CHAPTER V

RESULTS AND DISCUSSION

The purpose of this research is to synthesize poly(PE-b-PP) as a compatibilizer for PE/PP blend. This chapter provides the identification information of the poly(PE-b-PP) and the characterization information of compatibilised PE/PP blends with various poly(PE-b-PP) contents. The thermal properties, mechanical properties and morphology of the copolymer and the blends were obtained and verified.

5.1 Functionalization of PP and PE by hydroxyl group

5.1.1 Chain structure of PE/PP block copolymer diisocyanate linkage

On the basis of this result, a plausible products of the block copolymerization is proposed as shown in (Figure 5.1.1)
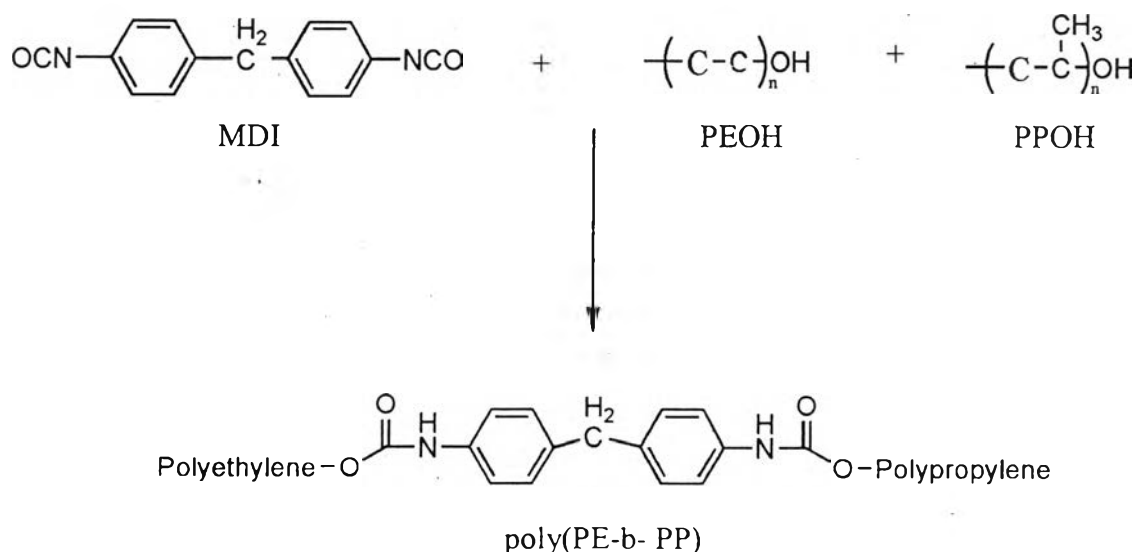

Figure 5.1.1. The block copolymerization

In addition, beside poly(PE-b-PP), there have others 2 byproducts of the reaction which are poly(PE-b-PE) and poly(PP-b-PP). Moreover there are others two products that end chain with hydrogen (not hydroxyl, OH) that are PE, PP and the small amount of remaining reactant, that are PEOH, PPOH. The fractions of these byproducts are hardly to be quantified and it can not be completely fractionated by solvent extraction. Thus unidentified fraction distribution of the block copolymers will be along with what is identified as poly(PE-b-PP) throughout this study. However, the mixture identify as poly(PE-b-PP) had very good phase binding with the melted blend of PP/PE that will be later discuss. Consequently the mixture of poly(PE-b-PP) copolymer in this study poly(PE-b-PP), and various size of PP, PE comprised the phases that will dissolve in the melted blend of PP/PE without any difficulty.

From GPC results, the poly(PE-b-PP) has very wide molecular weight distribution (MWD) as resulted from the reaction of wide MWD of PPOH and PEOH with diisocyanate. In order to confirm the reaction that contribute to the block copolymer of poly(PE-b-PP) in this system, the IR spectrum of block copolymer obtained at 25 ^{0}C is illustrated in Figure 5.1.2. The peak of isocyanate (NCO) transmittance is 1530 cm^{-1}, $v_{c=o \, MDI} = 1711$ cm^{-1}, $v_{NH} = 3404$, 1599 and 814 cm^{-1}. Thus IR spectrum has identified the diisocyante linkage in poly(PE-b-PP) copolymer structure. More over the binding properties of poly(PE-b-PP) can be confirmed in SEM figure followed.

C^{13} NMR were not able to show the spectrum of diisocyanate linkage because of the overlapped peak of benzene rings of MDI and solvent (o-dichlorobenzene), so we could not identify diisocyanate linkage by C^{13}NMR. Furthermore peak of few – NCO- presence in poly(PE-b-PP) can not be observed because of other high peak of large molecular weight of PE and PP obscured the small peaks.
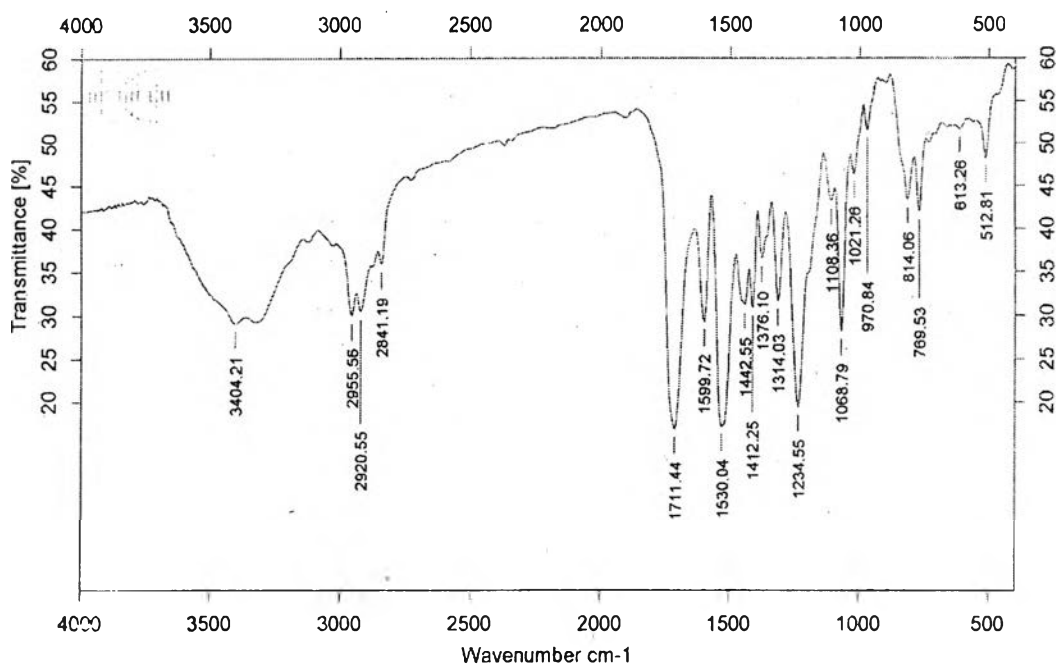
Figure 5.1.2 IR-spectra of poly(PE-b-PP)at 25 °C

