Polymer Bulletin 54, 417–426 (2005)
DOI 10.1007/s00289-005-0407-0

Polymer Bulletin

Compatibilizing Effects on the Phase Morphology and Thermal Properties of Polymer Blends Based on PTT and m-LLDPE

S.H. Jafari[1](✉), **A. Asadinezhad**[1], **A. Yavari**[1], **H.A. Khonakdar**[2], **F. Böhme**[3]

1) Department of Chemical Engineering, Faculty of Engineering, University of Tehran, 11365-4563, Tehran, Iran
2) Department of Polymer Processing, Iran Polymer and Petrochemical Institute (IPPI), 14965-115, Tehran, Iran
3) Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany
E-mail: shjafari@ut.ac.ir; Fax: +98-21-6957784

Received: 8 May 2005 / Revised version: 30 May 2005 / Accepted: 3 June 2005

Summary

Morphology and thermal characteristics of poly (trimethylene terephthalate) (PTT)/ metallocene linear low-density polyethylene (m-LLDPE) blends with different amounts of a terpolymer based on glycidyl methacrylate (GMA), employed as a possible compatibilizer, were systematically examined. DMTA results show two distinct peaks for all neat blends associated with each phase. Melt crystallization degree of both phases in all the blends was observed to be reduced compared to pure components, except for that of PTT-rich phase in those blends with PTT as the matrix which slightly increases. Addition of the terpolymer to the system is found to effectively reduce the droplet size of the dispersed phase and increase phase adhesion. Also it increases the crystallinity of PTT in the system with PTT as the matrix. The influence of the compatibilizer is ascribed to the chemical interaction of PTT functional end groups with GMA functionalities. The efficiency of the terpolymer as a compatibilizer beyond 5 wt% content decreases which can be ascribed to the interface saturation and formation of micelles in the bulk phases.

Introduction

Blending two or more polymers has emerged as a well-established route to produce new polymeric materials with desired performance. However, most of polymer pairs are intrinsically immiscible giving rise to lower mechanical properties [1]. Compatibilization is a convenient technique to improve interfacial adhesion and reduce the extent of coalescence which can be reached by introducing a block copolymer to the system or carrying out an *in situ* reaction between constituents [2-6]. In a compatibilized blend, part of the compatibilizer resides at the interface and interacts with the constituents. Below the critical micelle concentration, (CMC), at which the interface is saturated by the compatibilizer, all of the copolymer chains are concentrated on the interface. At concentrations higher than CMC, part of the copolymer forms the micellar aggregates which localize in one or both bulk phases

[7-9]. Formation of micelles affects the physical and mechanical properties of the system as indicated in the literature [10].

Poly (trimethylene terephthalate) (PTT), a promising aromatic polyester recently introduced by Shell Chemicals, combines many advantages of nylons and other polyesters [11]. PTT was reported to have an outstanding tensile elastic recovery and rapid crystallization rate [12]. Several studies have been made on aromatic polyester/LLDPE blends and reported to be immiscible due to some structural considerations and previous experimental findings [13-16].

This work deals with the investigation of morphology, crystallization, melting and dynamic mechanical behavior of PTT/m-LLDPE blends in the absence and presence of a glycidyl methacrylate-based terpolymer, added to the system in various quantities as a possible compatibilizer.

Experimental

Materials

All the materials used for this work were commercial products used as received without any further treatment. PTT grade CP 200 was obtained from Shell Chemicals. The intrinsic viscosity of PTT measured at 25°C in a 60/40 mixture of phenol and tetrachloroethane was 0.92 ml/g. A compatibilizer based on n-Butyl Acrylate Glycidyl Methacrylate Ethylene terpolymer, including 2-4 wt% GMA (glycidyl methacrylate), commercially known as Elvaloy$^{®}$PTW was obtained from Du Pont Ltd. A metallocene linear low-density polyethylene, m-LLDPE, grade 1023CA, was supplied by Exxon Mobile Chemicals. Prior to blending, the materials were dried for 24 h at 80°C in a vacuum oven, except for Elvaloy$^{®}$ PTW which was dried at 50°C for 4 h.

