

Characterization and Property Correlations of Amorphous Poly(alpha olefin)

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ABSTRACT: Amorphous poly(alpha olefins)[®] (APAOs) with various types and contents of comonomers, and molecular weight were characterized by general, thermal, rheological, and mechanical methods and their properties were correlated with their molecular parameters. It was found that they can be used as a modifier for isotactic poly-

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Key words: amorphous poly- α -olefin (APAO); thermal; rheological; mechanical properties

INTRODUCTION

Amorphous poly(alpha olefins)[®] (APAOs) are low molecular weight polypropylene or polypropylene-based copolymers with predominantly atactic molecular structure. These are polymerized with propylene or copolymerized with propylene and ethylene or 1-butene by Ziegler-Natta supported pro-catalyst and an alkyl aluminum cocatalyst. So, APAOs have three distinctive types: homopolymers of propylene, copolymers of propylene and ethylene, and copolymers of propylene and 1-butene. The tacticity and molecular weight of APAOs are controlled through a proprietary polymerization technique, which results in a versatile melt viscosity, melting point, freezing point, and mechanical strengths.^{1–4}

The Ziegler-Natta catalyst being used includes titanium tetrahalide mixed with an enhanced support composed of magnesium halide and aluminum trihalide, and alkyl aluminum cocatalyst includes as trialkyl aluminum and alkyl aluminum halide. Polymerization was done in a stirred batch reactor with average residence time of about 1–3 h at 65–75°C (28–39 kg cm⁻²).

There are many APAOs with different molecular weights, comonomers types and contents, but the main characteristics of those materials are low molecular weight and low crystallinity. So, these characteristics can provide easy processing, good adhesion to a wide variety of substrates, good compatibility

with solvents, oligomers and polymers, low temperature flexibility as well as toughening of propylene-based polymers.

Possible applications of APAOs include hot melt adhesive and sealant, laminations, bitumen modification for roofing and road paving, mineral filler and polymer alloy compounding, as well as modifier of plastics and elastomers. However, regardless of numerous possible applications, investigations on APAOs are rare, especially regarding the characteristics of APAOs and application for modifier of other plastics.

In this article, we characterized six grades of APAO with different comonomer type and contents, and molecular weight for the purpose of using APAOs as a modifier of isotactic homo polypropylene and block copolymer.

Characterizations were performed using nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimeter (DSC), gel permeation chromatography (GPC), and advanced rheometries expansion system (ARES). Correlations were made between the physical properties and molecular characteristics of the APAOs.

EXPERIMENTAL

Material

Six types of UBETAC[®] APAOs (Amorphous Poly Alpha Olefin, Ube Industries, Japan) were used for characterizations. And commercial isotactic and atactic polypropylene (KPIC 1088[®], KPIC APP[®] Korea Petrochemical Industrial Corp., Korea) were used for the purpose of comparison. Molecular characteristics and basic physical properties of the samples

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determined from our experiments described below are listed in Table I.

NMR and GPC measurements

^{13}C -NMR spectra were recorded on a Varian Unity-Inova-300 nuclear magnetic resonance spectroscopy for the analysis of comonomer contents and isotacticity of each APAO grade. To calculate isotacticity,^{5,6} we calculated the content of mm-triad methyl group ($-\text{CH}_3$) of PP using each pentad methyl peak resonating between 19 and 22 ppm following the relationship;

$$\text{mm}\% = \frac{S_{\text{mm}}}{S_{\text{total methyl}}} 100$$

where $S_{\text{mm}} = S_{\text{mmmm}} + S_{\text{mmmr}} + S_{\text{rmmr}}$ and $S_{\text{total methyl}}$ is the total area of all methyl peaks.

The molecular weight and molecular weight distribution of APAOs were determined by gel permeation chromatography (GPC). Tetrahydrofuran (THF) was used as carrier solvent, and the calibration curve was established by using standard polystyrene.

Thermal properties

Thermal properties were determined by differential scanning calorimeter (DSC, Perkin-Elmer Pyris II). Specimens were heated from 25°C to 200°C at 10°C min⁻¹ and kept for 1 min and cooled down to 30°C at 10°C min⁻¹ to measure crystallization temperature. Samples were reheated to determine melting temperature.

