

# Effective Nucleating Chemical Agents for the Crystallization of Poly(trimethylene terephthalate)

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**ABSTRACT:** This study focused on the crystallization promotion of poly(trimethylene terephthalate) (PTT), with an aim at engineering thermoplastics applications. The effects of organic sodium (Na) salts, including Na stearate, Na benzoate, disodium-*p*-phenolsulfonate (2Na-*p*-PS), disodium-*p*-hydroxybenzoate (2Na-*p*-HB), and the sodium ionomer of poly(ethylene-*co*-methacrylic acid) (Na-EMAA), were investigated as nucleating chemical agents with differential scanning calorimetry and capillary viscometry. For comparison, the effect of fine talc powder was also examined. The chemical agents were generally more effective than fine talc powder. Na stearate and Na benzoate caused large-scale decomposition of PTT. 2Na-*p*-PS was quite thermally stable

and caused little decomposition. 2Na-*p*-HB was the most efficacious of the nucleating chemical agents and caused mild decomposition. Na-EMAA was the most thermally stable and induced an increase in melt viscosity. A remarkable improvement in the crystallization rate of PTT was successfully attained at a minimum polymer decomposition cost by the introduction of a suitable amount of 2Na-*p*-PS, 2Na-*p*-HB, or Na-EMAA or by the concurrent proper incorporation of both of the latter two agents. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 590–601, 2004

**Key words:** polyesters; thermoplastics; crystallization; nucleation; viscosity

## INTRODUCTION

Poly(trimethylene terephthalate) (PTT) was recently introduced as a commercial aromatic polyester polymer, joining such others as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). This semicrystalline polymer is industrial produced by the condensation of 1,3-propanediol (PDO) with either terephthalic acid or dimethyl terephthalate. Recent breakthroughs in PDO synthesis has made it available in industrial quantities, and this offers new opportunities for the carpet, textiles, film, packing, and engineering thermoplastics markets.<sup>1</sup>

Numerous studies concerning the crystal structure and mechanical properties of PTT have been reported.<sup>2–13</sup> Crystalline structure analysis has revealed that PTT has a triclinic crystalline structure and each cell contains two chemical repeat units, where its aliphatic part takes a highly coiled structure of gauche-gauche conformation. A comparison study by Ward et al.<sup>3</sup> showed that PTT has very good tensile recovery

properties, which rank in the unexpected descending order PTT > PBT > PET.

The thermal behavior and crystallization kinetics of PTT have also been extensively studied.<sup>14–21</sup> In general, the glass-transition temperature has been found in the range 42–75°C, depending on the thermal history; the melting temperature ( $T_m$ ) was about 228°C, close to the 225°C of PBT and much lower than the 265°C of PET. The well-known Avrami equation and secondary nucleation theory describe the crystallization kinetics well. However, a large discrepancy has been found among the reported values of the equilibrium melting point ( $T_m^0$ ); reported values include 237°C,<sup>15</sup> 244°C,<sup>14</sup> and 252°C.<sup>20</sup> The last value is closest to the  $250 \pm 4^\circ\text{C}$  for PBT reported by Fairkov et al.<sup>22</sup> Pyda et al.<sup>15</sup> investigated the heat capacity of PTT by quantitative thermal analysis with adiabatic calorimetry and standard differential scanning calorimetry (DSC) and estimated the heat of fusion for the 100% crystalline PTT ( $\Delta H^0$ ) to be  $30 \pm 2$  kJ/mol. Chuah<sup>19</sup> studied, using DSC, the bulk isothermal crystallization kinetics and compared the crystallization rate of PTT with those of PBT and PET. PTT's crystallinity, growth rate, Avrami rate constant, and crystallization half-time ( $t_{1/2}$ ) were between those of PBT and PET when compared at the same undercooling degrees. PTT did not follow the odd–even effect, contrary to the widely believed concept that aromatic polyesters with odd numbers of methylene units are more difficult to crystallize than those with even numbers.

