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APPENDICES

APPENDIX A

DIFFERENTIAL SCANNING CALORIMETER (DSC) CHARACTERIZATION
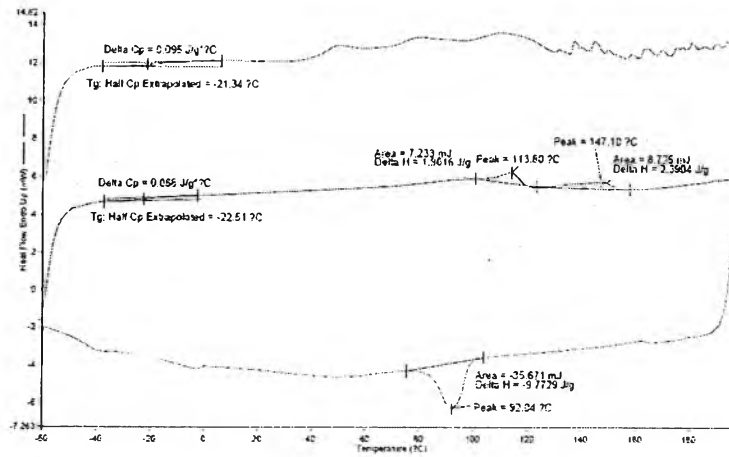
A-1 DSC curve of polymer synthesized

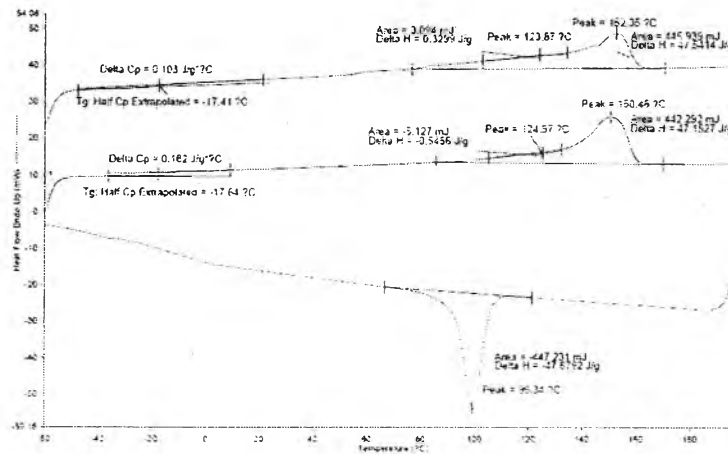**Figure A-1** DSC curve of PP-*co*-EP (Polymer 1)

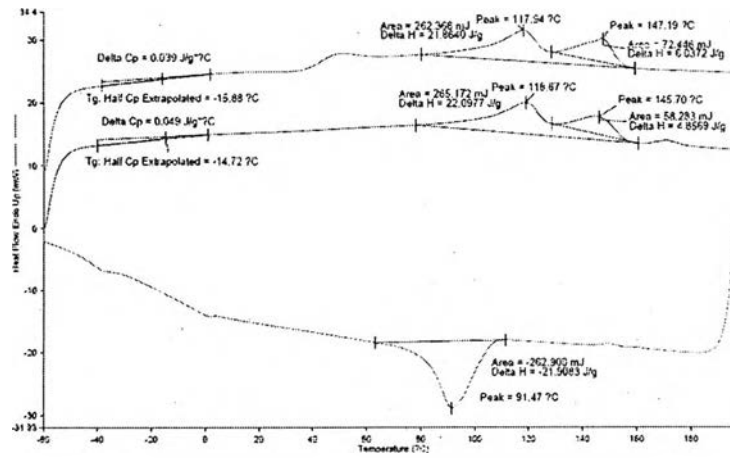**Figure A-2** DSC curve of PP-*co*-EP (Polymer 2)

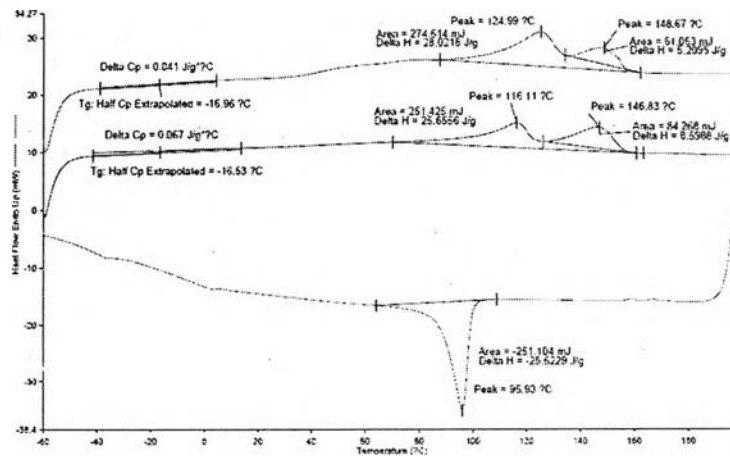**Figure A-3** DSC curve of PP-*co*-EP (Polymer 3)

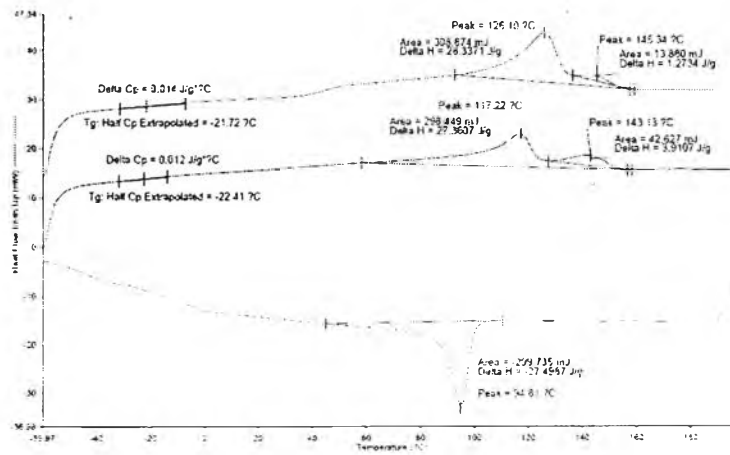**Figure A-4** DSC curve of PP-*co*-EP (Polymer 4)

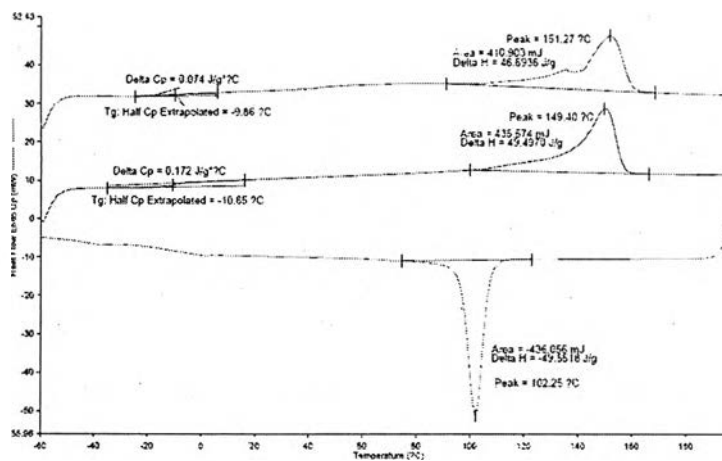**Figure A-5** DSC curve of PP-*co*-EP (Polymer 5)

Figure A-6 DSC curve of polypropylene (Polymer 6)
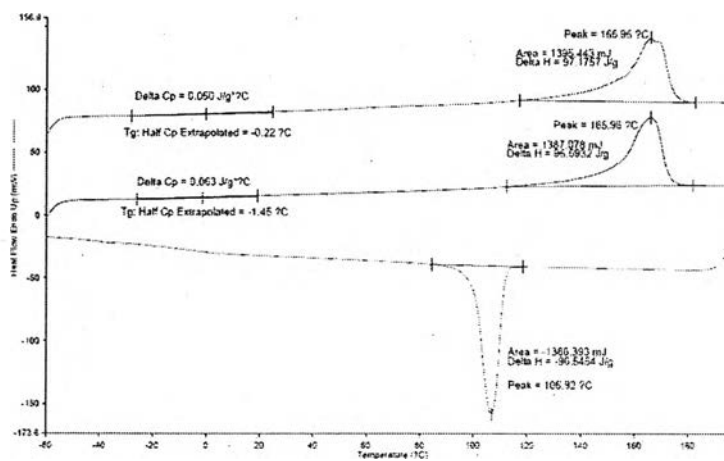
A-2   DSC curve of polymer blend

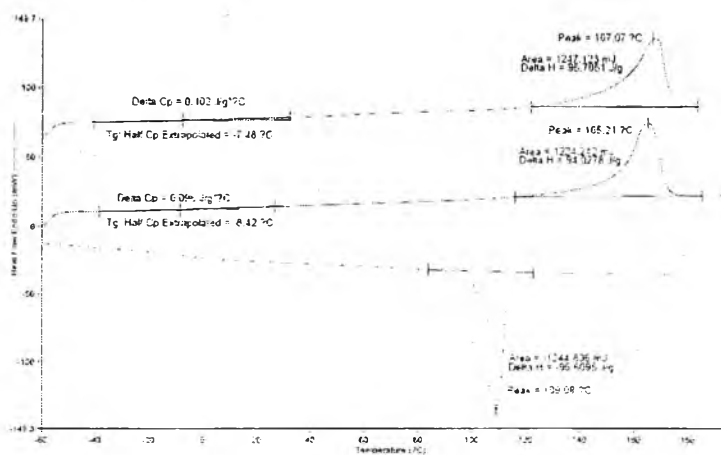Figure A-7 DSC curve of polypropylene (EP00)

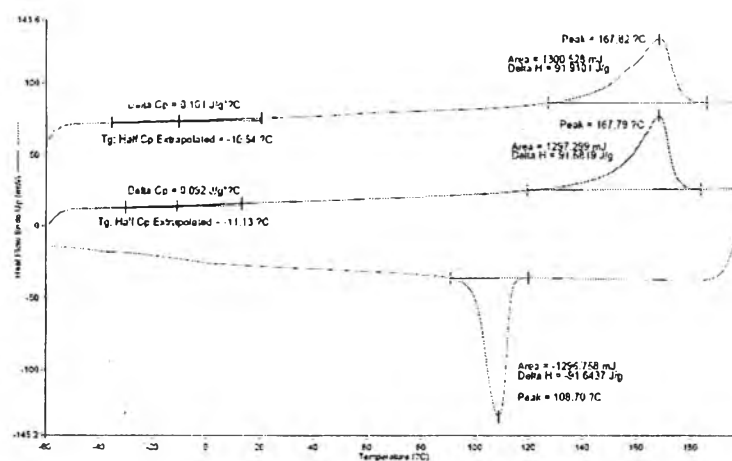Figure A-8 DSC curve of 5% PP-*b*-EP/PP polymer blend (EP05)

