

New Synthesis Methods for Polypropylene-*co*-Ethylene-Propylene Rubber

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ABSTRACT: In this research, the reinforcement of polypropylene (PP) was studied using a new method that is more practical for synthesizing polypropylene-*block*-poly(ethylene-propylene) copolymer (PP-*co*-EP), which can be used as a rubber toughening agent. This copolymer (PP-*co*-EP) could be synthesized by varying the feed condition and changing the feed gas in the batch reactor system using Ziegler–Natta catalysts system at a copolymerization temperature of 10°C. The ¹³C-NMR tested by a 21.61-ppm resonance peak indicated the incorporation of ethylene to propylene chains that could build up the microstructure of the block copolymer chain. Differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and dynamic mechanical analysis (DMA) results also confirmed these conclusions. Under

these conditions, the morphology of copolymer trapped in PP matrix could be observed and the copolymer T_g would decrease when the amount of PP-*co*-EP was increased. DMA study also showed that PP-*co*-EP is good for the polypropylene reinforcement at low temperature. Moreover, the PP-*co*-EP content has an effect on the crystallinity and morphology of polymer blend, i.e., the crystallinity of polymer decreased when the PP-*co*-EP content increased, but tougher mechanical properties at low temperature were observed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3609–3616, 2007

Key words: polypropylene-*co*-poly(ethylene-propylene) copolymer; synthesis; rubber toughening; Ziegler–Natta; polypropylene

INTRODUCTION

Isotactic polypropylene (iPP) is a typical semi-crystalline polymer that has been used to produce various products. However, it has a mechanical properties limit. It is well known that iPP has poor mechanical properties in the low-temperature range (0°C in the normal refrigerator) under its glass transition temperature (T_g). The general method to improve the mechanical properties of iPP is to blend iPP with a rubbery material such as poly(ethylene-propylene), copolymer (EPR), ethylene-propylene-diene terpolymer (EPDM), or any other copolymer.^{1–3} The iPP/EPR blends, called toughened polypropylene, have been widely used in consumer products and automotive industry. However, the strong incompatibility of EPR and iPP has presented a considerable problem in the modification of mechanical properties of iPP/EPR blending systems/methods.⁴

Copolymers are interesting alternatives as important materials to improve mechanical properties of iPP. The propylene-*co*-poly(ethylene-propylene) copolymer is one of the polymers that can be used for the rubber toughening of PP. Examples of the

syntheses and characterization of PP-*co*-EP have been reported.^{5–11}

Coates and colleagues⁵ reported the synthesis of a syndiotactic polypropylene-*block*-poly(ethylene-propylene) with a metallocene catalyst system. Fukui and Murata⁶ also reported the synthesis of polypropylene-*block*-poly(ethylene-*co*-propylene), using metallocene catalyst systems. However, these catalysts are not only expensive but are also rapidly deactivated by moisture and oxygen. Until now, the metallocene catalysts have remained difficult to operate and use practically.

Nitta et al.⁷ reported that the PP/EPR blends and polypropylene-*block*-poly(ethylene-*co*-propylene) can be synthesized by a short-period polymerization method. Mori et al.⁸ reported the synthesis of a polypropylene-*block*-poly(ethylene-propylene) by high-pressure-type and stopped-flow polymerization methods using the Ziegler–Natta catalyst.

However, the short-period polymerization and stopped-flow polymerization methods are not practical and are too complicated in polymer synthesis fields, as they must be controlled by a computer to generate sudden changes in gas feed conditions in 0.2 s.

Fan et al.⁹ reported that fraction of structure and properties of iPP/EPR in situ blend was synthesized by spherical Ziegler–Natta catalyst in two stages: the liquid phase propylene homopolymerization, and then the gas phase ethylene-propylene copolymerization.

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However, all the above-mentioned methods are not practical to use in the industrial applications. To overcome the problem, this work presents a new and simple method for the synthesis of polypropylene-*co*-poly(ethylene-propylene) (PP-*co*-EP) copolymer, using the Ziegler-Natta catalyst for industrial production. The nuclear magnetic resonance (NMR) results confirmed the incorporation of ethylene (E) in the molecule of propylene (P). The results of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) show that less pure P and pure E are produced in the PP-*co*-EP polymers. The copolymer obtained can be used for 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 blending of PP with PP-*co*-EP polymers.

