

Study of Poly(trimethylene terephthalate) as an Engineering Thermoplastics Material

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ABSTRACT: Poly(trimethylene terephthalate) (PTT) was systematically studied as an engineering thermoplastics material. Crystallization rates, crystalline degrees, and mechanical properties of two commercial PTT polymers and one glass fiber-reinforced PTT compound were investigated and compared with those of poly(butylene terephthalate) (PBT). PTT raw polymers have crystallization temperature (T_c) values around 152°C, and their kneaded polymers show T_c values of about 177°C, about 15°C lower than the values of PBT polymers used in this study. From the exothermic heat values of DSC measurements, both PTT and PBT show the crystalline degree order greater than 30%. Injection-molded

PTT specimens and PBT specimens exhibit crystalline degrees from 18 to 32% and 23.8 to 30%, respectively. PTT polymers show higher tensile and flexural strengths, but lower impact strengths and elongations than those of PBT polymers. The low elongation behavior of PTT does not change with the intrinsic viscosity and the molder temperature. PTT-GF30 promotes better mechanical properties than those of PBT-GF30, close to those of PET-GF30. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1657–1666, 2004

Key words: polyesters; thermoplastics; crystallization; injection molding; mechanical properties

INTRODUCTION

Poly(trimethylene terephthalate) (PTT), also called poly(propylene terephthalate) (PPT), was recently introduced as a member of the commercial aromatic polyester polymers, joining with others such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). PTT is a semicrystalline polymer synthesized by the condensation of 1,3-propanediol (PDO) with either terephthalic acid or dimethyl terephthalate, followed by polymerization. Studies of PTT had never gone beyond academic interest until recent years because one of its raw materials, PDO, was very expensive and available only in small volume. Thus, PTT received considerably less attention, compared with PET and PBT. However, recent breakthroughs in PDO synthesis made PTT available in industrial quantities, thus offering new opportunities in carpet, textile, film, packing, and engineering thermoplastics markets.¹

Numerous studies on the crystal structure and mechanical properties of PTT have been reported.^{2–13} Analysis of the crystalline structure of PTT shows that the aliphatic part of PTT takes a highly coiled structure of *gauche-gauche* conformation. PTT has a triclinic crystalline structure, each cell of which contains two chemical repeat units, with the cell parameters a

$= 0.464$ nm, $b = 0.627$ nm, $c = 1.864$ nm, $\alpha = 98.4^\circ$, $\beta = 93.0^\circ$, and $\gamma = 111.1^\circ$.⁴ Ward et al.³ performed a comparison study of the three polyester fibers and found that PTT has a very good tensile elastic recovery property. It was ranked in the unexpected descending order of PTT > PBT > PET. Jakeway et al.² studied the deformation of crystalline structure of PTT and PBT by drawing monofilaments *in situ* in a wide-angle diffractometer, where changes in the fiber period d -spacing along the c -axis were measured as a function of strain. They found that the deformation was reversible in both PBT and PTT below their critical strains, on the order of about several percent. Furthermore, the (002) crystal lattice spacing of PTT changes monotonically with increasing macroscopic strain, suggesting that the lattice responds immediately to the applied stress; on the other hand, the crystal lattice of PBT does not change up to 4% of strain.² This microscopic reversible crystal chain deformation was attributed to PTT's three methylene units arranged in a highly contracted and a very compliant *gauche-gauche* conformation.^{4,5}

Thermal behavior and crystallization kinetics of PTT have also been extensively investigated.^{14–21} In general, the glass-transition temperature is in the range of 42–75°C, depending on the thermal history; the melting temperature is about 228°C, which is almost equal to that of PBT (about 225°C) and is much lower than that of PET (about 265°C). The well-known Avrami equation and secondary nucleation theory could well describe the crystallization kinetics of the polymers. However, a large discrepancy is found

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among the reported values of the equilibrium melting point T_m^o , 237°C,¹⁵ 244°C,¹⁴ and 252°C.²⁰ The last value is close to $250 \pm 4^\circ\text{C}$ of the T_m^o value of PBT reported by Farikov et al.²² Pyda et al.¹⁵ investigated the heat capacity of PTT, by a quantitative thermal analysis with adiabatic calorimetry and standard differential scanning calorimetry (DSC) and estimated the heat of fusion for a 100% crystalline PTT to be 30 ± 2 kJ/mol. Chuah¹⁹ studied the bulk isothermal crystallization kinetics and compared the crystallization rate of PTT with that of PBT and PET, using DSC. Based on the analysis of crystallinity growth rate, the Avrami rate constant K and crystallization half-time were determined. Surprisingly, it was found that PTT's crystallization rate is between that of PBT and PET when compared at the same undercooling degree, contrary to the widely believed concept that aromatic polyesters with odd numbers of methylene units are more difficult to crystallize than the even-numbered polyesters. PTT does not follow the odd–even effect. Among the three polyesters, PBT has the highest crystallization rate K , about an order of magnitude faster than PTT, which in turn is an order of magnitude faster than that of PET.¹⁹

The crystallization rate for a semicrystalline polymer is important in practical applications. The slow crystallization behavior of PET is useful in producing transparent beverage bottles and films, where low crystallinity is an essential factor. However, this becomes the fatal shortcoming in the application as an injection-molding engineering thermoplastic, where short molding cycle time is required. Its application as the injection-molding material is limited in the fiber-reinforced form, where some chemical nucleating agents are usually added to further improve the crystallization rate. Even so, PET is still not widely accepted in the injection-molding market, despite its cheap price and good mechanical properties. On the other hand, because of the rapid crystallization rate, PBT has grown to be one of the most successful thermoplastic engineering polymers, now widely used as the parts of electric and electronic equipments and automobiles. With the good behaviors of flexibility and electric insulation, associated with the low glass-transition temperature and low water absorption character, it has become one of the essential materials generally used for electric or electronic connectors.