Instruments

PTT/m-LLDPE blends were prepared in a conical twin-screw extruder (DACA Micro-Compounder). The screw speed of 100 rpm and temperature of 230°C were used for blend preparation. Two sets of PTT/m-LLDPE blends with PTT content of 75 and 25 wt% were made with varying amounts of the compatibilizer (Elvaloy$^{®}$ PTW content of 0, 2.5, 5 and 10 %wt, with respect to the total weight of the blend). The micro-compounder showed a high torque on initial feeding which progressively dropped indicating uniformity of melts blends.

Morphology of cryogenically fractured surfaces of the extruded strands, after coating with a thin layer of gold, was investigated with a scanning electron microscope, (SEM), model S-360, Cambridge Instruments.

Dynamic mechanical properties of the samples were examined by a 2980 DMA V1.4O (TA Instruments) to determine the viscoelastic properties in bending mode. Rectangular specimens of dimension 10 mm × 40 mm × 0.5 mm were employed for testing. Samples were heated from -150°C to 100°C at a heating rate of 3 K/min and frequency of 1 Hz.

Differential scanning calorimetry measurements were performed on a DSC (Polymer Laboratories, UK) with samples of about 10 mg sealed in aluminum pans under nitrogen atmosphere. The samples were first heated at a rate of 10 K/min from 0°C to 250°C and kept there for 5 min in order to erase all thermal history, subsequently cooled down to 0°C at the same rate and the dynamic crystallization behavior were recorded. Melt crystallization degrees of the samples, after normalization, were calculated in terms of heat of fusion for 100% crystalline polymer based upon literature data (30 KJ/mol for PTT [17] and 7.6 KJ/mol for m-LLDPE [18]). The second heating scan within the same range at 10 K/min was also applied to examine the melting behavior of the crystallized blends.

Results and Discussion

DMTA Studies

Figure 1 shows tan δ curves of the pure components along with those of neat blends. Two substantial peaks are present in tan δ curve of pure m-LLDPE, one relates to its glass transition and the other is associated with the crystalline phase transition which is well-documented in the literature [19], while PTT shows only a single peak corresponding to its glass transition. Each blend exhibits two discernible peaks, which means that the blend is comprised of two distinct phases. The low-temperature peak occurs at T_g of m-LLDPE-rich phase and the high-temperature one falls between amorphous transition (T_g) peak of PTT and crystalline transition peak of m-LLDPE. The tan δ peaks of the blends show no shift toward each other suggesting the system is immiscible which has frequently been reported on similar systems in the literature [13-16].