Rheological properties

Rheological properties were measured by Advanced Rheometries Expansion System (ARES, Rheometries) at various temperatures and frequencies with a 25-mm parallel plate fixture. The test specimen was prepared by compression molding. Dynamic frequency sweep mode was performed in nitrogen atmospheres at constant strain of 15% and oscillatory angular frequency ranging between 0.1 and 400 rad s⁻¹ at 150, 160, and 170°C. Dynamic temperature sweep mode was performed at a constant frequency (1rad s⁻¹) from 60°C to 190°C. The measurement was performed by loading the specimen at 190 °C in the molten state. And the instrument was programmed to cool down at 4°C min⁻¹ from 190°C to 60°C, and then to heat up at 4 °C min⁻¹ from 60°C to 190°C.

Mechanical properties

Tensile properties and flexural modulus were measured by Universal Test Machine (UTM, Instron 4302,

TABLE I
General and Physical properties of Homo PP and 6 APAO Grades

Sample name	Grade name	Comonomer		General properties				Mechanical properties			
		Type	Content	M_n (10 ⁴ g mol ⁻¹)	M_w (10 ⁴ g mol ⁻¹)	M_w/M_n	Isotacticity	Hardness (shore D)	Izod Impact Strength (kgf cm cm ⁻¹)	Flexural modulus (kgf cm ⁻²)	Tensile strength at yield (kgf cm ⁻²)
R10	KPIC 1088	-	-	4.83	22.59	4.67	0.970	77.0	2.1	153.00	350
H18	UBE 2180	-	-	0.80	3.68	4.61	0.560	27.2	N/B	500	24
E28	UBE 2280	ethylene	4.3	0.81	3.62	4.46	0.494	17.0	N/B	100	13
E33	UBE 2330	ethylene	7.8	0.40	1.81	4.59	0.443	5.2	N/B	-	8
E38	UBE 2385	ethylene	7.4	0.84	3.62	4.29	0.448	5.0	N/B	-	8
E58	UBE 2585	ethylene	13.0	0.87	3.55	4.09	0.398	4.0	N/B	-	4
B78	UBE 2780	1-butene	32.0	0.90	4.08	4.56	0.602	2.0	N/B	-	3
BPA	KPIC APP	-	-	0.15	2.4	15.6	0.527	8	N/B	-	6

USA), hardness by Shore D (Toyoseiki, Japan), and impact strength by Izod impact tester (Toyoseiki, Japan). All mechanical properties were measured by the corresponding ASTM methods.

RESULTS AND DISCUSSION

General properties

Accurate comonomer content and isotacticity determined by NMR analysis are given in Figure 1 and Table I. Among ethylene copolymerized APAOs (E28, E38, and E58), polydispersity decreases with increasing comonomer content though their molecular weights are similar, and it is smaller than that of homo APAO(H18). In contrast, B78, though its comonomer content is very high, polydispersity is similar to H18. It is also shown in Table I, which shows that isotacticity and crystallinity of all APAOs are much smaller than that of homo polypropylene and it is decreasing with increasing ethylene content. This means that all APAOs have predominantly amorphous structure.

Rheological properties

Figure 2 shows the complex viscosities of six APAO grades and a commercial isotactic homo polypropylene as a function of frequency at 170°C. All APAOs show frequency independent behavior and their dynamic viscosities are much smaller than that of homo polypropylene (R10) because of their low molecular weight though they have similar polydispersity with homo polypropylene as seen from the GPC data.

All samples show semicircle in Cole-Cole plots (Fig. 3). Wisniewski et al. observed that drift from semicircle is not present for homopolymer and compatible polymer blends, but present for incompatible blends at low frequencies.⁷ Our results show no drift implying that they are relaxed following a single mechanism. Very low plot of E33 is due to its extremely low melt viscosity.

The curves of the storage modulus (G') and the loss modulus (G'') taken at two different temperatures are shown in Figure 4. Han and Chuang⁸⁻¹⁰ found that all homogeneous viscoelastic fluids showed temperature independence of G' when plotted against G'' . Our results show that E38 and B78 are temperature independent, but H18 shows a little deviation from superposition at low frequency. Kang et al.¹¹ observed this kind of deviation from ionomer based on propylene terpolymer, and suggested that it could be caused by different microstructure at each temperature, probably due to the difference in relaxation or degree of physical ionic crosslinkings. But in our results, the slight deviation of homo

