ISSN : 0974 - 7478 Volume 9 Issue 2

Macromolecules

An Indian Journal

Full Paper

MMAIJ, 9(2), 2013 [58-67]

Mechanical, thermal, rheological and morphological behavior of poly (trimethylene terephthalate)/high impact poly (styrene) blends compatibilized with poly (styrene-co-ethylene-co-butylene-co-styrene)-g-maleic anhydride

Kedar Jadhav, Pravin Kadam, Shashank Mhaske*
Department of Polymer Engineering, Institute of Chemical Technology, Matunga, Mumbai-400 019,
Maharashtra, (INDIA)
E-mail : stmhaske@gmail.com; st.mhaske@ictmumbai.edu.in

INTRODUCTION

The development of polymer blends, composites and laminates is of great economic importance for the plastics industry and for other industries where the use of such products is becoming increasingly common. Advanced polymer modification techniques have grown in importance during the last two decades as the “point of diminishing returns” has been approached in improving the performance/price balance by altering just the chemical structures of polymers. Most pairs of polymers are immiscible with each other. Even worse is the fact that they also have less compatibility than would be required in order to obtain the desired level of properties and performance from their blends. Compatibilizers are often used as additives to improve the compatibility of immiscible polymers and thus improve the morphology and resulting properties of the blend.

Poly (trimethylene terephthalate) (PTT) is a newly commercialized crystalline polymer with growing applications in fibers, films, and engineering plastics. This polymer was reported to have outstanding tensile elastic recovery, good chemical resistance, a relative low melting temperature, and a rapid crystallization rate. As an engineering thermoplastic, it was found to have mechanical properties similar to those of poly (ethylene terephthalate) (PET), while its processing characteristics are similar to those of poly (butylene terephthalate) (PBT). Thus, it combines some of the advantages of PET and PBT[1]. In addition, PTT possesses all of the advantages of thermoplastic polyesters, such as their dimensional stability, solvent resistance, and abrasion resistance and can be employed under moist conditions where nylon cannot be used. The performance of glass fiber reinforced PTT was also found to be better than that of reinforced PET or PBT and some of its mechanical properties are comparable to those of glass fiber reinforced nylon. Since its commercialization in 1998, PTT has been widely studied, especially with regard to its fiber properties, structure formation, crystal structure, and thermal and crystallization behaviors[2]. However, the low heat distortion temperature, low melt viscosity, poor optical properties, and pronounced brittleness of unreinforced PTT at low temperature have restricted its use as a desirable engineering plastic. Some of these deficiencies could be improved by developing PTT composites or blends with suitable polymers in which it retains its excellent properties. Polymer blending is a straightforward, versatile, and relatively inexpensive method of creating a new polymer material which has the desirable properties of all the constituent components. PTT blends are expected to possess a wide range of features that will broaden the applications of the homo-polymer. Recently, a considerable amount of research work pertinent to PTT blends was reported[3]. Much attention has been focused on the development and investigation of binary polymer blends, which allow the combination of desirable properties of different polymers with exceptional advantages over the development of novel polymer materials. Most of them focused on the mixtures of two amorphous components, or mixtures of amorphous and crystalline components. However, polymer blends containing two crystalline components are less frequently discussed. Both poly (ethylene terephthalate) (PET) and poly (trimethylene terephthalate) (PTT) are semicrystalline aromatic polyesters. PET is the most important polyester with satisfactory thermal stability and mechanical properties, which have been widely used as fibers, bottles, packages, etc for many years[4].While PTT is a relative new polymeric material that developed by Shell Chemical Co. Since its commercial introduction in 1998, there has been an increased interest in PTT for fiber and engineering thermoplastic applications[5]. PTT has shown better tensile elastic recovery but lower modulus than PET[6]. Polymer blending is widely recognized as the most common method for developing new polymeric materials. It is also expected that blending of PET and PTT will offer an interesting route to combine the complementary properties of both polymers. Opperman et al.[7] have prepared PET/PTT blend fibers by melt spinning. They found that PTT significantly improves recovery during cyclic deformation of PET fibers at a concentration of 10 wt%. The experimental results also revealed that PET/PTT blend fibers are dyed more easily than pure PET and PTT fibers.

In this paper Poly (styrene-co-ethylene-co-butylene-co-styrene)-g-maleic anhydride (SEBS-g-MA) (containing 0.5 wt% MA level) is utilized as a compatibilizer for the PTT/HIPS blend so as to improve its performance properties. The SEBS-g-MA compatibilized PTT/PP blends were characterized for mechanical, thermal, morphological and rheological properties.

MATERIALS AND METHODS

Materials

Poly (trimethylene terephthale) (0.93 IV) was amiably supplied by Futura Polyesters Pvt. Ltd., Chennai, India. High Impact Poly (styrene) (HIPS) (SH731) was procured from Supreme Petrochemicals Pvt. Ltd., Mumbai, India. SEBS-g-MA was obtained from Aldrich Chemicals, USA. All the materials were used as obtained without modification or treatment.

Methods

Prior to blending, PTT and HIPS pellets were dried at 100 ± 5°C for 4 – 5 hours in an air-circulating oven. The drying is essential to remove the moisture absorbed or adsorbed by the materials. This protocol was followed for all the batches. Also for the compatibiliser, was dried at 80°C.