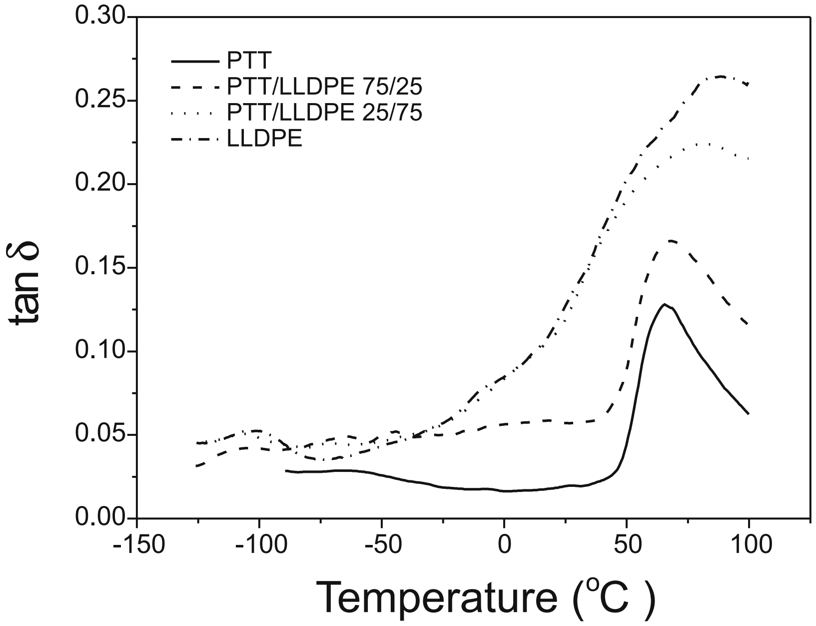


Figure 1. Temperature dependence of tan δ for the pure constituents and neat blends.

Melting and Crystallization Behavior

Figure 2 shows DSC cooling thermograms of two neat polymers along with PTT/m-LLDPE 75/25 blend at different contents of the compatibilizer. PTT reveals a melt crystallization exotherm at 204°C while that of m-LLDPE occurs at 114°C. Two

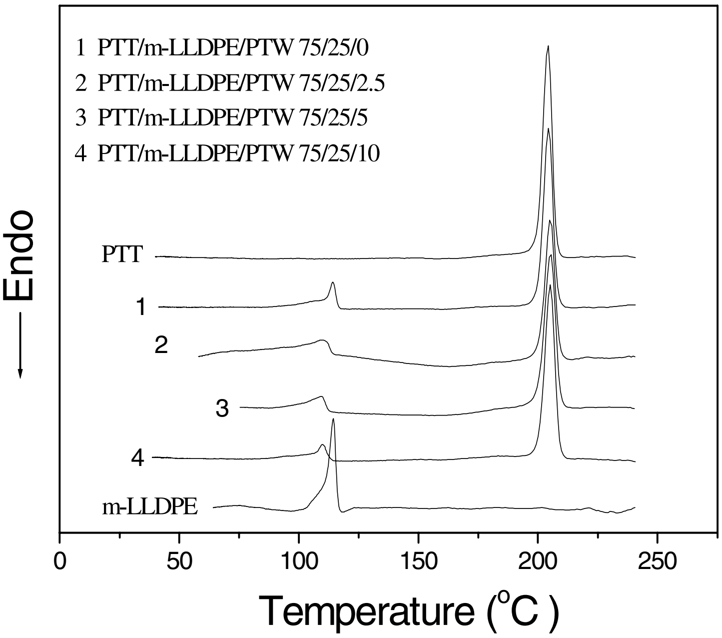


Figure 2. DSC thermograms at cooling scan of PTT/m-LLDPE 75/25 along with neat components.

discernible peaks associated with melt crystallization corresponding to matrix (PTT) and dispersed phase (m-LLDPE) are present in the blends and blending causes no change in melt crystallization temperature of PTT and m-LLDPE. However, the addition of 2.5, 5 and 10 wt% compatibilizer shifts the melt crystallization temperature of m-LLDPE-rich phase from 114°C to 111°C, 109°C and 109°C, respectively which is attributed to the dispersed state of the minor phase as well as the role of the compatibilizer in reducing the dispersed phase size [20] which will be discussed more in the phase morphology section. The melt crystallization temperature matrix phase (PTT) shows no variation. It seems that the effect of the compatibilizer beyond 5 wt% concentration is suppressed owing to micelle formation in bulk phases of the blend.

DSC cooling thermograms of PTT/m-LLDPE 25/75 blends at different contents of the compatibilizer along with two neat components are illustrated in Figure. 3. Similarly, two discernible peaks corresponding to matrix (m-LLDPE) and dispersed phase (PTT) appear in the curves. Introduction of 2.5 wt% compatibilizer shifts the melt crystallization of m-LLDPE-rich phase from 114°C to 112°C, interpreted as a reduction in melt crystallization ability of m-LLDPE, and further addition of the compatibilizer does not affect the melt crystallization of m-LLDPE. In other words, beyond 2.5 wt% concentration of the compatibilizer, micelle formation occurs. It is also observed that melt crystallization of PTT-rich phase shows no change upon addition of the compatibilizer which is ascribed to the dispersed state of PTT [20].