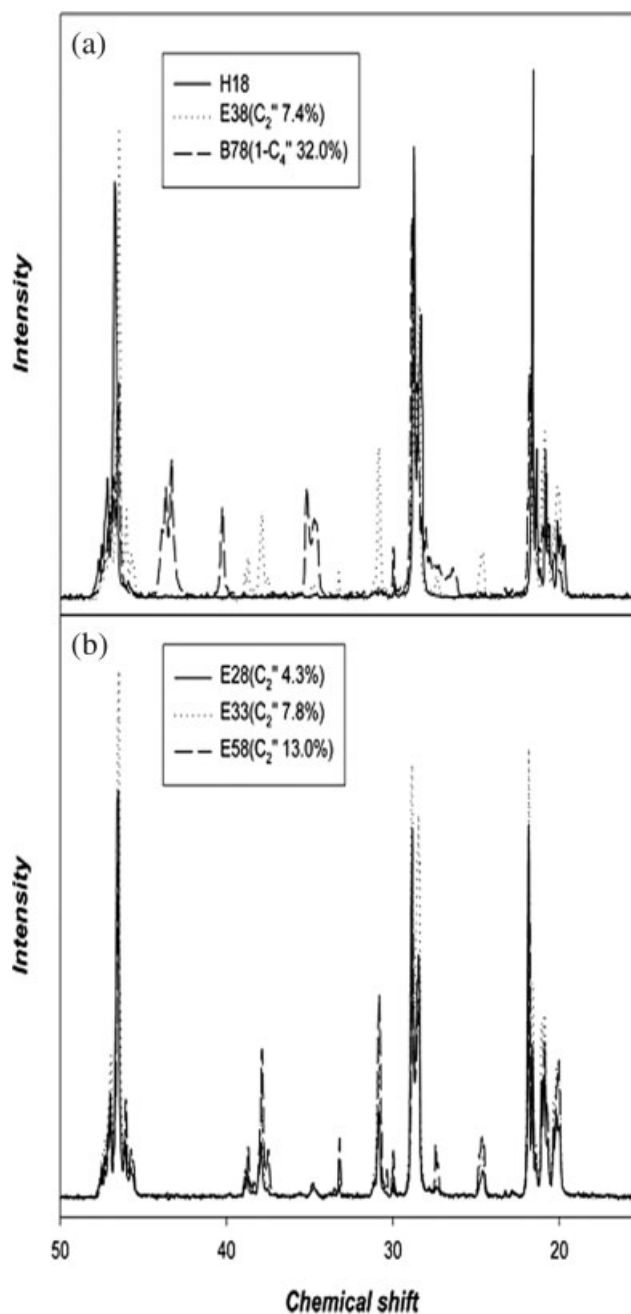


Figure 1 The results of NMR analysis for the APAOs for different comonomer types (a) and comonomer content (b).

APAO grade (H18) probably comes from the experimental condition. The lower test temperature of H18 is 160°C which is close to the melting temperature (157.5°C). Then, the ratio of the viscous portion to the elastic portion is different from that of fully melted ones, which can cause different relaxation behavior. So all APAO grades are supposed to be originally homogeneous viscoelastic fluids.

Figure 5 shows the temperature dependence of complex viscosities of the APAOs. For all samples viscosity increase in a similar fashion until the onset of freezing which is consistent with the Arrhenius

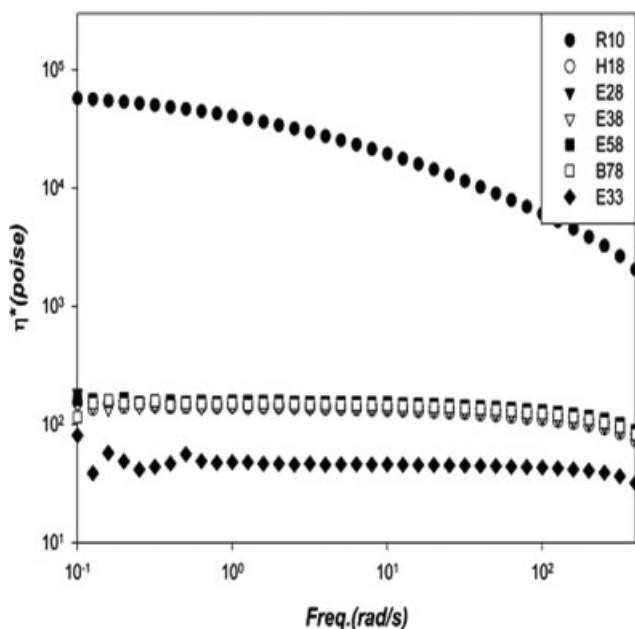


Figure 2 Dynamic viscosities of homo polypropylene and 6 APAO grades at 170 °C.