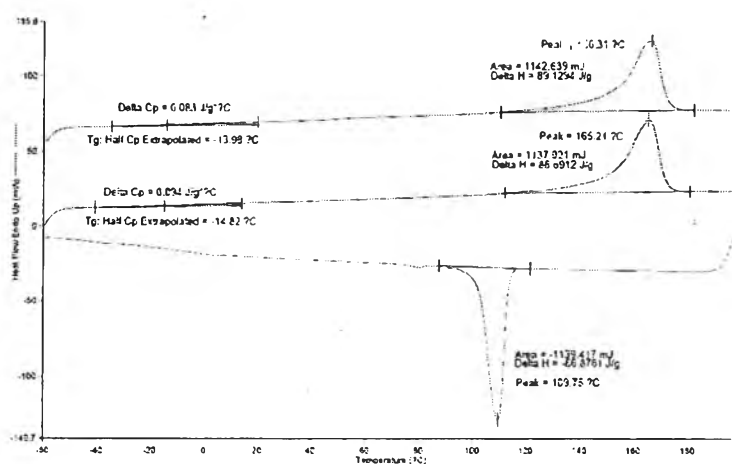**Figure A-9** DSC curve of 10% PP-*b*-EP/PP polymer blend (EP10)

Figure A-10 DSC curve of 15% PP-*b*-EP/PP polymer blend (EP15)
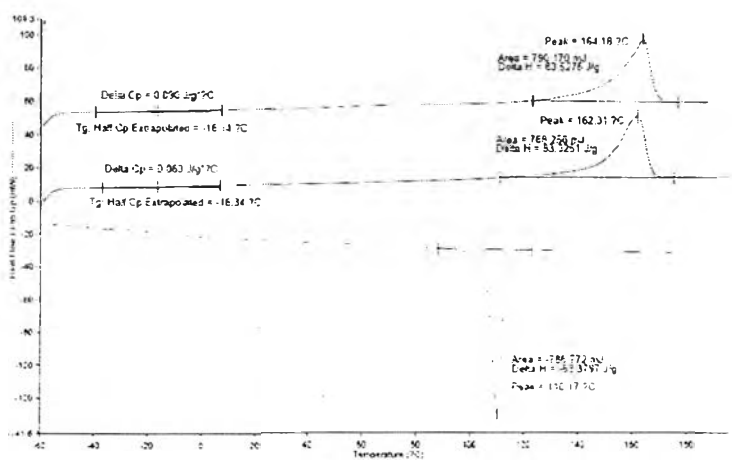
Figure A-11 DSC curve of 20% PP-*b*-EP/PP polymer blend (EP20)

APPENDIX B

NUCLEAR MAGNETIC RESONANCE (NMR) CHARACTERIZATION

B-1 Triad distribution of polypropylene-*b*-poly(ethylene-propylene) copolymer and calculated from ^{13}C-NMR spectrum

Table B-1 ^{13}C-NMR chemical shift and assignment for polypropylene-block-poly(ethylene-propylene) copolymer

Region	Chemical shift (ppm)	Sequence assignment
A	45-48	$T_A = k[PPP+(1/2)(PPE+EEP)]$
B	36-39	$T_B = k[PEP+(1/2)(PEE+EEP)+EPE+(1/2)(PPE+EPP)]$
C	33.3	$T_C = k[EPE]$
D	29.1-31.5	$T_D = k[2EEE+(PPE+EPP)+(1/2)(PEE+EEP)]$
E	28-29.5	$T_E = k[PPP]$
F	27-28	$T_F = k[PEE+EEP]$
G	24-25	$T_G = k[PEP]$
H	19-22	$T_H = k[PPP+(PPE+EPP)+EPE]$

The following results are obtained:

$$k[EEE] = (1/2)(T_{DEF}+T_A+T_C+3T_G-T_B-2T_H) \tag{B-1}$$

$$k[PEE+EEP] = T_H+(1/2)T_B-T_A-2T_G \tag{B-2}$$

$$k[PEP] = T_G \tag{B-3}$$

$$k[EPE] = T_C \tag{B-4}$$

$$k[EPP+PPE] = (1/2)(2T_H+T_B-2T_A-4T_C) \tag{B-5}$$

$$k[PPP] = (1/2)(3T_A+2T_C-(1/2)T_B-T_H] \tag{B-6}$$
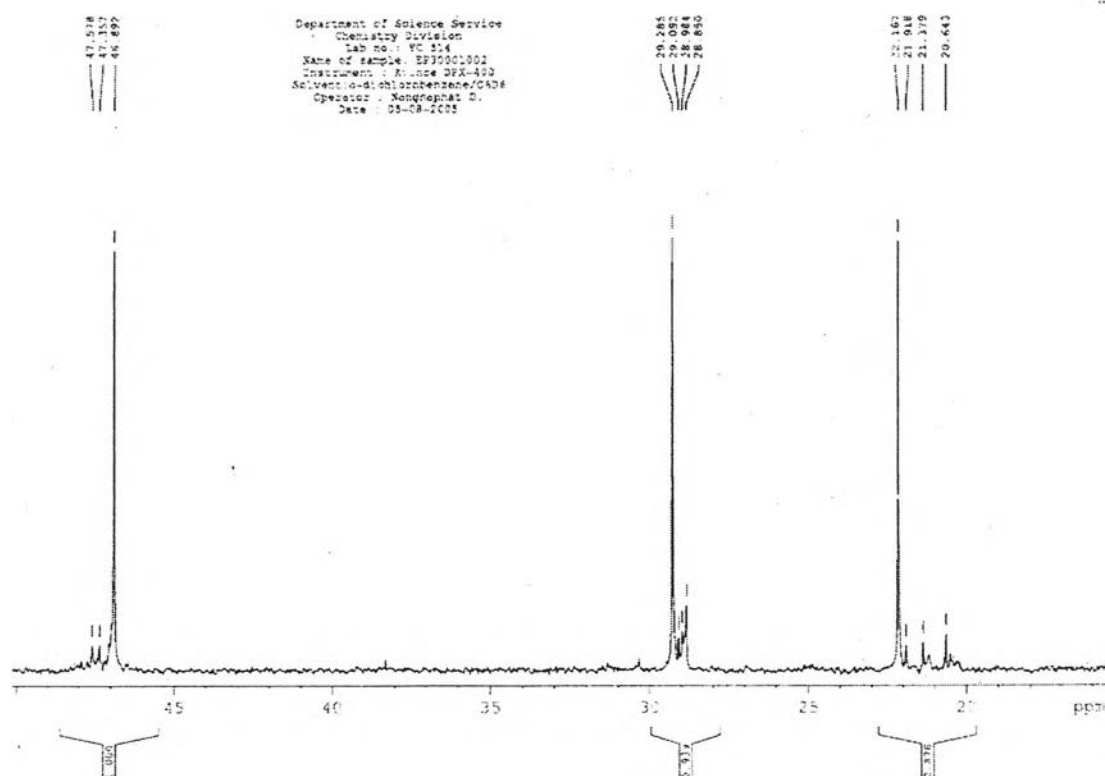
Figure B-1 ^{13}C-NMR spectrum of PP 30 psi 10 °C (Polymer 6)
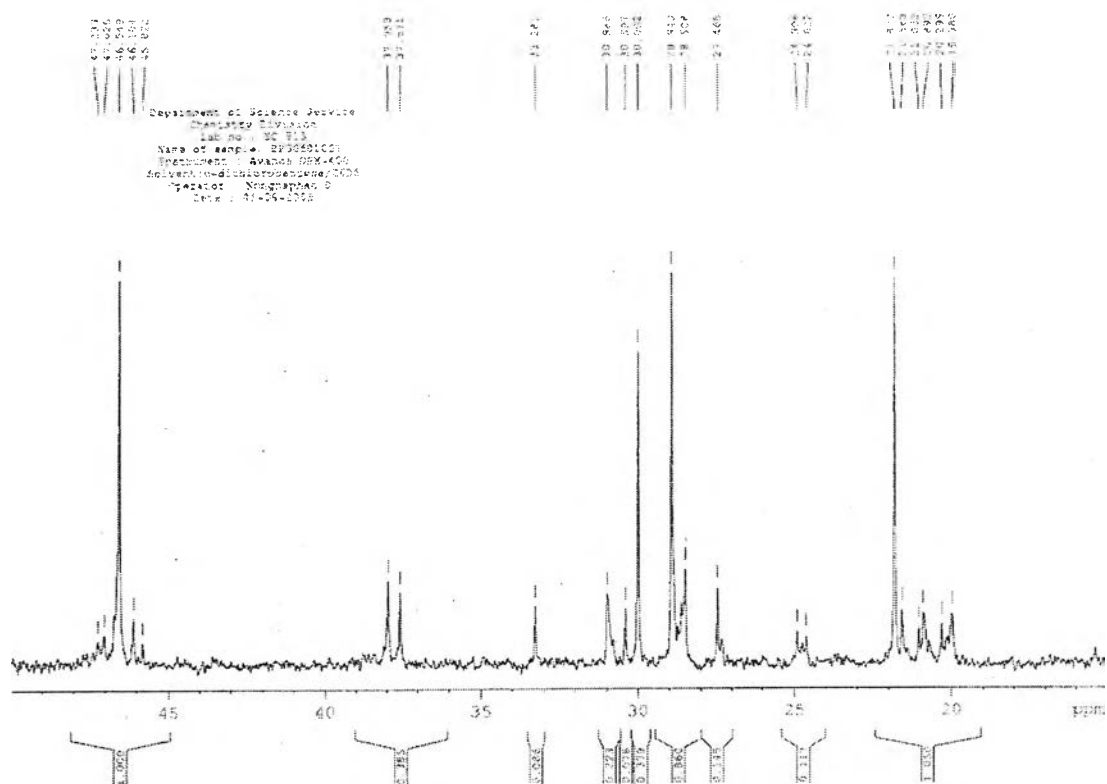
Figure B-2 ^{13}C-NMR spectrum of PP-*b*-EP; E/P 50/30 psi 10 °C (Polymer 3)
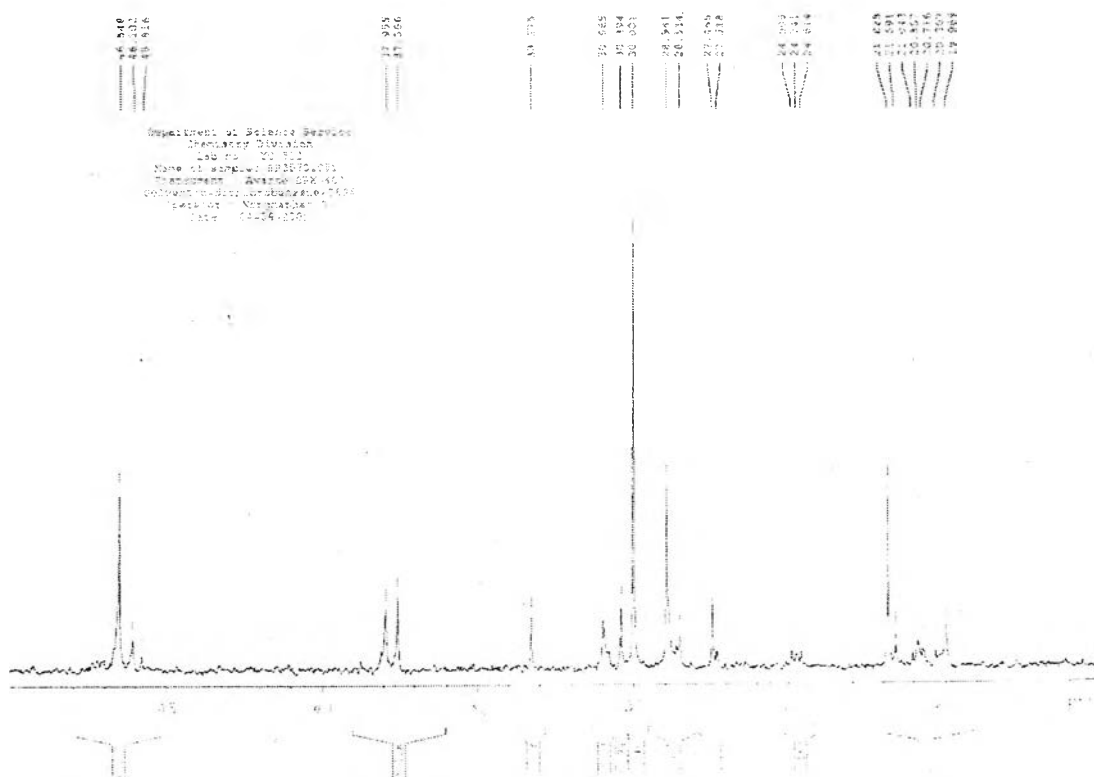
Figure B-3 ^{13}C-NMR spectrum of PP-*b*-EP E/P; 70/30 psi 10 °C (Polymer 5)

