

Effects of Nucleating Agents on Physical Properties of Poly(trimethylene terephthalate)/Glass-Fiber Composites

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ABSTRACT: Poly(trimethylene terephthalate) (PTT)/glass-fiber composites were investigated in the presence of nucleating agents. Sodium ionomer of poly(ethylene-co-methacrylic acid), disodium *p*-phenolsulfonate, and disodium *p*-hydroxybenzoate were adopted as the nucleating agents. Modified composites were systematically studied, including crystallization behaviors and both mechanical and melt viscosities, and were compared with PTT and poly(butylene terephthalate) composites without nucleating agents. All three sodium salts were found to be effective in accelerating the crystallization, but showed quite different characteristics upon closer investigation. Their efficacy at promoting the crystallization rates ranked in the order of disodium

p-hydroxybenzoate, disodium *p*-phenolsulfonate, and sodium ionomer. Besides the accelerating effects, sodium ionomer increased the melt viscosity and disodium *p*-phenolsulfonate showed nearly no influence on the melt viscosity of the PTT composite, whereas disodium *p*-hydroxybenzoate resulted in significant polymer decomposition. High crystallization rates and good mechanical properties were successfully obtained simultaneously, by suitably using *p*-phenolsulfonate or a combination of the other two agents. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 883–893, 2005

Key words: composites; crystallization; nucleation; injection molding; mechanical properties

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is a polymer belonging to the aliphatic–aromatic polyester family, which included poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). Industrial production of this polymer is made by the melt condensation of 1,3-propanediol (PDO) with either terephthalic acid or dimethyl terephthalate. Recent breakthroughs in PDO synthesis have made it available in industrial quantities, offering new opportunities in carpet, textile, packing film, and engineering thermoplastics markets.¹

So far, a number of analyses concerning the crystalline structure of PTT have been carried out.^{2–13} These analyses revealed that PTT has a triclinic symmetry, each cell contains two chemical repeat units, and the aliphatic parts assume a highly coiled structure of *gauche–gauche* conformation. A comparison study among the aforementioned three polyesters showed that PTT has a very good tensile elastic recovery property, ranking in the descending order of PTT > PBT > PET.³ The thermal behavior and crystallization kinetics have also been extensively investigated.^{14–21} In

general, the glass-transition temperature is in the range of 42–75°C, depending on thermal history, and the melting temperature (T_m) is about 228°C, close to the 225°C for PBT and much lower than the 265°C for PET. The Avrami equation and secondary nucleation theory well describe the crystallization kinetics. On the other hand, a substantial discrepancy is found among the reported values of the equilibrium melting point (T_m^0): 237°C,¹⁵ 244°C,¹⁴ and 252°C.²⁰ The last value is closest to the 250 ± 4°C for PBT.²² Chuah¹⁹ studied the bulk isothermal crystallization kinetics and found that the crystallinity growth rate, Avrami rate constant K , and crystallization half-time of PTT are between those of PBT and PET, compared at the same undercooling degrees.

Crystallization behavior is very important for a semicrystalline polymer in practical applications. For example, PET is not widely accepted in the engineering thermoplastics market, in spite of the low price and good mechanical properties, because its slow crystallization rate cannot meet the requirement of short molding time as an injection-molding material. On the other hand, because of the rapid crystallization rate, PBT has grown to be one of the most popular engineering thermoplastics, now widely used for making the parts of electric and electronic equipment and automobiles.

Because of its unique properties, such as excellent elastic recovery and resilience, PTT has been extensively researched as film, carpet, and clothing materi-

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als.^{1,23–28} By comparison, investigations with respect to its use as an engineering thermoplastic material are still scarce. However, the work performed by Dangayach et al.²⁹ showed that PTT might also be a promising engineering thermoplastic material, which imparts properties that are different from those of PET or PBT, where the key advantage is that it combines the desirable physical properties of PET (strength, stiffness, toughness, and heat resistance), while retaining the basic polyester benefits of dimensional stability, electrical insulation, and chemical resistance. Recently, one of the present authors³⁰ made a detailed comparison between PTT and PBT in both forms of the neat polymer and the glass-fiber-reinforced composite. The study revealed that PTT polymer has higher tensile and flexural strengths but lower impact strengths and elongations at room temperature than those of PBT polymer. The low elongation characteristic is one of those major disadvantageous factors in practical applications such as electronic connectors, for which a good hinge character is essential. Thus, it might be more proper to use PTT in the fiber-reinforced form. Nevertheless, although having high mechanical strengths, the glass-fiber-reinforced PTT composite showed stronger mold-temperature dependency than that of the glass-fiber-reinforced PBT composite (because of the comparatively slow crystallization rate of PTT), particularly under mold temperatures < 80°C.

The relatively slow crystallization rate is considered to be one of those major problems that may restrict PTT from being commonly used as an engineering thermoplastics material. Therefore, the improvement of crystallization rate is necessary, especially for those cases where short molding times are required. Under the circumstances, using nucleating agents is taken as one of the practical means. In a previous work,³¹ effects of talc powder and various sodium salts were investigated as nucleating physical additives and nucleating chemical agents in PTT polymer, respectively. This work is devoted to the improvement of crystallization rates for PTT/glass-fiber composites. Sodium ionomer of poly(ethylene-*co*-methacrylic acid), disodium *p*-phenolsulfonate, and disodium *p*-hydroxybenzoate were used as the nucleating agents. Physical properties of modified PTT/glass-fiber composites, including crystallization behaviors, mechanical properties, and melt viscosities, were systematically studied, and were compared with those of the unmodified PTT/glass-fiber and PBT/glass-fiber composites.