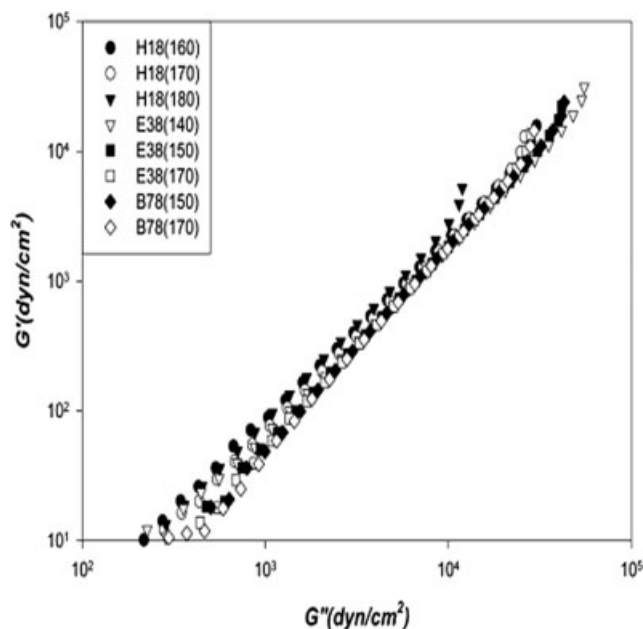


Figure 3 Cole-Cole plots for 6 APAO grades at 170 °C.

Figure 4 Log G' versus log G'' for different comonomer types at two temperatures.

relation. But after freezing is started, all samples show rapid increase in viscosity, and then become smooth flat. The rapidly increasing slope indicating freezing rate is the sharpest with homo APAO (H18). And though their molecular weight is similar, slope is decreasing with increasing comonomer content as $E28 \approx E33 > E38 \approx E58 > BPA > B78$. With similar comonomer content of E33 and E38, slope of low molecular weight (E33) is sharper than that of

high molecular weight (E38). This means comonomer interrupt the crystallization which results in slow freezing, and the effect is remarkable in high molecular weight sample. For atactic polypropylene (KPIC APP[®], BPA), though its crystallinity and isotacticity are similar with H18, freezing rate is much slower than that of H18, even slower than that of E58 with very low crystallinity. Generally, commercial by-product APP have small amount of nonpuri-

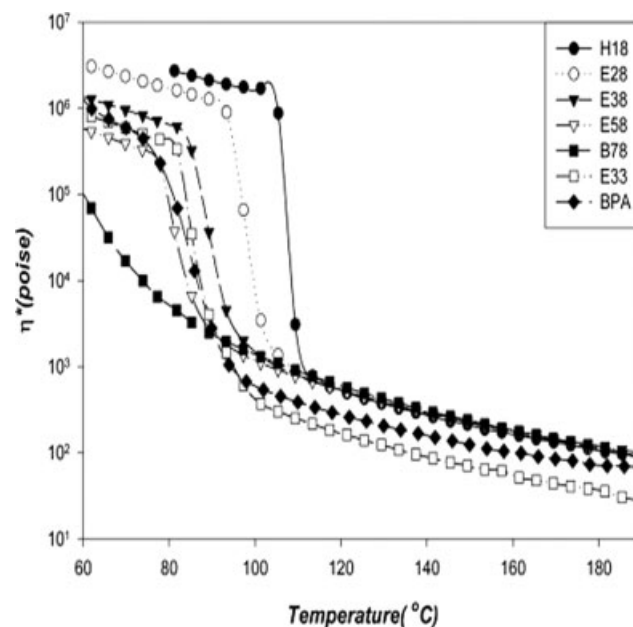
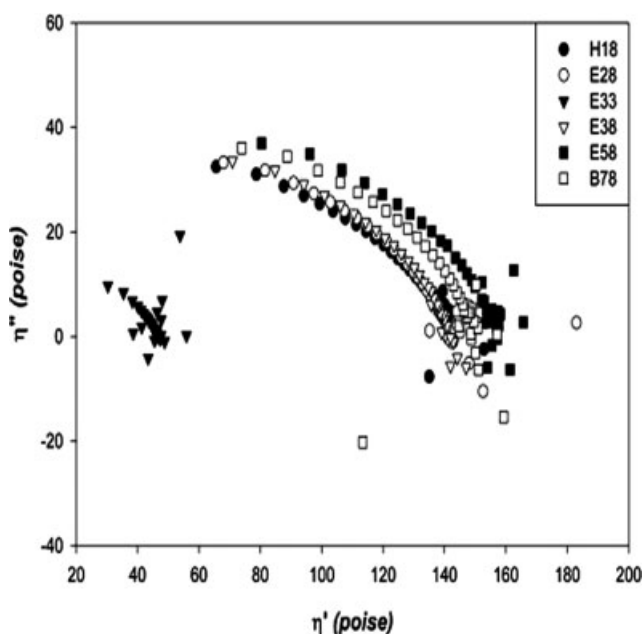


Figure 5 Temperature dependence of complex viscosities for 6 APAO grades.