Because of the unique mechanical properties and its lower melting temperature, giving better processing ability than that of PET, this makes it possible to use PTT as films, carpets, and clothing materials. A number of studies aimed at these purposes are found in the literature.^{9,23–26} However, useful information about its properties as an engineering thermoplastics material is still scarce. A pioneering work performed by Dangayach et al.²⁷ shows that PTT might be a promising engineering thermoplastics material, which imparts

different properties from those of PET or PBT. The key advantage is that it combines the desirable physical properties of PET (strength, stiffness, toughness, and heat resistance), while retaining basic polyester benefits of dimensional stability, electrical insulation, and chemical resistance.

In crystalline thermoplastics, crystalline degree is one of the most important variables that determine mechanical and physical properties of the final products. It is known that crystalline degrees of the final products are usually affected by the processing conditions. Injection molding is commercially one of the most important fabrication methods to mold engineering thermoplastics, and PBT is one of the fastest semicrystalline engineering thermoplastic materials, particularly well suited for injection-molding applications, given that its high crystallization rate ensures short processing cycles and excellent thermodynamically and dimensionally stable parts. This study focuses on the basic properties of PTT as an injection-molding engineering thermoplastic. Crystallization rates, crystalline degrees, and mechanical properties of two commercial PTT polymers and one glass fiber-reinforced PTT compound were studied and compared with those of PBT. Possible usage and problems that might be met in practical applications are discussed.

EXPERIMENTAL

Two commercial PTT polymers with different intrinsic viscosities were used. One was Corterra CP509200 (Shell Chemicals, Houston, TX) with an intrinsic viscosity of 0.92 dL/g (measured in a 50/50 mixture of methylene chloride and trifluoroacetic acid at 30°C); the other was Sorona 3GT (DuPont, Boston, MA) with an intrinsic viscosity of 1.04 dL/g. Two PBT polymers (Yicheng, Shanghai, China) with intrinsic viscosities of 0.95 and 1.10 dL/g, which were measured in a mixture of 50/50 phenol and 1,1,1,2-tetrachloroethane mixture at 30°C, were chosen for comparisons. For the simplicity of description, hereafter, these polymers are abbreviated as PTT-1, PTT-2, PBT-1, and PBT-2, respectively, in the increasing order of intrinsic viscosities.

Melt rheology—the relationship of melt viscosity versus shear rate—is important for a polymer, because it affects the way the polymer behaves in extrusion and injection-molding processes. Thus, rheology curves were measured on a Toyoseiki Capirograph 1C capillary viscometer.

It is popularly known that the crystallization rate of a raw semicrystalline polymer becomes faster once kneaded. Therefore, the kneading effect was checked in this study. Kneading was accomplished on a 35-mm corotating twin-screw extruder (Legahadong, Zhang Jia Gong, China). Barrel temperature was maintained between 240 and 255°C resulting in a melt tempera-

ture of about 270°C. Strands were quenched in cold water and cut into pellets by a rotating cutter. Polymers with lower intrinsic viscosities were used to make compounds with chopped E-type glass fibers, which were 3 mm long and 13 μm in diameter and had been treated by a silane coupling agent. The glass fiber concentrations in the compounds were controlled to be 30 wt %. Compounding was accomplished on the same extruder, following the same procedure for kneading, with an additional condition that glass fibers were added into the polymer melts from a feeder, which was mounted about two-thirds along the length of the barrel. No nucleating agents were used in this study.

DSC measurements were performed on a Pyris Diamond DSC apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT). Samples with masses of about 5 mg were sealed in the DSC aluminum pans with lids and heated at the rate of 20°C/min to 280°C. Peak temperatures of the endothermic curves observed during the heating were defined as the melting temperature (T_m). Samples were maintained at 280°C for 3 min under a nitrogen atmosphere to eliminate possible previous thermal histories, then cooled at the rate of 20°C/min. Peak temperatures of the exothermic curves obtained during the cooling were defined as the crystallization temperature (T_c). From the exothermic heat of ΔH , which is caused by crystallization, the area enclosed between an exothermic curve and the base line, the crystalline degree is calculated as follows:

$$X_{\text{DSC}} = \Delta H / \Delta H^\circ \quad (1)$$

where ΔH° is the fusion heat of fully crystalline polymer. Values of ΔH° , 30 and 32 kJ/mol, were adopted for PTT¹⁵ and PBT,²⁸ respectively.