APPENDIX C

DYNAMIC MECHANICAL ANLYSIS (DMA)
CHARACTERIZATION

C-1 DMA diagrams of PP-*b*-EP/PP polymer blend

These DMA diagrams showed E', E", and tanD at various frequencies of each sample.
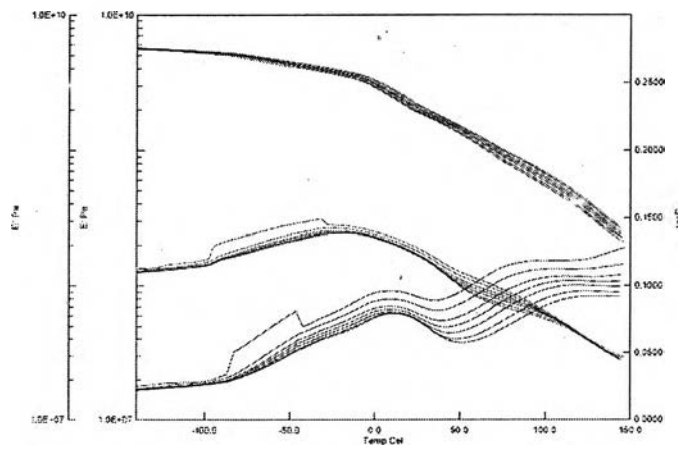
Figure C-1 DMA diagram of polypropylene (EP00)
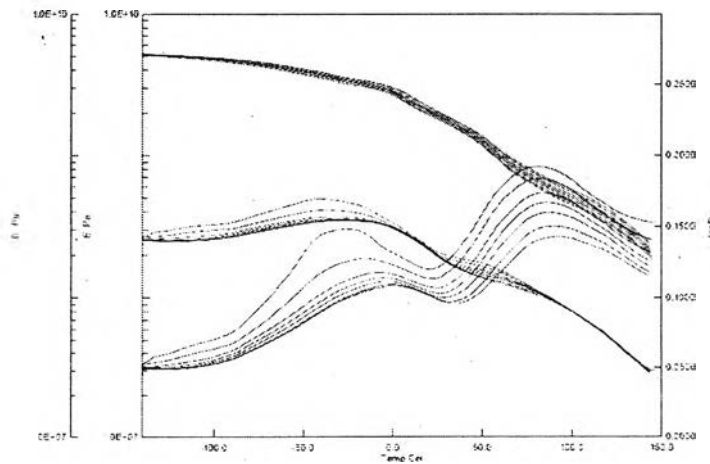
Figure C-2 DMA diagram of 5% PP-*b*-EP/PP polymer blend (EP05)
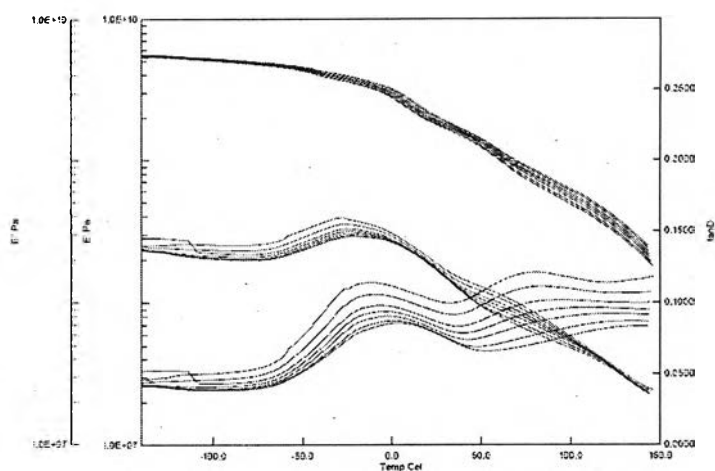
Figure C-3 DMA diagram of 10% PP-*b*-EP/PP polymer blend (EP10)
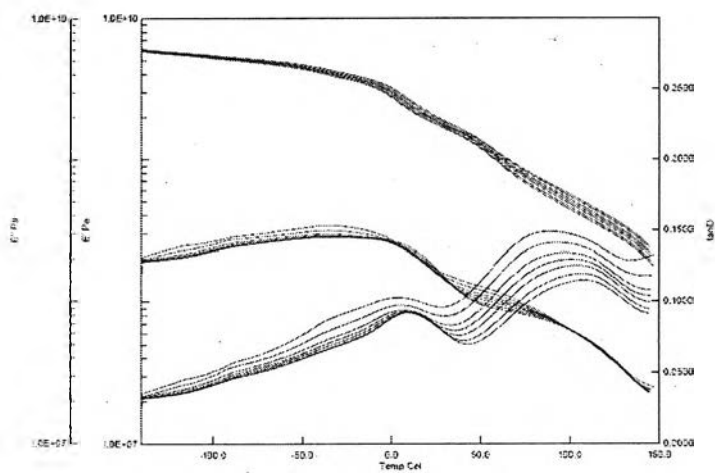
Figure C-4 DMA diagram of 15% PP-*b*-EP/PP polymer blend (EP15)
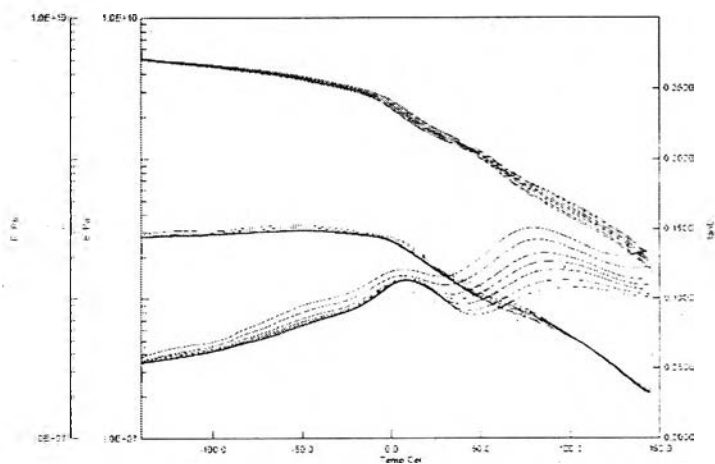
Figure C-5 DMA diagram of 20% PP-*b*-EP/PP polymer blend (EP20)

