

CHAPTER V

RESULTS AND DISCUSSION

This chapter provides information about the results concerning the polymerization reaction conditions such as polymerization temperature, ethylene feeding pressure, and characteristics of copolymers obtained and influence of poly(P-co-EP) content on thermal and mechanical properties of PP/ poly(P-co-EP) polymer blend at room temperature and low temperature.

5.1. Synthesis of copolymer

5.1.1 Polymer synthesis condition

All synthesized conditions and name definitions of synthesized polymers are shown in Table 5.1. Polymers are synthesized in gas phase polymerization at 30 psi constant propylene feeding pressure by $\text{TiCl}_4/\text{MgCl}_2/\text{DEP-TEA}$ catalytic system. Polymerization progress can be observed through mass flow meter.

The effects of ethylene feeding pressure and ethylene cooperated polymerization time were investigated in the range of 50 to 70 psi and 0 to 60 min respectively. The polymerization temperatures were in the range of 10 to 60 C°. The copolymerization was performed in hexane, 7×10^{-5} M of Titanium concentration and 0.305 M of triethylaluminium with 167 of $\text{Al}_{(\text{TEA})}/\text{Ti}$ molar ratio and 30 ml total solution volume.

Firstly, the pure polypropylene was fed to the reactor for 10 mins and the gas changed to ethylene abruptly and the fed continue for 30 min. before the termination of the catalyst by quench in acidic methanol.

Table 5.1 Polymer name and condition

Sample name	Polymerization temperature (C°)	Ethylene feeding pressure (psi)	Polymerization time (min/min) [P/E]
Polymer 1	60	50	10/60
Polymer 2	40	50	10/60
Polymer 3	10	50	10/30
Polymer 4	10	60	10/30
Polymer 5	10	70	10/30
Polymer 6	10	-	10

5.1.2 Microstructure of copolymer

The microstructures of polymer were investigated by ^{13}C -NMR spectrometer at 120 °C. Sample solution used mixed solvents of *o*-dichlorobenzene and benzene- d_6 . Figure 5.1 shows a typical ^{13}C -NMR spectrum of the synthesized poly(P-*co*-EP) (Polymer5) and Figure 5.2 shows a typical ^{13}C -NMR spectrum of polypropylene (Polymer 6) for comparison. The spectrum of Polymer 5 and Polymer 6 are clearly difference which indicates the cooperation of ethylene in propylene polymer chain in Polymer 5. Moreover, the chemical shift assignment for ^{13}C resonances of Polymer 5 is similar to reported block copolymer obtained by Yoshifumi et al. (Figure 5.3) [12]. From the feed condition and NMR spectrums, we can conclude that copolymer obtained can be characterized as block copolymer.

From the NMR peak integral of methylene and methyl carbons, the mole fractions of propylene/ethylene unit in the block copolymer (Polymer 5) were determined as 37/63 mole% [33-36].

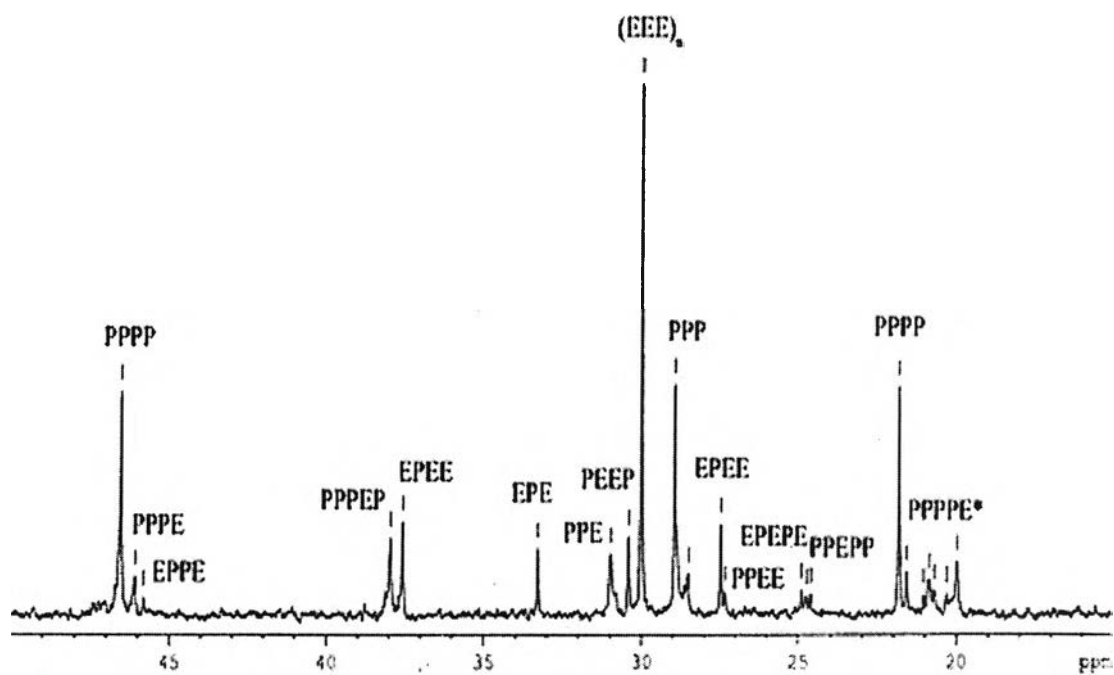


Figure 5.1 ^{13}C -NMR spectrum of the copolymers obtained (Polymer 5 of Table 1)

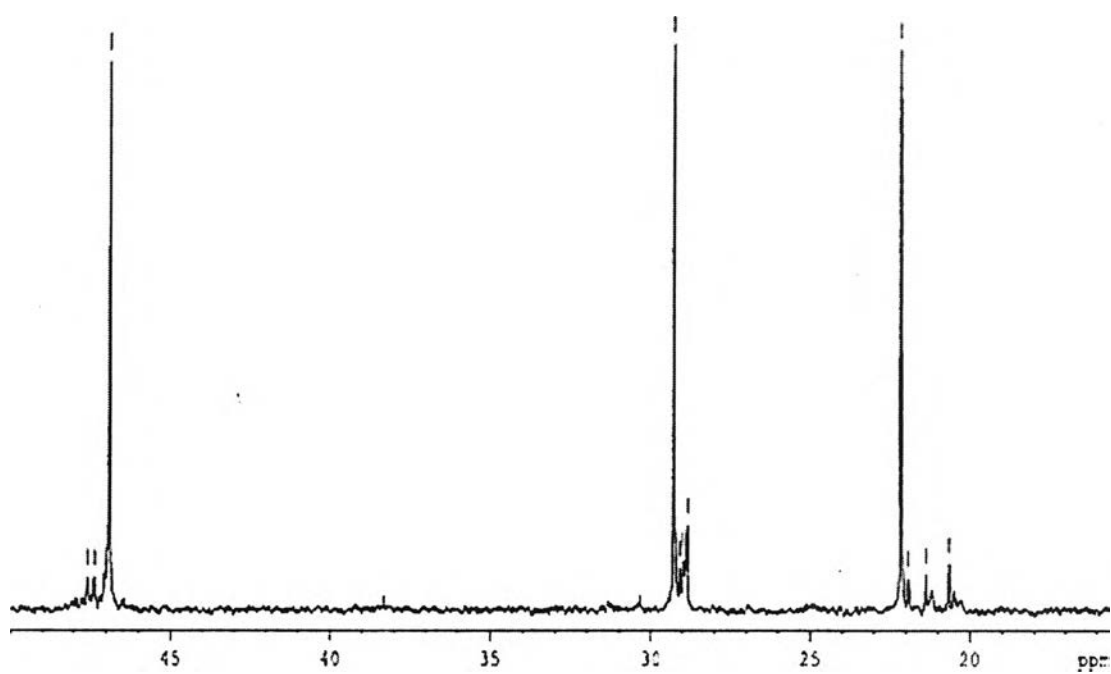


Figure 5.2 ^{13}C -NMR spectrum of the polypropylene obtained (Polymer 6 of Table 1)