Injection-molded ASTM specimens were prepared by the injection-molding method, using a molder that includes cavities of a tensile test bar (ASTM type I, with the thickness of 3.2 mm), a flexural test bar (with the thickness of 6.4 mm), and a notched Izod impact test bar (with the thickness of 3.2 mm). Pellets of neat polymers and compounds were dried in a vacuum oven at 120°C for more than 10 h, before the injection molding. Barrel temperatures were set from 240 to 255°C (from the hopper side to the nozzle of the injection-molding machine). Mold temperatures were set in the range of 20 to 120°C. Injection pressures were adjusted to obtain the best specimens in the range of 410–820 kg/cm², according to the melt viscosities. Total injection and pressure-holding time was set as 20 s for neat polymers and 10 s for compounds; cooling time was set at 20 s for neat polymers and 10 s for compounds. Mechanical tests following the ASTM standards (D638, D790, and D256) were performed with test specimens that equilibrated at 50% relative

humidity and temperature of 23°C. Stress–strain curves with the drawing rate of 5 cm/min were measured on an Instron tensile machine (Instron, Canton, MA), which is equipped with a circulating hot-air chamber. Crystalline degrees of neat polymer samples, which were cut from the dumbbell head part of injection-molded ASTM tensile test bars, were investigated on a density instrument (SMK-301; Shimadzu, Kyoto, Japan), which reads to four digits below the decimal points. Distilled water was used as the working floating liquid. The crystalline degree X_c was calculated from

$$X_c = \frac{\rho(\rho - \rho_a)}{\rho(\rho_c - \rho_a)} \quad (2)$$

where ρ is the density of the sample, ρ_c is the density of a 100% crystalline polymer, and ρ_a is the density of a 100% amorphous polymer. Values of ρ_c and ρ_a were, respectively, adopted as 1.4412 and 1.2990 g/cm³ for PTT²⁵ and 1.404 and 1.280 g/cm³ for PBT.^{29,30}

RESULTS AND DISCUSSION

Figure 1 shows melt flow curves of the PTT, PBT neat polymers, and the 30 wt % glass fiber–reinforced compounds, measured at 270°C, a temperature considered to be approximately the actual temperatures of melts inside the cylinders, in the extrusion process and the injection-molding process of this study. Melt flow curves are thought to be important in polymer processing because, together with thermal properties, they determine both extrudability and moldability. As shown in Figure 1, PTT-1 displays the melt flow curve very close to that of PBT-1, and PTT-2 exhibits its melt flow curve close to that of PBT-2. Thus, PBT polymers chosen here to make the comparison study with PTT polymers are considered to be proper. Before and after the kneading process, no apparent changes were observed among the melt flow curves of the neat polymers. Melt flow curves of 30 wt % glass fiber–reinforced compounds, where raw PTT and PBT polymers with lower intrinsic viscosities were used, are also shown in the same figure, described as PTT-GF30 and PBT-GF30, respectively. Over the whole shear rate range, PTT-GF30 shows values close to but slightly lower than those of PBT-GF30. Rheological similarities are expected in the injection-molding process between PTT-1 and PBT-1; PTT-2 and PBT-2; and PTT-GF30 and PBT-GF30, respectively.

Table I presents the melting point T_m , crystallization temperature T_c , half-value width ΔT_c of the crystallization peak, and exothermic heat ΔH of the neat polymers both before and after kneading and some compounds, which were obtained from calorimetric measurements with heating and cooling rates of 20°C/

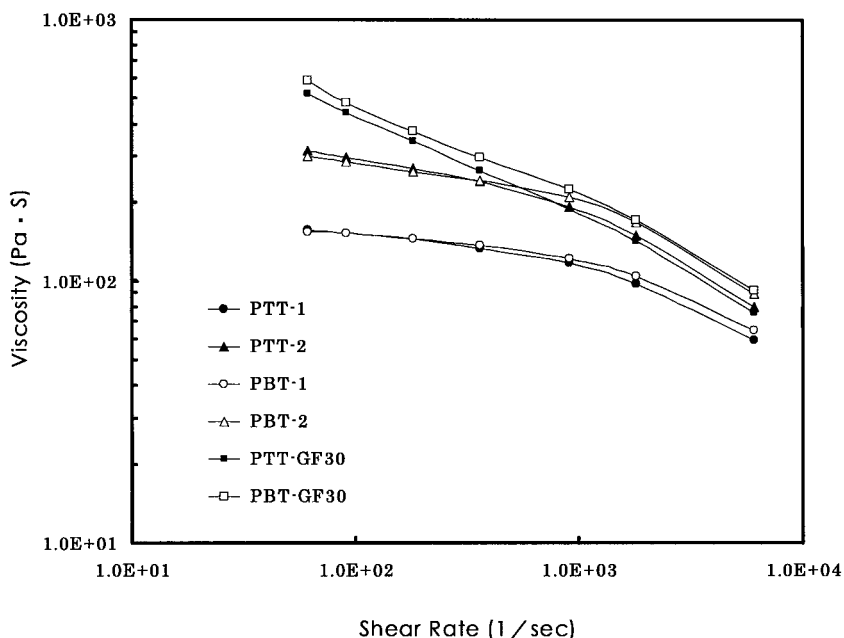


Figure 1 Melt flow curves of PTT and PBT polymers and 30 wt % glass fiber-reinforced compounds, which were measured at 270°C.