EXPERIMENTAL

A commercial-grade polymer, CORTERRA CP509200 [intrinsic viscosity: 0.92 dL/g (when measured in a 60/40 mixture of phenol and tetrachloroethane at 30°C); Shell Chemicals, Houston, TX], was used to prepare PTT/glass-fiber composites. A sodium iono-

mer of poly(ethylene-*co*-methacrylic acid) (mole ratio = 85:15 of ethylene groups to methacrylic acid groups, in which approximately 50% of the methacrylic acid groups were neutralized by sodium ions) was adopted. Disodium *p*-phenolsulfonate and disodium *p*-hydroxybenzoate were synthesized by the neutralizations of *p*-phenolsulfonic acid and *p*-hydroxybenzoic acid with sodium hydroxide, respectively, and their neutralization levels were 90 and 95%, respectively. These three kinds of sodium salts were used as chemical nucleating agents. For simplicity of description, the sodium ionomer, *p*-phenolsulfonate, and disodium *p*-hydroxybenzoate are hereafter abbreviated as A1, A2, and A3, respectively. E-type glass fibers (3 mm long and 13 μm in diameter), which had been treated by a silane coupling agent, were used as the reinforcing material.

Raw PTT polymer, nucleating agents, and glass fibers were first blended into mixtures. The contents of glass fibers in the mixtures were 30 wt %. Composites were obtained by melt mixing on a 25-mm corotating twin-screw extruder. In the extrusion process, barrel temperatures were set to be 255°C, resulting in a practical melt temperature of about 270°C. Strand extrudates were quenched through a cold-water bath and cut into pellets by a rotating cutter. As a reference, a PTT/glass-fiber composite (PTT/GF) without nucleating agents was prepared using a similar procedure.

For comparison, a PBT/glass-fiber composite (PBT/GF), which has the glass-fiber content of 30 wt %, was also prepared using a raw PBT polymer, synthesized by the condensation of 1,4-butanediol with dimethyl terephthalate. The raw PBT polymer showed its melt flow curve very close to that of the PTT raw polymer, when measured under the melting condition of 270°C, shown in Figure 1. Melt flow curves of PBT/GF and PTT/GF are also shown in the same figure. As can be seen, these two curves are also very close to each other.

Crystallization behavior was investigated by differential scanning calorimetry (DSC), on a Pyris Diamond DSC apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT). Both nonisothermal and isothermal measurements were performed. Samples with masses of about 5 mg were sealed in the DSC aluminum pans. They were heated at a constant rate of 20°C/min to 280°C and maintained at this temperature for 3 min under a nitrogen atmosphere. Peak temperatures of the endothermic curves, observed during the heating, were defined as the melting temperature (T_m). In the nonisothermal measurement, samples were cooled at a constant rate of 20°C/min. Peak temperatures of the exothermic curves, obtained during the cooling, were defined as the crystallization temperature (T_c). Crystallinity was estimated with the following equation:

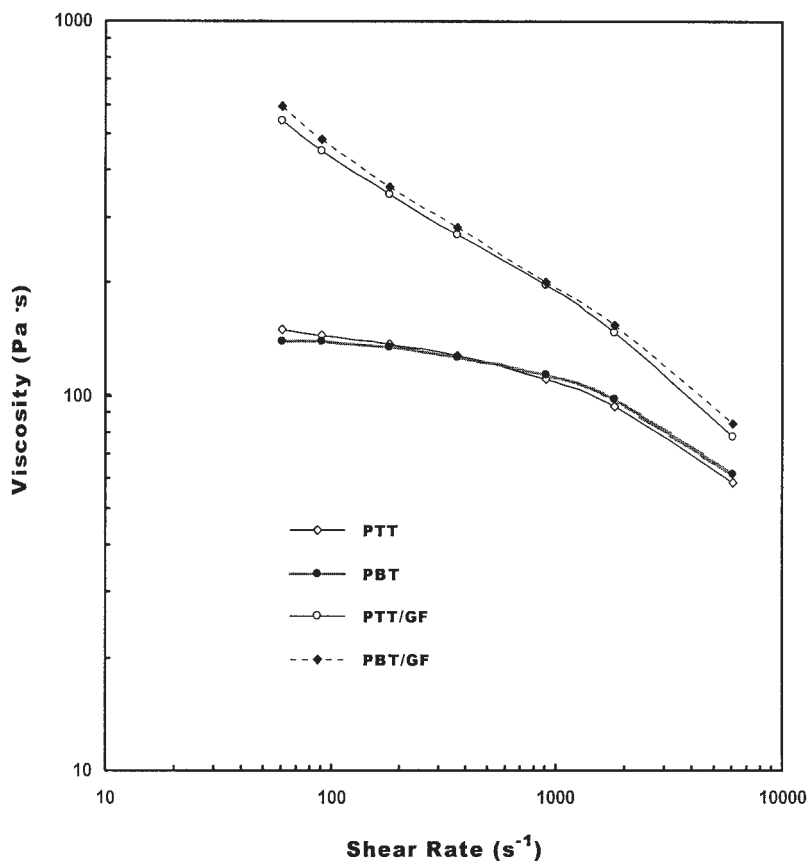


Figure 1 Melt flow curves for the raw polymers of PTT and PBT and their glass-fiber-reinforced composites (PTT/GF, PBT/GF), measured at 270°C.

$$\text{Crystalline degree} = \Delta H / \Delta H^\circ$$

in which ΔH is the exothermic heat caused by the polymer crystallization and ΔH° is the fusion heat of fully crystalline polymer. Exothermic heats were normalized by the polymer weight percentage in the crystallinity calculations. In the isothermal measurements, samples were quenched at a cooling rate of 150°C/min to the desired temperatures. Exotherms were measured as the function of time, until crystallizations were complete. Crystallization half-time ($t_{1/2}$), which is the time needed for crystalline degrees to reach their halves of the ultimate values, was determined from these exotherms.