APPENDIX D

DYNAMIC MECHANICAL ANLYSIS (DMA) CHARACTERIZATION
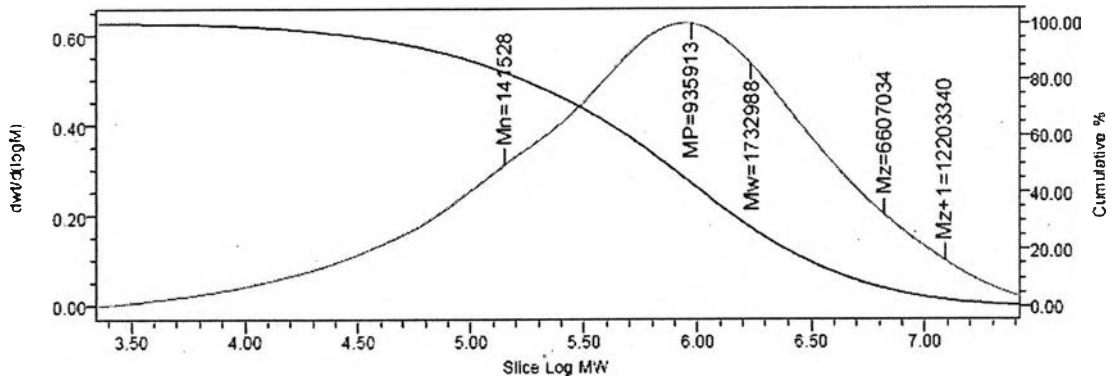
Figure D-1 GPC curve of polymer PP-*b*-EP (Polymer 5)
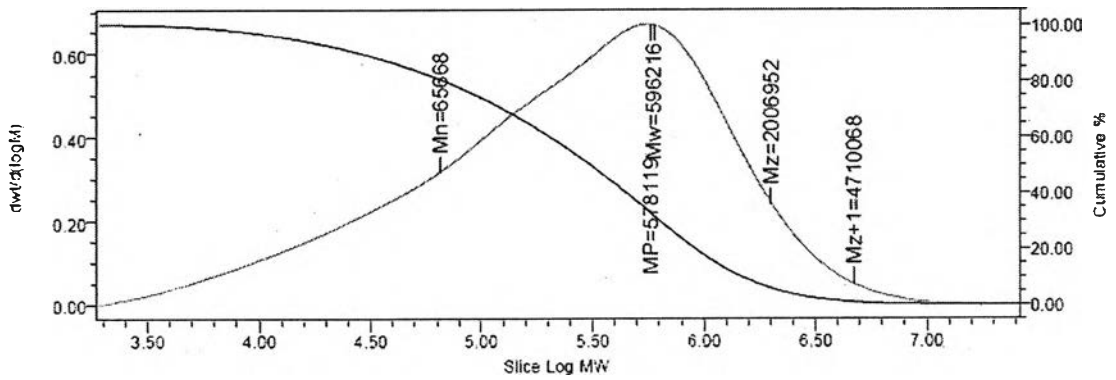
Figure D-2 GPC curve of polymer PP synthesized (Polymer 6)
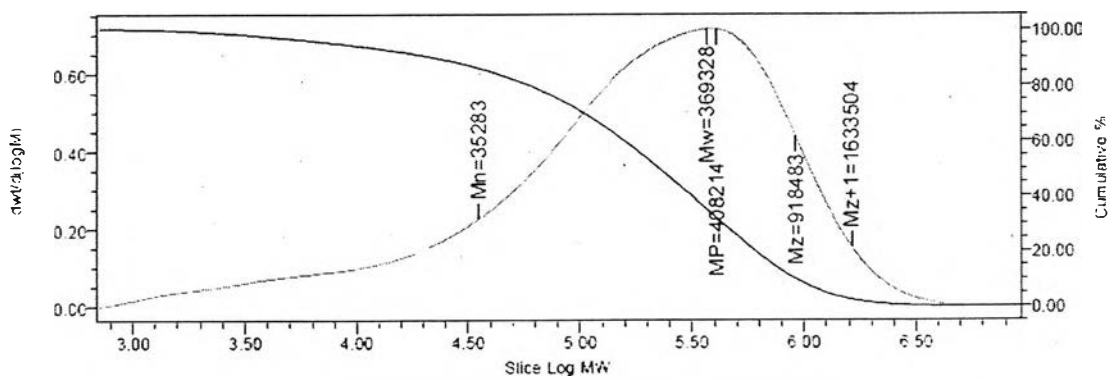
Figure D-3 GPC curve of polymer PP (EP00)
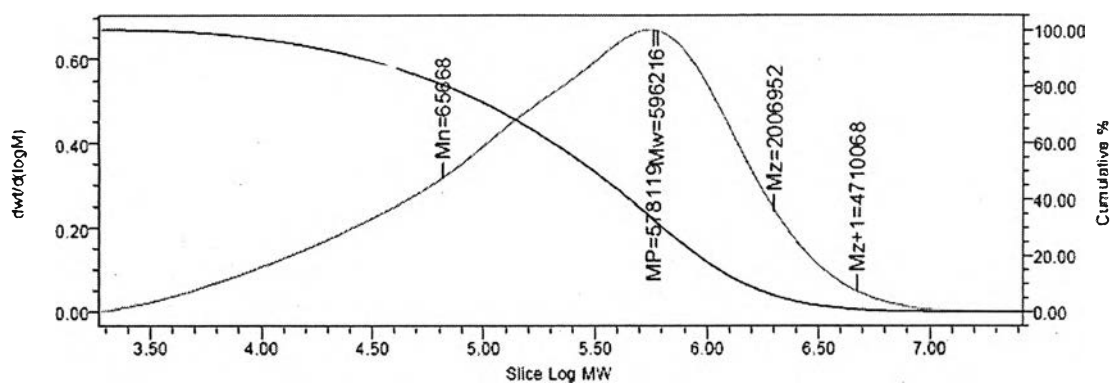
Figure D-4 GPC curve of 10% PP-*b*-EP/PP polymer blend (EP10)
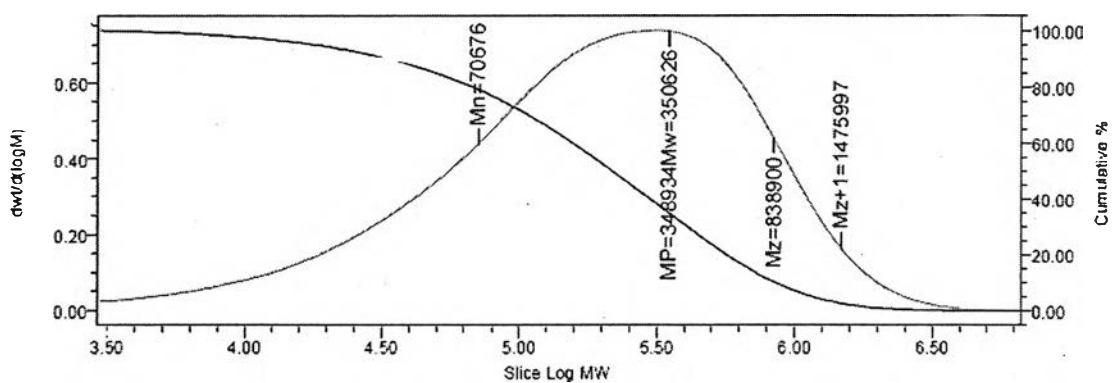
Figure D-5 GPC curve of 20% PP-*b*-EP/PP polymer blend (EP20)

APPENDIX E

THE SUBMITTED PAPER TO
JOURNAL OF APPLIED POLYMER SCIENCE

New Synthesis Methods for Polypropylene co Ethylene-Propylene rubber

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Abstract

In this research, the reinforcement of polypropylene (PP) was studied by using the new appropriate method for synthesizing polypropylene-*block*-poly (ethylene-propylene) copolymer (PP-*co*-EP), which can be utilized as rubber toughening agent. This copolymer (PP-*co*-EP) could be synthesized by varying the feed condition and change of feed gas in the batch reactor system by using Ziegler-Natta catalysts system at copolymerization temperature of 10 °C. The ^{13}C-NMR tested by 21.61 ppm resonance peak indicated the incorporation of ethylene to propylene chains that could build the microstructure of the block copolymer chain. DSC, SEM, and DMA results also confirmed these conclusions. From this circumstance, the morphology of copolymer trapped in PP matrix could be observed and the copolymer T_g would decrease if higher amount of PP-*co*-EP were increased. It was found from DMA study that PP-*co*-EP is good for the polypropylene reinforcement at low temperature. Moreover, the PP-*co*-EP content affected to the crystallinity and morphology of polymer blend. It was found that the crystallinity of polymer decreased when the PP-*co*-EP content increased, but tougher mechanical properties under low temperature were observed.

Keywords: Polypropylene-*co*-Poly (Ethylene-Propylene) copolymer, synthesis, rubber toughening, Ziegler-Natta, Polypropylene

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1. Introduction

Isotactic polypropylene (iPP) is typical semi-crystalline polymer which produces various products but it has a mechanical properties limit. It is well known that iPP has poor mechanical properties at low temperature range (0 °C, freezing in the normal refrigerator) under its glass transition temperature (T_g). The general method to improve mechanical properties of iPP is blending of iPP with rubbery material such as poly (ethylene-propylene) copolymer (EPR), ethylene-propylene-diene terpolymer (EPDM), or other copolymer [1-3]. The iPP/EPR blends called toughened polypropylene, which find the wide applications in consumer products and automotive industry. Nevertheless, the strong incompatibility of EPR and iPP is important trouble in modification of mechanical properties of iPP/EPR blend systems [4].

Copolymers are interested alternative way as important materials to improve mechanical properties of iPP. The propylene-co-poly (ethylene-propylene) copolymer is one of polymers that used for rubber toughening of PP. Examples of syntheses and characterizations of PP-co-EP are reported [5-11].

Coates et al. also reported the synthesis of a syndiotactic polypropylene-block-poly(ethylene-propylene) with a metallocene catalyst system [5]. Beside that works, Y. Fukui and M. Murata also reported the synthesis of polypropylene-block-poly(ethylene-co-propylene) by using metallocene catalyst systems [6]. However, these catalysts are expensive and rapidly deactivate on moisture and oxygen. Till now, the metallocene catalysts are still difficult to appropriately operate and to practically utilize.

K. Nitta et al. reported that polymer blend of PP/EPR blend and polypropylene block-poly(ethylene-co-propylene) was synthesized by short-period polymerization method [7].

H. Mori et al. reported the synthesis of a polypropylene-block-poly(ethylene-propylene) by high-pressure-type stopped-flow polymerization system by using Ziegler-Natta catalyst [8].

The short-period polymerization and stopped-flow polymerization methods are not practical and complicate in polymer synthesis fields. Because, these methods must be controlled by computer to generate suddenly changes in gas feed condition in 0.2 sec.

Z. Fan et al. reported fraction of structure and properties of iPP/EPR in-situ blend was synthesized by spherical Ziegler-Natta catalyst in two stage of liquid phase propylene homopolymerization and gas phase ethylene-propylene copolymerization [9].

However, all these mentioned methods are not appropriate to perform in the industrial applications. To overcome these problems, this work represents the new simple method for synthesis of polypropylene-co-poly(ethylene-propylene) (PP-co-EP) copolymer by using Ziegler-Natta catalyst which might apply to use in the industrial production. The NMR results confirmed the corporation of Ethylene (E) in the molecule of propylene (P). The DSC and DMA results show that less pure P and pure E produced in the PP-co-EP polymers. The obtained copolymer can be utilized as the rubber toughening of polypropylene. The DMA results show the advantage in the low temperature range below T_g of the pure PP in the blend of PP with PP-co-EP polymers.