All the compositions studied in the present work along with their coding system are presented in TABLE 1. The pre-dried components were dry blended in desired ratio before feeding to co-rotating twin-screw extruder (Model MP 19 PC, APV Baker Ltd, U.K), having L/D of 25:1. Mixing speed of 40 rpm was maintained for all the compositions. The extrudate from the die was quenched in a tank containing water at 20-30°C and then pelletized. Processing conditions such as temperature profile in different zones and the extruder die as well as speed of blending etc. for melt blending are given in TABLE 2.

The extrudate were pelletized using Boolani's pelletizer machine. The rpm of the pelletizer was maintained between the ranges of 60-80. Since the systems studied were incompatible with each other, thus they showed high die swell. Thus, the extrudate had to be grinded in a grinder where it was too thick for pelletization.

The pre dried (90°C for 4-5 hours in an air circulating oven) pellets of blends were injection molded using family mould cavity in a microprocessor-based injection molding machine (Boolani Industries Ltd., Mumbai, India). The family mould have tensile, flexural and impact test specimen cavities. The processing conditions for injection molding are given in TABLE 2. The test specimens pertained to ASTM standards (Tensile - ASTM D638, Flexural – ASTM D790, Impact – ASTM D256).

TABLE 1 : Prepared uncompatibilized and compatibilized blends of PTT/HIPS

Code	Poly(trimethylene terephthalate)		HIPS		SEBS-g-MA
	Gm	%	gm	%	
CPTT	800	100	0	0	0
PTT/HIPS=90/10	720	90	80	10	0
PTT/HIPS =80/20	640	80	160	20	0
PTT/HIPS =70/30	560	70	240	30	0
PTT/HIPS =60/40	480	60	320	40	0
PTT/HIPS =50/50	400	50	400	50	0
PTT/HIPS =20/80	300	20	500	80	0
CHIPS	0	0	800	100	0
PTT/HIPS/SEBS-g-MA=90/10/5	800	100	0	0	40
PTT/HIPS/SEBS-g-MA =80/20/5	720	90	80	10	40
PTT/HIPS/SEBS-g-MA =70/30/5	640	80	160	20	40
PTT/HIPS/SEBS-g-MA =60/40/5	560	70	240	30	40
PTT/HIPS/SEBS-g-MA =50/50/5	480	60	320	40	40
PTT/HIPS/SEBS-g-MA =20/80/5	400	50	400	50	40

TABLE 2 : Processing conditions used for preparing PTT/HIPS blends

Process		Temperature Profile (°C)						Screw Speed
Blending	Extrusion	Zone1	Zone2	Zone 3	Zone4	Die	WaterBath	40 rpm
		120	190	230	245	240	25-30	
Sample Preparation	Injection Molding	Zone 1	Zone 2	Nozzle	Mold	Cooling Time		Injection Pressure
		180	240	250	30-40	30 sec		98 Kg/cm^2

Characterization

The following methods were employed for determining the specific properties of the polymer blend. Flow chart of the study is shown in Figure 1.