It's hard to confirm the existing of urethane linkage by C^{13}NMR because other solvents which not contained the benzene rings are hard to find. The C^{13}NMR of poly(PE-b-PP) , poly(PP-b-PP) and poly(PE-b-PE) were shown were shown in A.1-A.5

All molecular weights of PEOH, PPOH and copolymers were shown in Table 5.1.1. The molecular weights of all poly(PE-b-PE) are different from each others because of the low solubility of copolymer in trichlorobenzene used as solvent in GPC. Similarly criteria applied to all poly(PE-b-PP). The molecular weight of poly(PP-b-PP) can not detect because copolymer can not dissolve in trichlorobenzene. Thus we chose the appropriate molecular weight to represent the copolymer and analyse all results of this work according to the chosen molecular weights.

As shown in Table 5.1.2. The PEOH has larger molecular weight compared to PPOH. Consequently, the molecular weights of poly(PE-b-PP) are higher than PPOH.

The ΔH of the melted blend of pure PE/PP lower than all of the poly(PE-b-PP) addition samples, this implied that the cystallinity of melted blend of pure PE/PP are increased when added with poly(PE-b-PP).

Table 5.1.1 The molecular weight of all synthesized poly(PE-b-PP) for each times.

sample name	Mn	Mw	MWD
PEOH	155,069	1,170,320	7.547073
PPOH	45,347	395,482	8.721203
poly(PE-b-PE)_1	271,251	1,191,696	4.393331
poly(PE-b-PE)_2	23,542	1,009,068	42.862070
poly(PE-b-PE)_3	143,700	1,198,896	8.343020
poly(PE-b-PP)_1	46,624	582,905	12.502200
poly(PE-b-PP)_2	19,622	544,242	27.736403
poly(PE-b-PP)_3	57,550	828,787	14.401066

In other words, the copolymer enhanced the crystallization of both PE and PP in the melted blend of PE/PP. From the highest ΔH, the largest percent of crystallinity is at 6% poly(PE-b-PP) in PE/PP. This may be the results in the highest reinforcement because of the formed crystal that contribute to the highest tensile properties. In addition, portion of Tm that represented the PP crystal in PE/PP were increased from pure PE/PP in all the composition of added poly(PE-b-PP). Usually Tm describing the quality of crystallinity in polymer blend (form crystalline and decrease entanglement polymer blend). This can be concluded that the addition of poly(PE-b-PP) alter both the quality and quantity of the crystallinity of PE/PP.

The chain structure of polymer blend and block copolymer was studied by DSC analysis of crystalline segregated samples. After stepwise annealing of the samples at different temperatures, the long PP and PE segments can form crystalline lamellae of different thickness according to their sequential lengths, and these lamellae will melt at different temperatures [31]. By recording the endothermic curves of the polymer blend and block copolymer in a DSC scan, we are able to judge the sequential contribution of PE/PP blend and role of poly(PE-b-PP) in crystallinity as shown in figure 5.1.3.

The melting peak at about 130-140 °C correspond to the melting temperature of PE crystal and the peak above 140 °C correspond to the melting temperature originate from PP crystal. However the appearance of the curves of PE/PP blend and poly(PE-b-PP) are similar. In the cases of adding poly(PE-b-PP) to PE/PP blend, the melting temperatures of PP increase (as shown in Table 5.1.2.)

Table 5.1.2 Characterization of polymers

polymer	Mw×10^{-4a}	MWD^a	Heating 1(°C)^b				Cooling (°C)^b			Heating 2(°C)^b			
			Tm$_{1.1}$	Tm$_{1.2}$	Tg$_1$	ΔH$_1$ (J/g)	Tc$_1$	Tc$_2$	ΔH$_2$ (J/g)	Tm$_{2.1}$	Tm$_{2.2}$	Tg$_2$	ΔH$_3$ (J/g)
PEOH	117.3	7.5	145	nd	nd	181.4	110	nd	123.6	137	nd	nd	118.9
PPOH	39.5	8.7	nd	156	-5	40.7	100	nd	58.8	nd	154	-5	51.4
poly(PE-b-PE)	na	Na	135	nd	nd	255.4	108	nd	83.2	132	nd	nd	84.1
poly(PP-b-PP)	na	Na	93	158	-7	32.5	102	nd	28.7	nd	153	-8	29.7
poly(PE-b-PP)	58.3	12.5	130	153	-6	71.7	113	120	96.7	129	152	-7	59.3
PE/PP+ 0%poly(PE-b-PP)	32.4	6.1	135	151	-6	68.3	98	110	67.1	135	151	-6	64.7
PE/PP+ 3%poly(PE-b-PP)	na	na	136	163	nd	131.6	111	nd	133.7	134	164	nd	137.3
PE/PP+ 6% (poly(PE-b-PP)	na	na	138	166	nd	137.9	109	nd	134.7	138	164	nd	137.8
PE/PP+ 12%poly(PE-b-PP)	na	na	138	165	nd	122.9	109	nd	122.3	136	163	nd	122.3
PE/PP+ 20%poly(PE-b-PP)	na	na	137	164	nd	119.9	109	nd	120.9	136	164	nd	113.9

^{a} Determined by gel permeation chromatography, PS standard
^{b} Determined by DSC
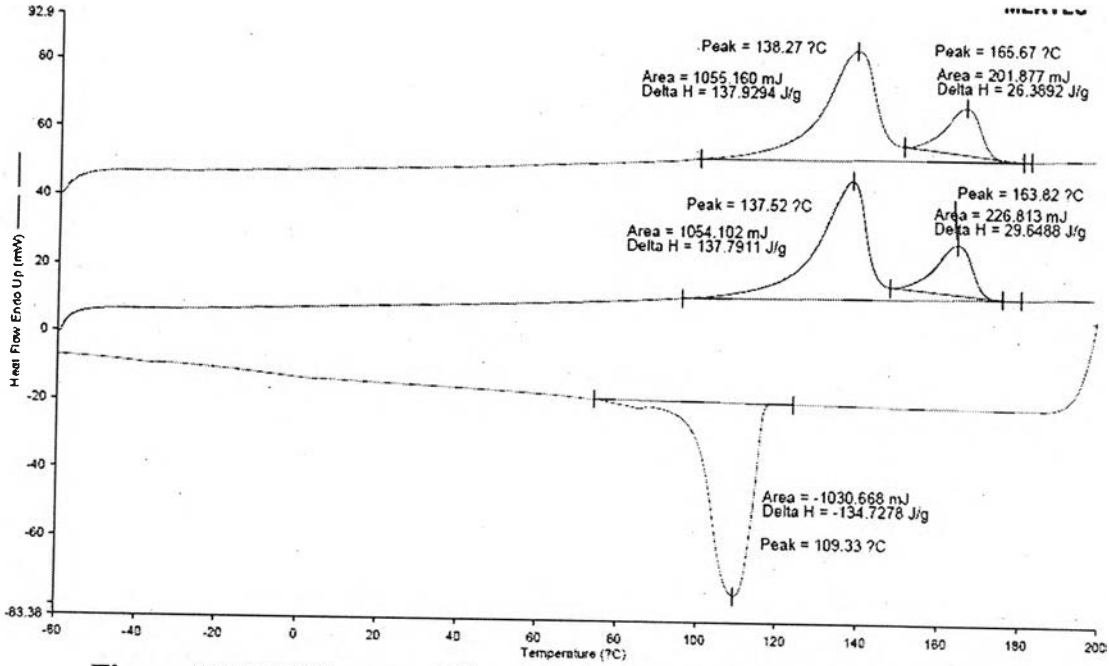na not available
nd not detected