2. Experimental

2.1 Material

Ethylene and Propylene (polymerization grade) and Triethylaluminum (AlEt$_3$; TEA) were obtained from Bangkok Polyethylene Co., Ltd., Thailand. TiCl$_4$ was purchased from Merck Ltd. Anhydrous MgCl$_2$ was supplied from Sigma-Aldrich Inc., Phthalic anhydride, diethylphthalate (DEP, used as an internal donor) and n-decane were purchased from Fluka Chemie A.G. Switzerland. Hexane was donated from Exxon Chemical Thailand Ltd. Solvents were distilled over sodium/benzophenone under argon atmosphere before use. Ultra high purity (UHP) argon (99.999%) was obtained from Thai Industrial Gas Co., Ltd. and was further purified by passing through molecular sieves 3Å, BASF catalyst R3-11G, NaOH and phosphorus pentoxide (P$_2$O$_5$) in order to remove traces of oxygen and moisture. Commercial grade polypropylene and was donated from Thai Polyplastic Industry Public Co,, Ltd.

All chemicals were manipulated under purified argon and all operations were carried out under an inert atmosphere of argon using a vacuum atmosphere glove box and/or standard Schlenk techniques.

2.2 Preparation of catalyst

Anhydrous magnesium chloride (MgCl$_2$), n-decane and 2-ethyl-1-hexanol were added into a schlenk tube and heated to 130 °C for 2 h under magnetic stirring and argon atmosphere. Then phthalic anhydride was introduced into the solution and stirred until MgCl$_2$ was completely dissolved. The resulting, uniform solution was cooled to room temperature, and wholly dropped wise of titanium tetrachloride (TiCl$_4$) kept at -20 °C under stirring. The temperature was then raised to 110 °C, and diethylpthalate was injected in. The mixture was maintained at this temperature for 2 hours. After the reaction for 2 hours, the solid portion was collected from the reaction mixture and again suspended in 20 ml of titanium tetrachloride and reacted at 120 °C for 2 hours, respectively. After these, it was again collected then washed with n-decane and n-hexane for 2 and 3 times, respectively. The resulting solid was subjected to vacuum dry to form a powder in gray color which needed to be stored under argon atmosphere.

2.3 Synthesis of polypropylene-co-poly(ethylene-propylene) copolymer

Polymerization was carried out in 100 ml stainless steel autoclave reactor with magnetic stirrer in hexane by using MgCl$_2$/DEP/TiCl$_4$-TEA catalytic system. The polymer was synthesized in a two-stage reaction process. First, solvent, cocatalyst and catalyst were added into the reactor. Subsequence put into liquid nitrogen to stop the reaction between the catalyst and cocatalyst. After that, the reactor was evacuated to remove argon and then taken out of liquid nitrogen and heated up to polymerization temperature. The first stage of polymerization concerned with propylene homopolymerization by feeding only propylene gas into the reactor with duration of 10 minutes. The reactor was heated under the controlled temperature to start the polymerization reaction. The second stage to cooperate the ethylene in the PP structure was successively done by suddenly feeding the pure ethylene gas to a stirred reactor with duration of 30 minutes. The mixture was quenched by addition of

HCl/methanol solution after completion of the reactions. The obtained polymer that precipitated out was washed with excess methanol and dried at room temperature.

2.4 Blending and molding of polymer

Polypropylene (PP) and Polypropylene-co-poly(ethylene-propylene) copolymer (PP-co-EP) were combined by melt mixing method on digital hot plate at 220 °C whit 5, 10, 15, and 20 percentage of PP-co-EP. After that, polymer blended was molded with LAB TECH Automatic Hydraulic Hotpress LP-50 M/C 9701 in aluminium mould at 200 °C 1500 psi. Then, polymer blended was cool down at room temperature. Sample size for tensile testing is 20×100×0.5 mm and 10×40×0.5 for DMA

2.5 Characterization

Differential scanning calorimetry analyses of polymers were carried out using Perkin-Elmer Diamond DSC that was calibrated for temperature and melting enthalpy using indium as a standard. About 10 mg weights of samples were sealed in aluminum sample pans for the measurement. The samples were heated from -60 to 200 °C at scanning rate of 40 °C/min under N_2 atmosphere.

^{13}C-NMR spectra of the polymers were measured on Avance DPX400 NMR spectrometer at 120 °C. o-Dichlorobenzene and Benzene-d_6 were used as solvent to prepare the polymer solution.

The morphologies of all polymer fracture surface were investigated by JSM-5410LV Scanning Microscope. The samples for SEM analysis were coated with gold particles by ion sputtering device provide electrical contact to the specimens.

Dynamic mechanical properties of blending polymers were characterized using Perkin-Elmer DMA-Pyris Diamond. All the experiments were operated at 1 Hz in tension mode over the temperature range -140 to 150 °C with 1.5 °C/min and sample size were 10×50×0.5 mm, using liquid nitrogen as a cryogenic medium.

The molecular weight and molecular weight distribution were determined using gel permeation chromatography (GPC, Waters 2000) with Styragel HT6E column at 135 °C by 1,2,4-Trichlorobenzene as a solvent.

3. Results and discussion

3.1 Synthesis of copolymer

Figure 1 shows a typical ^{13}C-NMR spectrum of the synthesized PP-co-EP (Polymer5). The chemical shift assignments for ^{13}C resonances are similar to those reported by Yoshifumi et al. [6]. The mole fractions of propylene/ethylene unit (P/E unit) in the block copolymer were determined as 37/63 mole% from the peak areas of methylene and methyl carbons [12-15]. From ^{13}C-NMR spectrum, the peak at 21.61 ppm showed the characteristic of propylene (P) that has the ethylene (E) laid in the adjacent of PPPPE which indicated the cooperation of E in the P chain. Because only the pure propylene was allowed in the reactor at the beginning, the first polymerization product in the reactor was the propylene pure chains only. (with the duration of 10 minutes) The second step of polymerization allowed E to react in the reactor (with the duration of 30 minutes), so the discovery that E corporate in the P 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 E incorporation as the consequences. Unfortunately, because of the batch reactions, the variation in the partial pressure of propylene and ethylene changed with time during the synthesis prevailed against the exact quantitative calculations of the cooperation of E in the P chain.
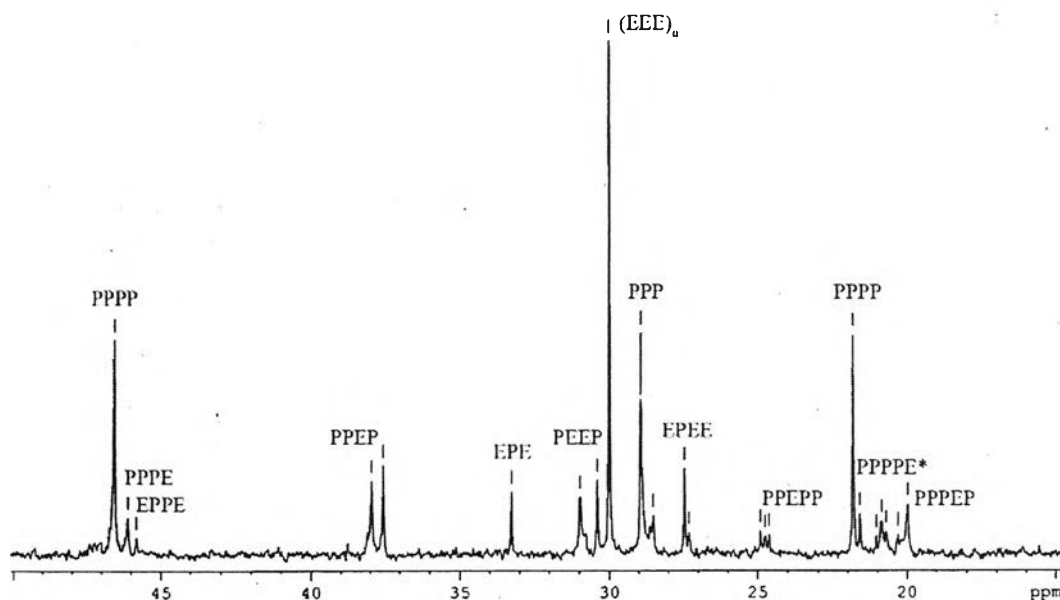

Figure 1 ^{13}C-NMR spectrum of PP-co-EP copolymer (Polymer5)

Table 1 showed the effects of polymerization temperature and pressure of corporate ethylene gas by being added in the reactor on the glass transition temperature (T_g), melting temperature (T_m), and temperature of crystallization of PP-co-EP products from DSC results. In addition to the NMR result, the DSC graphs of T_g of copolymer showed that there are two phase in the PP-b-EP block copolymer because the DSC results were clearly shown two T_m in the synthesized polymers. The first phase, PP is dominate and the other phase have the E in contributions.

From Table 1 we can conclude that the higher polymerization temperature give the lower of glass transition temperature of the products. This might be because of the more incorporation of E in the P chain at higher polymerization rate. Usually, the lower T_g in the block copolymer will result from the incorporation of the low T_g component (E) in the higher T_g matrix (P). The lower of the T_g also confirm NMR results that the E has cooperation in the PP chain with out serious segregation of pure PP because no clear pure component T_g of PP (-10° to 0°C) was detected. Moreover, synthesized polymers have the dispersed phase of the ethylene-propylene rubber even at the rector temperature of 60 °C. Usually At higher temperature, the polymerization will give result in the higher chain transfer rate (Polymer 1, Polymer 2 and Polymer 3) which shorten the progressive chains of PP and most likely that the E cannot totally corporate on the PP chain.