EXPERIMENTAL

Materials

Ethylene and propylene (polymerization grade) and triethylaluminum (AlEt₃; TEA) were obtained from Bangkok Polyethylene Company (Bangkok, Thailand). TiCl₄ was purchased from Merck. Anhydrous MgCl₂ was supplied by Sigma-Aldrich; phthalic anhydride, diethylphthalate (DEP, used as an internal donor) and *n*-decane were purchased from Fluka Chemie A.G. (St. Gallen, Switzerland). Hexane was donated by Exxon Chemical Thailand (Bangkok, Thailand).

The solvents were distilled over sodium/benzophenone under argon atmosphere before use. Ultra-high-purity (UHP) argon (99.999%) was obtained from Thai Industrial Gas Company (Bangkok, Thailand) and was further purified by molecular sieves -3 \AA , BASF catalyst R3-11G, NaOH, and phosphorus pentoxide (P₂O₅), to remove traces of oxygen and moisture. Commercial-

grade polypropylene was donated by the Thai Polyplastic Industry Public Company (Bangkok, Thailand).

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

Preparation of catalyst

Anhydrous magnesium chloride (MgCl₂), *n*-decane, and 2-ethyl-1-hexanol were put 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 stirring at -20°C . The temperature was then raised to 110°C, and diethylphthalate was injected in. The mixture was maintained at this temperature for 2 h. After the 2-h reaction, the solid portion was collected from the reaction mixture and again suspended in 20 mL of titanium tetrachloride and reacted at 120°C for another 2 h. It was then collected and later washed with *n*-decane and *n*-hexane for 2 and 3 times, respectively. The resulting solid was next vacuum dry to form a powder in gray color which must to be stored under argon atmosphere.

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

Polymerization was carried out in a 100-mL stainless steel autoclave reactor with magnetic stirrer in hexane, using a MgCl₂/DEP/TiCl₄-TEA catalytic system. The polymer was synthesized in a two-stage reaction process. First, the solvent, co-catalyst, and catalyst

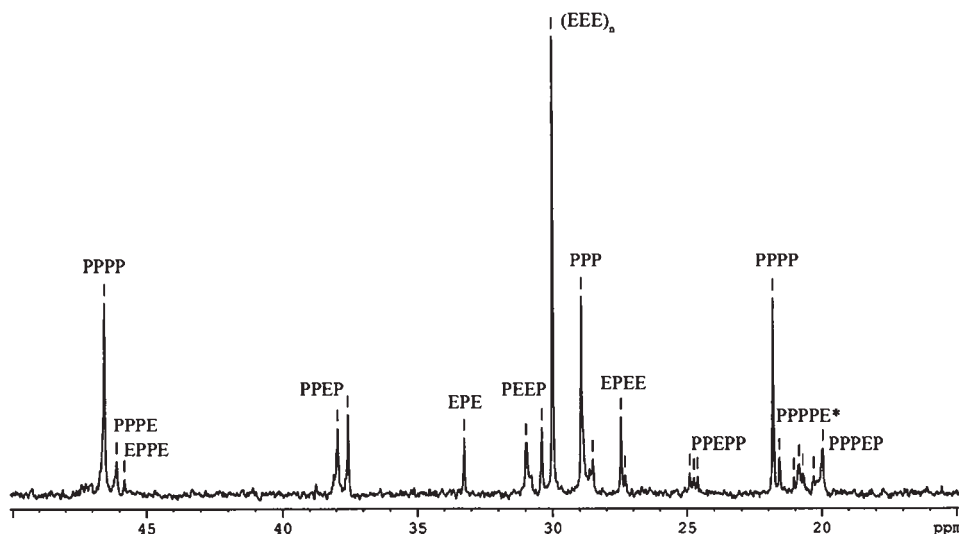


Figure 1 ¹³C-NMR spectrum of PP-*co*-EP copolymer (polymer 5).

TABLE I
Characterization of Polymers by DSC

Polymer ^a	Temp (°C)	P _E (psi)	Mn	MWD	Heat 1 ^b			Heat 2 ^b			
					T _g	T _{m1}	T _{m2}	T _g	T _{m1}	T _{m2}	T _c
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

nd, not detected.

