

Thermal Properties of Poly(trimethylene terephthalate)/Poly(ethylene terephthalate) Melt Blends

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Abstract: The thermal behavior, morphology, ester-interchange reaction of Poly(trimethylene terephthalate) (PTT)/Poly(ethylene terephthalate) (PET) melt blends were investigated over the whole composition range (x PTT/($1-x$)PET) using a twin-screw Brabender. The melt blends were analyzed by differential scanning calorimetry (DSC), nuclear magnetic resonance spectroscopy (¹³C-NMR), and scanning electron microscopy (SEM). Single glass transition temperature (T_g) and cold crystallization temperature (T_c) were observed in all melt blends. Melt blends were found to be due to the ester-interchange reaction in PTT/PET blend. Also the randomness of copolymer increases because transesterification between PTT and PET increases with increasing blending time. This reaction increases homogeneity of the blends and decreases the degree of crystallinity of the melt blends. In PTT-rich blends, mechanical properties decrease with increase of PET content compared with that of pure PTT. And, in PET-rich blends, tensile modulus decreases with increase of PTT content, but tensile strength and elongation is similar to that of pure PET.

Keywords: PTT, PET, Transesterification, Thermal behavior, Blend, Morphology

Introduction

Polymer blends have received great scientific and industrial interest during the last several decades. It is a common and versatile way to develop new material with a desirable combination of its properties. Most polymers are thermodynamically immiscible. They are physical mixtures of structurally different polymers, which adhere together through the action of secondary bond force, with no covalent bonding between them. So it is difficult and almost impossible (in most case) to obtain good mechanical properties from polymer blends based on the Rule of Mixtures. It was thought that compatibility of crystallizable polymer would rarely happen[1-3].

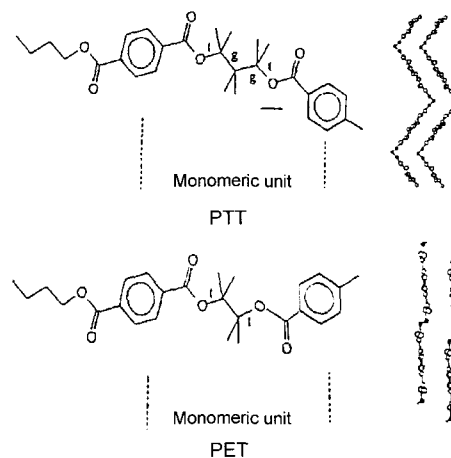
Especially, there has been great interest in polyester blends from the viewpoints of industrial applications and academic interest[4,5]. Several authors have studied on the transesterification reaction that occurs in polyester blends during melt processing[6]. In general, transesterification reaction in the polyester blends readily takes place at the above and near melting point, which produced block copolymers at first and random copolymers were produced with the passage of time.

PET has been used for filament and molding mostly because of excellent crystallinity, physical, and mechanical properties, but it has poor dye-ability and static resistance. To improve these properties, many researches for copolymerization or mechanical blending with other polymers have been done constantly[7].

Recently, interest of many researchers in PTT is increasing because the price of 1,3-propanediol that is the raw material

of PTT has been lowered. Though strength of PTT is inferior to that of PET and its melting temperature and T_g are lower than that of PET by 20-30 °C, but PTT has not only as excellent elastic recovery as nylon but also as superior physical properties as PET. For these reasons, PTT is considered as the most promising candidate for a replacement of PET[8].

Such differences in physical property of PET and PTT result from molecular characteristic difference of two polymers. It is well known that the number of methylene unit influences the physical properties of many polycondensation polymers such as polyamide and polyester, which is called the odd-even effect. As shown in Scheme 1, PET molecules are fully extended with two carboxyl groups of each terephthaloyl



Scheme 1. Molecular structure of PTT and PET.

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group in opposite directions, and all openchained bonds are trans with successive phenylene groups at the same inclination along the chain[9]. PTT has a conformation with bonds of the O-(CH₂)₃-O unit having the sequence of trans-gauche-gauche-trans, leading to a concentration of the repeating unit. The opposite inclinations of successive phenylene groups along the chain force the molecular chains to take on an extended zigzag shape[5].