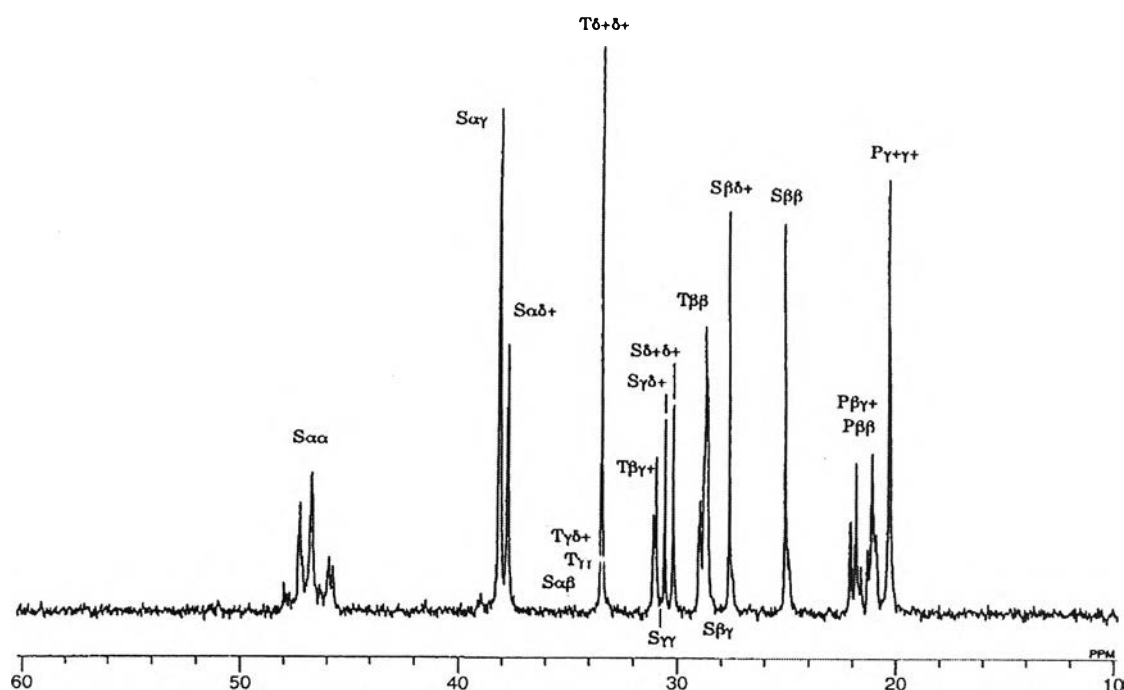


Figure 5.3 ^{13}C -NMR spectrum of the polypropylene *-block-*poly(ethylene-co-propylene) from Yoshifumi Fukui and Masahide Murata reported [12]

From ^{13}C -NMR spectrum, the peak at 21.61 ppm showed the characteristic of propylene unit (P) that has the ethylene unit (E) laid in the adjacent of PPPPE and PPPE which indicated the cooperation of ethylene in the propylene chain. Because the pure propylene was allowed in the reactor at the beginning, the first polymerization in the reactor was the propylene pure chains only (with the duration of 10 minutes). The second step of polymerization allowed ethylene to react in the reactor (with the duration of 30 minutes), so the discovery that ethylene cooperated in the propylene chain will support the formation of the block copolymer of PP and EP in the second stage. These showed that at least some of the PP chain will be survived through the second stage of the reaction and have ethylene incorporation as the consequences. Unfortunately, the variation in the partial pressure of propylene and ethylene during the synthesis prevailed against the exact quantitative calculations of the cooperation of ethylene in the propylene chain.

5.1.3 Thermal properties of copolymer

Table 5.2 showed the effects of copolymerization temperature and feeding pressure of ethylene gas to the reactor on the glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c) of PP and poly(P-co-EP) products obtained from DSC and molecular weight (M_n and M_w) and molecular weight distribution (MWD) obtained from GPC.

The DSC results were operated by heat-cool-hold-heat cycle between -60 to 200 °C at 40 °C/min scanning rate under argon atmosphere. The GPC results were run at 135 °C and used 1, 2, 4-Trichlorobenzene (TCB) as a solvent.

In addition to the NMR result, the DSC graphs showed that there are two phases in the poly(P-*h*-EP) block copolymer. The first phase, PP is dominate and the other phase have the E in contributions. So that DSC results were clearly shown two T_m in the synthesized polymer (Figure 5.4). The DSC curved obtained have three parts which was spitted in each step. Heat 1 represented the first heating which indicated the obtained raw polymer characteristics from reactor. After the first heating, the samples will be subjected to the cooling and T_c was observed. The Heat 2 represented the T_g and T_m that resulted from the cooling which clearly show the two different T_m according to the type of the crystal (Figure 5.5).

From Table 5.2 we can conclude that the higher is the polymerization temperature, the lower is the glass transition temperature. However, synthesized polymer has the dispersed phases of the ethylene-propylene rubber at the reactor temperature of 60 °C. Because at higher temperature, the chain transfer rates (Polymer 1 to Polymer 3) are higher which resulted in shorten the progressive chains. As the consequence, the higher of the feeding ethylene pressure give the lower glass transition temperature (Polymer 3 to Polymer 5). These may result from the low range T_g of EP part of the molecules.

Furthermore, from GPC, the molecular weights of copolymer (Polymer 5) and PP synthesized (Polymer 6) can be shown in Table 5.2. The M_w of Polymer 5 is higher than M_w of polymer 6 because Polymer 5 has the contribution from the ethylene feed gas to extend the PP chain while no ethylene contribution in Polymer 6.

The part of PP in Polymer 5 is similar to what obtain as Polymer 6 because the polymer 6 have the contribution from P as same as Polymer 5 but no contribution from E because the reactions were quenched abruptly after feeding PP. The Polymer 6 was obtained as a blank to represent the PP phases in the copolymer.