Figures 4 and 5 demonstrate the DSC thermograms at the second heating scan of PTT/m-LLDPE 75/75 and 25/75 blends respectively, in various quantities of compatibilizer along with two base polymers. All the blends exhibit two melting endotherms corresponding to PTT-rich and m-LLDPE-rich phases. The magnitude of

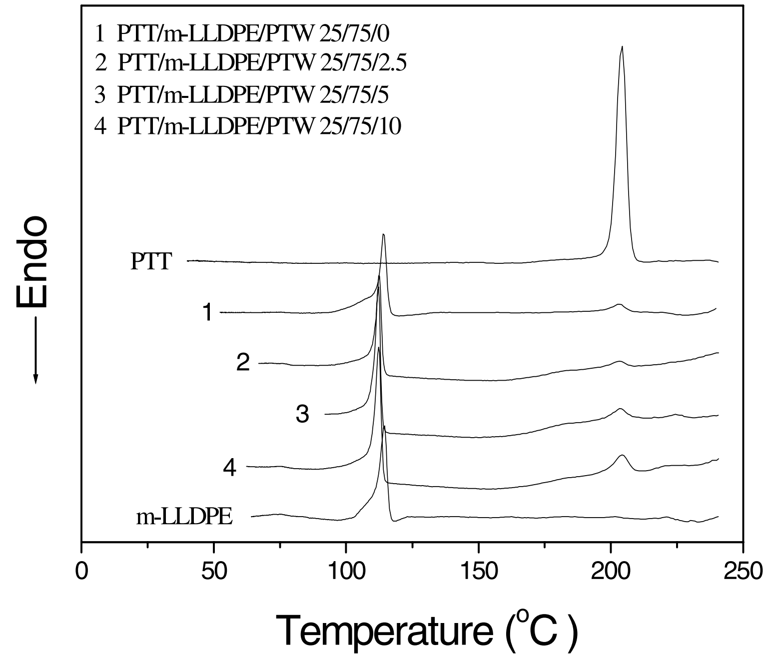


Figure 3. DSC thermograms at cooling scan of PTT/m-LLDPE 25/75 along with neat components.

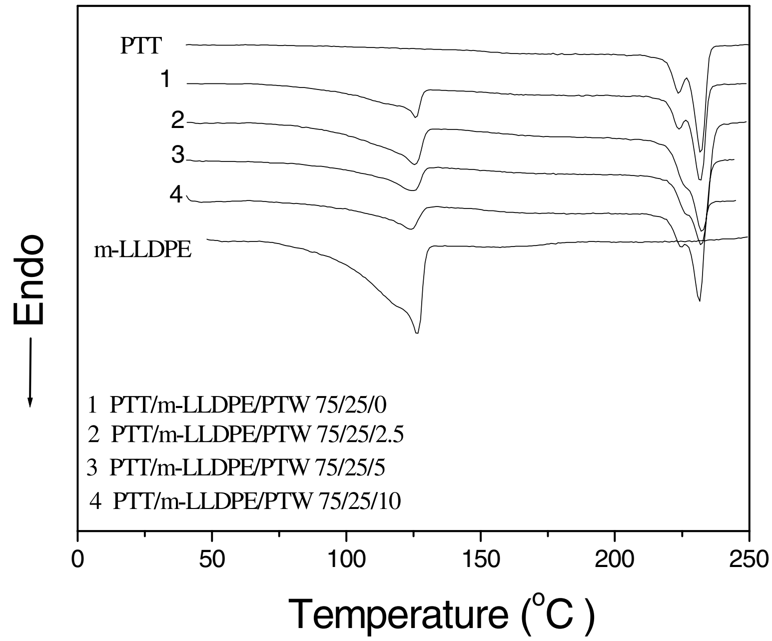


Figure 4. DSC thermograms at the second heating scan of PTT/m-LLDPE 75/25 along with neat components.