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

^b Ramp rate = 40°C/min both heating and cooling; heating 1 – cooling – heating 2 from -60° to 200°C.

were added into the reactor, and subsequently placed in some liquid nitrogen to control the reaction between the catalyst and co-catalyst. After that, the reactor was evacuated to remove both the argon and the liquid nitrogen, and then heated up to polymerization temperature. The first stage of polymerization is the propylene homopolymerization, to feed only propylene gas into the reactor for 10 min. The reactor was then heated under the controlled temperature to start the polymerization reaction. The second stage is to incorporate the ethylene into the PP structure by successively feeding the pure ethylene gas into a stirred reactor for a duration of 30 min. The mixture was then quenched in the HCl/methanol solution after the completion of the reaction. The polymer obtained that precipitates out is to be washed thoroughly in methanol and finally dried at room temperature.

Blending and molding of polymer

Polypropylene (PP) and the PP-*co*-EP were combined by the melt-mixing method on a digital hot plate at 220°C with 5%, 10%, 15%, and 20% of PP-*co*-EP. The

polymer blend was then was molded with LAB TECH Automatic Hydraulic Hotpress LP-50 M/C 9701 in an aluminum mold at 200°C 1500 psi. Then, the polymer blend was cooled down at room temperature. The sample size for tensile testing is 20 × 100 × 0.5 mm and 10 × 40 × 0.5 for DMA.

Characterization

DSC analyses of polymers were carried out using Perkin-Elmer Diamond DSC, calibrated for temperature and melting enthalpy, with indium as the standard. Each sample, ~ 10 mg in weight, was sealed in an aluminum pan for further measurement before being heated from -60 to 200°C at a scanning rate of 40°C/min under N₂ atmosphere.

¹³C-NMR spectra of the polymers were measured on an Avance DPX400 NMR spectrometer at 120°C, while *o*-dichlorobenzene and benzene-*d*₆ were used as solvents to prepare the polymer solution.

The morphologies of all polymer fracture surfaces were investigated with a JSM-5410LV scanning electron microscope (SEM). The samples for SEM analysis

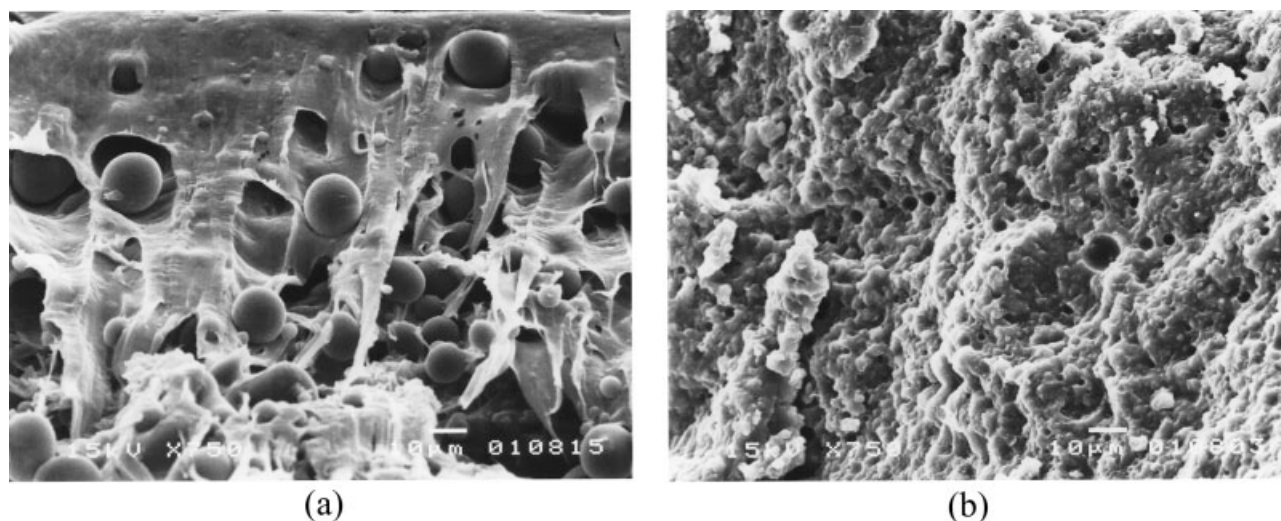


Figure 2 SEMs of cryogenic polymer fracture surface. (a) Polymer fracture of PP-*block*-EP (polymer 5); (b) polymer fracture of PP (polymer 6). ×750.