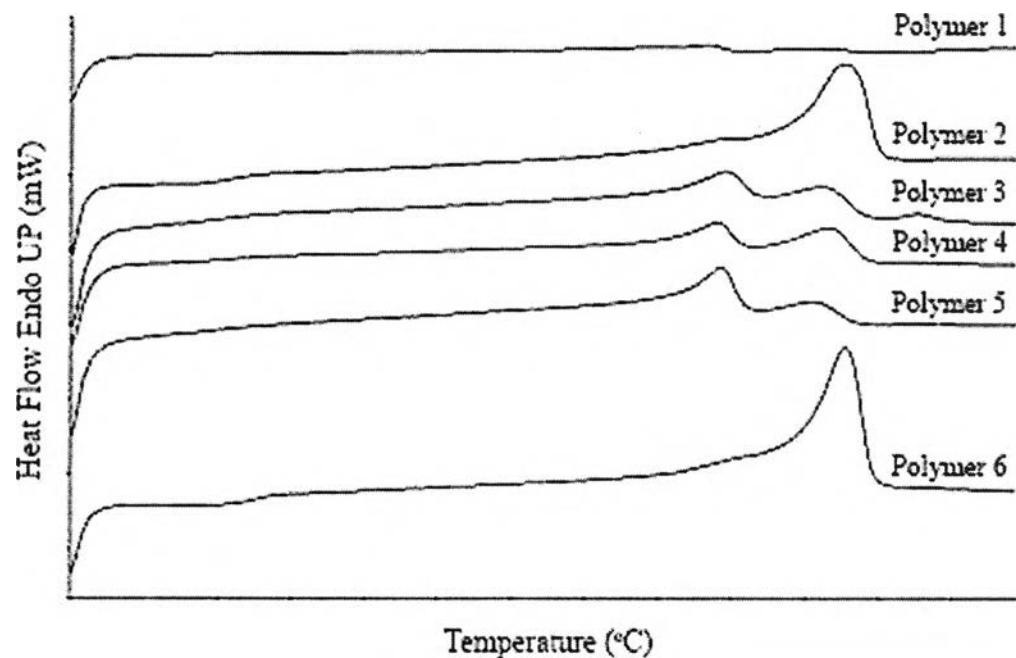


Figure 5.4 DSC Heat 2 result of each polymer

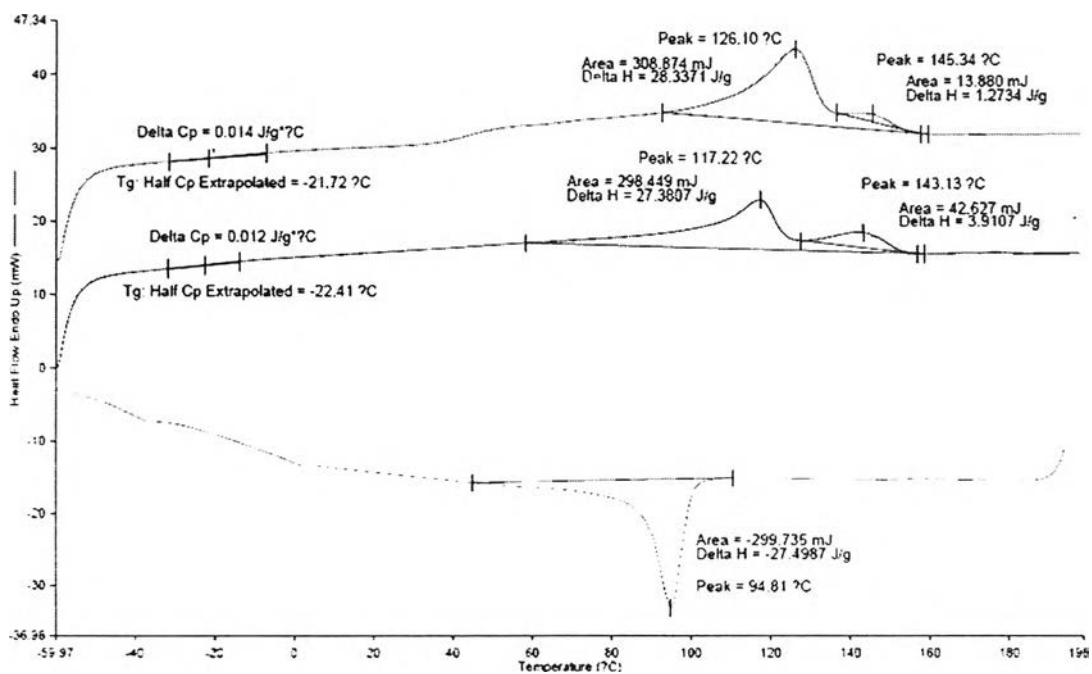


Figure 5.5 DSC curve of poly(P-b-EP) (Polymer 5 of table2)

Table 5.2 Thermal properties and molecular weight of polymer

Polymer ^a	Temp (°C)	P _E (psi)	M _w ^b	M _n ^b	MWD ^b	Heat1 ^c (°C)			Heat2 ^c (°C)			T _c ^c (°C)
						T _g	T _{m1}	T _{m2}	T _g	T _{m1}	T _{m2}	
Polymer 1	60	50	na	na	na	-21.34	nd	nd	-22.51	113.80	147.10	92.04
Polymer 2	40	50	na	na	na	-17.41	123.87	152.35	-17.64	124.97	150.48	99.34
Polymer 3	10	50	na	na	na	-15.88	117.94	147.19	-14.72	118.67	145.70	91.47
Polymer 4	10	60	na	na	na	-16.96	124.99	148.67	-16.53	116.11	146.83	95.93
Polymer 5	10	70	1,732,988	141,528	12.24	-21.72	126.10	145.34	-22.41	117.22	143.13	94.81
Polymer 6	10	-	596,216	65,658	9.08	-9.86	Nd	151.27	-10.85	Nd	149.40	102.25

^a Synthesis by TiCl₄/MgCl₂/DEP-TEA, Al/Ti = 167, propylene pressure feeding constant = 30 psi

^b Determine from GPC

^c Determine from DSC

5.1.4 Morphology of polymers

The SEM micrograph of cryogenic polymer fracture surfaces show difference polypropylene and polypropylene cooperated with ethylene morphology (Figure 5.6). In Polymer 5, morphology of phase separation of block copolymer can be observed. The minor phase of EP can be seen as the phase separated droplets in the fracture surface picture. In the pure polypropylene micrographs of Polymer 6, the droplet characteristics can not be observed. These two phase characteristics can also be observed from the DSC results.