In this work, the thermal properties and transesterification, and phase behavior of the melt blends that is caused by structural similarity between PET and PTT will be investigated through the thermal analysis, nuclear magnetic resonance analysis and morphological analysis.

Experimental

Materials

We used PTT chips with intrinsic viscosity (I.V.) of 0.92 dl/g, and PET chips with intrinsic viscosity of 0.68 dl/g. The intrinsic viscosity of each sample in a 50:50 mixed solvent of phenol and 1,1,2,2-tetrachloroethane were measured at 20 °C using capillary viscometers of the Ubbelohde type. We dried the chips in a vacuum oven at 60 °C for 10 h prior to melt processing to remove moisture from the chips completely.

Measurements

The following PTT/PET blends were prepared by melt mixing: 90/10, 70/30, 50/50, 30/70, 10/90. The mixing was performed with twin screw Brabender(PL331) extruder at screw speed of 50 rpm and temperatures that were set at 275 °C for 10 min according to the blending time.

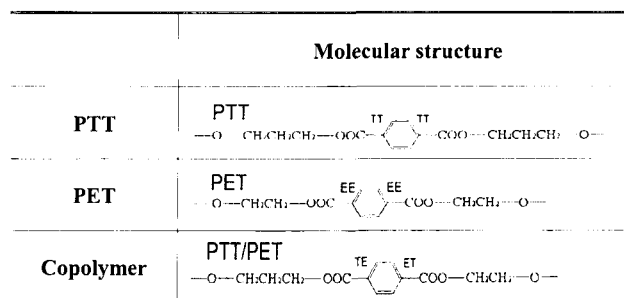
Thermal properties of PTT/PET blends were measured using a differential scanning calorimeter (DSC, TA 2010, Dupont). The samples were heated at 10 °C/min under nitrogen from 30 °C to 300 °C, held at this temperature for 3 min, and subsequently cooled down to 30 °C at a cooling rate of 10 °C/min. Thermogravimetric analysis was carried out using TGA(Perkin-Elmer TGA-7 analyzer). TGA experiment was performed at a scanning rate of 20 °C/min, from 50 to 700 °C under nitrogen atmosphere.

¹³C-NMR of the PTT/PET blends was measured by a Bruker AMX300 NMR spectrometer at 300.13 MHz. The samples used for the measurement were prepared by dissolving the PTT/PET blends in 1/3(v/v) mixed solvent of deuterated trifluoroacetic acid and chloroform. The morphology of fracture surface was observed using a scanning electronic microscopy (Hitachi 4200, Japan). The fractured surfaces were sputtered with gold before viewing.

Results and Discussion

Thermal Properties of the Blends

Scheme 2 shows the molecular structure of PTT/PET copolymer.



Scheme 2. PTT/PET Copolymer structures.

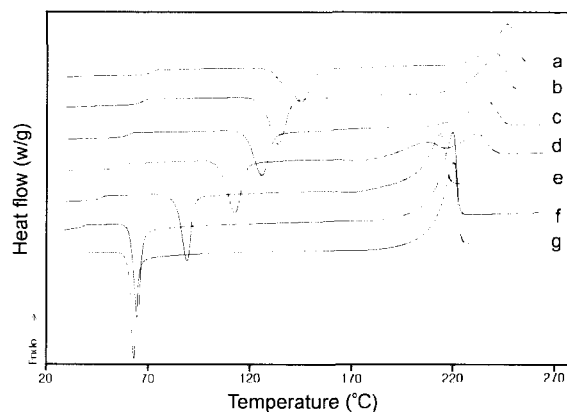


Figure 1. DSC thermograms of PTT/PET melt blends; (a) Pure PET, (b) 1/9, (c) 3/7, (d) 5/5, (e) 7/3, (f) 9/1 ratio, (g) Pure PTT.