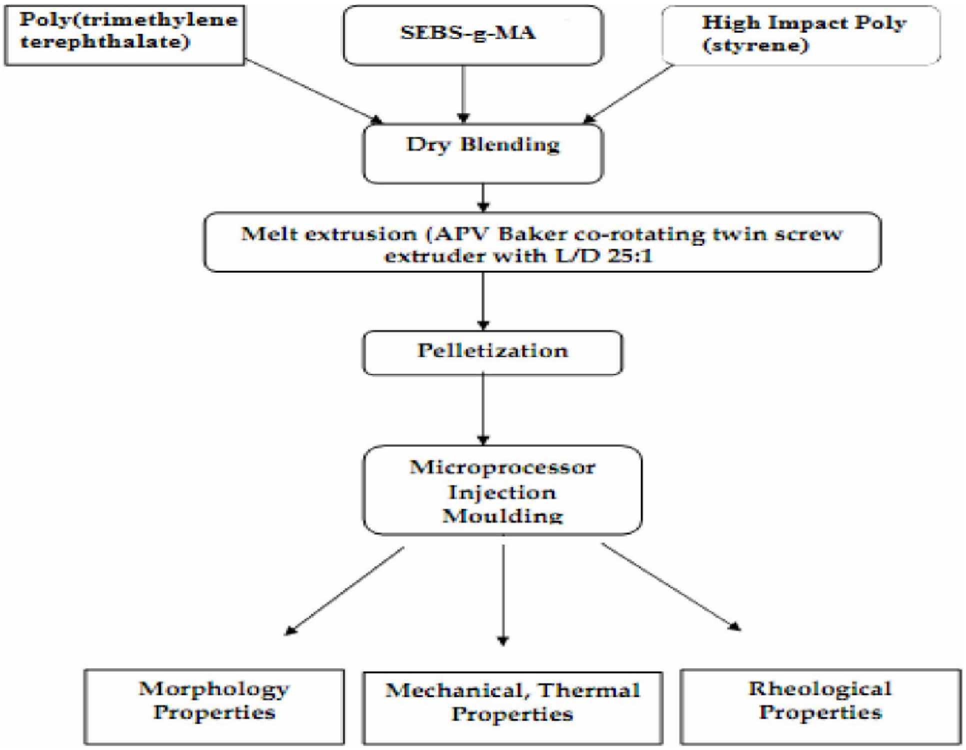

Figure 1 : Flow chart of the study from preparing to analyzing PTT/HIPS blends

Mechanical properties

Tensile (tensile strength, tensile modulus and percentage elongation at maximum load) and flexural (flexural strength and flexural modulus) properties were measured at ambient condition using a Universal Testing Machine (LR-50K, Lloyds Instrument, UK), according to ASTM procedures D638 and D790; at a crosshead speed of 50 mm/min and 2.8 mm/min respectively. The notch for impact test was made using a motorized notch-cutting machine (Polytest model 1, Ray Ran, UK). Notched Izod impact strength was determined at ambient condition according to ASTM D256, using impact tester (Avery Denison, UK) employing a 2.7J striker, having striking velocity of 3.46 m/s.

Thermal properties

Differential Scanning Calorimetric (Q 100 DSC, TA instruments Ltd., India) characterization was done to investigate the crystallization and melting behaviour of the prepared nanocomposites. Two consecutive heating scans were determined to minimize the influence of possible residual stresses in the material due to any specific thermal history. Scanning rate of 10°C/min was maintained for both heating and cooling cycle; whereas nitrogen gas purge rate was maintained at 50 ml/min. Melting temperature (T_m) was determined from the second heating scan, while the crystallization temperature (T_c) from the only cooling scan.

Rheological properties

Rheological properties of different compositions were measured using Haake rheometer RT10 parallel plate viscometer. Melt viscosity (η) as a function of shear rate (γ) was measured at 250°C. The shear rate was varied over 0.001s^{-1} to 1000s^{-1}. The samples were predried before rheological analysis. The test was also carried out in oscillatory mode with frequency range varying from 0.01 to 40 Hz at 250°C. Phase angle $\tan \delta = G3 / G2$ was determined as a function of frequency ω (rad /s).

Morphological properties

The morphology of PTT/HIPS blends were investigated using SEM with a JSM-840, JEOL instrument at an accelerating voltage of 10 KV. The electrons emitted from the electron gun were focused on the object surface. The secondary electrons emitted from the sample were monitored by suitable detectors. The adjustment of the magnification depends on the size of the scanned surface. The samples were taken from injection molded tensile specimen. The dumbbells were randomly chosen and etched in hot toluene to remove one of the phases. Gold sputtering devices were used to coat polymer samples, which have a most pronounced surface topography with a conducting metal layer.

RESULTS AND DISCUSSION

Mechanical properties

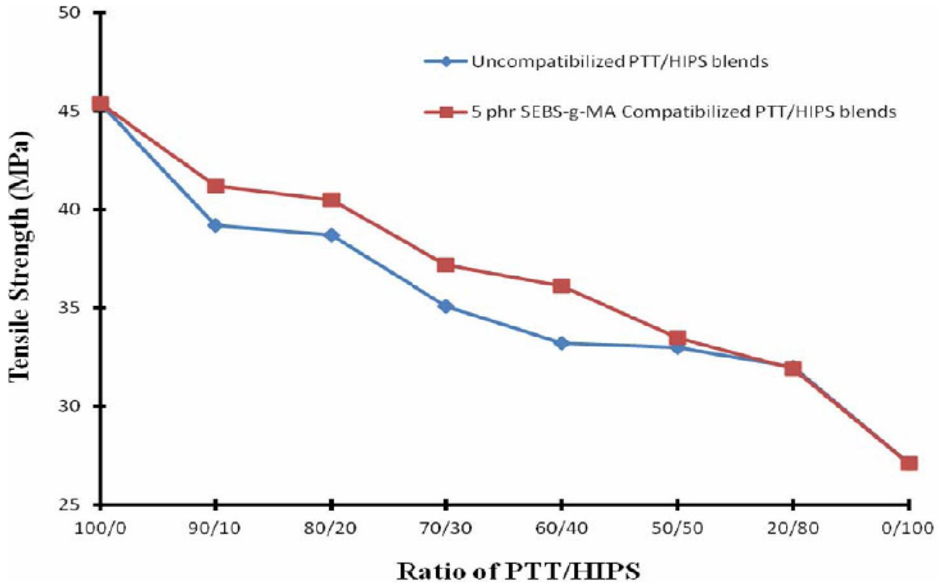

Figure 2 : Tensile strengths obtained for uncompatibilized and compatibilized PTT/HIPS blends