Table 1 Characterization of polymers by DSC

Polymer [a]	Temp (C°)	P_E (psi)	Mn	MWD	Heat 1 [b]			Heat 2 [b]			T_c
					T_g	T_{m1}	T_{m2}	T_g	T_{m1}	T_{m2}	
Polymer 1	60	50	-	-	-21.34	nd	nd	-22.51	113.80	147.10	92.04
Polymer 2	40	50	-	-	-17.41	123.87	152.35	-17.64	124.97	150.48	99.34
Polymer 3	10	50	-	-	-15.88	117.94	147.19	-14.72	118.67	145.70	91.47
Polymer 4	10	60	-	-	-16.96	124.99	148.67	-16.53	116.11	146.83	94.81
Polymer 5	10	70	141,528	12.24	-21.72	126.10	145.34	-22.41	117.22	143.13	95.93
Polymer 6	10	-	65,658	9.08	-9.86	nd	151.27	-10.85	nd	149.40	102.25

[a] Synthesis by $TiCl_4/MgCl_2$/DEP-TEA, Al/Ti = 167, propylene pressure feeding constant = 30 psi
[b] Ramp rate = 40°C/min both heating and cooling, heating1-cooling-heating2 from -60° to 200°C
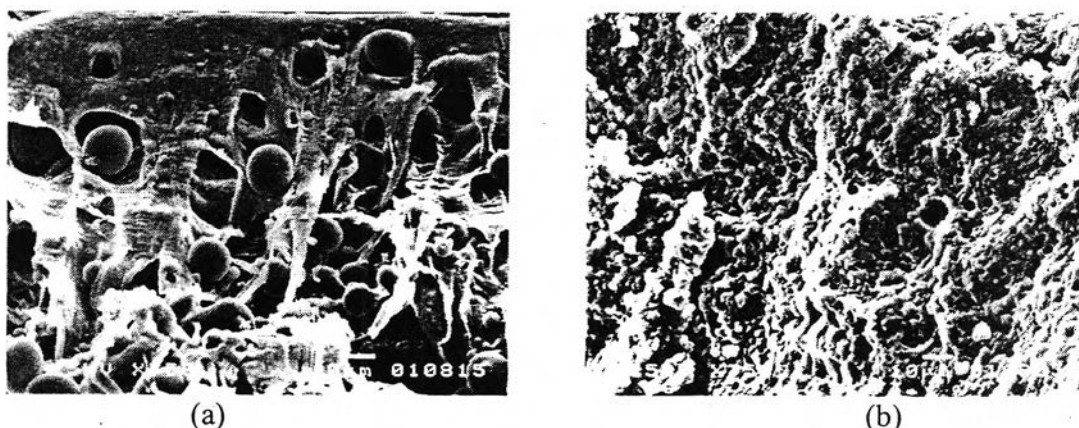nd = not detected

Figure 2 SEM micrographs of cryogenic polymer fracture surface: (a) polymer fracture of PP-block-EP (polymer 5), (b) polymer fracture of PP (polymer 6) (750×)

As the consequence, the higher of the feeding ethylene pressure also give the lower glass transition temperature (Polymer 3, Polymer 4, and Polymer 5) at the same reactions' temperatures. These may result from the more incorporation of E, because the higher concentration of E is increased with increase the pressure of the system. The higher concentration of E presented at the reactions, the higher incorporation of E onto PP chain and the samples. Unfortunately, with the limit of DSC scanning temperature (from -60°C to 200°C), the T_g of the pure E at -100°C was not confirmed. However the lower T_g of PP according to the corporation of E in these systems also supported the incorporation of E onto PP chains without substantial termination of the active site of PP.

In Polymer 6, only the P was allowed in the reactor, the polymer formed is the PP only. Because the time for PP to react is the same time as others samples before supply the E to the reactor, the polymer formed will represent the PP chains before the cooperation of E. The clear T_g of PP was observed at -9°C which clearly higher than the T_g of the corporate polymer with E. The molecular weight of PP6 and the T_m confirm the high quality of PP produced. If we further corporate E onto this PP, the polymer formed will have substantial characteristics of PP. Moreover, the higher T_m of Pure PP in polymer 6 than the others cooperation of E samples, show that the crystals of pure PP were affected by the cooperation of E and no clear separated peak T_m for pure PP was observed again after cooperation with E.

According to the DSC results, the appearance rubbery phase of block copolymer can by seen in SEM micrographs of polymer fracture. (Figure 2a) The minor phase of EP can be seen as the phase separated droplets in the fracture surface picture. In the pure PP micrographs (polymer 6, Figure 2b), the droplet characteristics can not be observed. These appearances supported the DSC results that represented the two phase characteristics.

3.2 Polymer blend

The influence of PP-b-EP incorporated in commercial grade polypropylene on T_g, T_m and T_c of polymer blend are shown in Table 2. The suffix number at the name of the blend stand for the weight% of PP-co-EP added to the blend. As it can be seen, T_g value decreases with an increase of PP-b-EP content (from 0 to 20%) while T_m and T_c value are not clearly affected. Generally, T_g is represented an amorphous part of polymer. The T_g value of pure polypropylene is approximately 0°C (EP00) and the T_g of the blend with PP-co-EP decrease when increase PP-b-EP copolymer content [7]. The T_g of polymer blend is raging from that of PP and synthesized PP-b-EP. From T_m and T_c result, it can be implied that EP molecule does not substancial affect the crystallinity of polypropylene [16]. Moreover, ΔH indicated the crystallinity of polypropylene. It was found that ΔH decreased with an increase of PP-b-EP content. Thus the addition of PP-b-EP can reduce the crystallinity of polypropylene [17]. Our results confirmed the previous works on the blend of PP and EP [7, 16, 17], thus our PP-co-EP produced can equally affect the properties of the PP as same as other reference but in the easier way of the preparations. Figure 3 show heat 2 DSC curve of PP (EP00) and polymer blend which T_m of polymer blend were similar to PP.

Table 2 Characteristics of polymer blend and polypropylene

Polymer[a]	Mn	MWD	Heat 1[b]			Heat 2[b]			Cool[b]	
			T_g	T_m	ΔH	T_g	T_m	ΔH	T_c	ΔH
EP00	35,283	10.47	-0.22	165.96	97.18	-1.45	165.96	96.59	106.92	96.54
EP05	-	-	-7.48	167.07	95.76	-8.42	165.21	94.03	109.08	95.61
EP10	56,474	4.09	-10.54	167.82	91.91	-11.13	167.79	91.68	108.70	91.64
EP15	-	-	-13.98	166.31	89.13	-14.82	165.21	88.69	109.75	88.88
EP20	70,676	4.96	-16.14	164.18	83.53	-16.34	162.13	83.33	110.17	83.38

[a]EP00, EP05, EP10, EP15, and EP20 refer to PP were added PP-b-EP 0%, 5%, 10%, 15%, and 20% respectively

[b]Ramp rate = 40°C/min both heating and cooling, heating1-cooling-heating2 from -60° to 200°C, ΔH =kJ/g
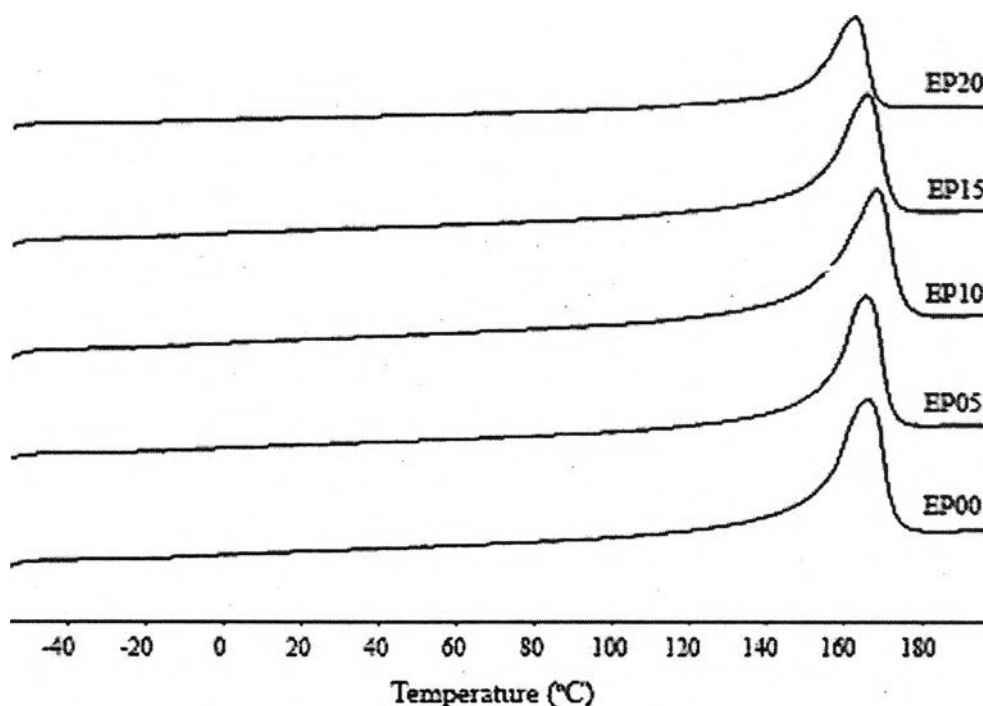