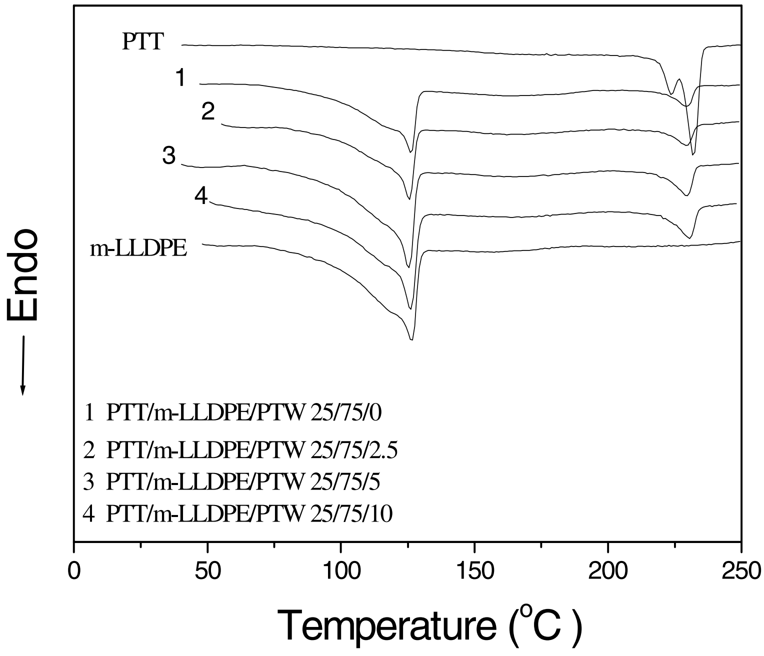


Figure 5. DSC thermograms at the second heating scan of PTT/m-LLDPE 25/75 along with neat components.

these two melting endotherms in the blends, especially for m-LLDPE, is significantly higher than that of the respective crystallization exotherms. This implies that both of the constituents, particularly m-LLDPE, have considerable cold crystallization which are not observable on DSC thermograms. In addition, neat PTT and PTT-rich phase of the blends demonstrate two adjacent melting peaks indicative of sequential melting behavior which has already been reported [21] and relates to melting process of crystallites with different stabilities.

A summary of DSC results including the melt crystallization temperature ($T_{c,m}$), melting peaks (T_m) and the degree of melt crystallization (X_c) for the blends and neat components is tabulated in Table 1. It can be observed from the table that the degree