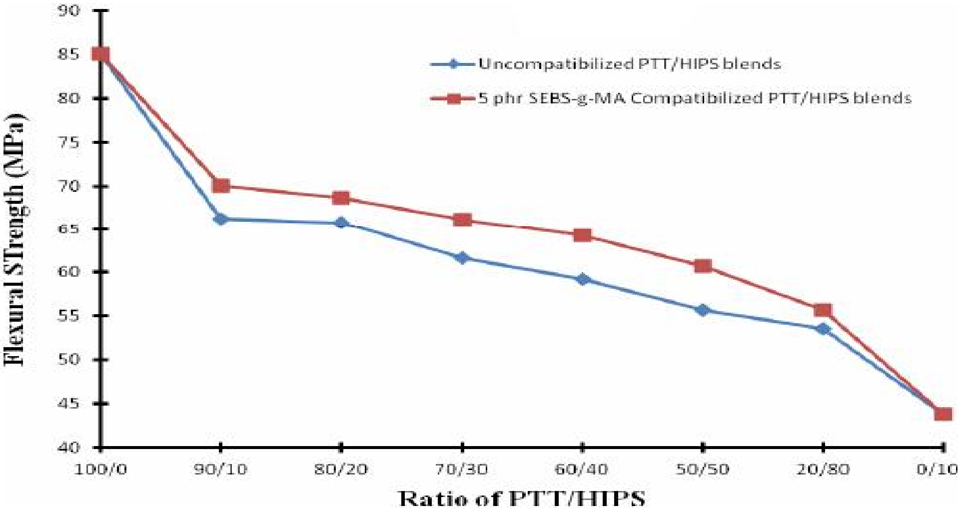

Figure 3 : Flexural Strengths obtained for uncompatibilized and compatibilized PTT/HIPS blends

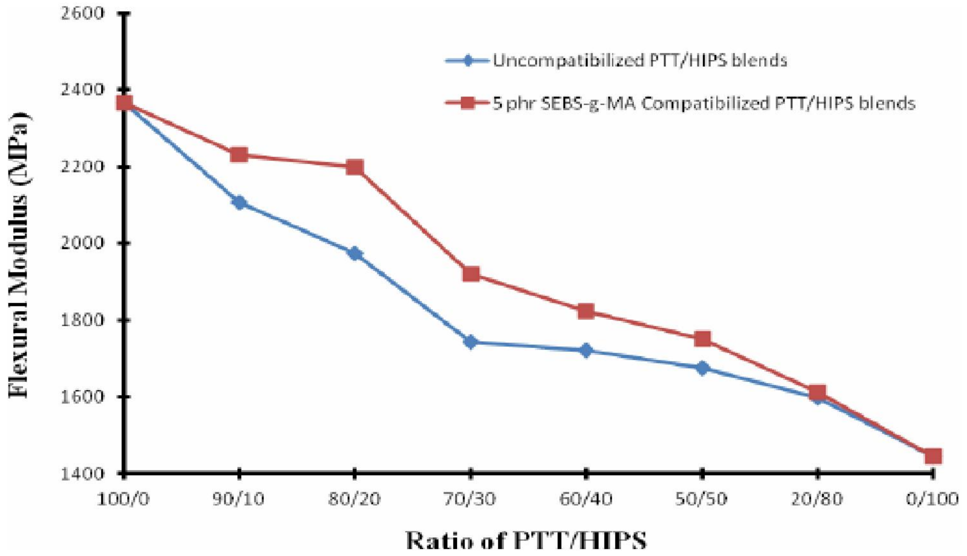

Figure 4 : Flexural Modulus values obtained for uncompatibilized and compatibilized PTT/HIPS blends

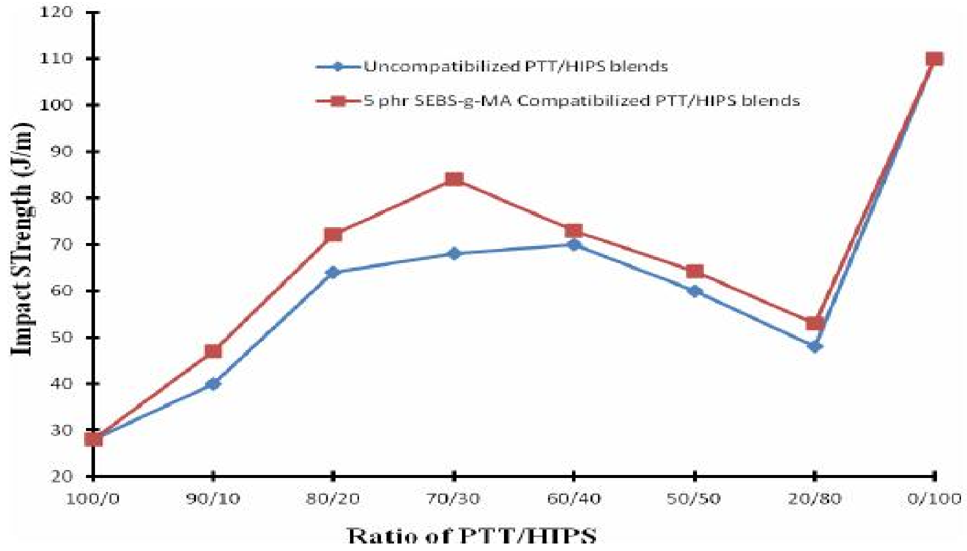

Figure 5 : Impact Strength values obtained for uncompatibilized and compatibilized PBT/PP blends