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Crystallization behavior is important for semicrystalline polymers in practical applications. The slow crystallization rate of PET is suitable for the production of transparent beverage bottles and films. However, this becomes a fatal shortcoming in applications as injection-molding engineering thermoplastics, where a short molding time is required. Thus, the application of PET as an injection-molding material is limited to the fiber-reinforced form, where some nucleating physical additives, usually chemical agents, are essentially used to increase the nucleus density to improve the crystallization rate, which is a combination of the linear growth rate of the crystals and the nucleus density. In response to this requirement, a great number of studies devoted to accelerating the crystallization rate have been reported,<sup>23,24</sup> and abundant patent literature, such as refs. 35–38, has been published in past decades. Fine particles, such as talc, kaolin, silicon oxide, titanium oxide, magnesium oxide, aluminum oxide, and barium sulfate, have been investigated as physical additives.<sup>23–27</sup> Organic alkali salts, particularly organic sodium (Na) salts such as Na benzoate, Na stearate, sodium-*o*-chlorobenzoate, disodium-*p*-phenolsulfonate (2Na-*p*-PS), disodium-*p*-hydroxybenzoate (2Na-*p*-HB), PET polymer–Na salt, and the sodium ionomer of poly(ethylene-*co*-methacrylic acid) (Na-EMAA), have been attempted as chemical agents (with which chemical reactions occur during the nucleus-formation process) and were found to be effective in the acceleration of the crystallization of PET.<sup>28–38</sup> Nevertheless, despite the many efforts made for the promotion of the crystallization rate, together with its cheap price and good mechanical properties, PET is still not widely accepted in the engineering thermoplastics market because its crystallization rate has never been successfully raised to the levels of other popular semicrystalline materials. However, because of its rapid crystallization rate, PBT has grown to be one of the most successful thermoplastic engineering polymers, now widely used in the parts of electric and electronic equipment and automobiles.

Because of its unique properties and  $T_m$ , which give it a better processing ability than PET, PTT can be used in applications for films, carpets, and clothing materials.<sup>1,39–43</sup> Studies on PTT as an engineering thermoplastic material are still scarce. However, pioneering work performed by Dangayach et al.<sup>44</sup> showed that PTT might be a promising material for engineering thermoplastics because it imparts different properties than those of PET or PBT, where its key advantage is that it combines the desirable properties of PET (strength, stiffness, toughness, and heat resistance) and retains the basic polyester benefits of dimensional stability, electrical insulation, and chemical resistance. I recently performed a more detailed comparison study<sup>45</sup> between PTT and PBT as engineering materi-

als in the form of both neat polymers and glass-fiber-reinforced composites; I studied the crystallization rates, crystalline degrees, mechanical properties, and mold-temperature dependences and found that the crystalline degrees and mechanical properties of the injection-molded test pieces had much stronger mold-temperature dependences than those of PBT because of PTT's comparatively low crystallization rate.

The slow crystallization rate is considered one of the major problems that restricts PTT from being widely used as an engineering thermoplastics material. Thus, nucleating agents, which are expected to effectively increase nucleus density and thereby modify the crystallization rate, are of considerable technological importance. Therefore, this study focused on the examination of effective nucleating chemical agents for PTT. Hereafter, by the term *effective nucleating chemical agents*, I refer to the chemical agents that are effective in accelerating the crystallization rate and at the same time have a comparatively small negative effect; that is, they cause comparatively little decomposition of the PTT polymer and are comparatively thermally stable and thus meet the strict requirements for practical application needs. The efficaciousness of several candidates, including Na stearate, Na benzoate, 2Na-*p*-PS, 2Na-*p*-HB, and Na-EMAA, were investigated by DSC and capillary viscometry in this study.

## EXPERIMENTAL

Two commercial PTT polymers with different intrinsic viscosities were used. One was Corterra CP509200 (PTT92; 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), and the other was Sorona 3GT (3GT; DuPont, Boston, MA), with an intrinsic viscosity of 1.04 dL/g. A PBT polymer that was synthesized by the condensation of 1,4-butanediol with dimethyl terephthalate and had an intrinsic viscosity of 0.95 dL/g (measured in a 50/50 mixture of phenol and 1,1,1,2-tetrachloroethane at 30°C) was chosen for comparison with PTT.

Melt rheology, the behavior of melt viscosity versus shear rate, is important in the determination of extrudability and moldability and closely relates to the molecular weight of a polymer, which affects the mechanical properties of the final products. In this study, melt viscosity curves were measured on a Toyo Seiki Capirograph 1C capillary viscometer (Toyo Seiki Seisaku-sho, Ltd., Tokyo, Japan) and were used to evaluate the states of polymer decomposition caused by chemical agents.