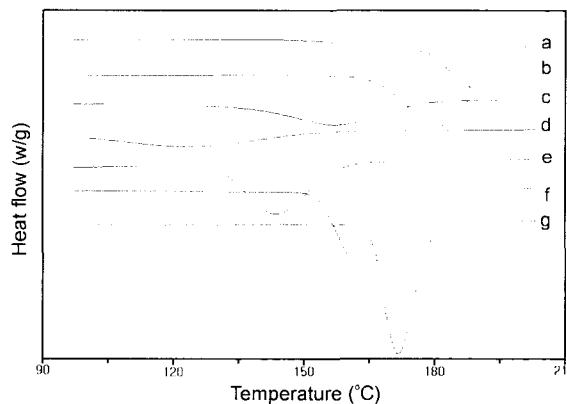


Figure 2. Recrystallization temperature of PTT/PET melt blends; (a) Pure PET, (b) 1/9, (c) 3/7, (d) 5/5, (e) 7/3, (f) 9/1 ratio, (g) Pure PTT.

PTT/PET blends were expected to be miscible blends because of structural similarity and molecular interaction. Pang *et al.* reported that the solution blends of PTT and PET were miscible in the amorphous region but immiscible in the crystalline region[10]. There are many researches for solution blends of PTT and PET but research for PTT/PET melt blends has been reported rarely. However most commercial blends

are prepared in the molten state. Thus we prepared the PTT/PET melt blends and investigated thermal properties of PTT/PET melt blends using DSC.

Figures 1 and 2 show the thermal behavior of PTT/PET blends during the second heating and cooling of the melt blends with different compositions. It is worth noting that thermal behavior of PTT/PET blends was measured during cooling after the first scan, because some crystallization occurs. And crystallization occurrence leads to increase of T_g because of the immobilizing effect of crystals. In this study, for rapid freezing, the sample melted at 275 °C was transferred to the DSC compartment after the DSC cell was quenched in liquid nitrogen externally, and then ultra-quenched sample was heated from 30 °C to 300 °C, held at this temperature for 3 min, and subsequently cooled down to 30 °C at a cooling rate of 10 °C/min. T_g of pure PET and PTT were 73.2 °C and 37.8 °C respectively.

In the DSC trace of the blends, a single glass transition temperature (T_g) and single cold crystallization temperature (T_{cc}) are always observed and increase with the increase of PET contents. The existence of a single T_g in the polymer blends is evidence for miscibility of polymers[11]. Because of the single T_g , it is considered that PTT polymer is compatible with PET polymer in the amorphous region and we confirmed that the blends are at homogeneous phase. Also crystallization velocity rate and T_g of PTT/PET blends increase with decrease in PET contents, because crystallization velocity rate of PTT is faster than that of PET. The Fox equation describes the relationship between the T_g and the blend composition.

$$1/T_g = (W_{PET}/T_{gPET}) + (W_{PTT}/T_{gPTT}) \quad (1)$$

where w_i is the weight fraction of the i th component in the copolymer (or blend) and T_g is the thermodynamic glass transition in absolute temperature units (K).

Predicted glass transitions and the determined values are

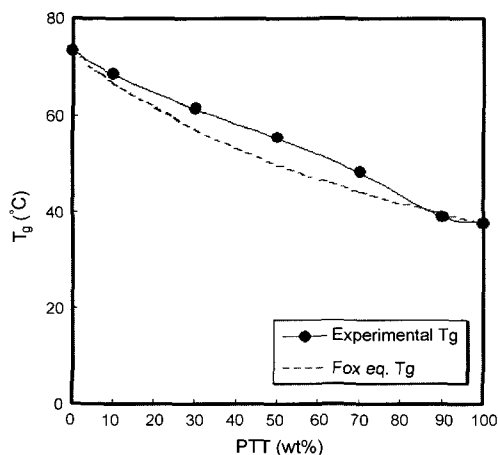


Figure 3. Experimental and Fox equation T_g of PTT/PET melt blends.

shown in Figure 3. It should be noted that all of the measured values are slightly above those predicted by the Fox equation and this difference is likely due to the PTT/PET copolymers produced by transesterification.