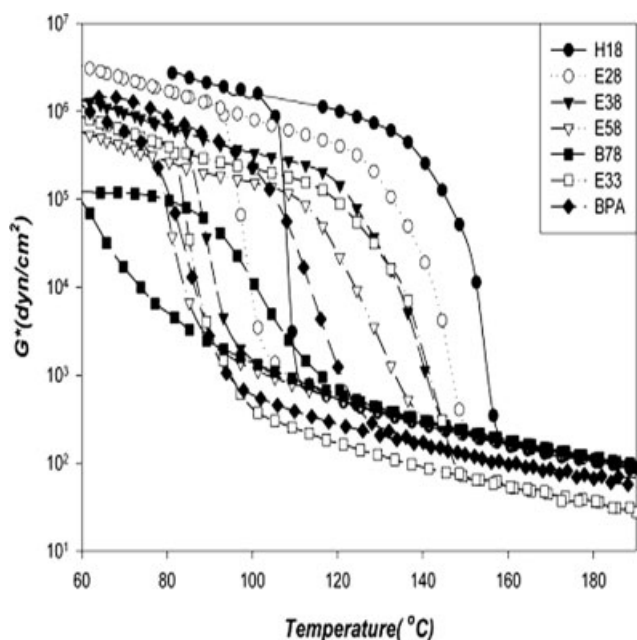


Figure 6 Temperature dependence of complex modulus for 6 APAO grades.

ficated isotactic PP, so it is supposed that this portion make to have APP high crystallinity and isotacticity, but cannot affect to increase freezing rate.

Figure 6 shows the temperature dependence of complex modulus for the APAOs. As temperature decreases, modulus increases in an approximately log-linear fashion, and then exhibits a sudden increase attributed to crystallization. As the temperature is increased again from 60°C to 190°C, the modulus gradually decreases until the onset of melting, and then rapidly decreases. All samples show irreversible behavior as temperature goes down and up. This supercooling effect is generally exhibited in semicrystalline polymer including isotactic polypropylene, and is caused by residual crystallinity. So, this explains that all APAOs have some crystallinity in spite of their predominant amorphous nature. For one APAO grade copolymerized with ethylene,

Tollefson¹² observed similar result with ours. The slope of complex modulus in freezing and melting process is the order of homo H18 > E28 ≈ E33 > E38 ≈ E58 > BPA > B78, and the degree of supercooling effect which can be supposed by the area of modulus difference is the same order. However B78 and BPA, though their crystallinity and isotacticity are somewhat higher compared with other APAOs, they show lower supercooling effect. With similar comonomer content of E33 and E38, lower molecular weight of E33 shows higher supercooling effect than that of E38.

Thermal properties

Thermal properties of APAOs, BPA, and isotactic polypropylene are listed in Table II. All APAOs have T_m and T_c although their crystallinity calculated by the heat of fusion is very low compared with general isotactic polypropylene (R10). This means all APAOs have predominantly atactic structure which is more remarkable with increasing comonomer contents, which is consistent with the result of rheological properties.

Figure 7 shows the shape of melting peaks of APAOs, homo polypropylene and BPA where H18, E28, E33, E38, and BPA exhibit two melting peaks. Generally, it is reported that polypropylenes have three types of crystalline structures, namely α , β , and γ form.^{13–16} In general crystallinity of isotactic polypropylene is very high and its crystalline structure is mostly α form, and exhibits only one melting peak. On the contrary APAO shows very low crystallinity and α form does not seem dominant any more, so it is supposed to exhibit two melting peaks in DSC curve. Also, the tendency to exhibit two melting peaks is decreased with increasing comonomer contents as E28 > E38 and for very high comonomer contents of E58 and B78 only one small melting peak is noted.