ASTM specimens were prepared by an injection-molding method, using a mold 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). Before the injection-molding, pellets obtained in the extrusion were dried in a vacuum oven at 120°C for more than 10 h. Barrel temperatures were set from 240 to 255°C, counting from the hopper side to the nozzle of the injection-molding machine. Injection pressures were adjusted to obtain

the best specimens around 550 kg/cm². Injection time, pressure-holding time, and cooling time were set as 1, 9, and 10 s, respectively. Mold temperatures were set either at 25 or 80°C. Mechanical tests following the ASTM standards (D638, D790, and D256) were performed with test specimens that had been equilibrated at 50% relative humidity and temperature of 23°C. At least five specimens were tested for each determination in the tensile, flexural, and impact tests.

Melt viscosity curves were measured on a Toyoseiki Capirographic 1C capillary viscometer (Toyo Seiki Seisaku-sho, Tokyo, Japan). They were used to evaluate the decomposition status of PTT polymer in the composites caused by chemical agents.

RESULTS AND DISCUSSION

Figure 2 illustrates the DSC traces of PTT/GF and PBT/GF, obtained in the nonisothermal DSC measurements, where the top two curves are heating scans and the bottom two curves are cooling scans. The values of T_m , T_c , ΔT_c (the half-value width of crystallization peak), ΔH^{exo} (the exothermic heat), and the crystalline degree for these two composites are summarized in Table I. The two composites had nearly equal melting

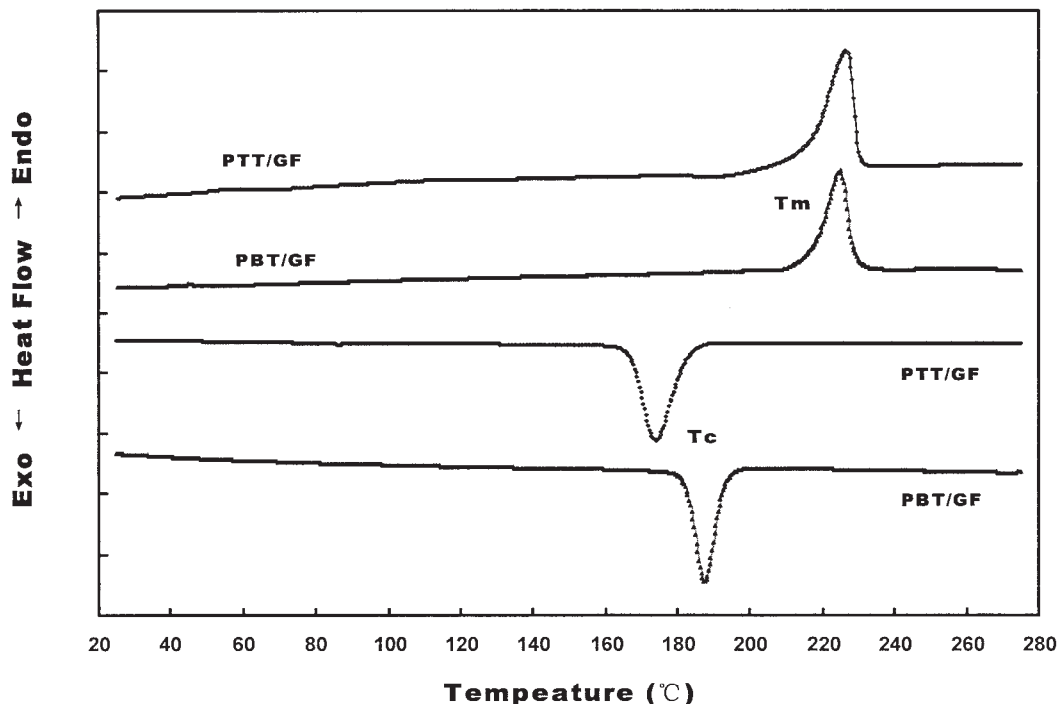


Figure 2 DSC traces for PTT/GF and PBT/GF, obtained under a heating rate of 20°C/min, melting condition of 280°C, 3 min, and a cooling rate of 20°C/min. The top two curves are heating scans, and the bottom two curves are cooling scans.

temperatures, and their crystallization degree values were also almost the same. The ΔH° values adopted in the calculation for PTT and PBT were 145.63 and 145.45 J/g, respectively, obtained by converting 30 kJ/mol of PTT¹⁵ and 32 kJ/mol of PBT³² with their repeating unit masses of 206 and 220, respectively. Although close crystallization degree values were observed for PTT/GF and PBT/GF, the result does not mean that these two kinds of composites have approximately equal crystallization rates; rather it should be explained as that PTT/GF is characterized by a level of achievable crystalline degree similar to that of PBT/GF. This is because the cooling rate of 20°C/min adopted in DSC measurements was slow enough for PTT/GF to nearly complete its crystallization. As can be seen from the table, the T_c and ΔT_c values for PTT/GF are 175.3 and 8.9°C, whereas the values for PBT/GF are 188.1 and 6.2°C, respectively. This indicates that the crystallization rate of PTT/GF is much slower than that of PBT/GF. Details are discussed below. Note also that the T_c value for PTT/GF

does not agree with the previously reported value.³⁰ This inconsistency came from the unstable commercial source of PTT raw polymer.