The CPTT has higher tensile strength than the all compositions of the blend, but the lowest impact strength. The addition of HIPS to PTT has certainly improved the toughness of the blend. The impact strength of the blend has significantly improved after addition of the 30% HIPS to PTT. The Figure 2 shows the tensile strength of all the blends with and without compatibiliser SEBS-g-MA. The addition of 5% compatibiliser has certainly improved the tensile strength of the blend. The improvement in tensile strength is large than that without one; the addition of compatibiliser has an effect on the blend giving the possible interfacial adhesion of the two blend components. The tensile strength decreases with the addition of HIPS & it is found that it is nearly same for PTT/HIPS (20/80) blend with and without compatibiliser. The possible cause for the same may be the lack of formation of SEBS-g-PTT in HIPS rich blend due to less PTT sites available for the compatibilization reaction. The flexural strength (Figure 3) has also shown the similar trend as tensile strength. The compatibiliser has increased the flexural strength but the effect is as pronounced as compared to the tensile strength. It is obvious form the Figure, that the flexural strength increased by the addition of the compatibiliser SEBS-g-MA to 90/10, 70/30 blends composition. The impact properties for all blends with and without compatibiliser are shown in the Figure 5. Addition of HIPS to the blend has improved the toughness of the blend. This can be stated that the addition of the other component, HIPS, in small amount has toughened the PTT. The impact strength of the blend has improved by the addition of the HIPS upto 40%, followed by the decrement in the value but still higher than virgin PTT. The 5 wt% compatibiliser improved the impact properties significantly for 60/40 blend. The main reason was that SEBS-g-MA is effective in improving the interface adhesion between the PTT and HIPS phases, which was the key factor affecting the mechanical properties, especially the impact energy of the blend. The addition of HIPS has significantly improved the impact strength of PTT, although the other mechanical properties of the blend have declined.

Thermal properties

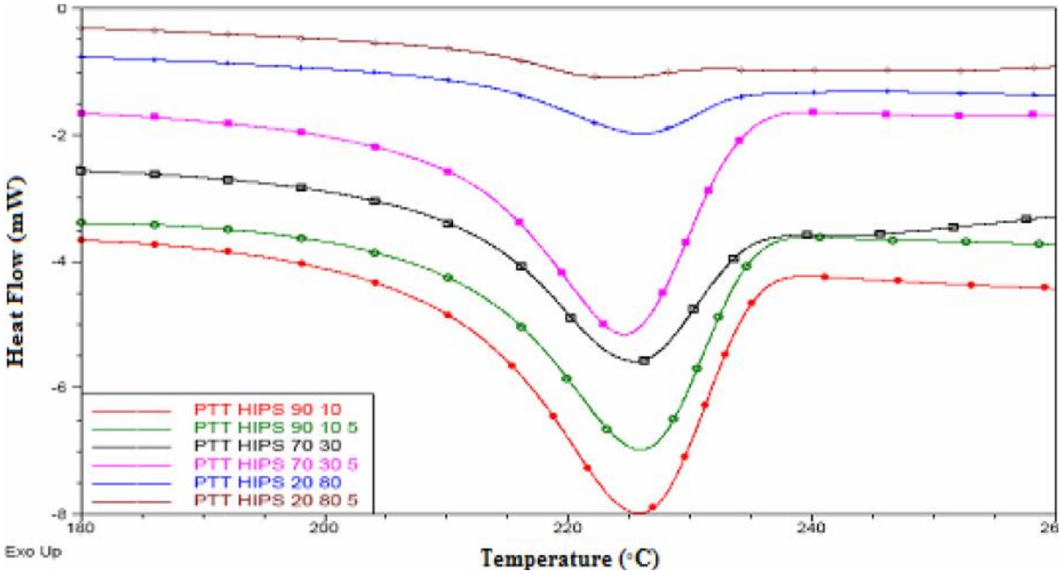

Figure 6 : DSC melting curves obtained for uncompatibilized and compatibilized PTT/HIPS blends

The blend has two Glass transition temperatures (Tgs'), indicating that the blends are phase separated in the amorphous phase. The lower temperature transitions observed between 40.7 and 47.2 °C were attributed to the Tg of the PTT amorphous phase. The higher temperature transitions observed from 98.2 °C to 94.1°C were the Tg of the HIPS phase. The variations of the two Tgs' values as a function of the compatibilized blend compositions are shown in Figure 8. It can be noticed that the variations of the two Tgs are composition dependent. When the HIPS content was increased from 0 to 80 wt%, the Tg (PTT-phase) shifted from 40.7 °C to 46.1 °C and then remained at 46.1 °C when the HIPS content was further increased above 80 wt%. In contrast, the Tg (HIPS-phase) decreased after the addition of PTT. These results are typical behaviors of