Figure 3 DSC curves of EP00, EP05, EP10, EP15, and EP20

Figure 4 shows the effect of PP-b-EP on dynamic mechanical properties of polymer blend. The result indicated that both PP and polymer blend have the similar values of E' in the range of -140 to 150 °C (Figure 4a). As shown in Figure 3b, E''of polymer blend is higher than PP at temperature lower than 0 °C. This result indicated that polymer blend can dissipate more energy than pure polypropylene (EP00) at low temperature (less than 0°C). Figure 4c shows the value of tanδ which determined from E''/E'. The tanδ of polymer blend is higher than pure polypropylene. It can be said that toughness of polymer blend increases in the range of low temperature when PP-co-EP presents in polypropylene blend. In addition, T_β peak, ascribed to glass transition in amorphous part, presented in polymer blend (Figure 4c). The broaden T_β peak is resulted from incorporation of EP molecule in amorphous PP region. [16] 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.
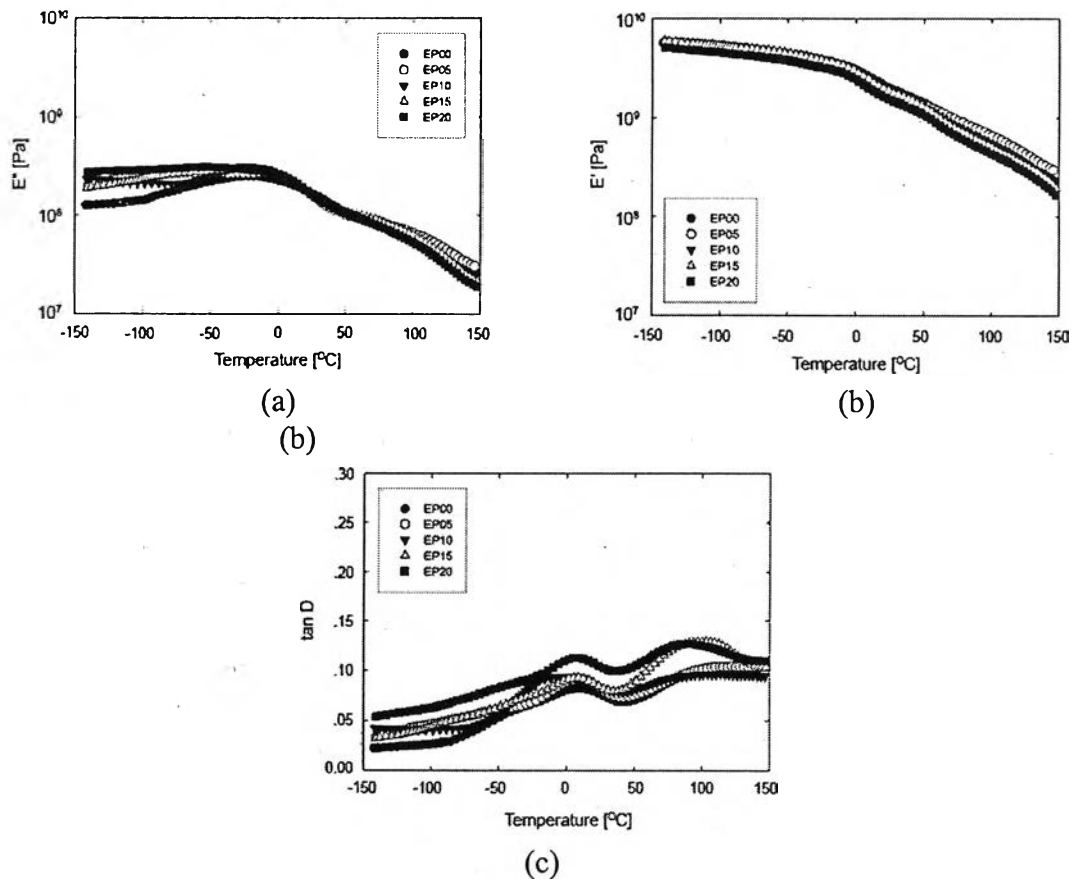
Figure 4 Temperature dependence of dynamic mechanical properties at 1 Hz: (a) storage modulus, (b) loss modulus, and (c) tanδ

As shown in Figure 5, SEM micrograph confirmed that polymer blend has greater toughness than PP. From room temperature fracture surface of polymer blends, these pictures showed rubbery morphology in addition to PP matrix. The blends have additional rubbery phase which stretch and binding the PP together. The more PP-*co*-EP added, the more stretch rubbery phase shown. This rubbery phase might be the reason for low temperature toughness of the blends.
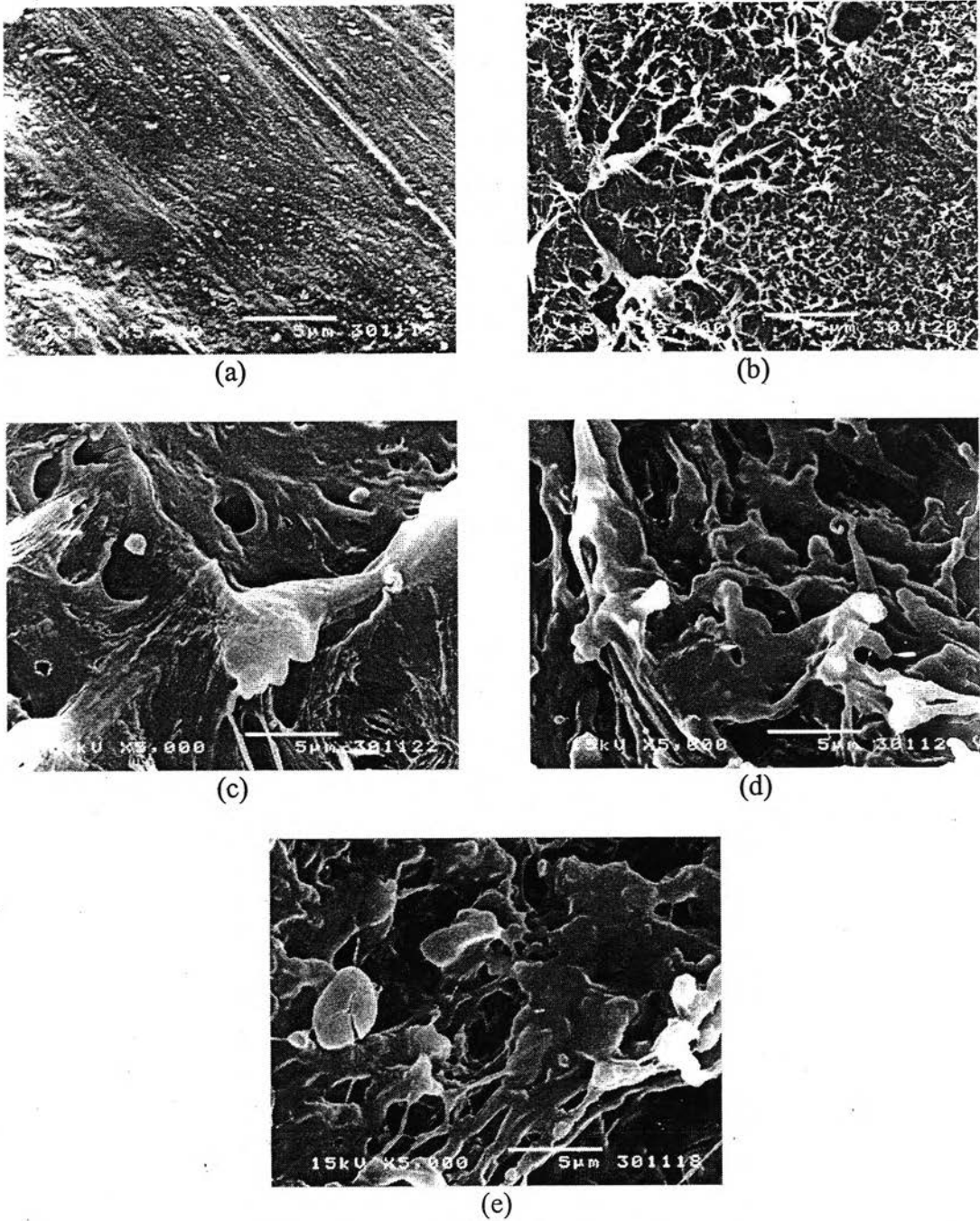
Figure 5 SEM micrographs of room temperature specimen fracture: (a) EP00, (b) EP05, (c) EP10, (d) EP15, and (e) EP20 (5000×)

Conclusions

The results presented PP-*co*-EP that synthesized by simple method. The ethylene content in the copolymer chain increased while increasing the ethylene fed pressure. The ^{13}C-NMR result indicated incorporation of ethylene in propylene chain. DSC and SEM showed rubbery material of copolymer resulted from lowering the T_g of the blends than the T_g of pure PP in the copolymers. The convenient condition from this work for synthesis PP-*co*-EP is 30 psi of propylene feeding and 70 psi of ethylene feeding pressure at 10 °C copolymerization temperature. The results of PP/PP-*b*-EP blends showed relation between PP-*b*-EP content with toughness, T_g, and crystallinity. From DSC, DMA, and SEM indicated the PP-*b*-EP include in amorphous region of PP and the polymer blends were lower T_g, and crystallinity but higher toughness than commercial grade PP in low range temperature. Therefore, we concluded that PP-*b*-EP is good rubber toughening agent for the polypropylene reinforcement at low temperature with simply prepared by the method described in this paper.

Acknowledgement

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APPENDIX F

THE PROCEEDING OF TECHNOLOGY AND INNOVATION FOR SUSTAINABLE DEVELOPMENT CONFERENCE (TISD2006)

New Synthesis Methods for Polypropylene co Ethylene-Propylene rubber

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Abstract

In this research, the new simple method for preparing of polypropylene-co-poly(ethylene-propylene) copolymer (PP-co-EP) was investigated. This copolymer was synthesized by using Ziegler-Natta catalyst at desired temperature. By changing the feed condition in Batch reactor, the copolymer can be synthesized. The microstructure of copolymer and melting temperature were characterized by ^{13}C-NMR and DSC. The NMR results stated that the copolymers were synthesized in the reactor. The properties of the copolymer were confirmed by DSC and SEM. The future usages of the copolymer in reinforcing the polypropylene have to be further investigated.

Keywords: Ziegler-Natta; Polypropylene; Ethylene-propylene copolymer

1. Introduction

It is well known that isotactic polypropylene (iPP) have poor impact properties at low temperature range (0°C, freezing in the normal refrigerator). The general methods to improve mechanical properties of iPP are the blending of iPP with rubbery material such as poly (ethylene-propylene) copolymer (EPR). The iPP/EPR blends are called toughened polypropylene, which find the wide applications in consumer products and automotive industry [1].

Copolymers are interested important materials to improve mechanical properties of iPP. The propylene-co-poly(ethylene-propylene) copolymer is one of polymers that used for rubber toughening of PP. Examples of syntheses and characterization of PP-co-EP are reported.[2-6]

Coates et al. also reported the synthesis of a syndiotactic polypropylene -block- poly (ethylene-propylene) with a metallocene catalyst system [2]. Beside that works, Y. Fukui and M. Murata also reported the synthesis of polypropylene-block-poly(ethylene-co-propylene) by using metallocene catalyst systems [3].

K.Nitta et al. reported polymer blend of PP/EPR blend and polypropylene -block- poly (ethylene-co-propylene) was synthesized by short-period polymerization method [4].

However, all method and catalyst system were reported are too difficult to perform in the application in industrials. This work represents new simple method for synthesis of polypropylene-co-poly(ethylene-propylene) copolymer which easy and can apply to use in the industrial production. The obtained copolymer can be utilized as the rubber toughening of polypropylene.

2. Experimental

2.1 Material

All chemicals were manipulated under purified argon using a vacuum atmosphere glove boxes and/or Schlenk techniques. Solvents were purified distilled over sodium/benzophenone under argon atmosphere before use. Ethylene and Propylene (polymerization grade) were obtained from National Petrochemical Co., Ltd., Thailand.