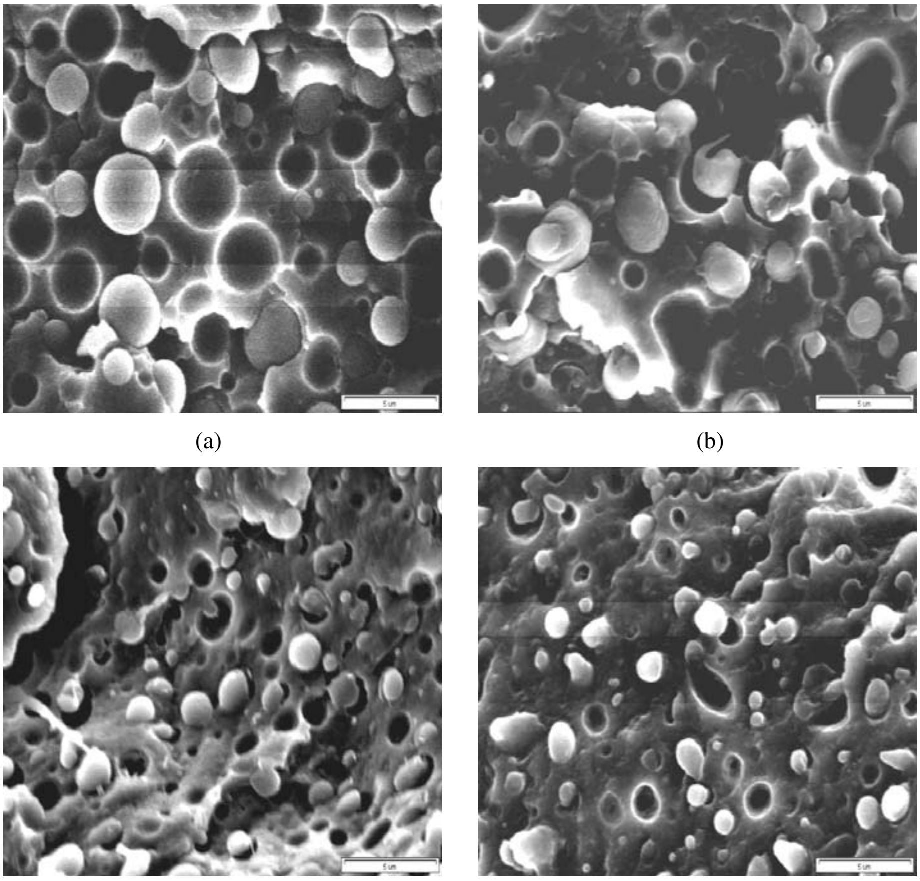
Table 1. Summary of DSC results of PTT/m-LLDPE/Elvaloy®PTW

Sample	X_c (%)		$T_{c,m}$(°C)		T_m (°C)	
	LLDPE	PTT	LLDPE	PTT	LLDPE	PTT
PTT	-	26	-	204	-	232
75/25	11	29	114	204	126	232
75/25/2.5	9	27	111	203	125	232
75/25/5	8	28	109	205	124	232
75/25/10	7	30	109	205	124	232
25/75	10	4	114	203	126	229
25/75/2.5	10	5	113	203	126	229
25/75/5	9	6	112	204	126	230
25/75/10	9	12	112	205	126	231
m-LLDPE	11	-	114	-	127	-

of melt crystallization of the blends is lower than that of neat components, except for that of PTT in those blends in which PTT is the matrix. In addition, crystallization degree of PTT phase in the blends with PTT as dispersed phase is much lower with respect to those blends with PTT as matrix which is ascribed to significantly fine dispersion in the former system [20]. It is also inferred from table data that the presence of PTT phase interferes with the melt crystallization phenomenon of m-LLDPE phase leading to reduce m-LLDPE crystallinity.

Phase Morphology

Figure 6a-d shows the SEM micrographs of PTT/m-LLDPE 75/25 blends with various amounts of the compatibilizer (0-10 %wt). It is deduced from this figure that the size of the dispersed domains decreases until addition of 5 wt% compatibilizer. This reduction may be due to the role of the compatibilizer to form an interphase giving rise to improve the interfacial adhesion. Huang [6] examined blends of PTT and polystyrene in the presence of a GMA-based copolymer as a compatibilizer and