Figure 5.1.3 DSC curve of the addition of 6%poly(PE-b-PP) to PE/PP blend .
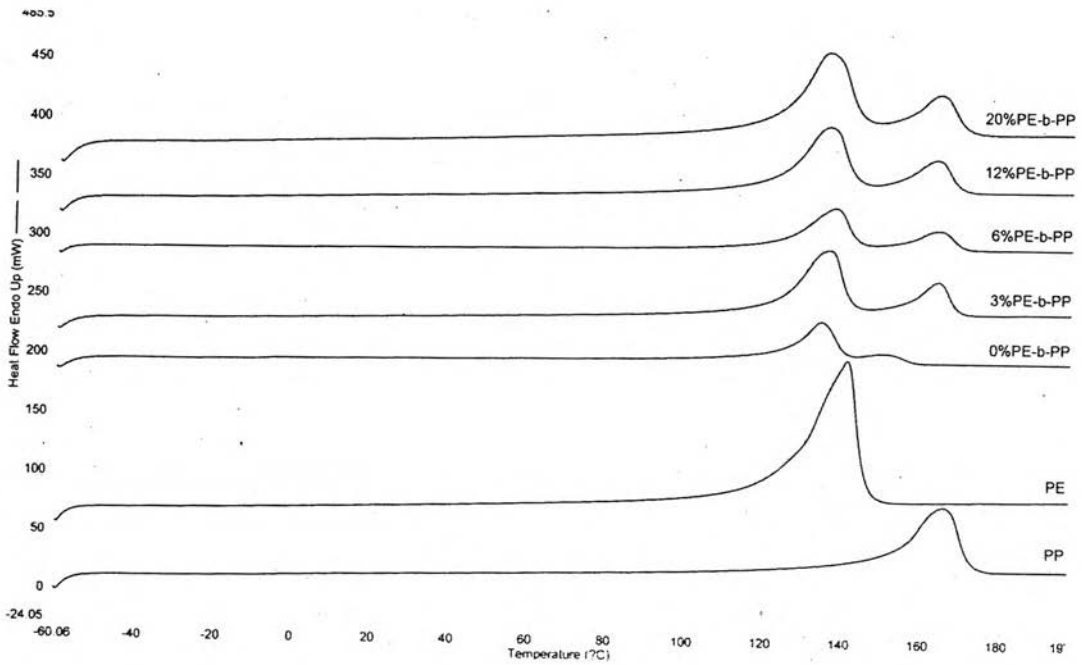

Figure 5.1.4 DSC endotherms of PP/PE blend , poly(PE-b-PE) and addition of

poly(PE-b-PP) to PE/PP blend after thermal segregation treatment.