Figure 8 shows the relationship between T_m and T_{mo} or T_{mt} , and T_c and T_{fo} or T_{ft} . T_{mo} and T_{mt} in

TABLE II
Thermal and Rheological Properties of Homo PP and 6 APAO Grades

Sample Name	T_m (°C, DSC)		T_m (°C, ARES)		T_c (°C, DSC)	T_f (°C, ARES)		ΔH_f (J g ⁻¹)	Crystallinity (%)
	T_{ml}	T_{mh}	T_{mo}	T_{mt}		T_{fo}	T_{ft}		
R10	–	165.2	–	–	119.9	–	–	141.7	68.1
H18	138.0	157.5	136	156	98.9	110	102	32.8	15.8
E28	128.1	149.5	126	148	86.5	106	94	23.3	11.2
E33	127.6	142.2	118	148	68.5	98	82	14.5	7.0
E38	123.3	141.5	118	144	72.2	102	84	17.2	8.3
E58	–	129.2	114	142	68.2	94	76	11.4	5.5
B78	–	90.5	90	120	53.2	78	54	24.5	11.8
BPA	108.8	144.5	73	128	74.3	98	71	35.0	16.8

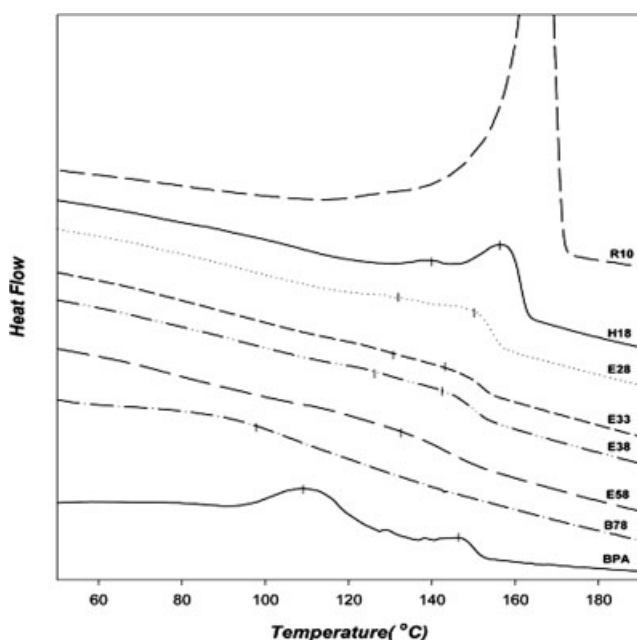


Figure 7 DSC thermogram for 6 APAO grades and homo polypropylene.

Table II mean the melting onset and termination temperature, and T_{fo} and T_{ft} mean the freezing onset and termination temperature measured by ARES shown in Figure 6. T_{ml} and T_{mh} measured by DSC is close to T_{mo} and T_{mt} measured by ARES, respectively, and they are well fitted. T_c is somewhat lower than T_{ft} . This may be caused by differ-

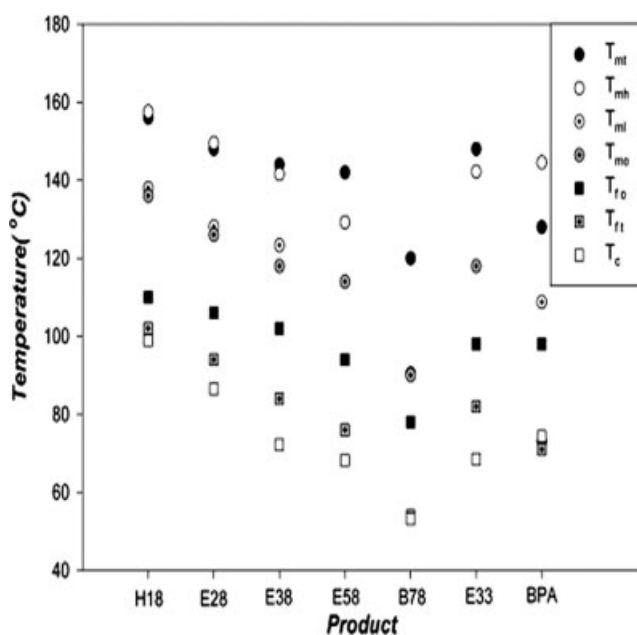


Figure 8 The relationship between T_m , T_c measured by DSC and T_{mo} , T_{mt} , T_{fo} , T_{ft} measured by ARES for 5 APAO grades.

ent cooling rates. The cooling rate of T_c measured by DSC is $10^\circ\text{C min}^{-1}$, and that of T_{fo} and T_{ft} measured by ARES is 4°C min^{-1} . From this result, it is supposed that rapid cooling makes crystalline temperature lower than that of slow cooling.