All PTT/PET blends show a single crystallization peak only. The fact that PTT/PET blends have a single T_g and T_{hc} peak. T_{hc} of PET and PTT was observed at 147.5 °C, 64.2 °C respectively and T_{hc} continuously increases with the increase of PET content. Also the T_{hc} peak shape of blends is becoming sharper with increase of PTT contents in the PTT/PET blends.

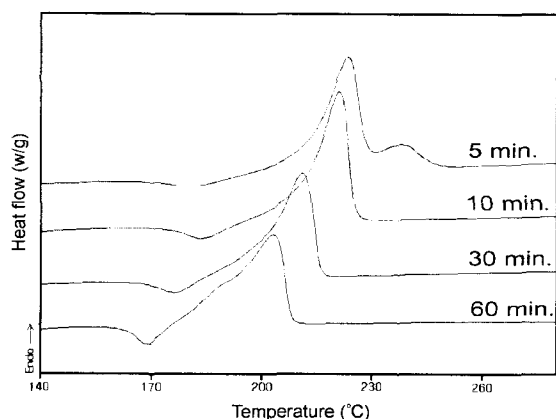
As can be seen in the Figure 1, it is shown that PET/PTT blends have a single endothermic melting peak in all blend composition except 5/5 blend. The 5/5 blend has double melting peak, and melting peak of 5/5 blend is broad. It could be expected that crystallization formation of PET and PTT would be affected by mutual presence. In other words, when crystal in the 5/5 blend was formed, the PTT and PET have their own crystal phase in the blend. On the other hand the blend can't form a perfect crystalline phase in 5/5 blend and melting peak of blend is broad compared with others.

Pure PET and PTT have one melting peak at 248 °C and 224 °C respectively. In case of PTT/PET blends, melting temperature of blends decreases with increase of PET contents in PTT-rich blends, and melting temperature of PET-rich blends decreases with increase of PTT contents. Also melting peak of blends is broad compared with pure PTT and PET. It was previously reported that T_m depression of a crystalline polymer in blends results from morphological, kinetic and esterification[12]. In this study, melting temperature depression of blends results from mutual existence and PTT/PET copolymer produced by ester exchange reaction. The degree of transesterification is proportional to the concentration of components and reaches the maximum in the 5/5 blend. Also when the polymer contents included in the other polymer matrix are less than 30 wt%, the polymer can't form its own crystal phase although it is sufficient to affect the glass transition and crystallization process of the matrix. But small amount of one component that was included in the other polymer matrix has a considerable effect on T_m of the major component.

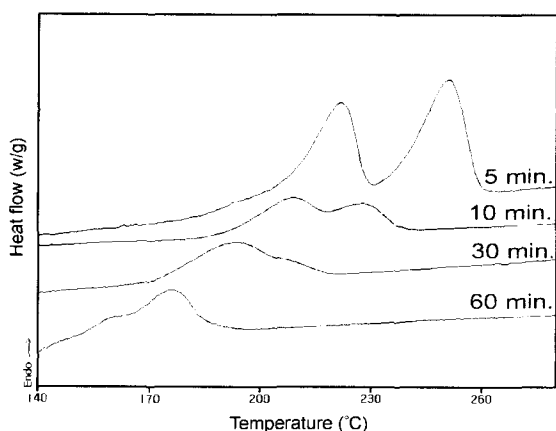
As can be seen in the melting behavior of PTT/PET blends, the blends possessed characteristics of PET when PET content is over 50 wt% in the blends, and the blends possessed characteristics of PTT when PTT content is over 50 wt% in the blend

Figure 4 shows the melting behavior of PTT/PET blends according to blending time and blend ratios. When blending time is within 10 min, double melting peaks can be observed for the blends. However, the double melting peaks were merged into one broad peak when blend time is over 10 min.