min. Figure 2 illustrates the typical DSC traces of the cooling process for the kneaded PTT-1 and PBT-1 polymers. In the figure, the areas enclosed between the exothermic curves and the base lines are the amount of ΔH caused by crystallization that were listed in Table I. Crystalline degrees are determined using the ratio of ΔH and ΔH^0 , from the values of 145.63 and 145.45 J/mol for PTT and PBT. These values were obtained by converting 30 kJ/mol of PTT¹⁵ and 32 kJ/mol of PBT²⁸ with their repeating unit masses of 206 and 220, respectively. Two PTT raw polymers show, respectively, the T_m values of 222.2 and 230.1°C, very close to 224.2 and 225.5°C of PBT

raw polymers used here. The peak temperatures of the endothermic curves of PTT raw polymers (i.e., the T_c values) are, respectively, 149.4 and 154.2°C, much lower than those of 167.1 and 171.8°C of PBT raw polymers. Compared with their corresponding raw base resins, T_c values of both kneaded PTT and PBT polymers become higher with approximate increases of T_c values 20°C, and the crystallization peaks become much narrower (ΔT_c decrease to about one-third values). This means that the crystallization rates of PTT and PBT are greatly improved through the extrusion process. Kneaded PTT neat polymers exhibit, respectively, T_c values of 177.7 and 176.9°C; however,

TABLE I
DSC Measurement Results Obtained Under Heating and Cooling Rates of 20°C/min

Material type	T_m (°C)	$\Delta H^{\text{heating}}$ (mJ/mg)	T_c (°C)	ΔT_c (°C)	$\Delta H^{\text{cooling}}$ (mJ/mg)	Crystalline degree (%)
PTT-1						
Raw base resin	222.2	82.6	149.4	29.5	48.6	33.4
After kneading	227.1	52.2	177.7	7.2	48.8	33.5
PTT-2						
Raw base resin	230.1	86.0	154.2	25.6	48.6	33.4
After kneading	229.2	56.4	176.9	7.8	47.0	32.2
PBT-1						
Raw base resin	224.2	50.3	167.1	14.5	45.9	31.6
After kneading	225.1	51.5	194.0	4.6	49.1	33.7
PBT-2						
Raw base resin	225.5	69.4	171.8	15.5	44.9	30.9
After kneading	224.8	49.4	190.2	5.5	45.6	31.3
PTT-GF30, Compounded	227.2	39.0	181.5	7.2	34.3	33.7
PBT-GF30, Compounded	225.1	35.9	187.3	6.1	33.9	33.3