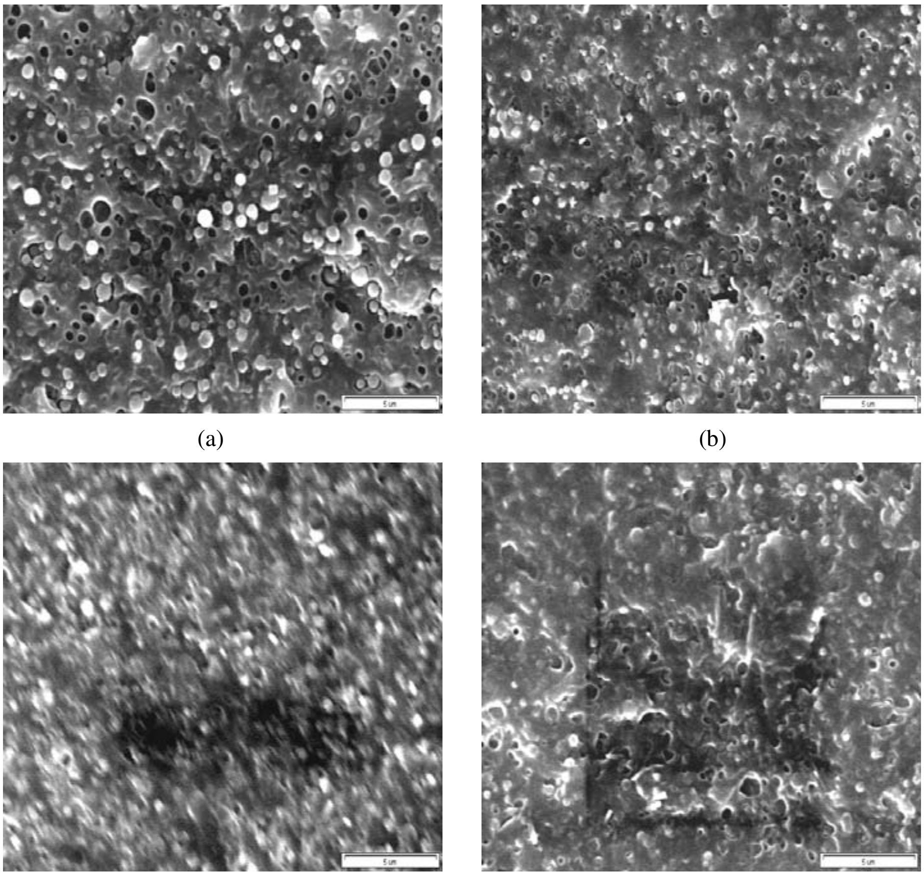


(a) (b) (c) (d)

Figure 6. SEM micrographs of PTT/m-LLDPE 75/25 at different compatibilizer contents, (a) 0 %wt ; (b) 2.5 %wt ; (c) 5 %wt ; (d) 10 wt%.

showed that GMA functionalities chemically interacts with carboxylic acid and hydroxyl end groups of PTT leading to formation of graft copolymers which anchor along the interface and reduce the interfacial tension and suppress coalescence. It also worth noticing that the possibility of physical interaction of Elvaloy®PTW with m-LLDPE can not be withdrawn. Moreover, as indicated in Figure 6c,d, further addition of the compatibilizer to the blends has no discernible effect on the droplet size meaning that the effectiveness of the compatibilizer has diminished which may be attributed to the saturation of the interface with the compatibilizer. Similar comments have also been given by Zhao et al. on compatibilized blends of poly(methyl methacrylate) and poly(butadiene) [22].

Phase morphology of PTT/m-LLDPE 25/75 blends with varying extent of compatibilization is illustrated in Figure 7a-d. Addition of the compatibilizer to this system reduces the droplet size as well, but only up to 2.5%wt compatibilizer suggesting a lower CMC value for this composition as compared with that of PTT/m-LLDPE 75/25. This may be associated with two factors, the lower diffusion coefficient of matrix phase toward the terpolymer due to much higher viscosity of


(a) (b)

(c) (d)

Figure 7. SEM micrographs of PTT/m-LLDPE 25/75 at different compatibilizer contents, (a) 0 %wt ; (b) 2.5 %wt ; (c) 5 %wt ; (d) 10 wt%.

m-LLDPE phase compared to PTT phase and lower reactivity of the compatibilizer with m-LLDPE phase than with PTT phase. This fact that PTT shows high reactivity to GMA-based copolymers has already been reported [6]. Moreover, in the system of PTT/m-LLDPE 25/75 the dispersed droplets are significantly smaller than those of PTT/m-LLDPE 75/25 having a finer dispersion. An explanation to this observation is that the dispersed droplets in PTT/m-LLDPE 75/25 can hardly be broken up to finer particles owing to high viscosity ratio of the latter system.