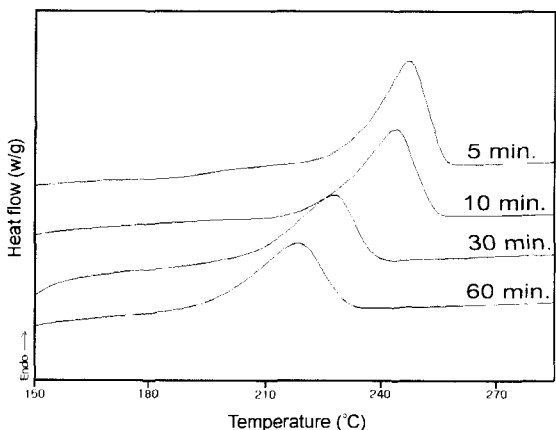
Thermodynamical depression of melting point was exhibited in PTT/PET blends and melting point of blends decreased with the increase of blending time. It should be noted that all the



(a) PTT/PET (7/3 wt%) melt blends

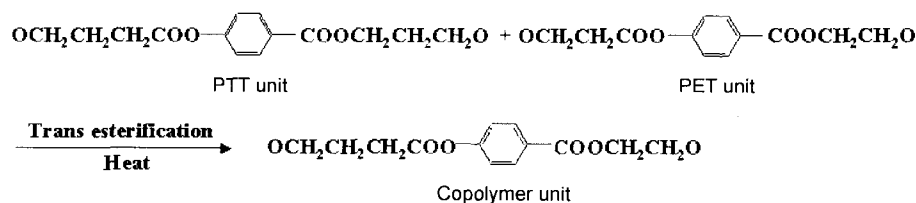


(b) PTT/PET (5/5 wt%) melt blends



(c) PTT/PET (3/7 wt%) melt blends

Figure 4. Melting behavior of PTT/PET melt blends at 275 °C.



Scheme 3. Ester-interchange reaction.

melting behaviors are mainly related to the transesterification.

TGA (Thermogravimetry Analysis)

TGA was used to investigate the thermal decomposition behaviors of PTT/PET blends. The TGA results of 1:9, 3:7, 5:5, 7:3, and 9:1 PTT/PET blends are shown in Figure 5. It is shown that the thermal decomposition temperatures of PTT/PET blends increase with increasing PET contents and one step thermal degradation was shown for all of the blends. The TGA result of PTT/PET blends indirectly suggests that the two polymers are miscible and the composition of blends affects thermal property.

Ester-interchange Reaction

Scheme 3 shows ester-interchange reaction in PTT/PET blend.

The intermolecular transesterification between PTT and PET was investigated by ¹³C-NMR methods. The result shows in Figures 6 and 7.

In the Figure 6, the propanediol 1,3-carbon peaks of PTT appear at 63 ppm(a), ethylene carbon peak of PET appears at 66 ppm(b), and 2,3,5,6-carbon of phenyl group appears at 132 ppm(f,g). 4-carbon peak of phenyl group in the PET/PTT blend appear 134 ppm(x).

The characteristic peak of transesterification was shown in Figure 8. The degree of transesterification in PTT/PET blends can be determined from the region corresponding to the

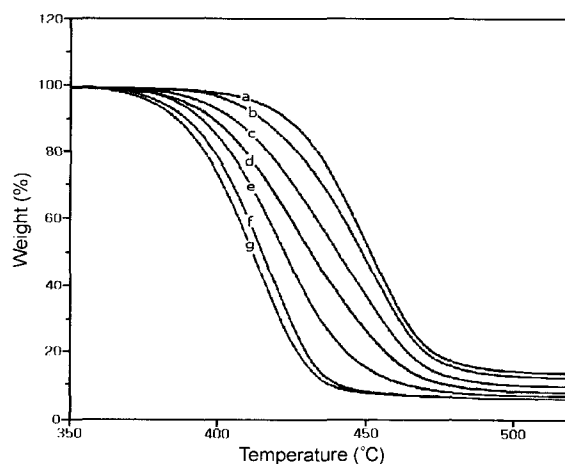


Figure 5. Thermogravimetry analysis of PTT/PET melt blends; (a) Pure PET, (b) 1/9, (c) 3/7, (d) 5/5, (e) 7/3, (f) 9/1 ratio, (g) Pure PTT.