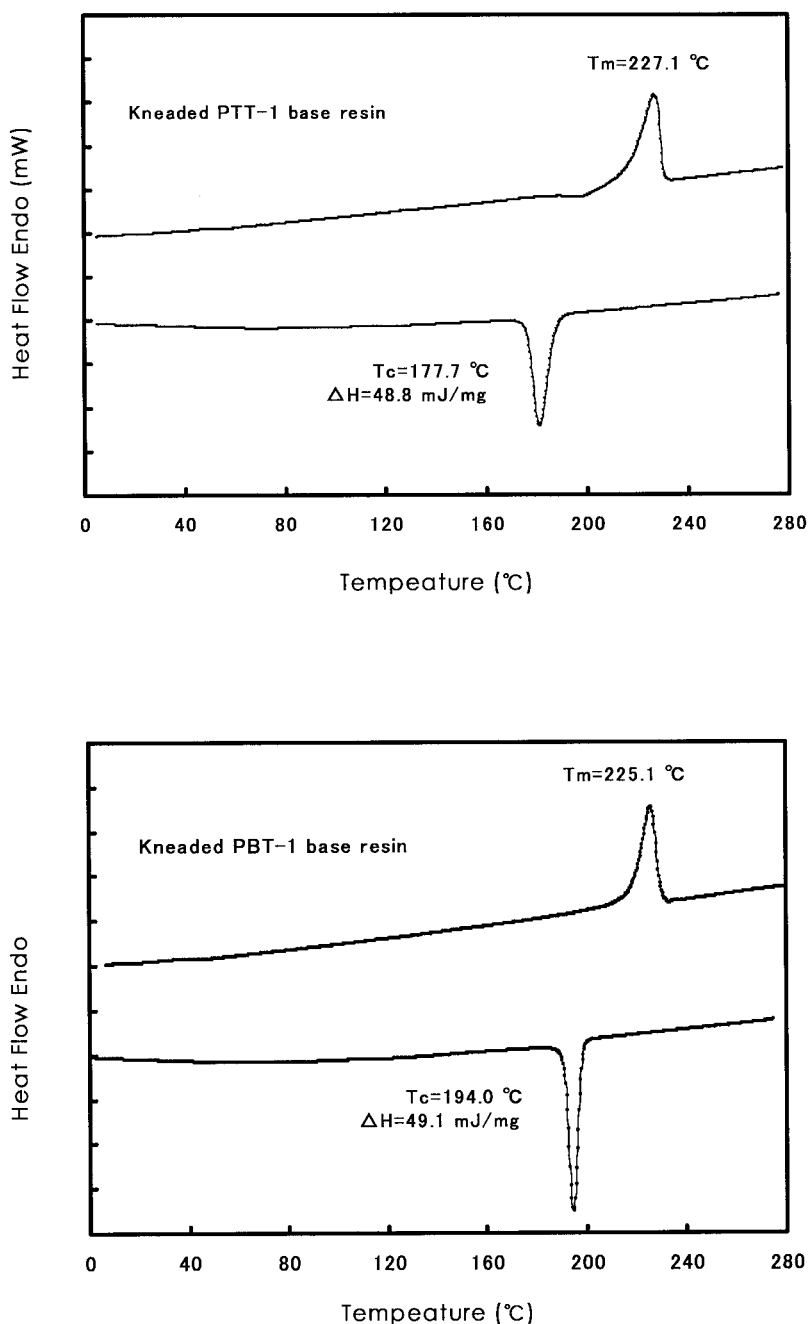


Figure 2 Typical DSC traces for kneaded PTT polymer and PBT polymer, under the heating rate of 20°C/min.

these values are much lower than those of kneaded PBT neat polymers, which are 194.0 and 190.2°C, respectively.

A similar result was also found between the PTT and PBT compounds, where the PTT compound shows a T_c value of 181.5°C, which is slightly higher than the corresponding value of the kneaded neat polymer, whereas the PBT compound shows a T_c value of 187.3°C, which is slightly lower than the corresponding value of the kneaded PBT neat polymer. It is noticed that PTT-1 and PTT-2 show only slightly different behavior, where there is a large in-

crease of T_m value for PTT-1 neat polymer, which has the unusually low T_m value of 222.2°C before kneading. It may be understood that the large increase of T_m value is connected with the large improvement of the crystallization rate through kneading, which leads to the production of comparatively perfect crystallites and gives the higher T_c value of 227.1°C, close to the literature value of 228°C. In addition, PTT shows similar levels of crystalline degrees with PBT in the DSC measurements, which is larger than 30%, either in the forms of kneaded neat polymers or compound. However, the result should not be directly understood in

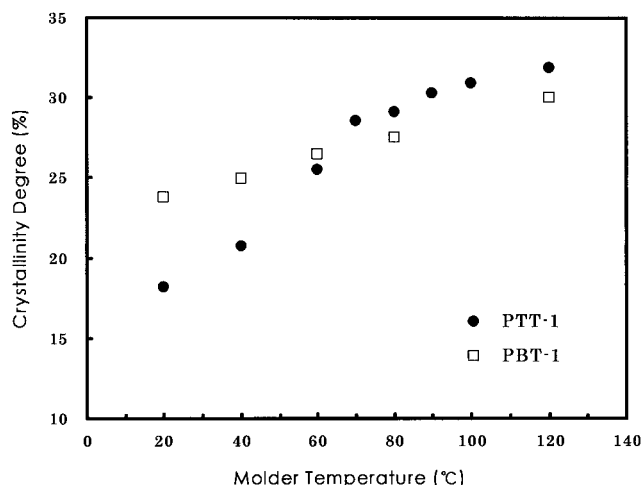


Figure 3 Molder temperature dependency of crystalline degrees of kneaded polymer specimens.

the way that PTT has a similar crystallization rate with PBT; instead it should be explained as that PTT has a similar level of achievable crystalline degree with PBT. The cooling rate of 20°C/min adopted in DSC measurements is thought to be slow enough for PTT to nearly complete its crystallization. In fact, as reported by Chuah,¹⁹ PTT has a slower crystallization rate than that of PBT. The result could also be readily understood from the fact that PTT has a melting point (or more exactly the equilibrium melting point T_m^0) that is nearly equal to that of PBT, but it shows much lower T_c values and broader crystallization peak curve measured during the cooling process than those of PBT.

The crystallization rate difference between PTT and PBT was also found among the injection-molded pieces. In this experiment, densities of samples, cut from the dumbbell head part of injection-molded ASTM tensile bars of kneaded neat polymers that were prepared at various molder temperatures, were investigated. Crystalline degrees were calculated from the densities. The results are shown in Figure 3. PTT specimens show crystalline degree values of 18 to 32%, and PBT specimens show values of 23.8 to 30%.

PTT specimens have stronger molder temperature dependency than PBT specimens. PTT specimens formed at molder temperatures below 60°C have lower values than those of PBT specimens formed under the same condition. This is another evidence that the crystallization rate of PTT is slower than that of PBT. However, the specimens prepared at molder temperatures above 60°C show the same or even slightly larger values of crystalline degrees than PBT specimens that were prepared under the same molder temperatures. In addition, PTT shows weaker molder temperature dependency above 80°C. To examine achievable maximum crystalline degrees of injection-molded articles, the following experiment was conducted with ASTM tensile specimens of PTT and PBT neat polymers. Specimens were annealed for 8 h at 180°C in a vacuum oven; their densities were checked before and after the annealing. Results are listed in Table II. The highest value of crystalline degrees for PTT specimens is 38.4%, slightly higher than the value of 35.9% for PBT specimens. These values are comparable to those obtained in DSC measurements shown in Table I. It is interesting that crystalline degrees of PTT specimens are close to its highest value of 38.4%, obtained by the annealing treatment. This implies that good-quality PTT articles that are dimensionally stable in practical applications can be obtained in practical production under the conditions of comparatively high molder temperature.