TABLE II
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, referring to PP, were added PP-*b*-EP 0%, 5%, 10%, 15%, and 20%, respectively.

^b Ramp rate = 40°C/min both heating and cooling; heating 1 – cooling – heating 2 from -60° to 200°C, $\Delta H = \text{kJ/g}$.

were coated with gold particles by ion sputtering device to provide electrical contact for the specimens.

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

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

RESULTS AND DISCUSSION

Synthesis of copolymer

Figure 1 shows a typical ¹³C-NMR spectrum of the synthesized PP-*co*-EP (polymer 5). The chemical shift assignments for ¹³C resonances are similar to those reported by Fukui et al.⁶ The mole fractions of pro-

pylene/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 the ¹³C-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, indicating 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 (for a duration of 10 min) The second step of polymerization allowed E to react in the reactor for a duration of 30 min, so that the discovered E incorporated in the P chain would support the formation of the block copolymer of PP and EP in the second stage. This shows that at least some of the PP chain will survive through the second stage of the reaction, with E incorporation as the consequence. 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.

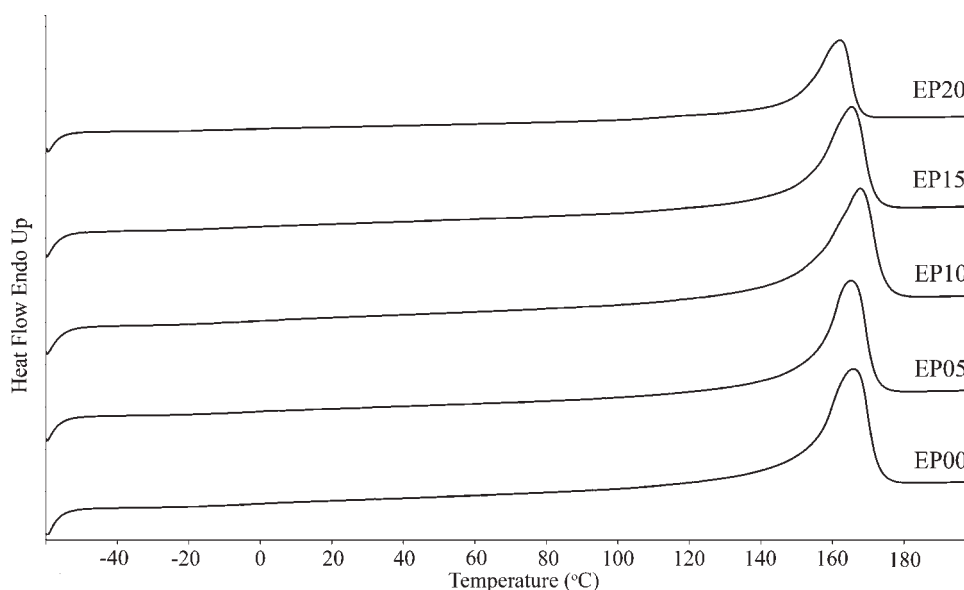


Figure 3 DSC curves of EP00, EP05, EP10, EP15, and EP20.