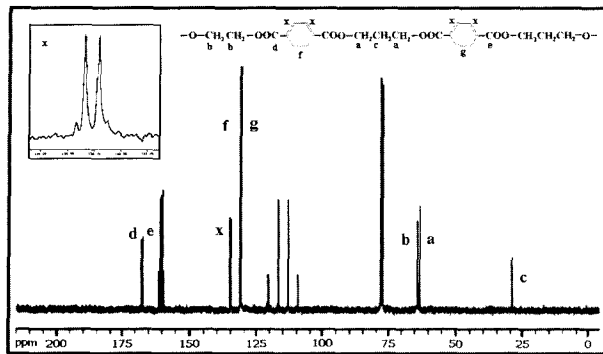


Figure 6. ^{13}C -NMR spectrum of PTT/PET (5/5 ratio) melt blends.

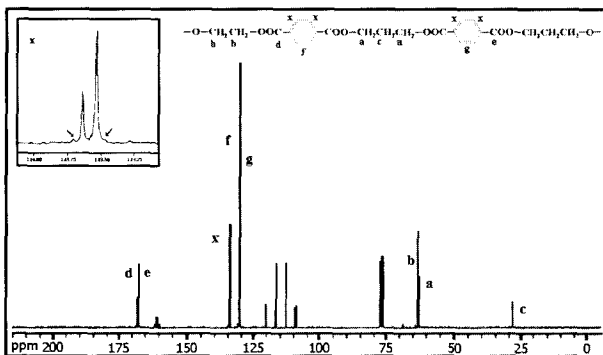


Figure 7. ^{13}C -NMR spectrum of PTT/PET (3/7 ratio) melt blends.

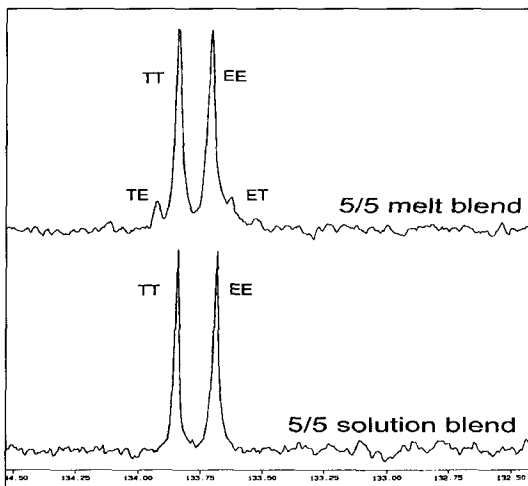


Figure 8. ^{13}C -NMR spectra of (5/5 ratio) melt blends and solution blends.

phenyl unit in the ^{13}C -NMR spectrum. In the solution blends, the doublet peak of phenyl unit was observed, but the peak of phenyl unit in the melt blends split in to a quartet. It was expected that the new peaks would be clearly observed at 133.9 ppm and 133.4 ppm resulting from copolymerization of PTT and PET. In other words, two peaks are evidence of

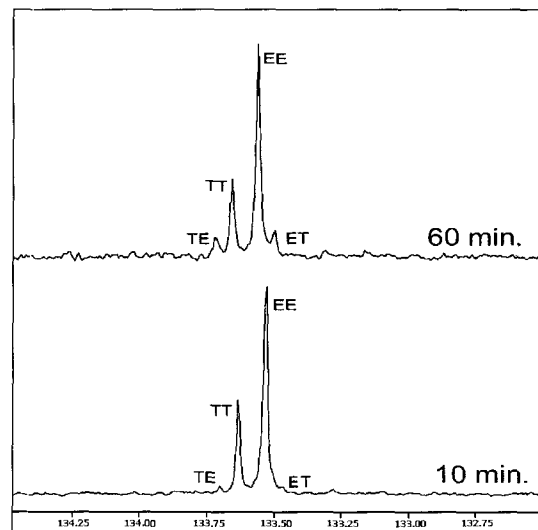


Figure 9. ^{13}C -NMR spectra of PTT/PET (3/7 ratio) melt blends with different blending time.

the fact that ester-interchange reaction occurs between two polymers during the melting process.