5.2 Mechanical Properties

5.2.1 Tensile mechanical properties

The tensile mechanical property was measured by tensile testing machine and each sample of polymer blend were tested for five samples and selected the maximum tensile strength from five samples. Figure 5.2.1 shows the tensile stress and tensile strain of uncompatibiliesd PE/PP, the results of each uncompatibilised PE/PP blends are rather different because if the sample has any little defect (bubbles, cracks, scratch) it will effect the tensile strength results.
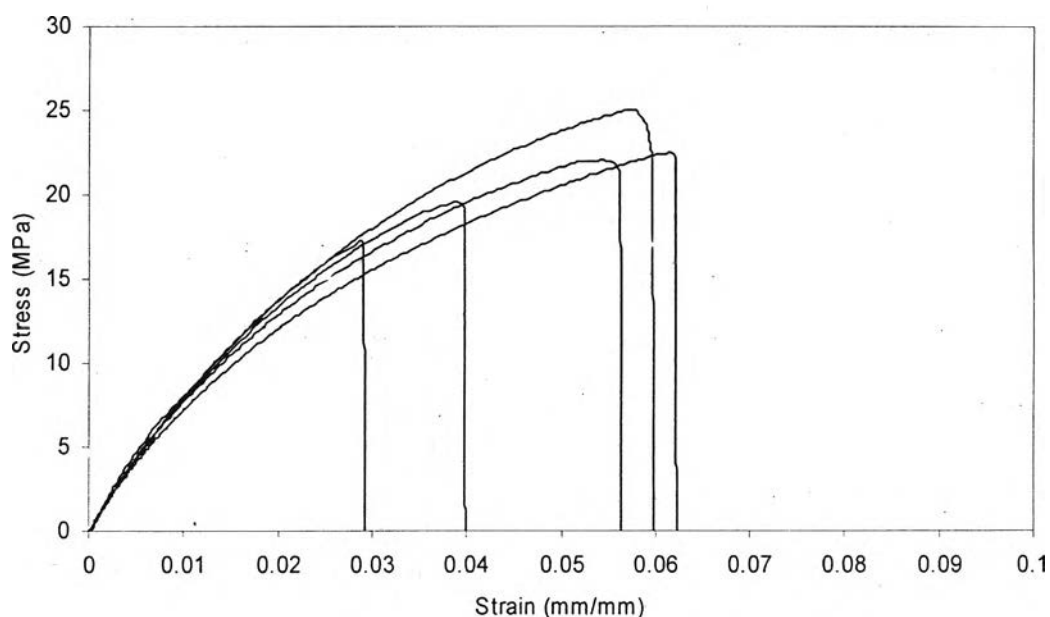
Figure 5.2.1 Tensile strength of PE/PP+ 0%poly(PE-b-PP)
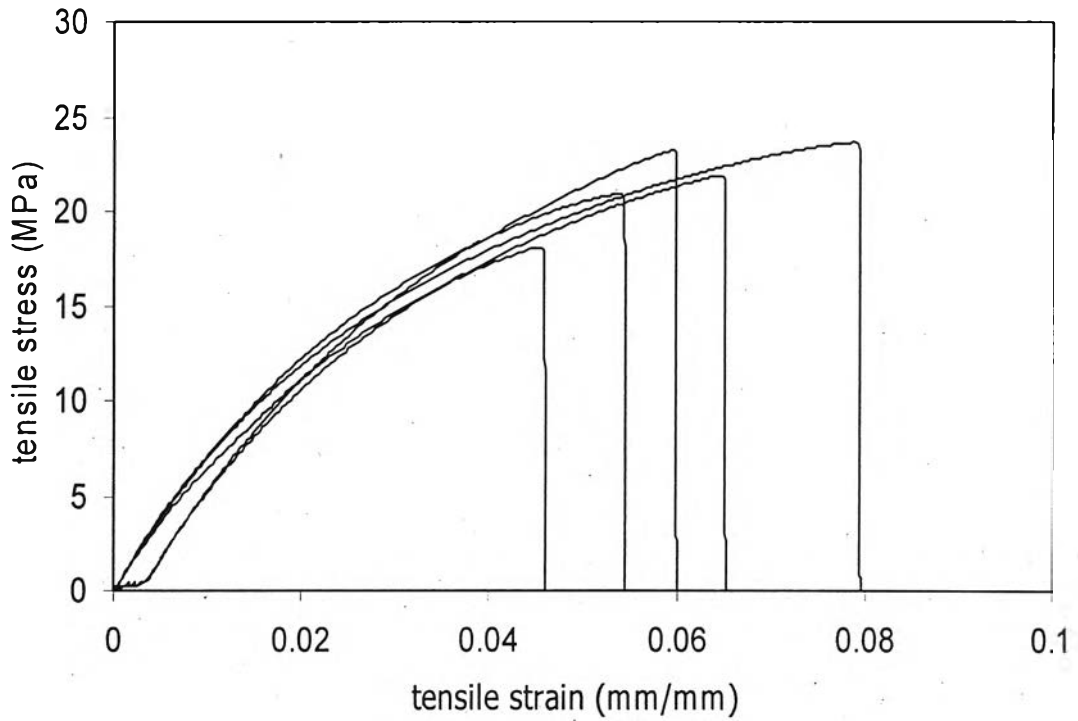
Figure 5.2.2 Tensile strength of 3% poly(PE-b-PP) in PE/PP blend
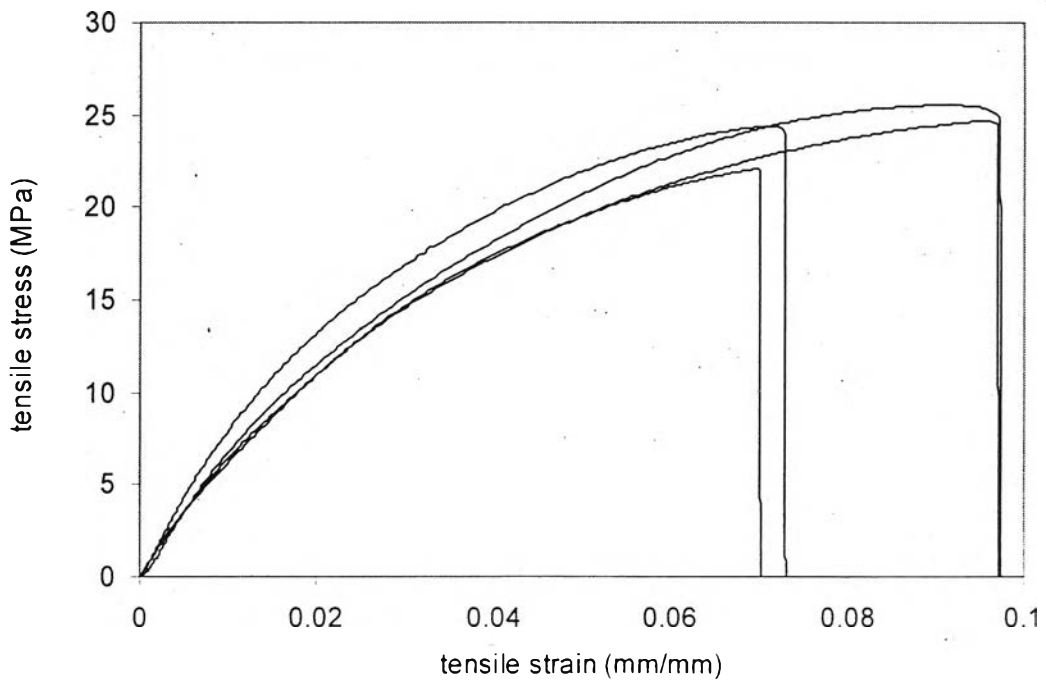

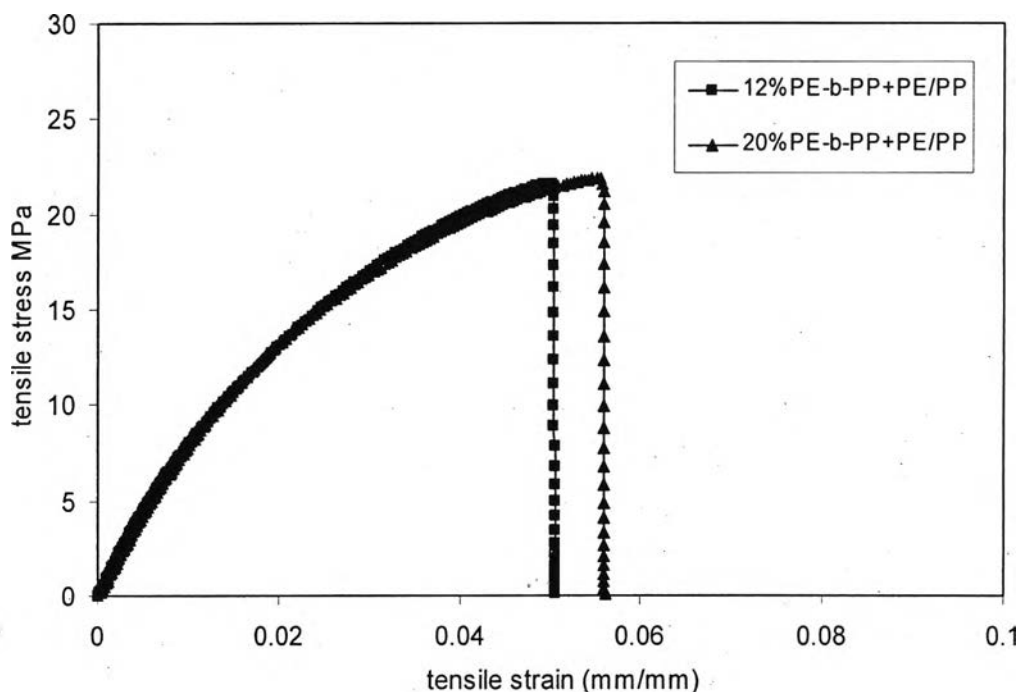**Figure 5.2.3** Tensile strength of 6% poly(PE-b-PP) in PE/PP blend