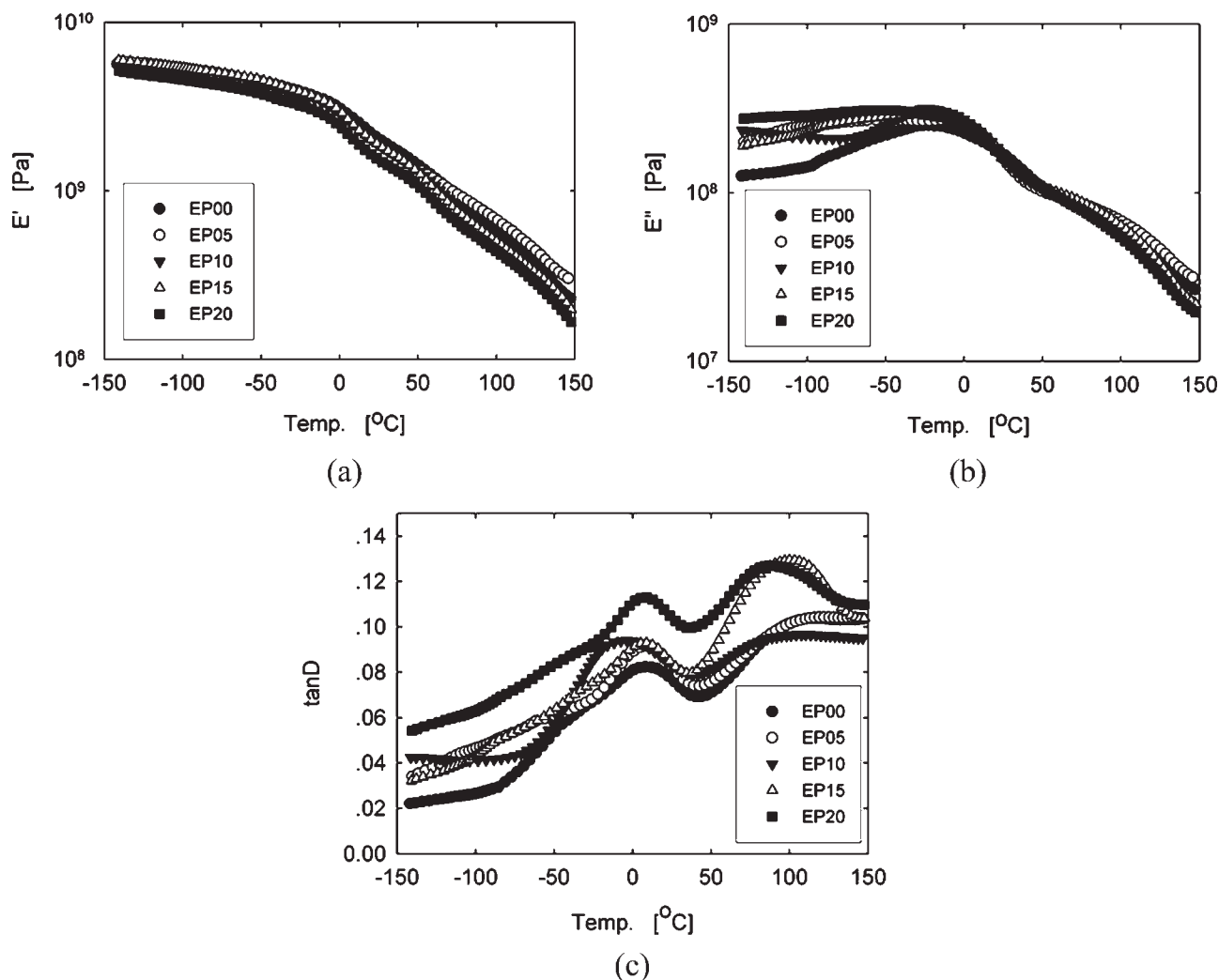


Figure 4 Temperature dependence of dynamic mechanical properties at 1 Hz. (a) Storage modulus; (b) loss modulus; (c) $\tan\delta$.

Table I shows the effects of polymerization temperature and pressure of corporate ethylene gas when added into the reactor at 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 show that there are two phases in the PP-*b*-EP block copolymer, as the DSC results clearly show two T_m in the synthesized polymers. In the first phase, PP is dominant and the other phase appears to have the E contribution.

From Table I we can conclude that a higher polymerization temperature gives the lower T_g of the products. This might be because there is more incorporation of E in the P chain at the 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 T_g also confirms the NMR results that E has cooperation in the PP chain without serious segregation of pure

PP because no clear pure component T_g of PP (-10 – 0°C) was detected. Moreover, synthesized polymers have the dispersed phase of the ethylene-propylene rubber even at the reactor temperature of 60°C . Usually at higher temperature, polymerization will give results in the higher chain transfer rate (polymer 1, polymer 2, and polymer 3), which shorten the progressive chains of PP; it is most likely that the E cannot totally incorporate on the PP chain.