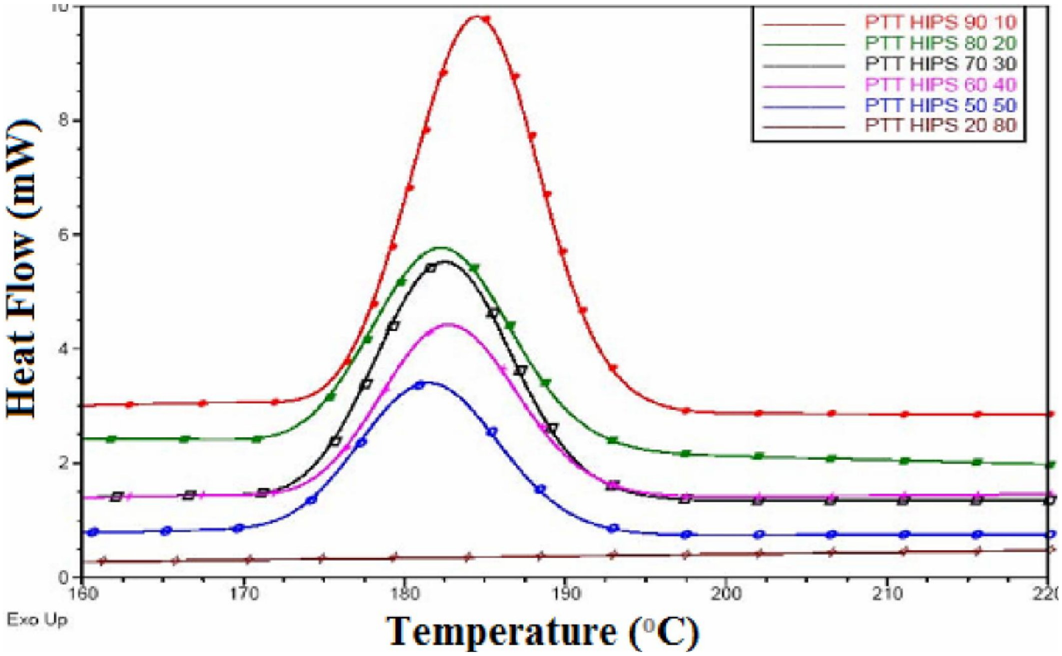

Figure 7 : DSC cooling curves obtained for uncompatibilized and compatibilized PTT/HIPS blends

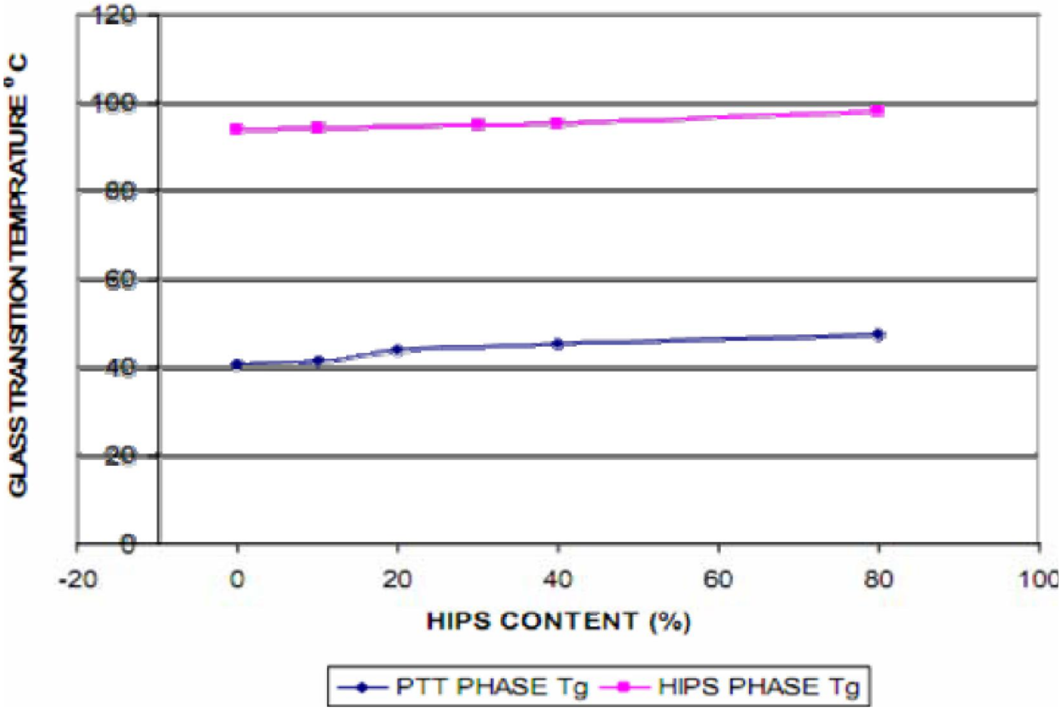

Figure 8 : Glass Transition Temperatures obtained for PTT and HIPS in the compatibilized PTT/HIPS blends

a partially miscible system. The results indicate that: (i) PTT is partially miscible with HIPS; (ii) the miscibility of the PTT/HIPS blends is improved slightly as the HIPS content is increased. The variations of the melting temperature Tm) PTT as a function of the blend compositions are shown in Figure 6. The Tm value shifts to lower temperatures with increasing HIPS content. In general, for a blend exhibiting some phase mixing, the presence of a second partially solubilized polymer will cause the melting temperature to decrease, due to the reduction in the chemical potential. This behavior is usually observed in the case of miscible or partially miscible blends. Accordingly, the variation of Tm indicates that the solubility of HIPS in the PTT-phase is slightly increased with increasing HIPS content.