Relationships among each property

Figure 9 shows the correlation of heat of fusion (ΔH_f) measured by DSC and isotacticity measured by NMR. A linear relationship except B78 and BPA is obtained where B78 shows high isotacticity but ΔH_f is similar to E28 and BPA shows the highest ΔH_f but isotacticity is smaller than H18.

Tensile strength and isotacticity gives a fair linearity except B78 and BPA and similar relationship is also obtained between hardness and isotacticity (Fig. 10). The relationship between tensile strength/hardness and crystallinity also shows a fair linearity except B78 and BPA (Fig. 11).

B78 and BPA having higher crystallinity and isotacticity than other copolymerized APAOs gives poor mechanical strengths. This means that the crystallinity and isotacticity of B78 presumably caused by structural self-arrangement of high content of 1-butene comonomer and those of BPA probably caused by contained small amount of isotactic PP can not affect mechanical strength. Impact strength of all APAOs is excellent, and as is seen in Table I, impact-stiffness balance of APAOs is well compared with commercial by-product APP.

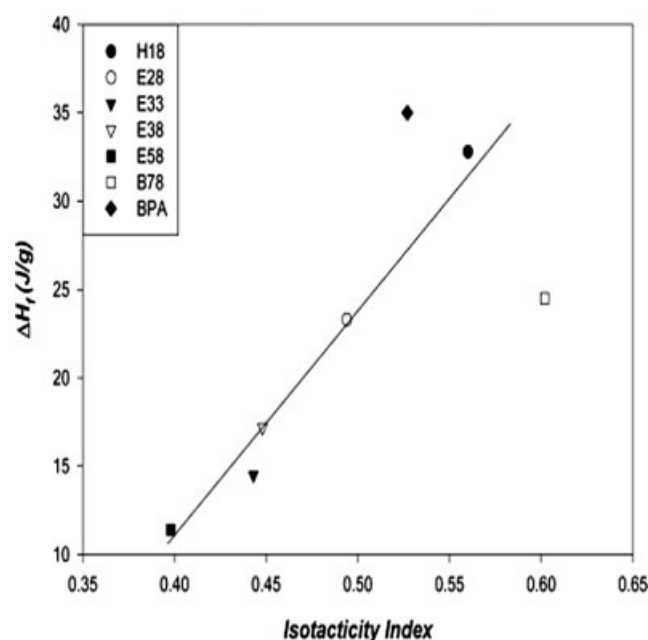


Figure 9 The correlation of heat of fusion (ΔH_f) versus isotacticity index for 6 APAO grades.