As a consequence, the higher feeding ethylene pressure gives the lower T_g temperature (polymer 3, polymer 4, and polymer 5) at the same reaction temperatures. These may result from the higher incorporation of E, because the concentration of E is increased along with the pressure of the system. The higher concentration of E presented in the reactions shows the higher incorporation of E onto the PP chain and the samples. Unfortunately, with the limit of the 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

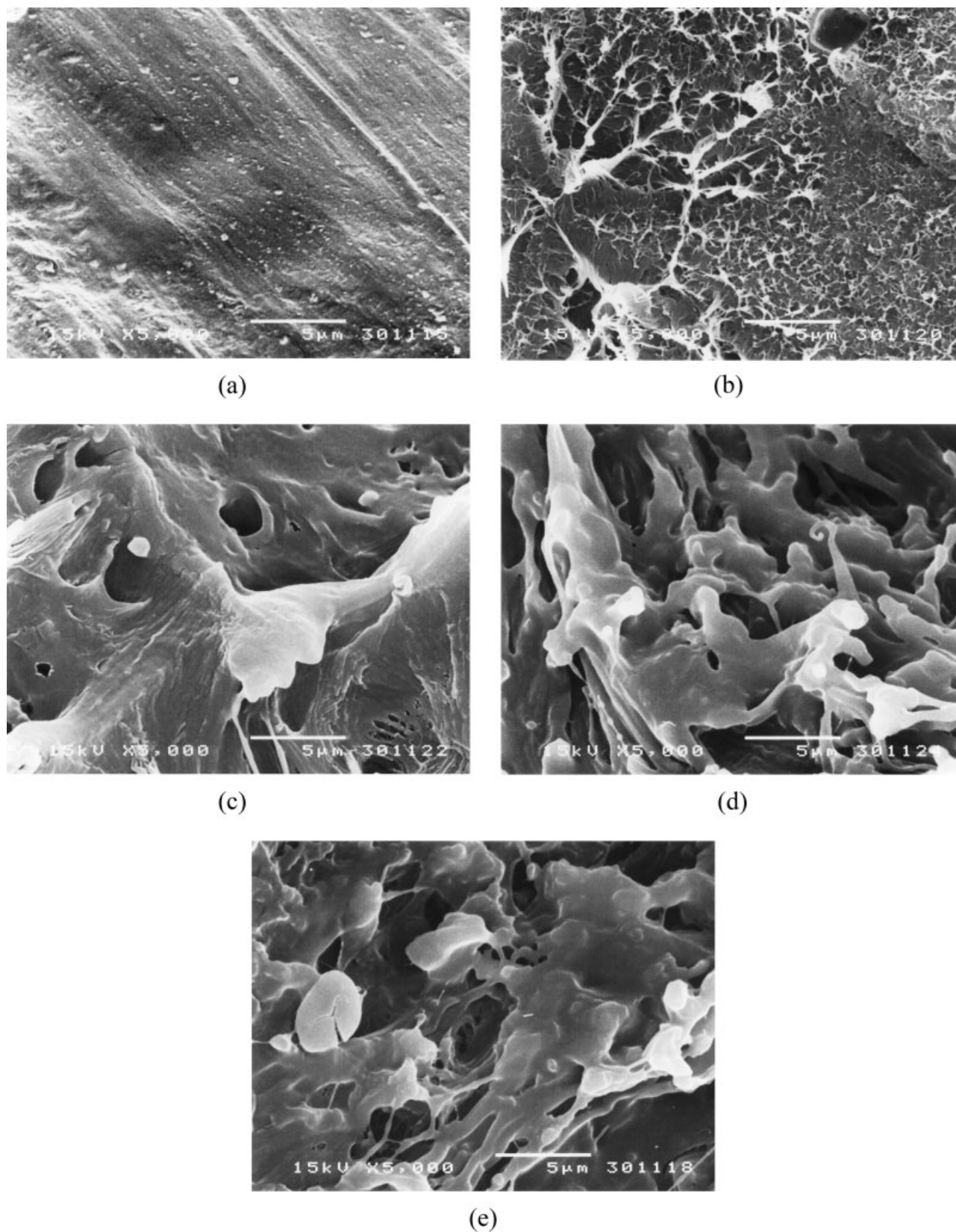


Figure 5 SEMs of room temperature specimen fracture. (a) EP00; (b) EP05; (c) EP10; (d) EP15; (e) EP20. $\times 5000$.