It is known that crystallization rates of the same type of materials can be compared by the parameters T_c and ΔT_c . Within this scheme, the higher the T_c value and the narrower the ΔT_c width are, the faster the crystallization rate is. In other words, high T_c and narrow ΔT_c width suggest a fast crystallization rate. Because PTT and PBT are not the same kind of materials, a direct comparison of crystallization rates cannot be made between PTT/GF and PBT/GF in a strict sense by T_c and ΔT_c . Nevertheless, because their T_m^0 values are very close (252°C for PTT²⁰; 250 ± 4°C for PBT²²), a direct comparison still seems to be reasonable. From this perspective, we conclude that PTT/GF has a much slower crystallization rate than that of PBT/GF. This was confirmed by the results of isothermal DSC measurements. As shown in Figure 3, PTT/GF needs longer times to complete its crystallization than does PBT/GF, particularly in the range of temperatures > 175°C. In the isothermal DSC measurements, crystallization rates are characterized by the parameter of $t_{1/2}$.

The above-cited thermal analysis data are consistent with the result previously obtained in the practical injection molding, in that PTT/GF showed a stronger dependency of tensile strength on the mold temperature than did PBT/GF.³⁰ Similar results obtained in this work will be shown again later. Thus, efforts to

TABLE I
DSC Results for PTT/GF and PBT/GF

Composite	T_m (°C)	T_c (°C)	ΔT_c (°C)	ΔH^{exo} (J/g)	Crystalline degree (%)
PTT/GF	226.4	175.3	8.9	33.8	33.2
PBT/GF	224.9	188.1	6.2	33.6	33.0

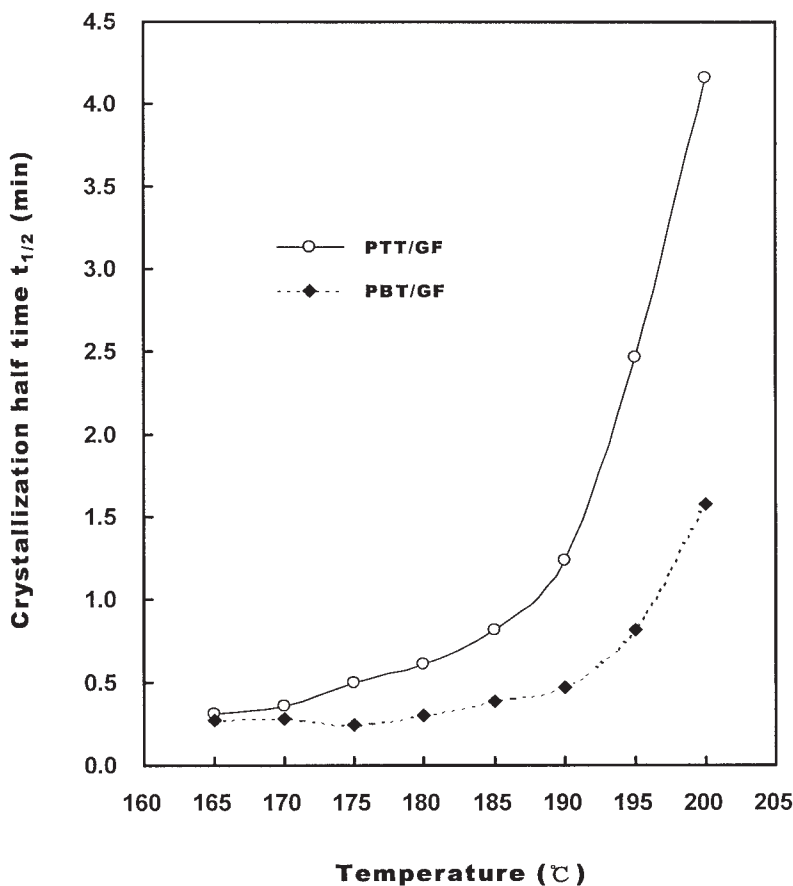


Figure 3 Temperature dependency of crystallization half-time ($t_{1/2}$) for PTT/GF and PBT/GF. Data were obtained in the isothermal measurement.

improve the crystallization rate of PTT/GF are desirable for practical applications, and are essential for the cases where short molding times are required.

Figure 4 shows typical DSC curves for different PTT composites modified by the nucleating agents. These curves were obtained during the cooling in DSC measurements, in which the cooling rates were 20°C/min, similar to those shown in Figure 2. For elucidation, some abbreviations are used in the figure and below. PTT/GF/1%A1 and PTT/GF/2%A1 denote the two modified PTT composites that contain A1 with the concentrations of 1 and 2 wt %, respectively. PTT/GF/0.6%A2 represents the modified composite that constitutes 2 wt % of A2. Similarly, PTT/GF/0.1%A3 and PTT/GF/0.3%A3 mean the modified composites, including A3 with the concentrations of 0.1 and 0.3 wt %, respectively. PTT/GF/1%A1/0.1%A3 refers to the modified composite in which 1 wt % of A1 and 0.1 wt % of A3 were simultaneously incorporated. For the purpose of comparison, the DSC trace of PTT/GF obtained during the cooling is again plotted in Figure 4. In general, all three of the nucleating agents under investigation effectively shifted the crystallization curve peaks to higher temperatures, and at the same time reduced the widths of the crystallization curve.