Figure 9 shows the peak intensity as a function of blending time. There are many reports regarding the ester-interchange reaction between polyester and polymer such as PET, PBT, PEN etc., in the melt blend[13].

In the PET/PBT melt blends, the relation between randomness and blending time was reported by Backson *et al.*[14]. He has reported that the resonance intensity of the peak, which was found with measuring the amount of hetero sequence, increases with increasing blending time. And he has explained that the degree of transesterification increases with increasing blending time and randomness of PET/PBT melt blends increases with increasing blending time. This indicates that block copolymer was produced by transesterification between two polymers and it was changed from block copolymer to random copolymer with increasing blending time. Therefore, in this study, it was concluded that melting point depression of PTT/PET blend is influenced by the ester-interchange reaction.

Morphology

Figure 10 shows SEM micrographs for freeze-fractured surfaces of the PTT/PET blends. All of these blends show no clear phase separation. It means that the blends are homogeneous because of structural similarity and transesterification between PTT and PET. And PTT rich blends show tougher surface than PET rich blends, but 5/5 ratio blends appear stiff surface than other blends. It is considered that each polymer crystallize competitively in 5/5 ratio blends.

Mechanical Properties

Figures 11 and 12 show the tensile modulus and tensile

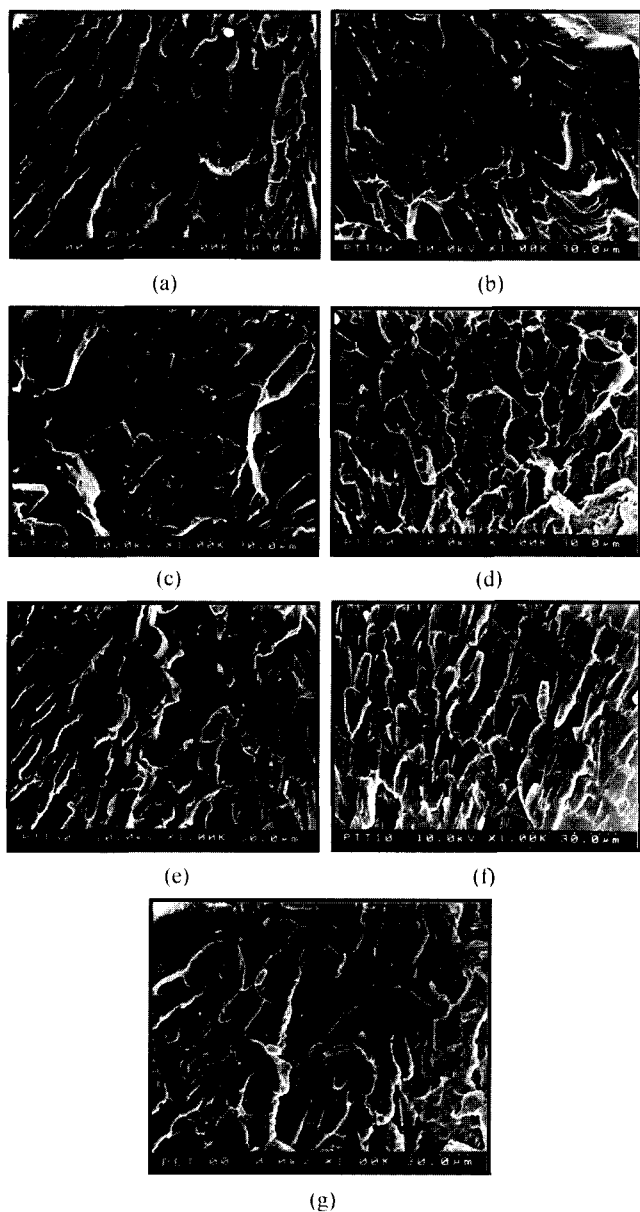


Figure 10. SEM photographs of PTT/PET melt blends; (a) Pure PTT, (b) 9/1, (c) 7/3, (d) 5/5, (e) 3/7, (f) 1/9 ratio.