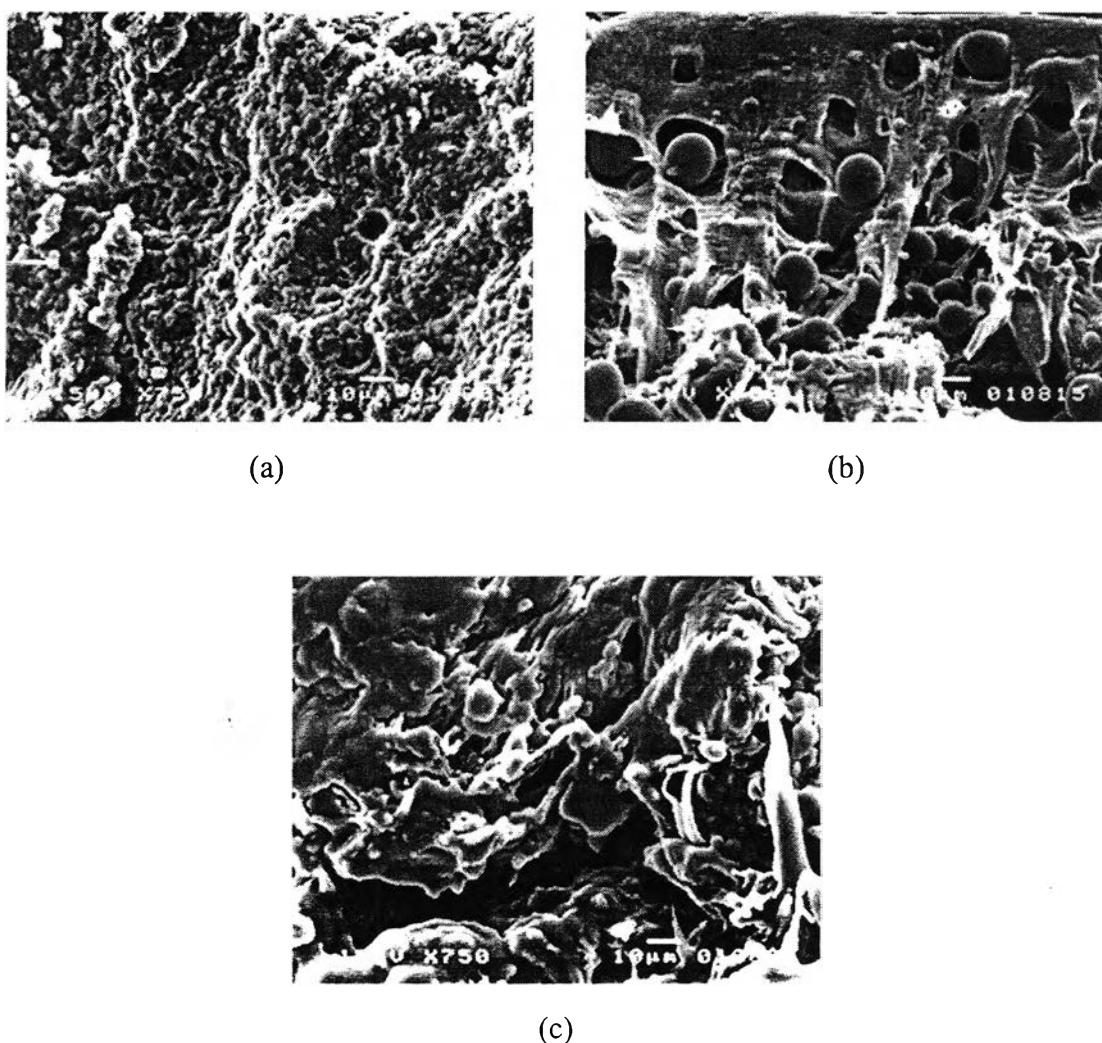


Figure 5.6 SEM micrographs of cryogenic polymer fracture surface: (a) polymer fracture of PP (polymer 6), (b) polymer fracture of poly(P-*b*-EP) (polymer 5) and (c) polymer fracture of poly(P-*b*-EP) (Polymer 3) ($\times 750$)

5.2. Polymer blend

5.2.1 Influence of poly(P-*b*-EP) content on thermal properties

The combinative influences of the blend between poly(P-*b*-EP) and commercial grade PP on T_g , T_m and T_c measured by DSC were shown in Table 5.3. When poly(P-*b*-EP) content in the blend increased, it can be seen that T_g values of the blend decreases from the pure commercial grade PP (EP00) while T_m and T_c values are not clearly different. Generally, T_g is presented the flexibility in amorphous part of polymer. The T_g value of commercial grade polypropylene was approximately 0°C (EP00) and successively decreases when more poly(P-*b*-EP) copolymer was added [18]. The T_g of the polymer blend resulted from the flexible EP part in the amorphous part of the blend. From T_m and T_c results, it can be implied that EP molecule does not directly affect the crystallinity quality of polypropylene [21]. Moreover, ΔH , which indicated the amount of the crystallinity in polypropylene, decreased with increasing poly(P-*b*-EP) content in the blends. In other words, the addition of poly(P-*b*-EP) can reduce the crystallinity of polypropylene and increase the amorphous part of the blends which will affect the toughness of the blend [37].

Moreover, Table 5.3 also showed molecular weight of polymer blends which should have molecular weight between block copolymer (Polymer 5 of Table 5.2) and commercial grade PP (EP00) and increase with increased block copolymer.

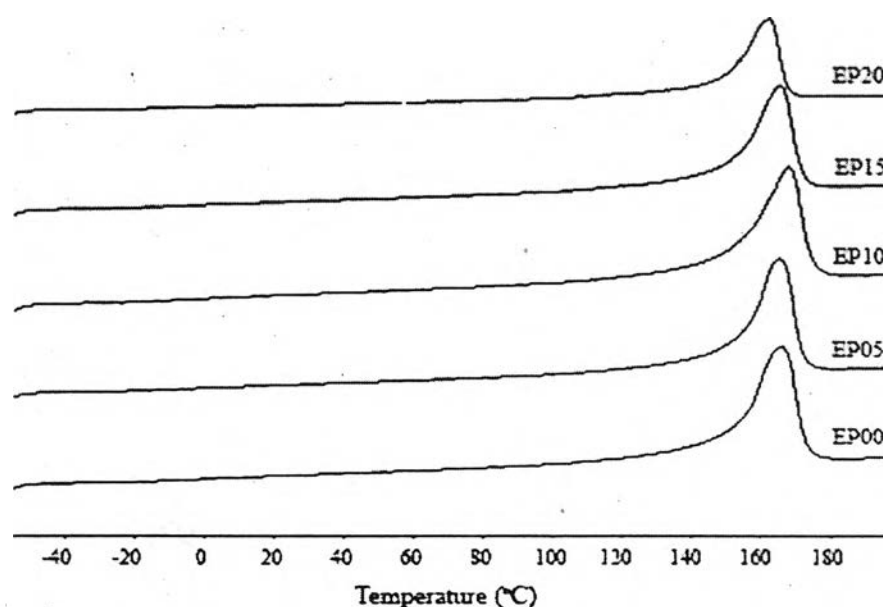


Figure 5.7 DSC curves of EP00, EP05, EP10, EP15, and EP20

Table 5.3 Thermal properties and molecular weight of polymer blends

Polymer	Mn ^a	Mw ^a	MWD ^a	Heat1 ^b			Heat2 ^b			Cool ^b	
				T _g (°C)	T _m (°C)	ΔH (kJ/g)	T _g (°C)	T _m (°C)	ΔH (kJ/g)	T _c ^c (°C)	ΔH (kJ/g)
EP00	35,283	369,328	10.47	-0.22	165.96	97.18	-1.45	165.96	96.59	106.92	96.54
EP05	na	na	na	-7.48	167.07	95.76	-8.42	165.21	94.03	109.08	95.61
EP10	56,474	231,205	4.09	-10.54	167.82	91.91	-11.13	167.79	91.68	108.70	91.64
EP15	na	na	na	-13.98	166.31	89.13	-14.82	165.21	88.69	109.75	88.88
EP20	70,676	350,626	4.96	-16.14	164.18	83.53	-16.34	162.13	83.33	110.17	83.38

^a Determine from GPC

^b Determine from DSC

Noticeable, PP synthesized (Polymer 6 of table 5.2) from experimental had higher molecular weight than commercial grade PP obtained from industry (EP00 of table 5.3) and molecular weight of polymer blend were laid between commercial grade PP and poly(P-*b*-EP).

Figure 5.7 show the second heating DSC curves of PP (EP00) and the polymer blend. Similar to EP00 or pure PP, the polymer blend also have only one T_m .

5.2.2 Influence of poly(P-*b*-EP) content on mechanical properties

The mechanical properties of polymer blend were investigated by DMA and tensile testing. Both specimen for DMA and tensile testing were rectangular characteristic.