Table II lists the analyzed values obtained in the DSC measurements for various modified PTT composites. The composites introduced with 1 or 2 wt % of A1 showed T_c and ΔT_c values of 185.8 and 3.3 or 188.6 and 2.6°C, respectively. The composite introduced with 0.6 wt % of A2 exhibited 188.1 and 4.0°C. Those introduced with 0.1 or 0.3 wt % of A3 gave values of 183.7 and 4.1 or 189.8 and 3.5°C, respectively. Interestingly, simultaneously using both A1 and A3 showed a synergistic effect, yielding T_c values > 190°C. The one that contains 0.5 wt % A1 and 0.1 wt % A3 showed 190.1 and 3.2°C, and the one composed of 1 wt % A1 and 0.1 wt % A3 resulted in 191.2 and 3.2°C. For a specific nucleating agent, T_c increased and ΔT_c decreased with its concentration in the modified PTT composites. Obviously, all the nucleating agents effectively promoted the crystallization rates of PTT composites, and the efficacy ranked in the order of A3, A2, and A1.

In comparison with PTT/GF, as can be seen from Tables I and II, modified PTT composites showed enhanced T_c values (10.5 to 15.9°C higher than the T_c value of PTT/GF) and reduced ΔT_c widths (to less than half that of PTT/GF), and also small increases in crystalline degrees. Besides, when compared to PBT/GF, those composites containing 2 wt % A1, 0.6 wt %

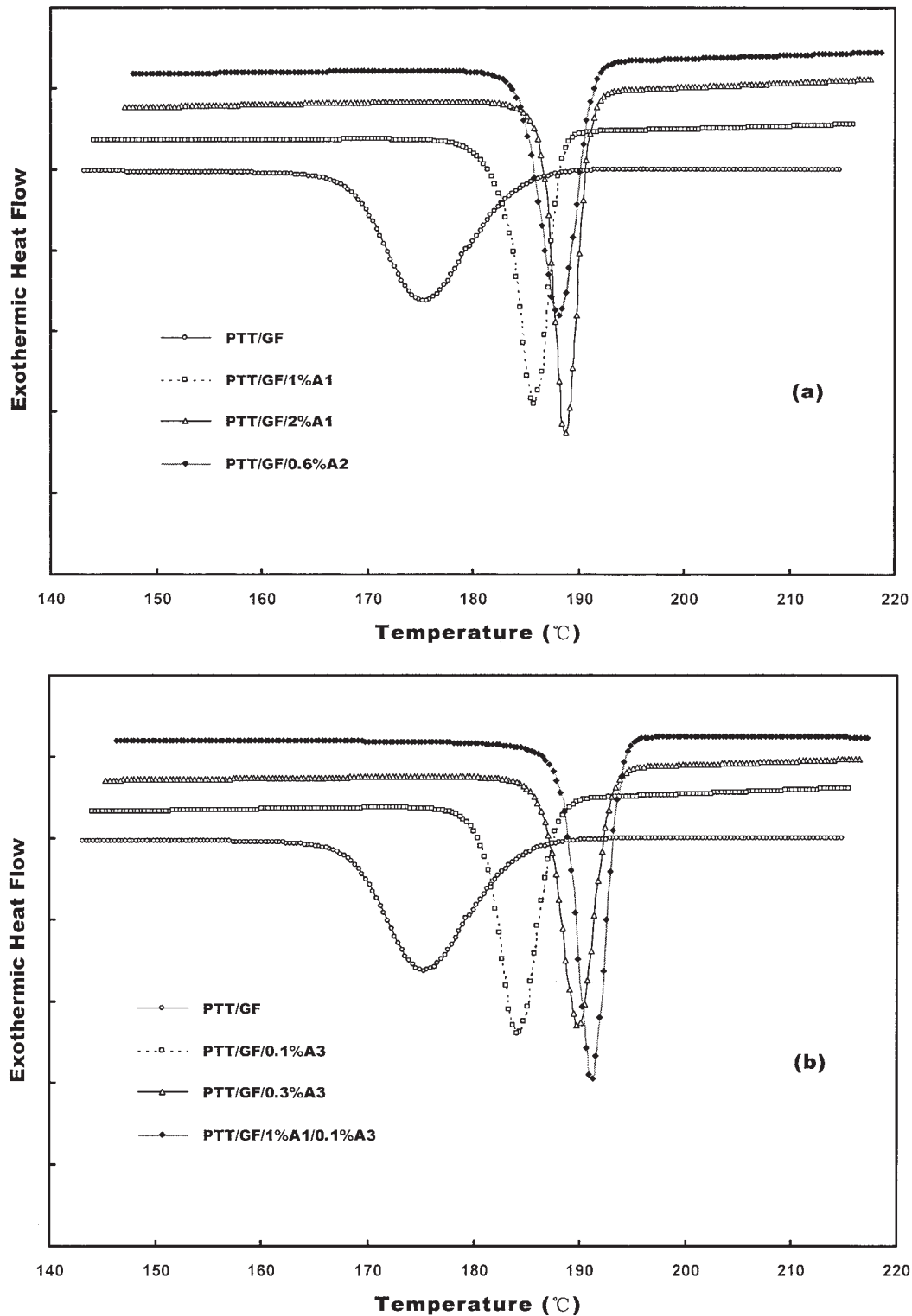


Figure 4 DSC traces for various kinds of PTT composites, which were modified by nucleating agents. The corresponding trace of PTT/GF is included as the reference. For clarity, the data are plotted in two graphs.

A2, both 0.5 wt % A1, and 0.1 wt % A3, and both 1 wt % A1, and 0.1 wt % A3, respectively, showed comparable T_c values and narrower ΔT_c widths. Thus, the latter four modified PTT composites are readily con-

sidered to have roughly the same order of crystallization rates as those of PBT/GF.