Comparison studies on the isothermal crystallization kinetics of PET, PTT, and PBT were made by Chen et al.¹⁸ and Chuah.¹⁹ It was found that PTT crystallizes at a rate between those rates of PET and PBT. Its Avrami rate constants were about an order of magnitude faster than PET and an order of magnitude slower than PBT at the same degree of undercooling. PET is known to crystallize very slowly, whereas PBT has a very fast crystallization rate. With these two extremes, melt-processed PET is generally quite amorphous, where PBT tends to be highly crystalline. PTT is surmised to show an intermediate level of crystalline degree between that of PET and that of PBT as

TABLE II
Crystalline Degree Changes of Injection-Molded Specimens of PTT Polymer and PBT Polymer, Before and After the Annealing Treatment of 180°C for 8 h Under Vacuum Atmosphere

Material	Molder temperature (°C)	Thermal history	Density (g/cm ³)	Crystalline degree (%)
PTT-1	20	As-formed	1.3087	7.5
		Annealed	1.3473	36.3
	80	As-formed	1.3372	28.9
		Annealed	1.3502	38.4
PBT-1	80	As-formed	1.3121	27.7
		Annealed	1.3220	35.9

TABLE III
Mechanical Properties of ASTM Specimens of PTT Polymer and PBT Polymer

Material type	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Notched Izod impact strength (J/m)
PTT-1					
Base resin	59.1	19	100.0	2.66	37
After keading	60.5	15	100.3	2.67	30
PBT-1					
Base resin	49.5	>200	83.8	2.43	41
After keading	57.5	45	89.1	2.57	39
PTT-2					
Base resin	65.4	16	101.4	2.71	30
After keading	64.4	15	102.9	2.64	30
PBT-2					
Base resin	50.2	>200	84.0	2.45	57
After keading	53.7	54	88.1	2.54	43

well. As shown in Figure 3, PTT specimens prepared at low molder temperatures show lower crystalline degree values than those of PBT specimens. However, the achievable maximum crystalline degree of PTT is slightly higher than that of PBT. As a result, specimens prepared at molder temperatures above 60°C show the same or even slightly larger values of crystalline degree than PBT specimens prepared under the same molder temperatures. This phenomenon is important and useful in practical injection molding.

Table III summarizes the ASTM mechanical properties of PTT and PBT polymer specimens, which were prepared at the molder temperature of 80°C. It includes tensile strength, elongation at breakage, flexural strength, flexural modulus, and notched Izod impact strength. PTT shows higher values of tensile and flexural strengths, but has lower impact strengths and elongations at break than those of PBT. Furthermore, the behavior of low elongation values does not change with its intrinsic viscosities. The data of PTT-2 neat polymer, which has a higher intrinsic viscosity, are in

good agreement with those reported by Dangayach et al.,²⁷ except the term of notched Izod impact strength. The injection-molding preparation conditions are considered to be the main origin that results in the notched Izod impact strength difference. The cycling time used in this study was a little longer than that adopted in the literature²⁷; thus crystallization proceeds more completely, which leads to the weaker value of notched Izod impact strength.

Table IV gives the molder temperature dependency of ASTM mechanical properties of two kneaded PTT and PBT polymer specimens that were injection-molded at a variety of molder temperatures. Although substantial molder temperature dependency is found for both PTT and PBT materials, PTT shows a stronger dependency than PBT. For a clear understanding, molder temperature dependencies of tensile strengths are further plotted and shown in Figure 4. The result is also the evidence that the crystallization rate of PTT is slower than that of PBT. In general, all the PTT specimens prepared over the molder temperature

TABLE IV
Molder Temperature Dependency of Mechanical Properties of Kneaded PTT Polymer and PBT Polymer

Material type	Molder temperature (°C)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Izod Impact strength (J/m)
PTT-1	20	49.2	2.35	12.7	97.2	2.57	33
	40	50.3	2.44	10.2	99.2	2.60	51
	60	53.6	2.56	5.4	99.1	2.61	45
	70	58.4	2.65	6.6	99.7	2.65	33
	80	60.5	2.69	14.8	100.3	2.67	30
	100	63.7	2.74	15.3	101.1	2.74	26
	120	61.5	2.82	7.2	101.8	2.80	25
PBT-1	20	53.8	2.53	197.7	83.9	2.42	55
	40	55.4	2.60	167.3	84.6	2.43	48
	60	56.8	2.69	70.4	86.1	2.46	44
	80	57.5	2.72	45.3	89.1	2.57	39
	120	58.1	2.69	31.8	89.9	2.64	40

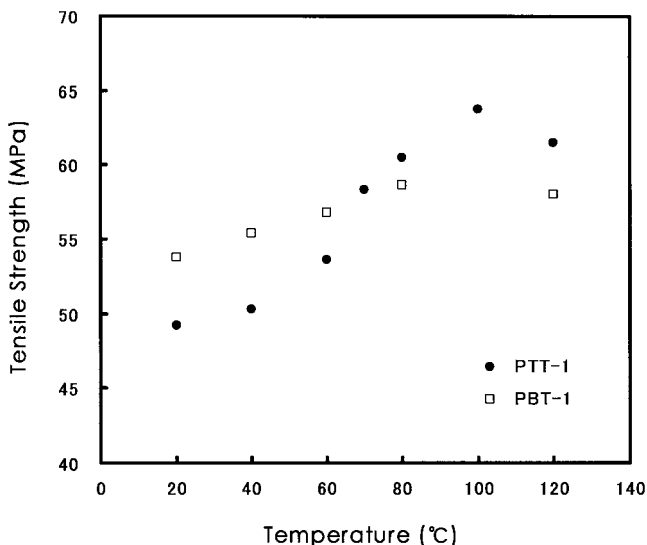


Figure 4 Molder temperature dependency of tensile strengths of kneaded PTT polymer and PBT polymer.