Figure 5.2.4 Tensile strength of 12% poly(PE-b-PP) and

20% poly(PE-b-PP) in PE/PP blend

Figure 5.2.2-5.2.4 show the tensile strength of 3, 6, 12 and 20% poly(PE-b-PP)

in PE/PP blends. There is only one sample for each 12 and 20% poly(PE-b-PP) in

PE/PP blends due to insufficient poly(PE-b-PP). Thus the only one results of these

tensile strength of 12 and 20% poly(PE-b-PP) , are represented the tensile strength of

these compositions and they may be inaccurate compared to as 5 samples of the low

concentration samples.

The results of tensile stress tests are shown in Figure 5.2.5. As the

concentration of poly(PE-b-PP) in melted blend of pure PE/PP increased, both the

tensile strength and the elongation at break increased. These show that the addition of

poly(PE-b-PP) to PE/PP can improve the reinforcement of polymer by increasing the

interfacial adhesion between PE and PP. At 6% poly(PE-b-PP) in PE/PP, the highest

tensile stress of the blend occurred, which resulted from more stiffness and toughness

of the samples. Thus the tensile properties of poly(PE-b-PP) in PE/PP were in agreement with DSC results as we discussed above that the 6%wt poly(PE-b-PP) has the most reinforcement characteristics. The reasons of decreasing tensile strength and elongation at break at 12% and 20% poly(PE-b-PP) contents might be because of the lower percent crystal in the samples together with the increase of PE, PP pure from poly(PE-b-PP) that have the higher molecular weight than the commercial PE/PP. The amount of high molecular weight might result in the more incompatible of PE/PP.
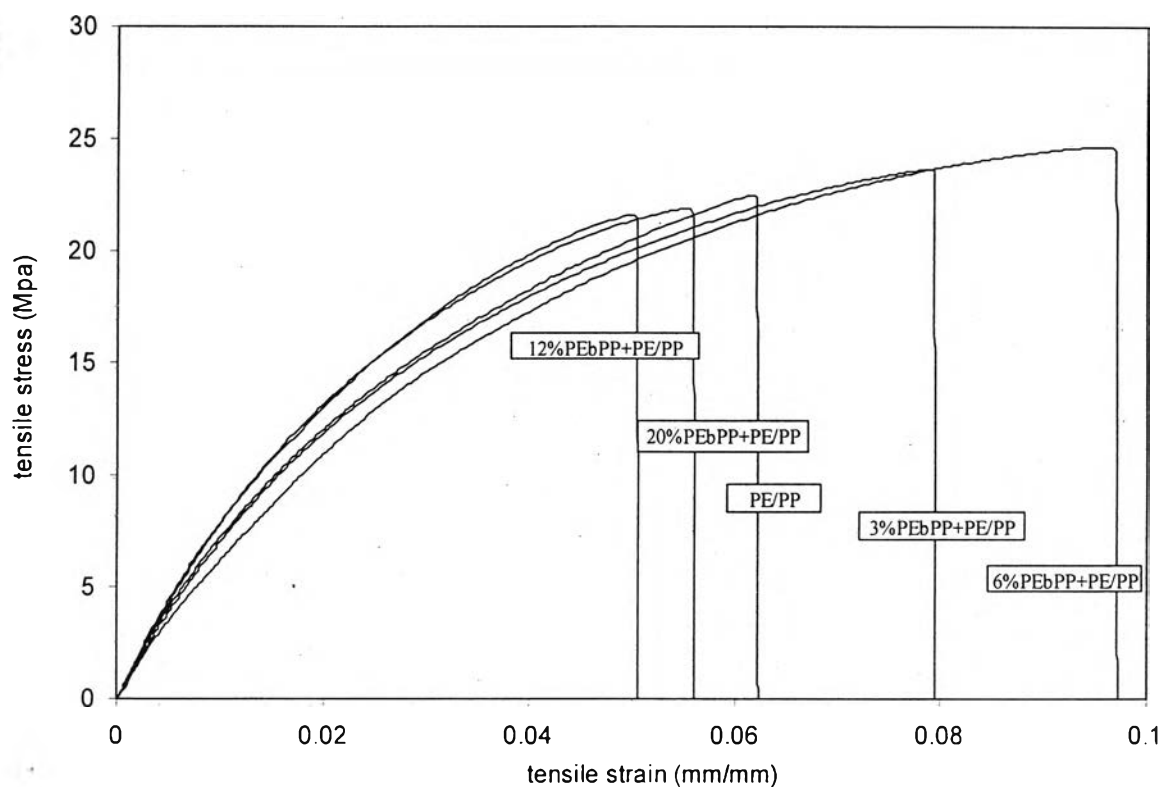

Figure 5.2.5 Additive effect of poly(PE-b-PP) to PE/PP blend on stress -strain behavior at 25 ^{0}C

5.2.2 Dynamic mechanical properties

Figure 5.2.6-5.2.8 compared the effects of temperature on the dynamic mechanical properties of compatibilized polymer blend. The DMA properties were measured for both pure components and melted mix of the pure components (PP, PE, PE/PP blend) and their physical blends (of PE/PP) with various poly(PE-b-PP) contents at 1 Hz. From Figure 5.2.6 , the compatibilized PE/PP blends show that the storage modulus (E') that decreased with increasing temperature as usual in thermoplastics. At low temperature DMA, PE has more stiffness and strength properties than PP especially below 0°C. In the melted blend of PE with PP, the moduli are lower than both pure components because PE and PP are immiscible and strong phase separation occurred. As already proof that PE and PP were immiscible because of structural consideration, though both exhibit the same spherulitic morphology, the two polymers may not be compatible in bulk since polyethylene crystallizes in the more stable orthorhombic form whereas isotactic polypropylene crystallizes in the monoclinic α-form thus the decrease of interfacial adhesion follows which causes loss of the mechanical properties of the blend.[32] After adding poly(PE-b-PP) to PE/PP, the storage modulus of various compositions of poly(PE-b-PP) all increased from the pure PE/PP at all temperature. The maximum of the average storage modulus was at 12%wt poly(PE-b-PP) in PE/PP blend. At 20%wt poly(PE-b-PP) in PE/PP, the samples are more ductile and less stiff than at 12% poly(PE-b-PP) content because the blend has too high portions of high molecular weight of PE, PP that contaminated in poly(PE-b-PP). As usual, the portions of high molecular weight in the blend will result in phase separation of the high molecular weight species easier than low molecular weight portions [33].