strength of PTT/PET blends films. For mechanical properties on the PET/PBT blends, Mishra *et al.* has reported that the modulus and tenacity of blends are increasing because of intercrystalline linkage between PET and PBT[7]. In this study, because of the homogeneity of blends, the ultraquenched melt blends have good mechanical properties. The tenacity and elongation of PTT-rich blend film are lowered with increasing PET content but tensile modulus of that is similar to Pure PTT film. In the PET-rich blend film, although tenacity and elongation of film are similar to or slightly higher than pure PET, tensile modulus of film decreased with increase of PET content. It could be explained that smaller amount

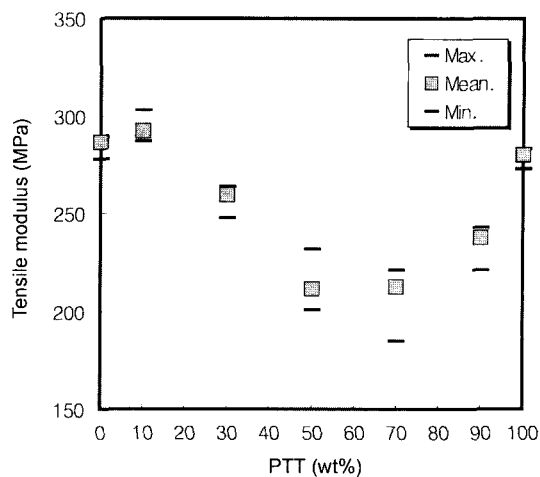


Figure 11. Tensile modulus of PTT, PET, and PTT/PET melt blends film.

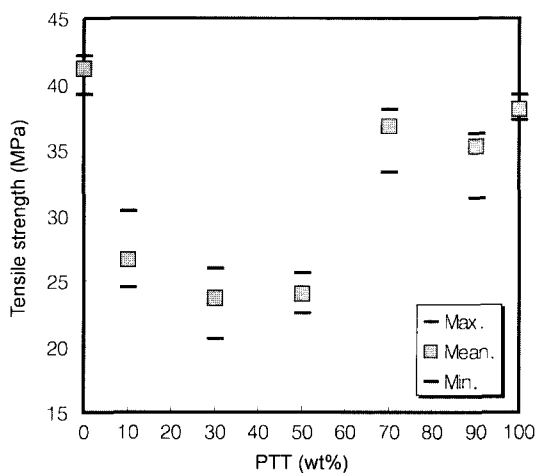


Figure 12. Tensile strength of PTT, PET, and PTT/PET melt blends film.

polymer would play for a detector to larger amount of polymer.

Conclusion

Melt blends of PET and PTT with the composite range 9/1, 7/3, 5/5, 3/7, 1/9 were prepared by a twin screw extruder. Thermal behaviors, mechanical properties, ester-interchange reaction and morphology of the blends were investigated.

It was confirmed that PTT/PET blends have the homogeneous blend system by thermal analysis. PET/PTT blend have a single T_g and single T_{hc} in the all blend composition, and the area of T_g region is similar in all blend composition. For the all blends, a single melting peak was showed and melting point depression was occurred. In particular, 5/5 ratio blend has two endotherm melting peaks. In this 5/5 ratio blend, each polymer component has its own crystal phase and

crystallization of one component disturbs other component. In PTT-rich blends, mechanical properties decrease with increase of PET content. And, in PET-rich blends, tensile modulus decreases with increase of PTT content, but tensile strength and elongation is similar to that of pure PET. The results showed that transesterification occurs between PTT and PET and crystallization of one component interferes with crystallization of other component.

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