TABLE 3 : Melting characteristics obtained for PTT/HIPS blends

Blends	Start (°C)	Onset (°C)	Maximum (°C)	Stop (°C)	Area (J/g)
CPTT	178.05	230.42	238.77	256.97	74.79
PTT/ HIPS=90/10	192.57	215.24	224.51	243.12	40.05
PTT/ HIPS =80/20	196.34	207.12	225.9	242.15	36.45
PTT/ HIPS =70/30	184.8	214.12	223.79	244.27	30.79
PTT/ HIPS =60/40	192.32	215.14	225.11	242.83	26.03
PTT/ HIPS =50/50	181.21	214.37	223.38	238.89	22.66
PTT/ HIPS =20/80	188.38	212.08	224.2	234.24	10.33
PTT/HIPS/SEBS-g-MA =90/10/5	176.56	210.73	225.91	248.57	34.87
PTT/HIPS/SEBS-g-MA =80/20/5	190.89	214.7	224.77	241.04	30.64
PTT/HIPS/SEBS-g-MA =70/30/5	168.67	209.36	224.58	248.21	37.98
PTT/HIPS/SEBS-g-MA =60/40/5	194.83	215.75	225.56	242.21	27.15
PTT/HIPS/SEBS-g-MA =50/50/5	172.97	210.53	223.38	242.83	10.93
PTT/HIPS/SEBS-g-MA =20/80/5	191.24	212.16	224.54	238.18	7.57

On the other hand, it also implies that PTT and HIPS are partially miscible. In contrast, the Tc value shifts slightly to higher temperatures as the HIPS content is increased (see Figure 7), indicating that much higher activation energy is needed for the organization of the neighboring PTT segments, due to the interference of the HIPS segments. This behavior, in turn, is characteristic of partially miscible blends.

TABLE 4 Cooling characteristics obtained for PTT/HIPS blends

Blends	Start (°C)	Onset (°C)	Maximum (°C)	Stop (°C)	Area (J/g)
CPTT	199.03	180.45	167.05	138.6	27.25
PTT/ HIPS =90/10	204.14	192.31	184.54	46.31	42.48
PTT/ HIPS =80/20	202.53	190.89	182.47	34.14	31.32
PTT/ HIPS =70/30	207.37	189.34	180.2	22.58	20.72
PTT/ HIPS =60/40	208.08	191.26	182.73	29.13	26.72
PTT/ HIPS =50/50	202.35	190.23	181.49	23.02	21.12
PTT/ HIPS =20/80	193.39	211.23	183.71	12.48	11.45
PTT/HIPS/SEBS-g-MA =90/10/5	207.73	191.7	183.78	37.18	34.11
PTT/HIPS/SEBS-g-MA =80/20/5	205.22	191.67	183.45	34.92	32.04
PTT/HIPS/SEBS-g-MA =70/30/5	203.43	190.45	181.93	31.82	29.19
PTT/HIPS/SEBS-g-MA =60/40/5	200.2	190.82	182.02	31.29	28.71
PTT/HIPS/SEBS-g-MA =50/50/5	203.78	191.33	182.32	14.18	13.01
PTT/HIPS/SEBS-g-MA =20/80/5	203.1	191.15	183.36	16.61	14.12

Figure 6 shows the effects of 5 wt% SEBS-g-MA on the melting behavior of the PTT/HIPS blends. It is clear that both the Tg and Tc values of the PTT-phase are shifted to higher temperatures in the presence of SEBS-g-MA. This indicates that excess energy is needed to initiate the movements or regular arrangement of the PTT segments, because of the SEBS-g-MA's compatibilization effect. However, the melting temperature showed no discernable changes in the compatibilized and uncompatibilised blends.

Rheological properties

The shear viscosity of a polymer melt is the most important function in characterizing the rheological behavior of the polymer melt; it will reflect the variation in interface interaction. The rheological properties of multiphase polymer blends are strongly influenced by their interfacial characteristics. Investigation of the rheological properties of blends can show information about the compatibilization effect, and can also reflect the correlation of rheology-morphology-mechanical properties of the blends.

Figure 9 shows the comparisons of the shear viscosity vs. shear rate plots for the PTT/HIPS blends at 250 °C with and without SEBS-g-MA compatibilization. When the SEBS-g-MA content was 5 wt%, the shear viscosity was increased compared with that of the corresponding uncompatibilized blend, implying an improvement in the adhesion between the phases.