From the loss modulus (E'') as shown in Figure 5.2.7, a α relaxation (indicating strong mobility of polymer molecules) can be seen for all compatibilized polymers and virgin PE, PP. These α relaxations, indicated by the peak in the E'' curves, occur at temperatures ranging from -115 to -100 °C and from -20 to 20°C for compatibilized polymers. For virgin PE/PP, relaxation temperatures occur at temperature ranging from -130 to -120°C and from -50 to 20 °C, which are lower than when consisted of poly(PE-b-PP). This showed that the a relaxation temperature of PE/PP blends composed of poly(PE-b-PP) increased due to increased in percent of crystallinity and less flexible amorphous part remained.

Figure 5.2.8 shows the effects of temperature on the tan delta responses of various blend and virgin PE/PP. It's well known that block copolymers should exhibit the glass transition of each of the respective homopolymer component as same as pure polymers [33,34]. The Tm above 30 °C has contribution for both PP and PE crystalline segments[35,36]. The $Tg2$ relaxation between -20 °C and +20 °C is the glass transition of polypropylene [35]. The $Tg1$ peak at about -125 °C represents the relaxation of the methylene group of PE.[36] Both Tg of PE and PP components in compatibilised PE/PP (with poly(PE-b-PP)) increase when compare with virgin PE/PP. For pure PE/PP blend, value of tan δ is high according to high quantity of amorphous phase, as has been concluded from Table 5.2.1. The lower prediction of Tg and the high magnitude of tanδ might result from the increase in the free volumes of the immiscible virgin PE/PP blend that directly affected the increase flexibility of the amorphous part when higher free volume obtained. The addition of poly(PE-b-PP) in PE/PP increase the Tg,Tm to the value of the pure component PE and PP. Because of the compatibilizer, the quantity of amorphous reduces while increase the
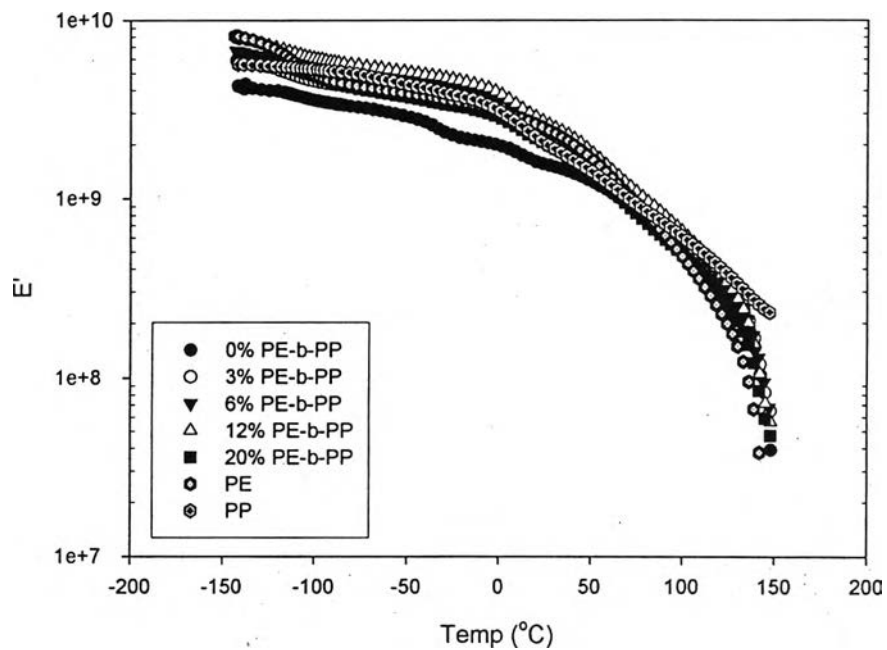
Figure 5.2.6 DMA curves (storage modulus (E') and temperature) for PE/PP and compatibilised PE/PP
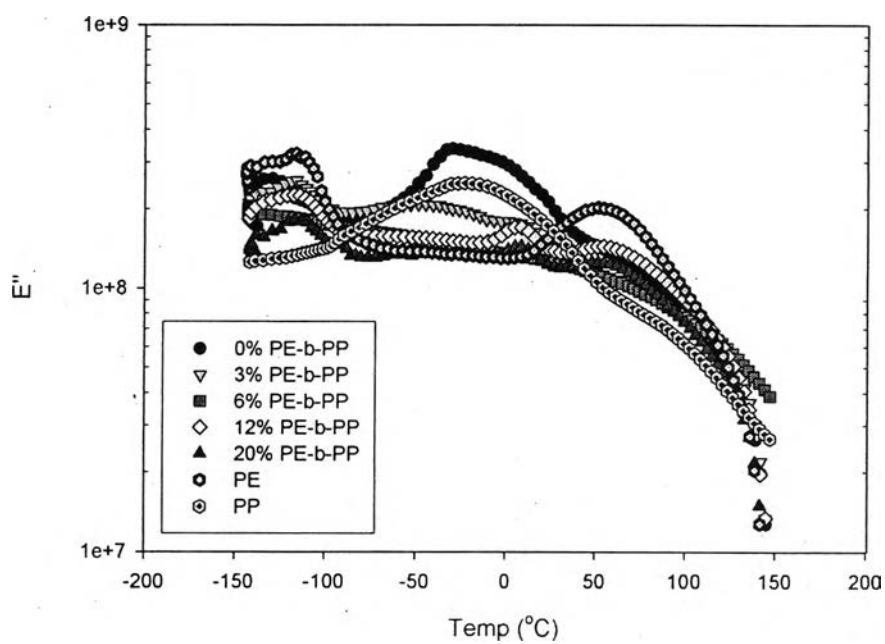