T_g of PP according to the incorporation of E in these systems also supports 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, and the polymer formed is the PP only. Because the time for PP to react is the same as other samples before the supply of 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 was 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 in the other cooperation of E samples shows 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 of the rubbery phase of the block copolymer can be seen in SEMs of polymer fracture [Fig. 2(a)] 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, Fig. 2(b)], the droplet characteristics cannot be observed. These appearances support the DSC results that represent the two phase characteristics.

Polymer blend

The influence of PP-*b*-EP incorporated in commercial-grade polypropylene on T_g , T_m , and T_c of polymer blend is shown in Table II. The suffix number at the name of the blend stands for the weight percentage of the PP-*co*-EP added to the blend. As can be seen, T_g value decreases with an increase of the PP-*b*-EP content (from 0% to 20%), while T_m and T_c values are not clearly affected. Generally, T_g represents 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 decreases with the increase of the PP-*b*-EP copolymer content.⁷ The T_g of polymer blend ranges from that of PP and synthesized PP-*b*-EP. The T_m and T_c results suggest that EP molecule does not substantially 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 confirm the previous work on the blend of PP and EP;^{7,16,17} thus, our PP-*co*-EP can affect the properties of the PP like other references but is better in that it has an easier preparation. Figure 3 shows heat 2 DSC curve of PP (EP00) and polymer

blend in which the T_m of the polymer blend was similar to PP.

Figure 4 shows the effect of PP-*b*-EP on the dynamic mechanical properties of the polymer blend. The result indicates that both PP and polymer blend have similar values of E within the range of -140 – 150°C [Fig. 4(a)]. As shown in Figure 3(b), the E of polymer blend is higher than PP at a temperature of $< 0^\circ\text{C}$. This means that the polymer blend can dissipate more energy than pure polypropylene (EP00) at low temperature ($< 0^\circ\text{C}$). Figure 4(c) shows the value of $\tan\delta$, which is determined by E''/E' . The $\tan\delta$ of polymer blend is higher than that of the pure polypropylene. It can be said that the toughness of the polymer blend increases within the range of low temperature, while PP-*co*-EP only presents in the polypropylene blend. In addition, the T_β peak, ascribed to glass transition in amorphous part, is present in polymer blend [Fig. 4(c)]. The broader T_β peak resulted from the incorporation of EP molecule in the amorphous PP region.¹⁶ Moreover, the T_g of E at $\sim -100^\circ\text{C}$ was not observed. This may suggest that the samples have too small an amount of PE molecules generated in amorphous phases to be detected by DMA.

As shown in Figure 5, SEM confirmed that the polymer blend has greater toughness than PP. From the room temperature fracture surface of polymer blends, these pictures show a rubbery morphology in addition to the PP matrix. The blends have an additional rubbery phase that stretches and binds the PP together. The more PP-*co*-EP added, the more the stretched rubbery phase can be observed. This rubbery phase might be responsible for the low-temperature toughness of the blends.

CONCLUSION

The results presented show that the PP-*co*-EP can be synthesized by a simple method. The ethylene content in the copolymer chain increased while increasing the ethylene feed pressure. The ^{13}C -NMR result indicated incorporation of ethylene in the propylene chain. DSC and SEM showed the rubbery material of the copolymer resulting from lowering the T_g of the blends further than the T_g of pure PP in the copolymers. The convenient condition shown in the present work for the synthesis PP-*co*-EP is 30 psi of propylene feeding and 70 psi of ethylene feeding pressure at a 10°C copolymerization temperature. The results of PP/PP-*b*-EP blends show a relationship among the PP-*b*-EP content with toughness, T_g , and crystallinity. DSC, DMA, and SEM indicated that the PP-*b*-EP included in the amorphous region of PP and the polymer blends have lower T_g and crystallinity, but higher toughness, than commercial-grade PP within the low-temperature range. We can conclude that PP-*b*-EP is a

good rubber toughening agent for polypropylene reinforcement at low temperature that can be simply prepared, using the method described.

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