Crystallization behaviors of modified PTT composites were further examined with isothermal measure-

TABLE II
DSC Results for Various PTT Composites Modified by Nucleating Agents

Composite	Na content (ppm)	T_m (°C)	T_c (°C)	ΔT_c (°C)	ΔH^{exo} (J/g)	Crystalline degree (%)
PTT/GF/1%A1	454	226.0	185.8	3.3	34.6	34.4
PTT/GF/2%A1	908	226.4	188.6	2.6	34.5	34.8
PTT/GF/0.6%A2	434	225.7	188.1	4.0	35.0	34.7
PTT/GF/0.1%A3	126	226.3	183.7	4.1	35.7	35.1
PTT/GF/0.3%A3	377	225.0	189.8	3.5	35.2	34.7
PTT/GF/0.5%A1/0.1%A3	453	226.1	190.1	3.2	34.8	34.5
PTT/GF/1%A1/0.1%A3	580	226.2	191.2	3.2	34.6	34.4

ments. The results are shown in Figure 5, where the crystallization rate is characterized by $t_{1/2}$. For comparison, the corresponding data of PBT/GF are also plotted. From this figure, it is obvious that the crystallization rates of modified PTT composites have been significantly improved. PTT/GF/1%A1 and PTT/GF/0.1%A3 showed $t_{1/2}$ values very close to that of PBT/GF up to 185°C, which is 15°C higher than that of PTT/GF. Moreover, the $t_{1/2}$ of PTT/GF/0.6%A2 coincided well with those data of PBT/GF up to 195°C. In particular, the crystallization rates of PTT/

GF/2%A1 and PTT/GF/0.5%A1/0.1%A3 had been accelerated to a level slightly higher than that of PBT/GF.

For engineering thermoplastic materials, mechanical properties are considered to belong to those most important terms in their practical applications. In this work, mechanical properties of modified PTT composites were studied using ASTM specimens, which were injection-molded under mold-temperature conditions of 25 and 80°C, respectively, and were compared with mechanical properties of PTT/GF and PTT/GF. Table

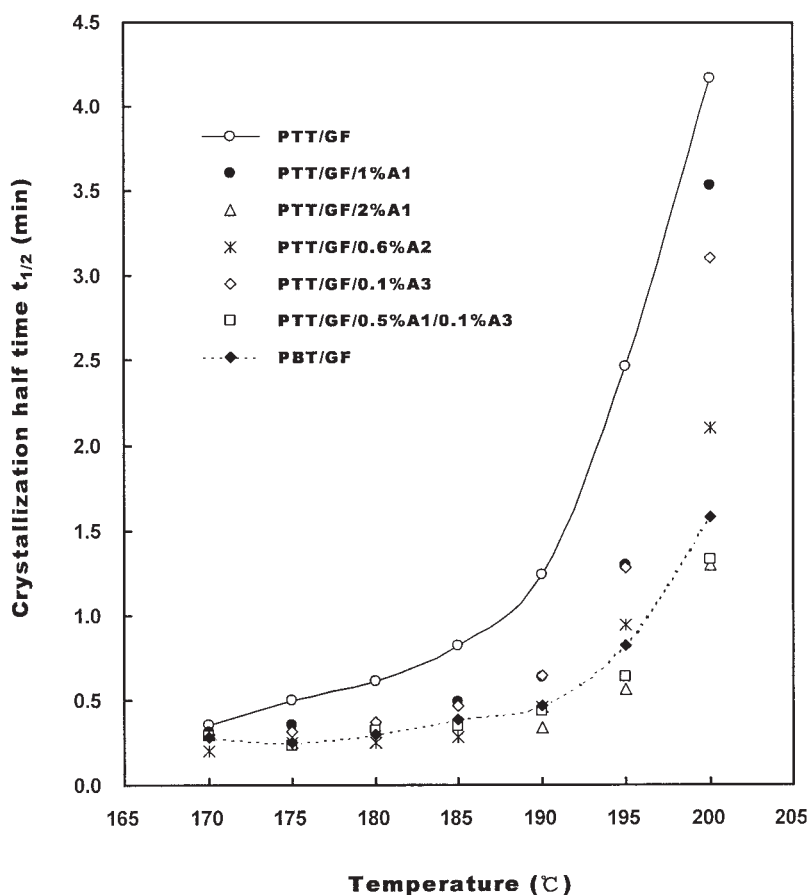


Figure 5 Crystallization half-time ($t_{1/2}$) for various modified PTT composites. The corresponding data of PTT/GF and PBT/GF are also included for reference.

TABLE III
Mechanical Properties of ASTM Specimens for Various Composites^a

Composite	Molder temperature (°C)	Tensile strength (MPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Notched Izod impact strength (J/m)
PTT/GF	25	120.1	213.6	9.06	115
PTT/GF/1%A1	25	124.9	184.9	8.39	76
PTT/GF/2%A1	25	130.6	195.0	8.86	76
PTT/GF/0.6%A2	25	139.9	214.0	9.34	73
PTT/GF/0.1%A3	25	139.0	210.0	9.25	79
PTT/GF/0.3%A3	25	130.8	182.3	9.50	78
PTT/GF/1%A1/0.1%A3	25	139.5	200.4	9.28	83
PBT/GF	25	121.9	195.8	8.56	126
PTT/GF	80	142.5	212.6	9.42	75
PTT/GF/1%A1	80	135.2	195.3	9.10	73
PTT/GF/2%A1	80	133.7	193.2	8.95	72
PTT/GF/0.1%A3	80	138.8	200.7	9.40	75
PTT/GF/0.3%A3	80	129.9	177.6	9.50	77
PTT/GF/0.5%A1/0.1%A3	80	143.3	205.7	9.33	77
PBT/GF	80	125.2	202.0	8.81	119

^a ASTM specimens were injection-molded under mold temperatures of 25 and 80°C.