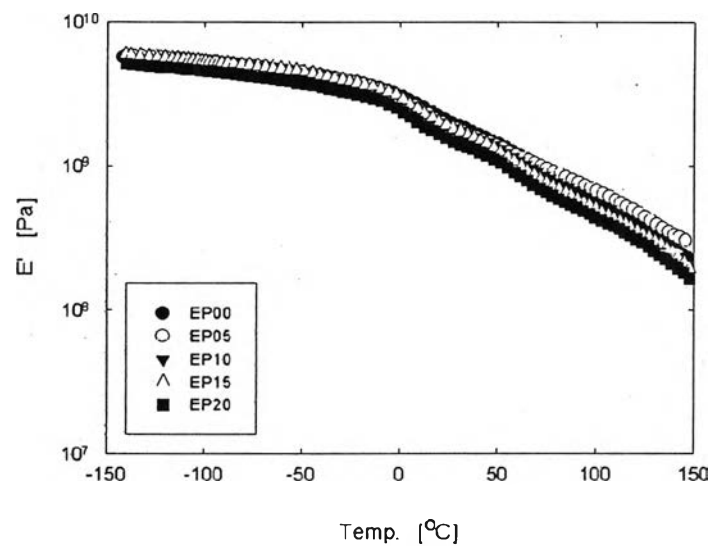
Figure 5.8 shows the effect of poly(P-*b*-EP) on dynamic mechanical properties of polymer blend. The rectangular specimen was tested in the range of -140 to 150 °C under nitrogen atmosphere. The tension mode of DMA was run at a variety of frequency but in these figure showed one frequency as 1 Hz.

The results indicated that both PP and polymer blend have the similar trend of E' (Figure 5.8a). As shown in Figure 5.8b, E'' of polymer blend is higher than PP at temperature lower than 0 °C. This indicated that the blend can adsorb more energy than the pure PP in the low temperature range. In order to clearly compare the different in E'' value of polymer blend, percentage of different E'' founded from curve integration area over polypropylene (Table 5.4) were calculated. This result indicated that polymer blend can adsorb more energy than polypropylene. Figure 5.8c shows the value of $\tan\delta$ which determined from E''/E' , $\tan\delta$ of polymer blend is higher than polypropylene. It can be said that toughness of polymer blend increases at low temperature when poly(P-*b*-EP) presents in polypropylene blend. From these result, toughness have significance increasing in 20% of poly(P-*b*-EP) content.

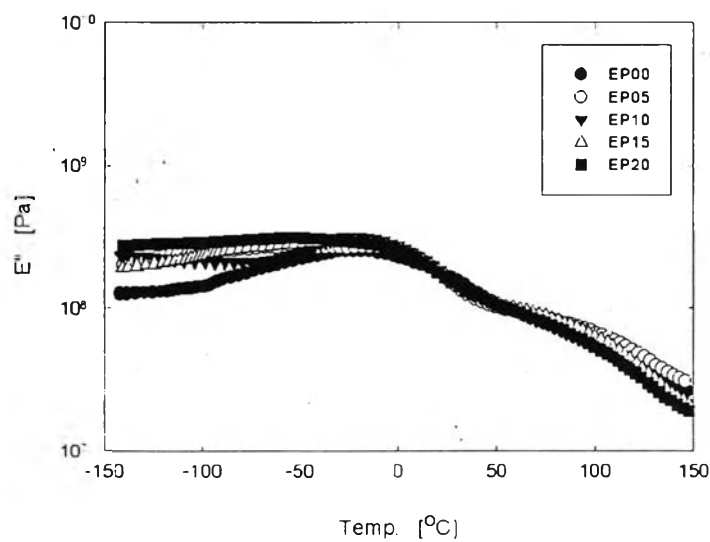
In addition, T_β peak, ascribed to glass transition in amorphous part, presented in polymer blend (Figure 5.8c). The broaden T_β peak is resulted from incorporation of EP molecule in amorphous PP region [21]. Moreover, the T_g of E at around -100°C

was not observed. This may conclude that the samples have small amount of only PE molecules generated in amorphous phases which cannot be detected by DMA.

From $\tan\delta$ curve (Figure 5.8c), two peak positions were detected as shown in Table 5.4. The first peak position laid around 8 °C and represented T_g of PP and other peak position, which has small intensity, were around T_m of PE which decreased with increase poly(P-*b*-EP) content. However, some conclusion were opposed another conclusion because the defect on some of the tensile and DMA specimen gave the unpleasant results.



(a)



(b)

Figure 5.8 Temperature dependence of dynamic mechanical properties at 1 Hz: (a) storage modulus, (b) loss modulus, and (c) $\tan\delta$

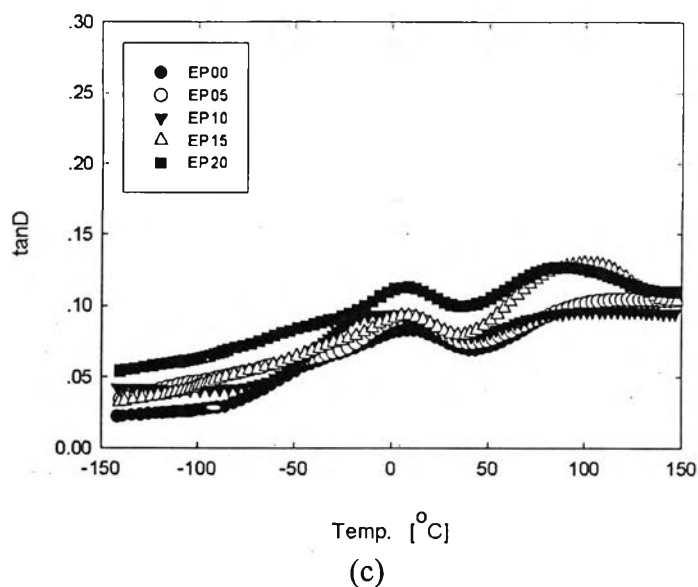


Figure 5.8 Temperature dependence of dynamic mechanical properties at 1 Hz: (a) storage modulus, (b) loss modulus, and (c) tanD (continue)

Table 5.4 Summaries of data from DMA and tensile testing

Polymer	Curve area ^a	% Increase ^b	Peak position of tanD		Toughness ^c
			1	2	
EP00	2.635E+10	-	8.07	114.55	3.500
EP05	3.555E+10	34.91%	7.92	121.99	0.737
EP10	3.450E+10	30.93%	-3.62	107.48	0.660
EP15	3.549E+10	34.69%	8.84	99.97	1.004
EP20	4.074E+10	54.61%	8.98	87.15	1.012
Blend ^b	na	na	na	na	0.553

^a Determine from curve integration between -140 to 0 °C

^b % Increase = (area of polymer blend – area of EP00)/ area of EP00 × 100

^c Determine from curve integration of tensile stress-strain curve

^d PE/PP blend

Figure 5.9 shows the effect of poly(P-*b*-EP) content on the tensile properties of polymer blend. The rectangular specimen was tested at room temperature. The speed test was 12.5 mm/min with 10 kN of load cell and 50 mm grip separation according to ASTM D 882-02.