range of 20–120°C show low values of elongation at breakage less than 16%, in particular that formed at 60°C, has the minimum of 5.4%. PBT specimens show elongation values of 31.8 to 197.7%, depending on the different molder temperature. The breakage elongation value and impact strength for a polymer are in some cases the important indices in practical applications. Unfortunately, PTT has much lower elongation values than those of PBT.

The low elongations of PTT are considered to be closely related to the glass-transition temperature T_g . PTT has comparatively high T_g values in the range from 42 to 75°C. It is well known that brittle failures take place with a semicrystalline thermoplastic polymer at temperatures below T_g , and ductile failures occur at temperatures between T_g and T_m , and T_g usually shifts to a higher temperature with the increase of crystalline degree. All the result described above were obtained at the ambient temperature of 23°C. Therefore, it is not surprising that PTT shows much lower values of elongations at breakage than those of PBT.

Figure 5 shows the typical stress–strain curves of ASTM tensile specimens of a PBT polymer and two PTT neat polymers at 23 and 46°C, where the strain is expressed in terms of extension ratio $\lambda = L/L_0$, where L represents the instantaneous length and L_0 represents the initial length of a tensile specimen. At 23°C, whereas PBT is ductile, PTT is brittle. PTT yields at strain of about 3.5% then strain-hardens, followed by the sudden catastrophic failure at strain of about 14% without necking. PBT shows a yield at strain of about 3.0% then strain-hardens, followed by a drop where necking occurs, and breaks at an elongation value greater than 200%. At 46°C, a temperature near T_g ,

PTT becomes rubbery, necking occurs during drawing, and its elongation increases to a value of 67%. The stress–strain curve of PTT at 46°C is very similar to that of PBT at 23°C. However, it needs to be pointed out here that the low elongation behavior at room temperature might be the fatal disadvantage for PTT, when used as an engineering thermoplastics material in the neat polymer form such as electronic connectors, for which the good hinge character is the essential term in some cases. Thus, it seems PTT is not suitable to be used for this purpose.

Table V shows the ASTM mechanical properties of the 30 wt % glass fiber–reinforced PTT and PBT compounds. Injection moldings were carried out at 20°C and 80°C. It is noticed that the values of PTT-GF30 obtained here are slightly inferior to those reported values by Dangayach et al.²⁷ The inconsistency is considered to arise from several factors. The reinforcement glass fibers and detailed extrusion conditions might be different. To examine the inherent mechanical properties, no nucleating agents were added to the PTT-GF30 compound, different from studies reported in the literature.²⁷ In addition, the injection-molding conditions are quite different: compared to preparation conditions of this study, the injection and holding pressures reported in the literature²⁷ were nearly one order lower. In this study, the same kind of reinforcement glass fibers and nearly the same extrusion and injection-molding conditions were used for the preparations of PTT-GF30 and PBT-GF30; thus the inherent mechanical properties of the two compounds could be directly compared, different from literature studies,²⁷

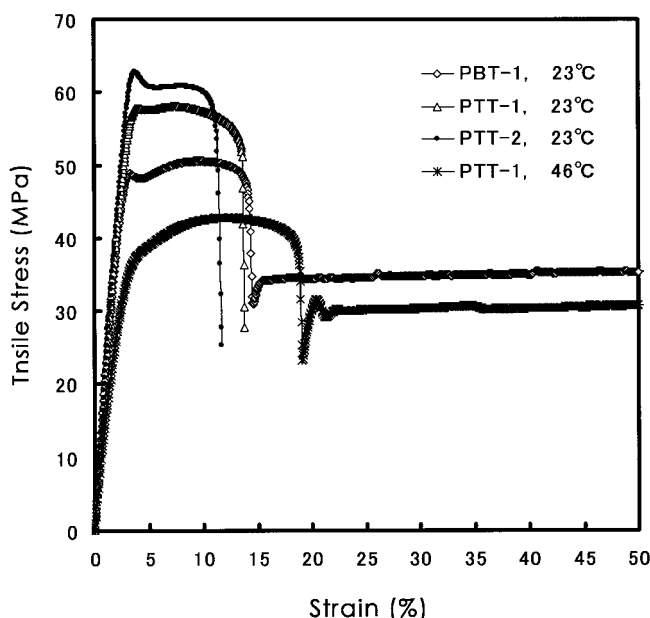


Figure 5 Stress–strain curves of PTT and PBT ASTM tensile bars at 23 and 46°C, which were prepared from the base polymers by injection molding.