Figure 5.2.7 DMA curves (loss modulus (E'') and temperature) for PE/PP and compatibilised PE/PP

crystallinity of PE and PP component. The smaller amorphous exhibit the higher temperature for relaxation that contribute in the higher Tg than the pure PE/PP when added poly(PE-b-PP).
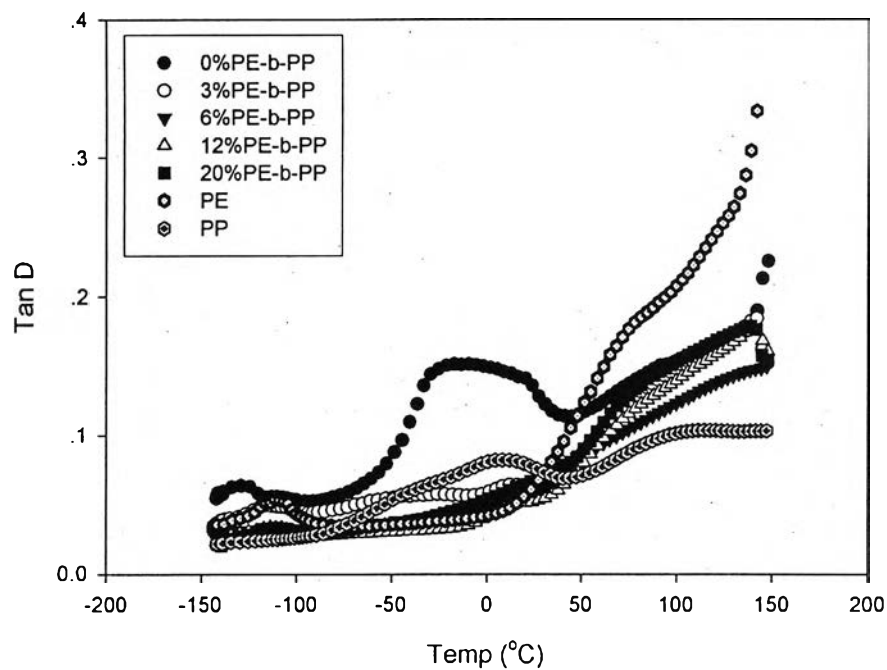
Figure 5.2.8 DMA curves (tanδ and temperature) for PE/PP and compatibilised

PE/PP

Table 5.2.1 Prediction of Tg,Tm from DMA experiment from Figure 5.2.8

| polymer	Tg_1	Tg_2	Tm
PE	-110	nd	nd
PP	nd	12	nd
0% poly(PE-b-PP)	-128	-2	nd
3% (poly(PE-b-PP)	-110	15	138
6% poly(PE-b-PP)	-110	12	141
12% poly(PE-b-PP)	-110	12	138
20% poly(PE-b-PP)	-110	16	141

5.3 Morphology

According to SEM picture, it clearly shows the differences of the rough surface particles and the bridge formation within PP matrix of PE/PP blend which continuously changed according to the concentration of poly(PE-b-PP). The addition of poly(PE-b-PP) to PE/PP blend vividly shows the smaller phase particles size as increased concentrations. Many studies [37-40] on polymer alloys have shown that for multiphase polymer systems, the toughening effect is determined by two factors. Firstly, the smaller the particles and the narrower the particles size distributions are, the better impact strength is. Secondly, the stronger is the adhesion between particle and the matrix; the better is the impact properties.

The SEM micrographs of compatibilized PE/PP blends (3%, 6%, 12%, 20% poly(PE-b-PP)) can be shown in Figure 5.3.1-5.3.2. Figure 5.3.1 shows the tensile fracture of PE/PP and compatibilised PE/PP, while indicated that the interfacial adhesions, and therefore the compatibility of the PE and PP phases, are better than uncompatibilized PE/PP. In room temperature fracture experiments, the PE are in the form of tough rubbery polymer compare to PP. These might be shown as the stretch rubbery structure in the blends. The cryogenic fracture of the similar blends will result in the clear domain size because at the cryogenic temperature both PE/PP are in the glassy states and the fractures cut directly to the cross-sections of the segregation size in the blends.
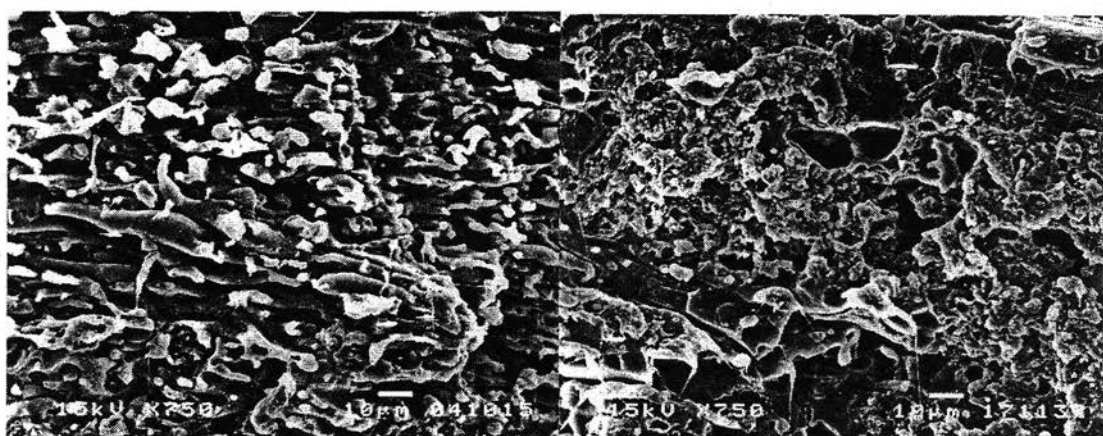
Figure 5.3.2 shows the cryogenic fracture of PE/PP and compatibilized PE/PP, while indicated that the clearly decrease domain sizes (dispersion of PE in PP) and finer particle size distributions. As might be confirmed by the SEM, the phase segregation decrease deliberately but the clear second dots of PE/PP are capture in the