From tensile testing results, it was found that the elongation of polymer blends increases with increasing of poly(P-*b*-EP) content. However these values are less than pure commercial grade PP. Because of the phase separation between commercial grade PP and ethylene part in poly(P-*b*-EP) occurred, these mainly deteriorate the impact properties of PP [38-40]. From these results, poly(P-*b*-EP) obtained could not use as rubber toughening for PP at ambient temperature. However, at lower temperature (below 0°C) the produced poly(P-*b*-EP) may be important for mechanical properties. Moreover, polymer blends had percentage of poly(P-*b*-EP) content more than 5% poly(P-*b*-EP) had higher tensile elongation than pure polyethylene/polypropylene blend (PE/PP blend)

From all mechanical properties results, it can be concluded that the method, poly(P-*b*-EP) synthesis, which used in this research is simpler than other industrial process. According to DMA results, the poly(P-*b*-EP) copolymer can also increase toughness of PP at low temperature. However, from Tensile and DMA result, the block copolymer can not reinforce the PP at room temperature. Moreover the defects in the specimens and the preparation methods have profound effect to the mechanical properties.

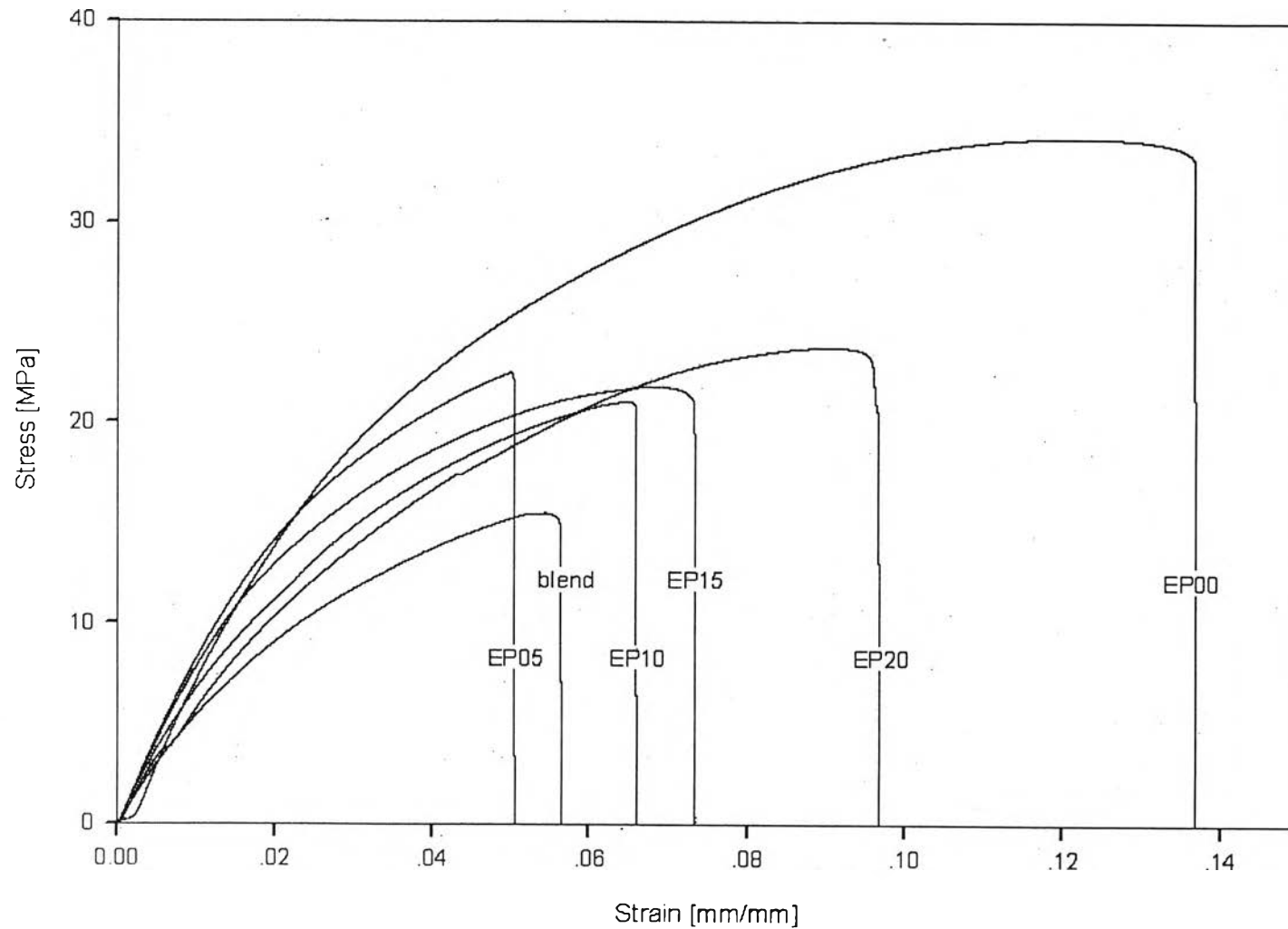


Figure 5.9 Stress-strain curve of polymer at room temperature (blend mean PE/PE blend)

5.2.3 Influence of poly(P-*b*-EP) content on morphology

The morphology of all polymer blends can be observed from SEM micrograph. The SEM micrographs of polymer fracture and cryogenic polymer fracture surfaces show influence of difference poly(P-*b*-EP) content on polymer blend morphology. Figure 5.10 and Figure 5.11 show polymer fracture surfaces of tensile specimen. Figure 5.12 and Figure 5.13 show cryogenic polymer fracture surfaces of polymer.

In figure 5.10 and figure 5.11, SEM micrographs show influence of poly(P-*b*-EP) content on morphology at ambient temperature. Contrast to tensile strength results, SEM confirmed that polymer blend has greater toughness than polypropylene morphology. From tensile fracture surface of polymer blend showed higher rubbery characteristic than PP and have phase separation with clearly boundary in figure 5.11. So, the toughness of polymer blend is lower than the pure polypropylene. But, increase block copolymer contributed to large rubbery size and higher toughness when block copolymer content increased.

However, the difference morphology can not observe in figure 5.12 and figure 5.13 when SEM capture the cryogenic polymer fracture surfaces of polymer blend. Because at cryogenic temperature or liquid nitrogen temperature which lower than T_g of polypropylene, both PP and PP/ poly(P-*b*-EP) blend behave like glassily polymer that have brittle characteristic equally to all component, so the cryogenic polymer fracture surfaces of all systems were similar to each others.