2.2 Preparation of catalyst

Anhydrous magnesium chloride (MgCl₂), decane and 2-ethylhexanol were added into a schlenk tube and heated to 130 °C for 2 h under magnetic stirring and argon atmosphere. Then phthalic anhydride was introduced into the solution and stirred until MgCl₂ was completely dissolved. The resulting, uniform solution was cooled to room temperature, and wholly dropped wise of titanium tetrachloride (TiCl₄) kept at -20 °C under stirring. The temperature was then raised to 80 °C, and diethylpthalate was injected in. The mixture was maintained at this temperature for 2 hours. After the reaction for 2 hours, the solid portion was collected from the reaction mixture. The solid portion was again suspended in 20 ml of titanium tetrachloride and again reacted at 120 °C for 2 hours. After these, the solid portion was again collected then washed with decane and with hexane 3 times. The resulting solid was subjected to vacuum dry to form a powder in gray color which needed to be stored under argon.

2.3 Synthesis of polypropylene-co-poly(ethylene-propylene) copolymer

Polymerization was carried out in 100 ml stainless steel autoclave reactor with magnetic stirrer in hexane by using TiCl₄/MgCl₂/DEP-TEA catalytic system. The polymer was synthesized in a two-stage reaction process. First, catalyst, cocatalyst and solvent were added into the reactor. The reactor was immediately put into liquid nitrogen to stop the reaction between the catalyst and cocatalyst. After that, the reactor was evacuated to remove argon. Then, the reactor was taken out of liquid nitrogen and heated up to polymerization temperature. The first stage of polymerization concerned with propylene homopolymerization by fed only propylene gas into the reactor. The reactor was heated under the controlled temperature to start the polymerization reaction. The second stage to cooperate the ethylene in the PP structure was successively done by suddenly feeding the pure ethylene gas to a stirred reactor. The mixture was quenched by addition of HCl/methanol solution after completion of the reactions. The obtained polymer that precipitated out was washed with excess methanol and dried at room temperature.

2.4 Characterization

Differential scanning calorimetry analyses of polymers were carried out using Perkin-Elmer Diamond DSC that was calibrated for temperature and melting enthalpy using indium as a standard. About 10 mg weights of samples were sealed in aluminum sample pans for the measurement. The samples were heated from -60

to 200 °C at scanning rate of 40 °C/min under N₂ atmosphere.

¹³C-NMR spectra of the polymers were measured on Avance DPX400 NMR spectrometer at 120 °C. o-Dichlorobenzene and Benzene-d₆ were used as solvent to prepare the polymer solution.

The morphologies of all polymers were investigated by JSM-5410LV Scanning Microscope. The samples for SEM analysis were coated with gold particles by ion sputtering device.
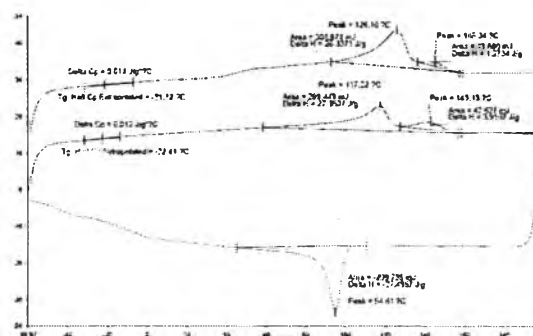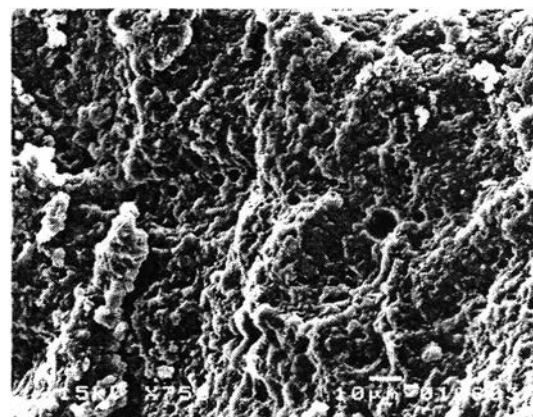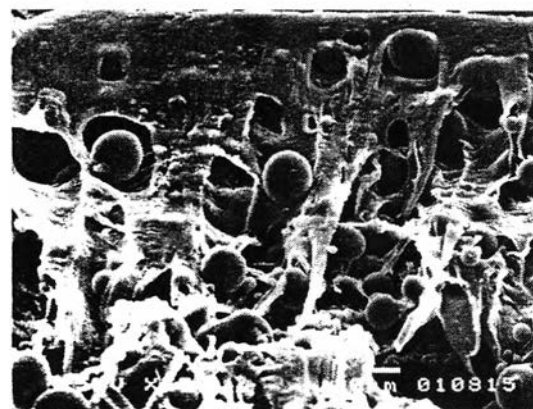

Figure 1 DSC curve of EP5

3. Results and discussion

(a)

(b)

Figure 2 SEM micrographs of polymer: A polymer fracture of PP, B polymer fracture of PP-block-EP

Figure 2 show a typical ^{13}C-NMR spectrum of the synthesized PP-co-EP (EP5). The chemical shift assignment for ^{13}C resonances is same as those reported by Yoshifumi et al. [3]. The mole fractions of propylene/ethylene unit in the block copolymer were determined as 37/63 mole% from the peak areas of methylene and methyl carbons [7-8]. From ^{13}C-NMR spectrum, the peak at 21.61 ppm showed the characteristic of Propylene (P) that have the Ethylene (E) laid in the adjacent of PPPPE which indicated the cooperation of E in the P 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. The second step of polymerization will allow E to react in the reactor, so the discovery that E cooperated in the P 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 E 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 E in the P chain.

Table 1 showed the effects of polymerization temperature and pressure of ethylene gas cooperated by being added in the reactor on the glass transition temperature and melting temperature of PP-co-EP products from DSC results. In addition to the NMR result, the DSC graphs of Tg of copolymer showed that there are two phase in the PP-b-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 Tm in the synthesized polymer.

From this table we can conclude that the higher polymerization temperature give the lower of glass transition temperature. However, synthesized polymer has the dispersed phase of the ethylene-propylene rubber at the rector temperature of 60 °C. Because at higher temperature will result in the higher chain transfer rate (EP1, EP2 and EP3) which shortening the progressive chains. As the consequence, the higher of the feeding ethylene pressure give the lower glass transition temperature (EP3, EP4, and EP5). These may resulted from the low Tg of EP part of the molecules, Figure 1 represent the DSC curves of EP4. The DSC curved obtained have three parts which was spitted in each step. Heat1 represented the first heating which indicated the raw polymer characteristic that obtained form reactor. After the first heating, the samples will be subjected to the Cooling and the temperature of crystallization, Tc, was observed. The Heat 2 represented the Tg and Tm that resulted from the cooling which clearly show the two different Tm according to the type of the crystal.

According to the DSC results, the appearance rubbery phase of block copolymer can by seen in SEM micrographs of polymer fracture. (Figure 2B) The minor phase of EP can be seen as the phase separated droplets in the fracture surface picture. In the pure PP micrographs, the droplet characteristics can not be observed. These appearances supported the DSC that represented the two phase characteristics.

Table 1 Characterization of polymers by DSC

Polymer	Temp (°C)	P_E (psi)	Heat 1(°C)			Heat 2 (°C)			Tc (°C)
			T_g	T_{m1}	T_{m2}	T_g	T_{m1}	T_{m2}	
EP1	60	50	-21.34	na	na	-22.51	113.80	147.10	92.04
EP2	40	50	-17.41	123.87	152.35	-17.64	124.97	150.48	99.34
EP3	10	50	-15.88	117.94	147.19	-14.72	118.67	145.70	91.47
EP4	10	60	-16.96	124.99	148.67	-16.53	116.11	146.83	94.81
EP5	10	70	-21.72	126.10	145.34	-22.41	117.22	143.13	95.93
PP	10	-	-9.86	-	151.27	-10.85	-	149.40	102.25

* Synthesis by TiCl$_4$/MgCl$_2$/DEP-TEA, Al/Ti = 167, propylene pressure feeding constant = 30 psi
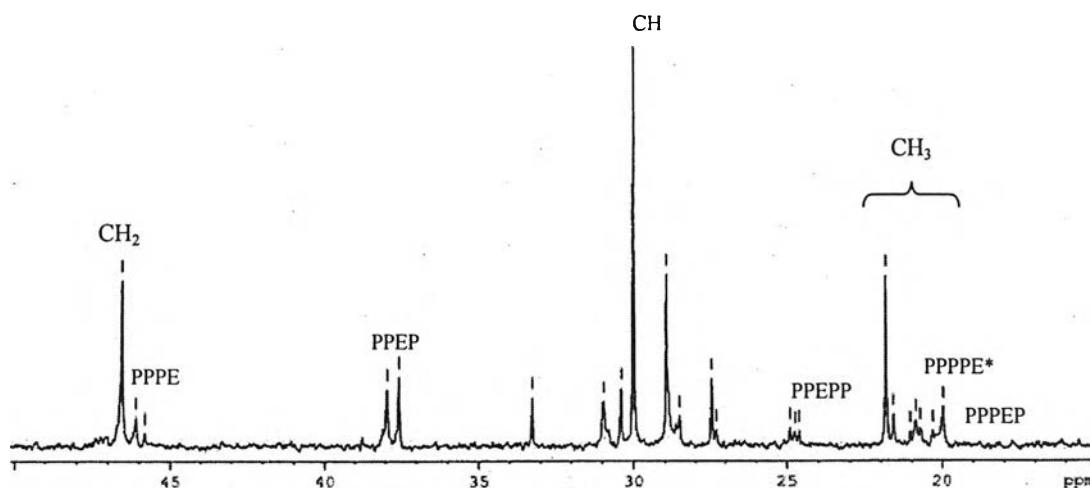
Figure 2 ^{13}C-NMR spectrum of PP-co-EP copolymer (EP4)

4. Conclusions

The results presented PP-co-EP that synthesized by simple method. The ethylene content in the copolymer chain increased while increasing the ethylene fed pressure. The NMR, DSC and SEM showed the success copolymerized of E in to the PP chains. The convenient condition from this work for synthesis PP-co-EP is 30 psi of propylene feeding and 70 psi of ethylene feeding pressure at 10 °C copolymerization temperature. The further effects on the combination of iPP with the PP-b-EP will be further evalutated.

Acknowledgement

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