12%, and 20%wt poly(PE-b-PP) which might be the reason for the weaker interfacial ability than the 6%wt poly(PE-b-PP). Those samples have lower tensile properties than the 6%wt poly(PE-b-PP). These phenomena can be confirmed by mechanical properties. However, the DMA properties of 12%wt poly(PE-b-PP) showed the superior properties than all the blends. This might be because of the amorphous part of 12%wt poly(PE-b-PP) are larger than the 6%wt poly(PE-b-PP), but the existing of the small segregations according to the high molecular weight PE could lower down the tensile properties of the 12%wt poly(PE-b-PP). As can be observed from the GPC data, the amount of PE large molecular weight portions from PEOH and poly(PE-b-PE) can give the separated phases of segregations in the blend especially with the high content of poly(PE-b-PP) in the blend.
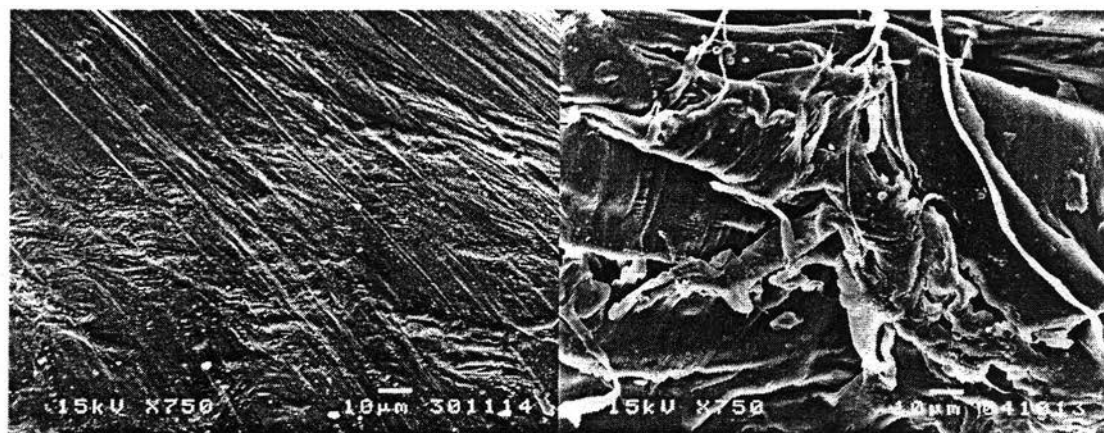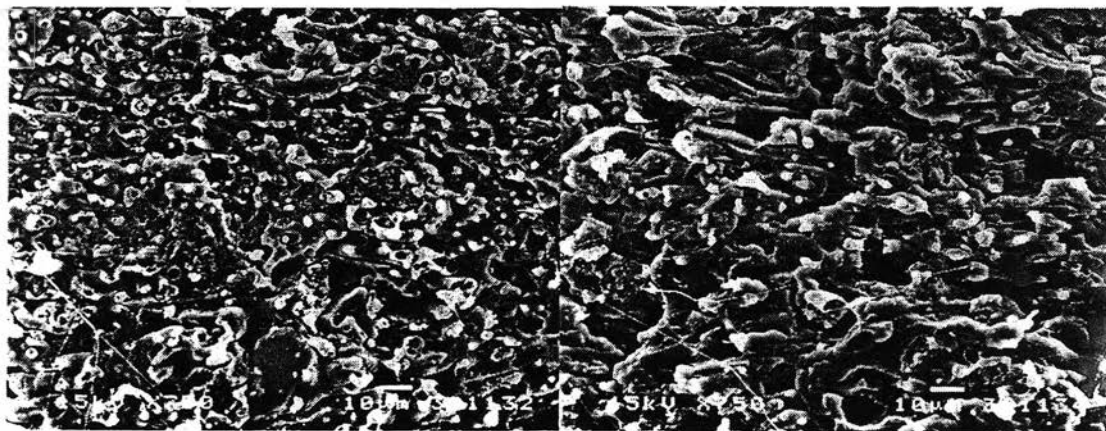
Figure 5.3.1 SEM of tensile fracture surface of a)PP b) PE/PP+ 0%poly(PE-b-PP)

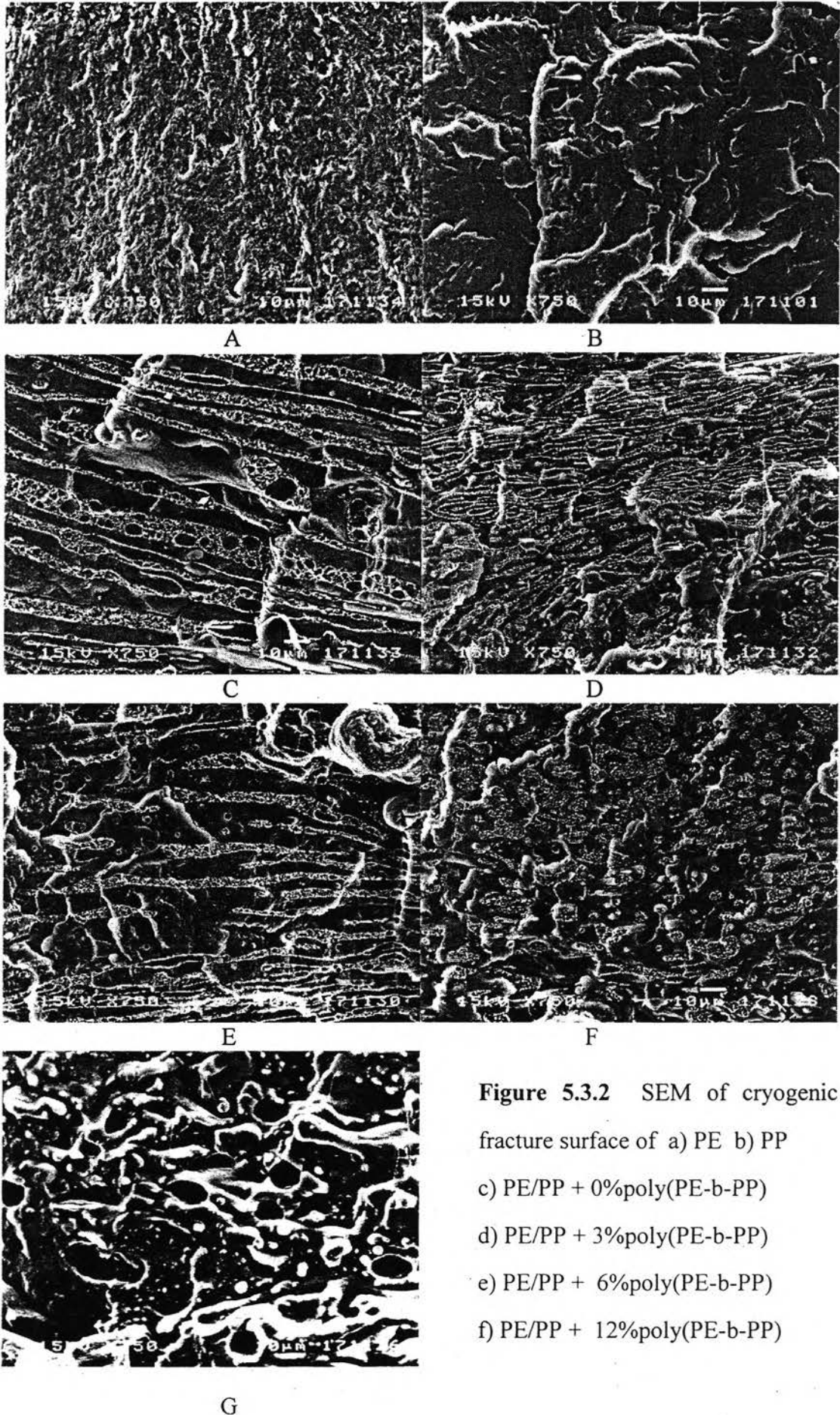c) PE/PP+ 3%poly(PE-b-PP) d) PE/PP+ 6%poly(PE-b-PP) e) PE/PP+ 12%poly(PE-b-PP) f) PE/PP+ 20%poly(PE-b-PP)

Figure 5.3.2 SEM of cryogenic fracture surface of a) PE b) PP
c) PE/PP + 0%poly(PE-b-PP)
d) PE/PP + 3%poly(PE-b-PP)
e) PE/PP + 6%poly(PE-b-PP)
f) PE/PP + 12%poly(PE-b-PP)