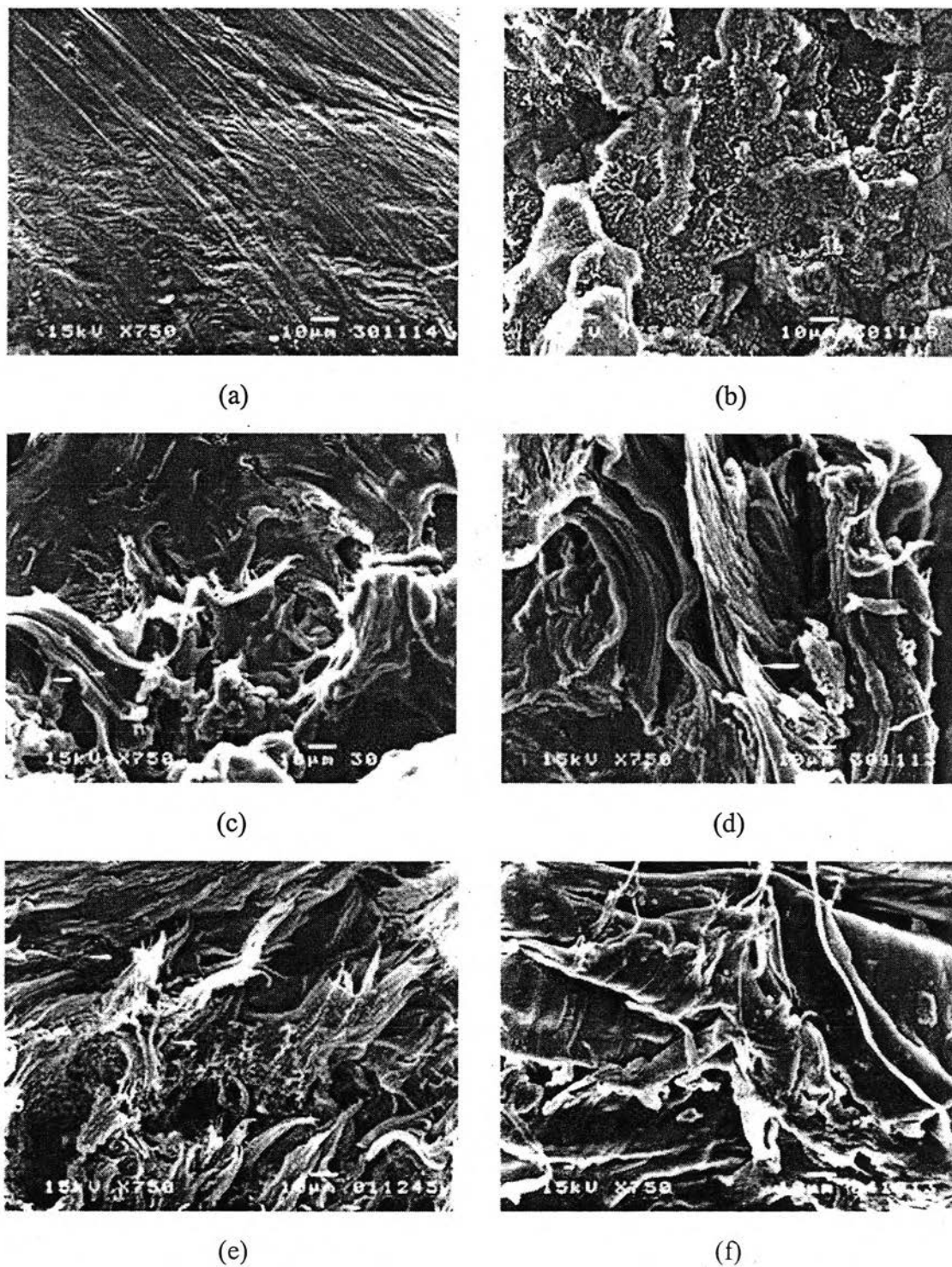


Figure 5.10 SEM micrographs of tensile specimen fracture: (a) EP00, (b) EP05, (c) EP10, (d) EP15, (e) EP20, and (f) PE/PP blend ($\times 750$)

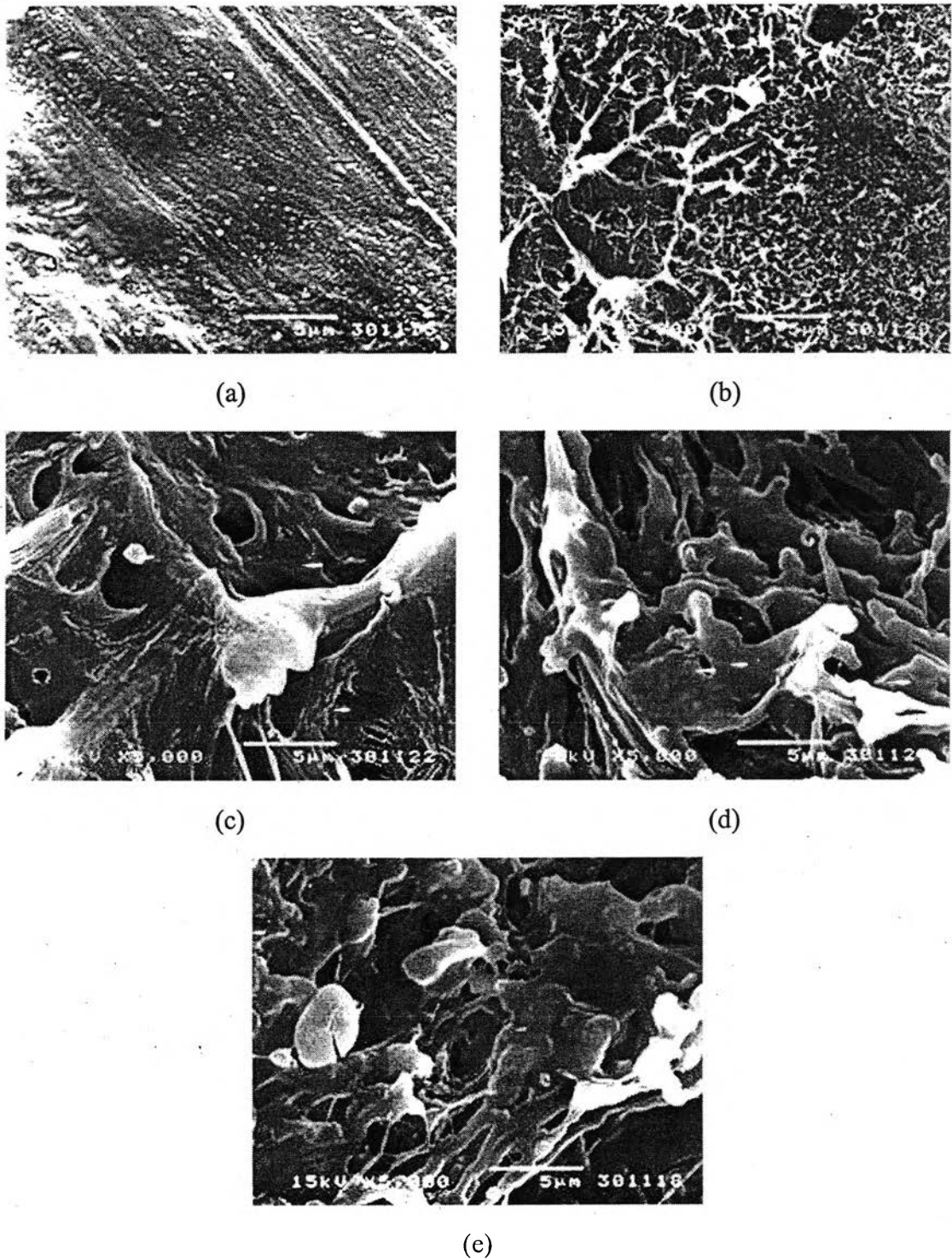


Figure 5.11 SEM micrographs of tensile specimen fracture: (a) EP00, (b) EP05, (c) EP10, (d) EP15, and (e) EP20 ($\times 5000$)