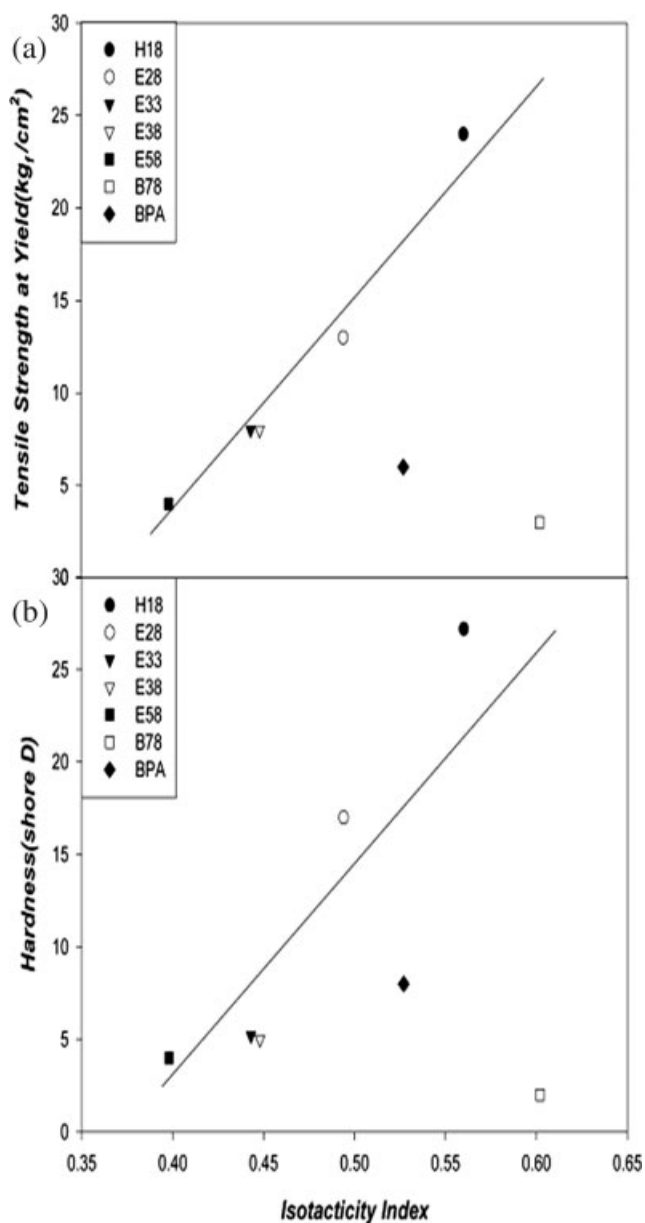


Figure 10 The relationship between tensile strength (a)/ hardness (b) and isotacticity for 6 APAO grades.

CONCLUSIONS

Molecular parameters and various properties of six APAO grades have been extensively studied and the following conclusions have been obtained.

1. All APAO grades showed predominantly amorphous structure, and supercooling effect caused by some crystallinity, which was decreased with increasing comonomer content and molecular weight.
2. Some APAOs having relatively small comonomer content showed two melting peaks, and their thermal properties were well fitted with rheological properties.

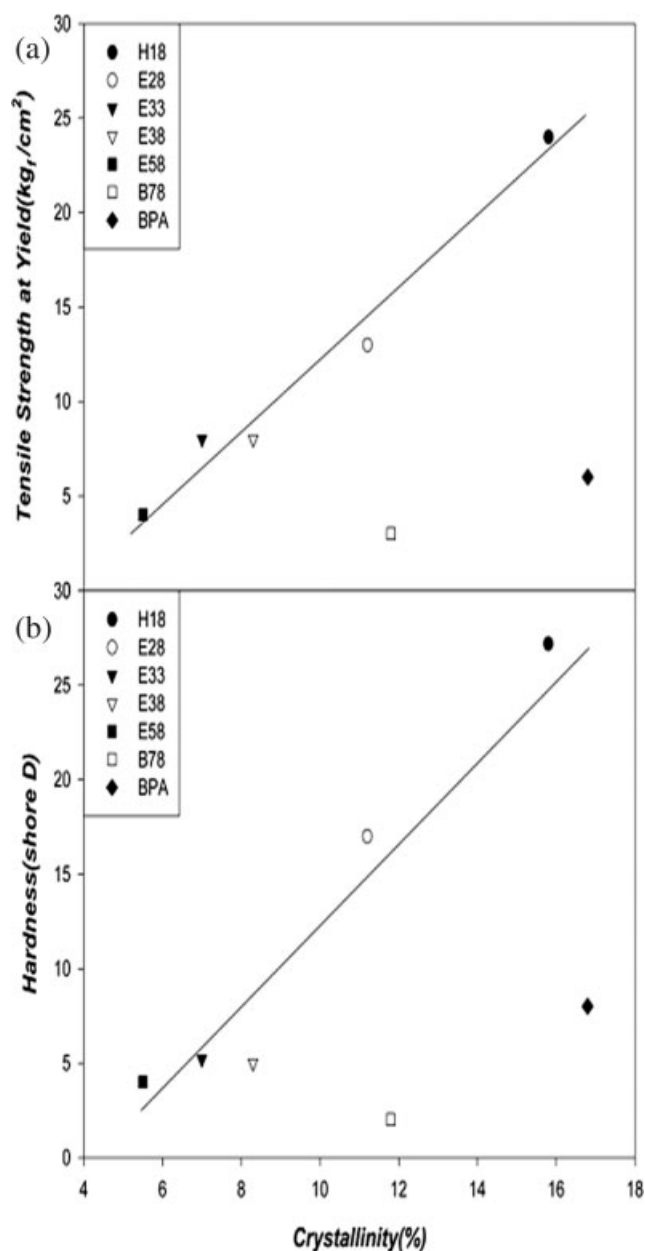


Figure 11 The relationship between tensile strength (a)/ hardness (b) and crystallinity for 6 APAO grades.

3. The correlation between mechanical strengths and molecular parameters of APAOs showed fair linear relationship except 1-butene copolymerized APAO and commercial by-product APP.
4. Any structural self-arrangement of high comonomer content or simply blended small amount of nonpurificated isotactic PP sensitively affected polymer characteristics, but could not affect mechanical strength.
5. APAOs have well impact-stiffness balance differently with by-product APP, and can be capable for modifier of isotactic polypropylene.

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