TABLE V
Mechanical Properties of ASTM Specimens of Various Glass Fiber-Reinforced Compounds

Material type	Molder temperature (°C)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Notched Izod impact strength (J/m)
PTT-GF30	20	120.1	9.77	3.7	213.6	9.06	115
	80	142.5	10.17	4.3	212.6	9.42	75
PBT-GF30	20	121.9	11.44	3.8	195.8	8.56	126
	80	125.2	11.63	3.9	202.0	8.81	119
PET-G30	80	143.6	11.59	3.6	230.8	10.86	70
	120	145.9	11.91	3.7	217.3	11.10	71

where the data of PBT-GF30 were taken from other literature.

To make a more complete comparison, the data of a 30 wt % glass fiber-reinforced PET compound that were obtained in our laboratory are also summarized in Table V. A chemical nucleating agent was added to PET-GF30 to promote its crystallization rate because the crystallization rate of a pure PET compound is too slow. ASTM specimens of PET-GF30 were formed under a slightly different condition for those of PTT-GF30 and PBT-GF30, where the barrel temperatures of the injection-molding machine were set at 270°C. In general, the mechanical properties of PTT-GF30 are better than those of PBT-GF30, close to those of PET-GF30. In particular, PTT-GF30 shows a stronger dependency of tensile strength on the molder temperature, compared to PBT-GF30. This was further investigated in detail, and the result is shown in Figure 6. The tensile strength of PTT-GF30 increases with the molder temperature and becomes nearly saturated at molder temperatures above 80°C. The strong molder temperature dependency at low-temperature range is once again considered to connect with the slower crys-

tallization rate of PTT. However, it is worth noting that problems of slow crystallization rate might be solved in large part by setting molders at comparatively high yet feasible temperatures in practicable injection moldings. Furthermore, additions of suitable nucleating agents can be expected to further promote the crystallization rate. Thus, PTT is considered to be a very promising engineering thermoplastics material, most probably being used in the fiber-reinforced form.

CONCLUSIONS

PTT was investigated as an engineering thermoplastics material for injection molding. Crystallization rates, crystalline degrees, and mechanical properties of two commercial PTT polymers and one glass fiber-reinforced PTT compound were systematically studied and compared with those of PBT.

DSC measurements show that T_c values of the two commercial PTT polymers are approximately 149.4 and 154.2°C, much lower than those of the two PBT polymers used in this study. Crystallization rates of both PTT and PBT improve greatly through an extrusion process, with an increase in T_c of about 15°C, although the large difference of T_c between PBT and PTT still remains. Kneaded PTT polymers exhibit, respectively, T_c values of 177.7 and 176.9°C, whereas kneaded PBT polymers reveal, respectively, values of 194.0 and 190.2°C. Glass fiber-reinforced PTT compound has a T_c value of 181.5°C, whereas glass fiber-reinforced PBT compound has a T_c value of 187.3°C. Crystalline degrees of both PTT and PBT in either forms of kneaded neat polymers or compounds are calculated to be an order larger than 30%.

Injection-molded PTT and PBT specimens have crystalline degrees from 18 to 32% and 23.8 to 30%, respectively. PTT has stronger molder temperature dependency than that of PBT. PTT specimens prepared at molder temperatures above 60°C show the same or even slightly higher crystalline degrees than those of PBT specimens. In addition, the molder temperature dependency of PTT becomes weaker above 80°C. Furthermore, the achieved maximum crystalline

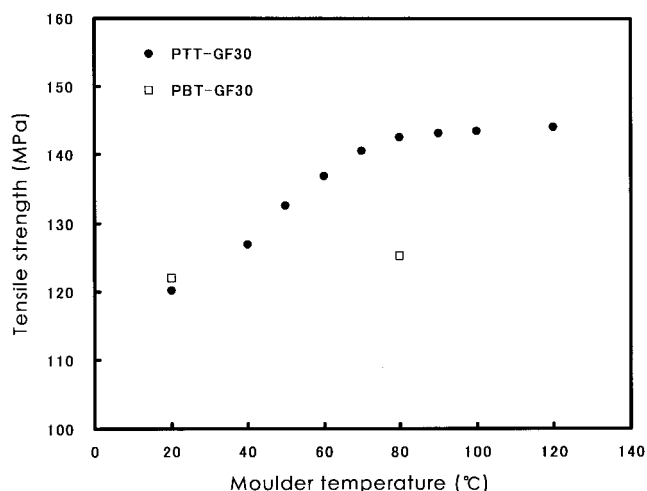


Figure 6 Molder temperature dependency of tensile strengths of 30 wt% glass fiber-reinforced PTT and PBT compounds.

degree of PTT is 38.4%, slightly higher than the 35.9% of PBT, obtained by an annealing treatment at 180°C.

PTT polymers exhibit higher tensile and flexural strengths and lower impact strengths and elongations than those of PBT polymers. The low elongation behavior of PTT does change with molder temperature and intrinsic viscosity. PTT-GF30 has mechanical properties close to those of PET-GF30 and better than those of PBT-GF30. Besides, PTT-GF30 shows the stronger molder temperature dependency of the mechanical properties than PBT-GF30 at molder temperatures lower than 80°C, although the dependency becomes very weak above 80°C. It seems that setting molders at comparatively high yet feasible temperatures is an effective way to overcome the disadvantage of PTT's slow crystallization rate in practicable injection moldings. Thus, PTT is thought to be a promising engineering thermoplastics material, used most probably in the glass fiber-reinforced form.

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