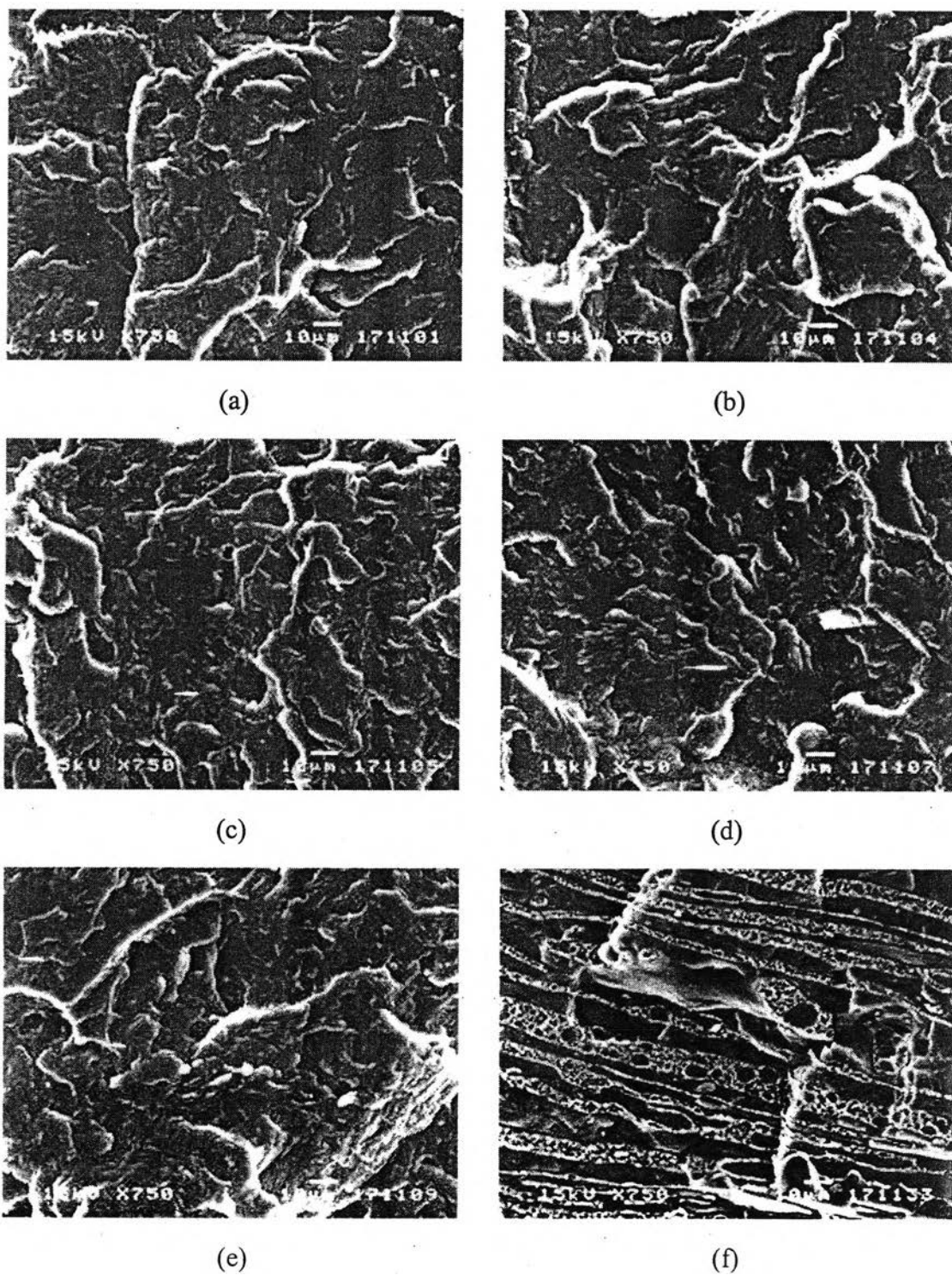


Figure 5.12 SEM micrographs of cryogenic polymer fracture: (a) EP00, (b) EP05, (c) EP10, (d) EP15, (e) EP20, and (f) PE/PP blend ($\times 750$)

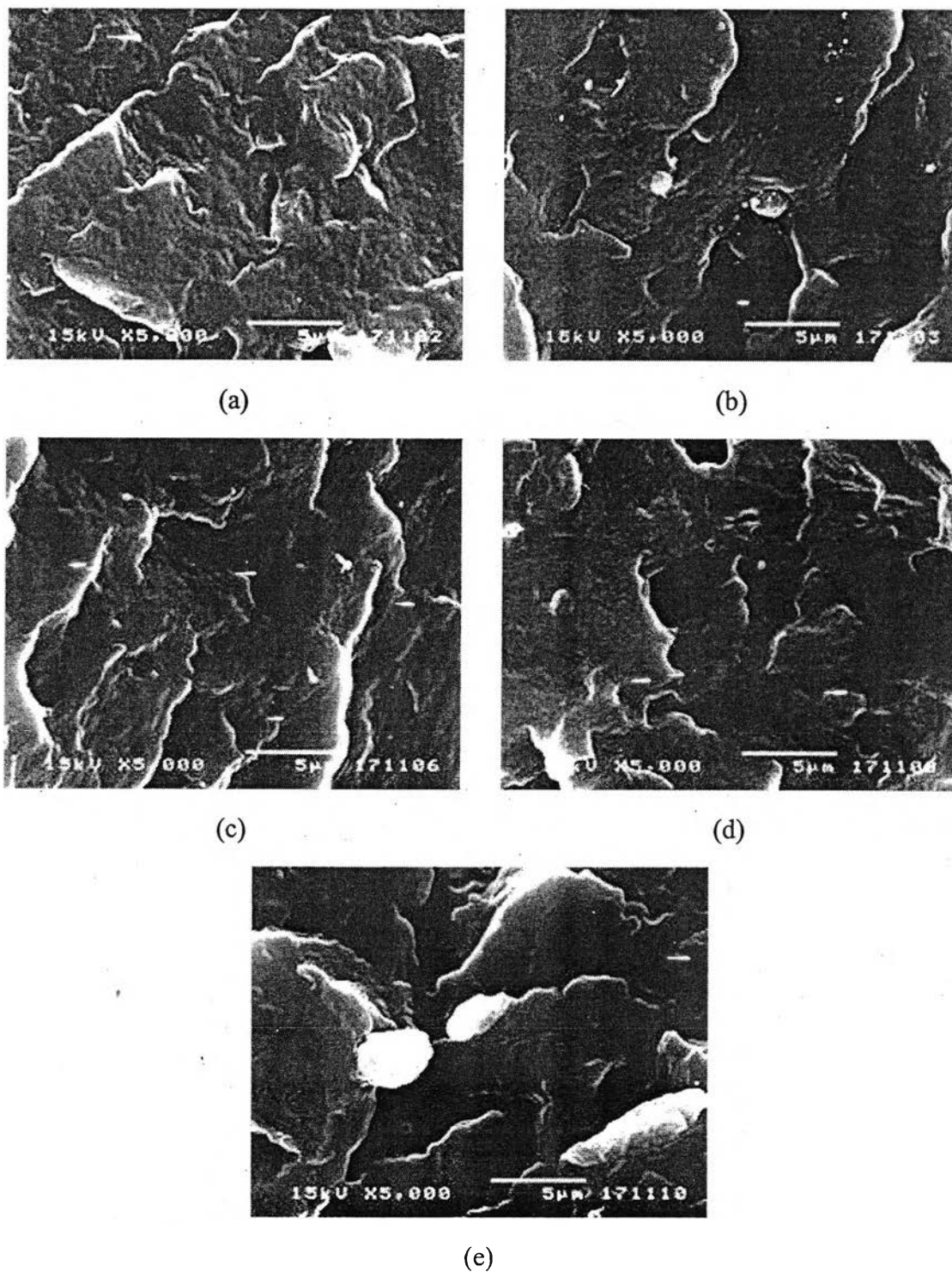


Figure 5.13 SEM micrographs of cryogenic polymer fracture: (a) EP00, (b) EP05, (c) EP10, (d) EP15, and (e) EP20 ($\times 5000$)