III summarizes the data of mechanical properties for various composites. As can be seen from the table, because of the difference of crystallization rates, mechanical properties of PTT/GF showed a large mold-temperature dependency, different from those of PBT/GF. When injection-molded under the mold-temperature condition of 25°C, all the specimens of modified PTT composites showed higher tensile strengths and lower notched Izod impact strengths than those of the specimens of PTT/GF, indicating the specimens of modified PTT composites were well crystallized. Moreover, the specimens of PTT/GF/0.6%A2, PTT/GF/0.1%A3, and PTT/GF/1%A1/0.1%A3, prepared at a mold temperature of 25°C, showed mechanical values close to those of PTT/GF prepared at a mold temperature of 80°C. In particular, the specimens of PTT/GF/0.5%A1/0.1%A3, prepared under the mold-temperature condition of 80°C, exhibited almost the same mechanical properties as those of PTT/GF. Nevertheless, it should be noted that specimens of PTT/GF/2%A1 and PTT/GF/0.3%A3, even prepared under the mold-temperature condition of 80°C, still showed tensile and flexural strengths that were inferior to those of PTT/GF, despite the high crystallization rates that are comparable to that of PBT/GF. Generally, mechanical properties of a composite reflect both the crystallization status and molecular weight of its composing polymer. The result obtained here suggests that the three nucleating agents show substantially different influences on the molecular weight of PTT polymer, relating to potential polymer decompositions, and the deterioration of mechanical properties using A3 as the nucleating agent should be ascribed to the lowering of PTT's molecular weight.

To evaluate the states of polymer decompositions caused by the additions of sodium salts, melt viscosity

curves were investigated. Figure 6 shows the curves for various modified PTT composites. As can be seen, three nucleating agents exhibited different behaviors. Compared to PTT/GF, those composites composed of A1 showed higher melt viscosities, and the composite to which A2 was added with showed little melt viscosity change, whereas those composites containing A3 had lower melt viscosities. Interestingly, the composite simultaneously introduced with both A1 and A3 exhibited a cooperative effect; its melt viscosity curve nearly coincided with that of PTT/GF. Because the contents of glass fibers in all the composites were controlled to be the same in this work, the rheological differences directly reflect the properties of polymer matrices. Thus, the polymer matrices of those composites that contain A1 and A3, respectively, should have either higher or lower melt viscosities than that of PTT/GF. Moreover, the two composites, modified with A2 or both A1 and A3, should have approximately the same melt viscosities of polymer matrices as those of PTT/GF. For the composite modified with both A1 and A3, the unchanged melt viscosity character is considered to be a result of the compensation effect of the opposite properties of the two nucleating agents.

The effects of the three nucleating agents were previously studied in the PTT compounds in which glass fibers were not incorporated.³⁰ It was found that A1 induces an increase in melt viscosity and A3 results in the decomposition of PTT polymer, and A2 has no apparent influence on the melt viscosity. Generally, the results obtained here in the PTT composites are in good agreement with that previously observed in the PTT compounds.

A number of papers were published in the last few decades, dealing with the problem of crystallization acceleration mechanism of sodium salts in PET.^{33–38}

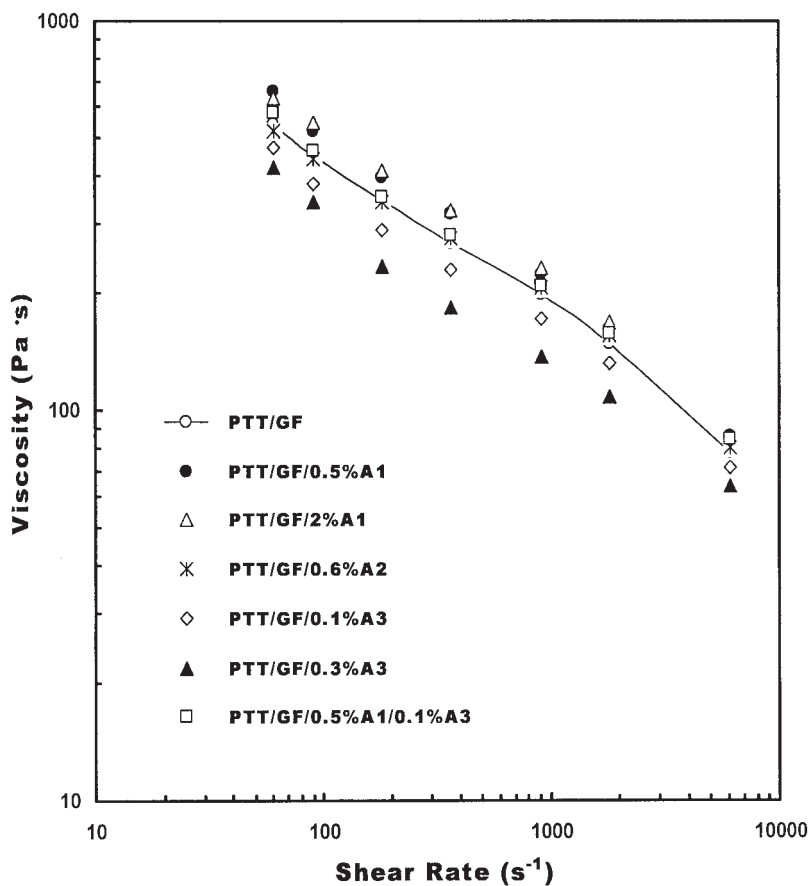


Figure 6 Melt flow curves for various kinds of PTT composites modified by nucleating agents. For comparison, the corresponding curve of PTT/GF is also plotted.