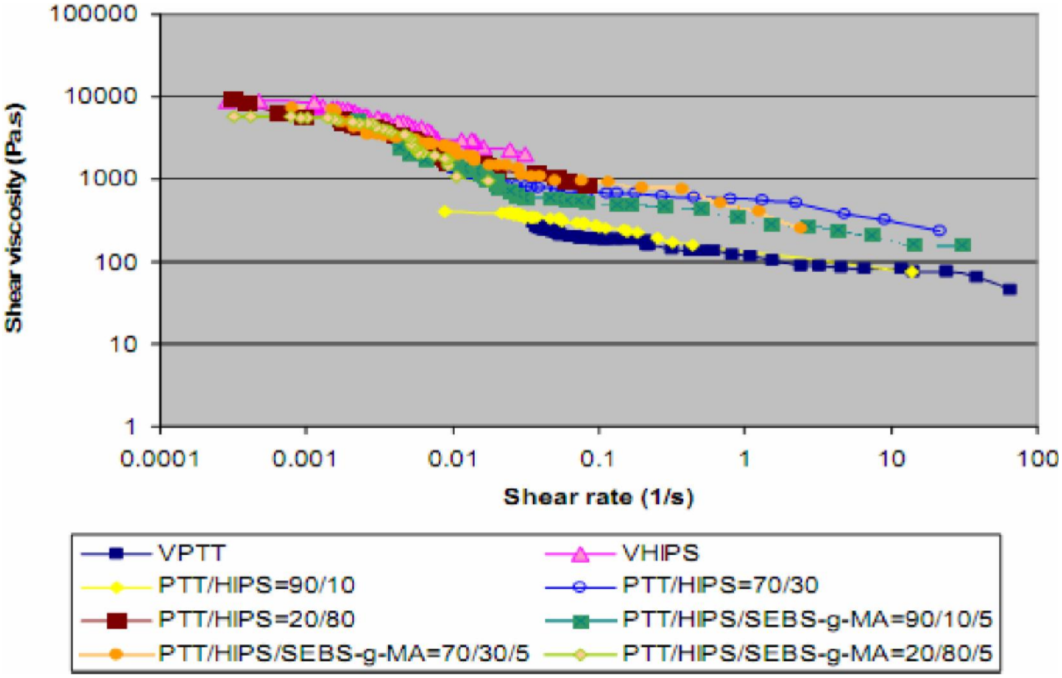

Figure 9 : Graph of viscosity vs shear rate obtained for uncompatibilized and compatibilized PTT/HIPS blends

Theoretically, there are the reaction between SEBS-g-MA and PTT due to –OH groups of the PTT in the matrix. The blend viscosity increased in the presence of SEBS-g-MA, indicating the formation of PTT-co-SEBS-g-MA copolymer which resulted in an increase in the flow resistance, due to the improved phase adhesion. This implies that the shear stresses can overcome the adhesion between the phases and result in a rapid decrease in the viscosity at high shear rates.

Morphological properties

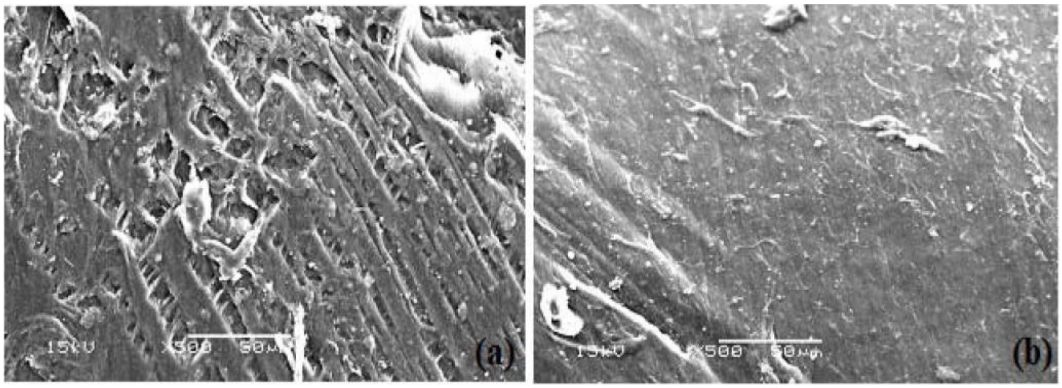

Figure 10 : SEM images obtained fort PTT/HIPS 80/20 (a) and PTT/HIPS/SEBS-g-MA (b)

Figure 10 (a) shows SEM micrographs of the PTT/HIPS (80/20) blend. PTT/HIPS was a biphasic blend. For the uncompatibilized blends, it can be seen that there is no evidence of interfacial interactions or adhesion, suggesting that the PTT and HIPS phases were incompatible. It was interesting that for the compatibilized blends there were broken fibers or small bumps on the fractured interfaces with evidence of their being drawn out; some unbroken fibers connecting the PTT and HIPS phases also appeared. It was concluded that these phenomena were the results of the reactive compatibilization, i.e., the reaction between the maleic acid functional groups of SEBS and the hydroxyl end groups of PTT formed polymer connections at the interfaces as seen from Figure 10 (b). These SEM morphological results provided evidence that SEBS-g-MA could improve the interfacial adhesion of PTT/HIPS during melt blending and consequently would theoretically enhance its mechanical properties.

CONCLUSION

The SEBS-g-MA is potentially reactive towards the carboxylic and/or hydroxyl groups at the chain ends of PTT. The mechanical properties like tensile strength, flexural strength of PTT/HIPS blend is lower than of virgin PTT, but was much higher than HIPS. The addition of the compatibiliser SEBS-g-MA has increased these properties, though the improvement in the impact properties of the blend was not significant. Rheological characterization has confirmed a molecular-weight buildup due to the interfacial reaction between the MA-grafted SEBS and PTT. Thermal analysis of the blend showed that the melting temperature of PTT has showed a slight decrease, while melting temperature of HIPS has showed a slight increase about 5°C. This was also confirmed through SEM analysis.

REFERENCES

[1] S.S.Dagli, K.M.Kamdar; Polym.Eng.Sci., **34**, 1709 **(1994)**.
[2] B.Boutevin, M.Khamlichi, Y.Pietrasanta; J.Robin; Polym.Bull., **34**, 117 **(1995)**.
[3] C.H.Tsai, F.C.Chang; J.Appl.Polym.Sci., **61**, 321 **(1996)**.
[4] H.Chieh-Chih, C.Feng-Chih; Polym., **38**, 2135 **(1997)**.
[5] W.R.Ashcroft, B.Ellis; Chemistry and Technology of Epoxy Resins Blackie; Glasgow UK, **(1993)**.
[6] K.C.Man, C.David; Polym.Intl., **43**, 281 **(1997)**.
[7] S.Yeong-Tarng, L.Mao-Song, C.Show-An; J.Polym.Sci.Part B-Phys., **40**, 638 **(2002)**.