Conclusions

Miscibility, morphology, thermal and dynamic mechanical properties of PTT/m-LLDPE blends with different amounts of a GMA-based terpolymer as a possible compatibilizer were studied. DMTA results showed two distinct peaks in all the blends associated with each component. DSC thermograms of the blends also revealed two separate melt crystallization peaks and two distinct melting peaks showing that two polymers crystallize separately to form their own crystallites. The melt crystallization degree of each phase in the blends is lower than that of neat components, except for that of PTT in those blends in which PTT is the matrix. In addition, crystallization degree of PTT phase in the blends with PTT as dispersed phase is significantly reduced which is ascribed to fine particle size in this system. It was verified that the presence of PTT retards the crystallization ability of m-LLDPE owing to the influence of the compatibilizer in changing the state of dispersion of minor component. The addition of the terpolymer to the system efficiently reduced the droplet size of the dispersed phase associated with the role of interfacial products in suppressing the coalescence. However, the effectiveness of the terpolymer as a compatibilizer beyond 5 wt% decreases which can be assigned to the formation of micelles in the bulk phases.

Acknowledgments. The authors gratefully acknowledge Du Pont and Exxon Mobil Chemicals companies for supplying the materials as well as Mrs. Sadr from IPPI for SEM examinations.

References

1. Utracki LA (2003) Polymer Blends Handbook, Kluwer Academic Publishers, Netherlands
2. Aravind I, Albert P, Ranganathaiah C, Kurian JV, Thomas S (2004) Polymer 45: 4925
3. Jafari SH, Pötschke P, Stephan M, Warth H, Alberts H (2002) Polymer 43 : 6985
4. Echevarria GG, Eguiazabal JI, Nazabal J (2004) J Appl Polym Sci 92 : 1559
5. Yang J, Shi D, Gao Y, Song Y, Yin J (2003) J Appl Polym Sci 88: 206
6. Huang JM (2002) J Appl Polym Sci 88: 2247
7. Noolandi J, Hong KM (1984) Macromolecules 17:1531
8. Fortelny I (2000) J Macromol Sci Phys B39: 67
9. Jeon HK, Kim JK (1998) Macromolecules 31:9273
10. Asaletha R, Groeninckx G, Kumaran MG, Thomas S (1998) J Appl Polym Sci 69: 2673
11. Hong PD, Chung WT, Hsu CF (2002) Polymer 43:3335
12. Hong PD, Chuang WT, Yeh WJ, Lin TL (2002) Polymer 43: 6879
13. Yang J, Shi D, Yao Z, Xin ZA, Yin J (2002) J Appl Polym Sci 84: 1059
14. Retolaza A, Eguiazabal JI, Nazabal J (2003) J Appl Polym Sci 87:1322
15. Kang TK, Yang KK, Park HD, Cho WJ, Ha CS (1999) J Appl Polym Sci 72: 989
16. Márquez M, Sabino MA, Rivero IA (1998) Polym Bull 41: 191

17. Pyda M, Boller A, Grebowicz J, Chuah HH, Lebedev BV (1998) J Polym Sci Polym Phys 36 : 2499
18. Teng H, Wenfei D, Shi Y, Jin X (2003) J Appl Polym Sci 88: 536
19. Orozco JAG, Rego JM (1991) J Appl Polym Sci 42: 1879
20. Tang T, Lei Z, Huang B (1996) Polymer 37: 3219
21. Srimoaon P, Dangseeyun N, Supaphol P (2004) Europ Polym J 40:599
22. Zhao H, Huang B (1998) J Polym Sci Polym Phys B36: 85