The high nucleation efficiency of sodium salts in PET was reported to relate to the products of sodium carboxylate chain ends ($-\text{COONa}$), which are created by chemical reactions during the mixing process between the sodium salts and ester linkages. Sodium carboxylate chain ends precipitate in the polymer melts as ionic aggregates and act as seeds in the subsequent crystallization process. In the chemical reactions, chain scissions occur and lead to the molecular weight reduction of PET polymer. The nucleating efficiency was ascribed to the presence of ionic end groups. In contrast with physical additives, the most effective chemical agents were those that are the most soluble ones in the polymer melt. Thus, solubility and reactivity are two important factors for chemical nucleating agents. Because of the similarity of chemical structures between PTT and PET, the same mechanism also seems applicable to describe the effects that sodium salts show in the PTT composites. The crystallization rate is a combination of the linear growth rate of the crystals and the nucleus density. We ascribe the enhanced crystallization rates of the modified PTT composites to increases in the nucleus density arising from the addition of nucleating agents.

The two sodium salts of low molecular weights studied in this work showed different behaviors in PTT composites. A2 was less effective in the crystallization rate acceleration but had little influence on the melt viscosity, and thus the molecular weight of PTT polymer, whereas A3 showed a strong efficiency in promoting crystallization rates and caused a substantial decomposition of PTT polymer, which results in the lowering of molecular weight. Their differences as nucleating agents shown in PTT are considered to closely relate to their chemical structures. Although they both have the soluble $-\text{ONa}$ groups, the other parts of chemical structures are different: one has the $-\text{SO}_3\text{Na}$ group; the other has the $-\text{COONa}$ group. This difference in chemical structures is considered to induce a difference in solubility and is mainly responsible for the different behaviors of the nucleating agents, as shown in PTT composites. Because A3 has a strong negative effect, causing the decomposition of PTT polymer, the added amount must be carefully controlled when applied as a nucleating agent in practical applications. As can be seen from Tables II and III, despite the high crystallization rate, comparable to that of PBT/GF, the composite containing 0.3 wt % A3

showed mechanical properties inferior to those of the composite containing 0.1 wt % A3. In contrast, A2 is a very good nucleating agent, having little negative effect on mechanical properties, although its promotive efficiency for the crystallization rates is lower than that of A2.

A1 showed the promotive effect on the crystallization rate, increased the melt viscosity, and lowered the mechanical properties. Its effectiveness as a nucleating agent is considered to surely relate to the sodium carboxylate groups, although details are very complicated and far from clear at present. This ionomer consists of hydrophobic organic backbone chains and a small amount of pendant carboxylic acid and sodium carboxylate groups. It has been reported that A2 plays the role of a nucleating agent and leads to very little reduction of molecular weight, and at the same time induces molecular motion because of the flexible chains in PET.³⁹ We analyzed the morphology of a PTT compound that contains 2 wt % A1 with TEM, and found that small isolated islands of A1 are distributed in the matrix of PTT polymer and fibril-like PTT lamellas grow from the surfaces of these isolated islands.³¹ The morphology of ionomer itself was reported to be rather complicated, being composed of crystalline and amorphous phases and clusters, and thus some fundamental issues remain unsolved.^{40,41} The phenomenon that A1 led to high melt viscosities for PTT composites is considered to relate to possible ionic and molecular crosslinkings between sodium carboxylate and carboxylic acid groups and residual hydroxyl groups of PTT polymer, and also to be relevant to its own comparatively high melt viscosity. It is easy to understand the deterioration of mechanical properties by the inferior mechanical properties of the ethylene-based chemical structure of the ionomer. Considering its accelerating efficiency of crystallization rate and the negative effect on mechanical properties, we cannot make the conclusion that A1 is a good nucleating agent, although it is popularly used for the crystallization rate acceleration in PET. However, its cooperative addition with a third nucleating agent seems to be one means of overcoming the shortcomings. Examples applied in this way can be found in Figure 4(b) and 5, and from Tables II and III. High crystallization rates were obtained with minimum costs to mechanical properties, while at the same time, the inherent melt viscosity of PTT/GF was maintained.

CONCLUSIONS

PTT/glass-fiber composites were investigated in the presence of nucleating chemical agents. Sodium ionomer of poly(ethylene-*co*-methacrylic acid), disodium *p*-phenolsulfonate, and disodium *p*-hydroxy-

benzoate were used as the nucleating agents. Crystallization rates were studied by both nonisothermal and isothermal DSC measurements, and were further examined by checking the mechanical properties of injection-molded ASTM specimens. Modified PTT composites were compared with PTT/GF and PBT/GF without nucleating agents. Injection moldings were carried out under the mold-temperature conditions of 25 and 80°C, respectively. Rheological behaviors were used to evaluate the decomposition status of PTT polymer in the composites caused by sodium salts.

In general, any one of the above three nucleating agents could substantially improve the crystallization rates. However, they showed quite different behaviors upon closer inspection. The efficacy for promoting crystallization rates ranked in the order of disodium *p*-hydroxybenzoate, disodium *p*-phenolsulfonate, and sodium ionomer. Although disodium *p*-phenolsulfonate showed nearly no negative effect, sodium ionomer and disodium *p*-hydroxybenzoate resulted in degradation of mechanical properties. In particular, high crystallization rates and good mechanical properties were successfully obtained simultaneously, by suitably using *p*-phenolsulfonate or both of the other two nucleating agents.

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