It is popularly known that the crystallization rate of a raw semicrystalline polymer is usually improved through a simple kneading process, even when no

nucleating additives or chemical agents are purposely added into it. Thus, in this study, raw polymers were kneaded and chosen as the reference samples; the samples with physical additives or chemical agents were compared to these reference samples to elucidate accelerating effects. Fine talc powder with an average particle diameter size of 0.5  $\mu\text{m}$  was used as a physical additive. Na stearate, Na benzoate, 2Na-*p*-PS, 2Na-*p*-HB, and Na-EMAA were selected as the nucleating chemical agents. Na stearate and Na benzoate were chemical reagent pure grade. 2Na-*p*-PS and 2Na-*p*-HB were synthesized by the neutralization of *p*-phenolsulfonic acid (also called *p*-hydroxybenzenesulfonic acid) and *p*-hydroxybenzoic acid with Na hydroxide, respectively. Their neutralization levels were 90 and 95%, respectively. An Na-EMAA with a molar ratio of 85:15 of ethylene groups to methacrylic acid groups, where approximately 50% of the methacrylic acid groups were neutralized by Na ions, was adopted.

PTT92 and 3GT raw polymers and their blends, containing either talc powder or Na salts, were kneaded on a 35-mm corotating twin-screw extruder. In this extrusion process, barrel temperatures were set between 240 and 255°C, which resulted in a maximum  $T_m$  of about 275°C. Strands were quenched in cold water and cut into pellets by a rotating cutter, and these pellets were dried at room temperature.

Nonisothermal DSC measurements were performed on a Pyris Diamond differential scanning calorimeter (PerkinElmer, Norwalk, CT). Samples of flakes, each with a total mass of about 6 mg and which were cut from the extruded pellets, were sealed in DSC aluminum pans with lids and heated at a rate of 20°C/min to a certain temperature above  $T_m^0$  and held at this temperature for a certain period under a nitrogen atmosphere to eliminate possible previous thermal histories. They were then cooled at a rate of 20°C/min. Various kinds of melting conditions were tested. The standard melting condition was strictly chosen as 280°C and 3 min, which was slightly higher than the temperatures of melts inside the extruder barrel. In this study,  $T_m$  was defined as the temperature at which the endothermic curve showed its endothermic maximum. Crystallization temperature ( $T_c$ ) was taken as the temperature at which the exothermic curve exhibited its exothermic peak value.

Isothermal crystallization measurements were carried out on the same DSC equipment. Samples were heated at 20°C/min to 280°C and kept at this temperature for 3 min; they were then quenched at 150°C/min to the desired temperatures. Exotherms were measured as the function of time until the crystallizations finished.  $t_{1/2}$ , which is the time needed for the crystalline degree to reach half of its ultimate value, was determined from these exotherms.

## RESULTS AND DISCUSSION

Figure 1 illustrates the DSC traces for the kneaded PTT92, 3GT, and PBT polymers, which were measured under melting conditions of 280°C for 3 min. The data for  $T_m$ , endothermic heat ( $\Delta H^{\text{endo}}$ ),  $T_c$ , half-value width of the crystallization peak ( $\Delta T_c$ ), and exothermic heat ( $\Delta H^{\text{exo}}$ ) of the neat polymers both before and after kneading are shown in Table I. The crystallization rates were described by the parameters  $T_c$  and  $\Delta T_c$  in the nonisothermal DSC measurements.  $\Delta H^{\text{endo}}$  and  $\Delta H^{\text{exo}}$ , which presented the heats absorbed for melting and emitted by crystallization, respectively, were determined from the areas enclosed by the endothermic or exothermic curves and the base lines and were used to calculate the crystalline degrees ( $X^{\text{exo}}$  and  $X^{\text{endo}}$ ) with the following equation:

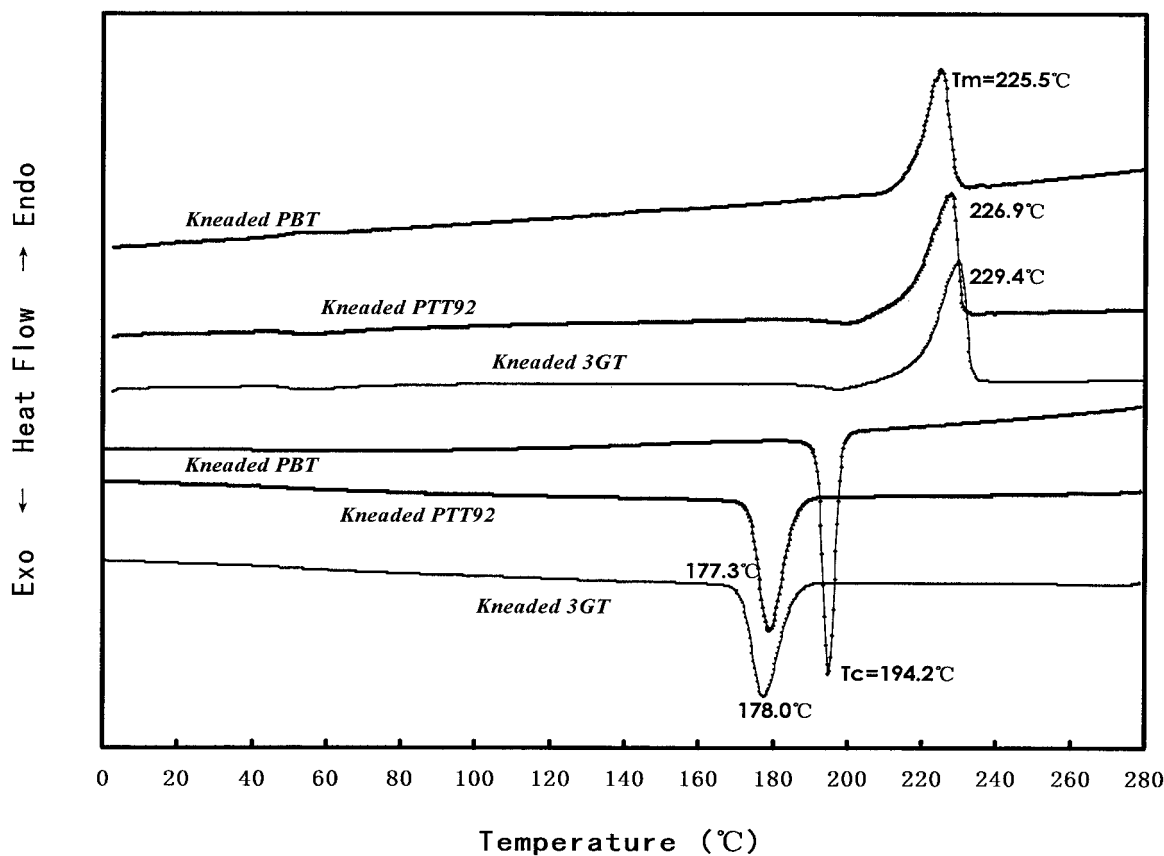
$$X^{\text{exo}} = \Delta H^{\text{exo}} / \Delta H^0 \quad \text{or} \quad X^{\text{endo}} = \Delta H^{\text{endo}} / \Delta H^0$$

The  $\Delta H^0$  values adopted for PTT and PBT were 145.63 and 145.45 J/g, respectively, which were obtained by the conversion of 30 kJ/mol of PTT<sup>15</sup> and 32 kJ/mol of PBT.<sup>46</sup>

The PTT92 and 3GT raw polymers had  $T_m$  values of 223.1 and 230.3°C, respectively, which were very close to the 224.2°C of the PBT raw polymer, and  $T_c$  values of 156.0 and 154.9°C, which were much lower than the 167.2°C of the PBT raw polymer. In addition, rather high crystalline degree values of about 58% were observed in the first heating runs, which were much larger than the value of 36% that was obtained in the cooling runs; this differed from that of the PBT raw polymer. The crystallization rates of PTT92, 3GT, and PBT were greatly improved through the extrusion process; the  $T_c$  values of the kneaded polymers were 177.3, 178.0, and 194.2°C, respectively, which were nearly 20°C higher than those of the corresponding raw polymers. The  $\Delta T_c$  values decreased to approximately one-third of those of the corresponding raw polymers. Further and similar to kneaded PBT, kneaded PTT92 and 3GT had crystalline degrees that were larger than 30% in both the heating and cooling runs.

The isothermal crystallizations of kneaded PTT92 and PBT were investigated. The results are shown in Figure 2, where the crystallization rate was measured with  $t_{1/2}$ . From Figure 2, it is clear that the crystallization rate of the kneaded PTT92 was much slower than that of the kneaded PBT, particularly at temperatures higher than 185°C. A similar case, not shown here, was also found for glass-fiber-reinforced composites. Thereby, efforts to improve the crystallization rate are desirable, particularly to meet the needs of fast injection-molding production.

Figure 3 presents typical DSC curves for PTT92 compound samples that contained 2 wt % fine talc



**Figure 1** DSC traces of PTT92, 3GT, and PBT obtained at a heating rate of 20°C/min, under melting conditions of 280°C for 3 min, and at a cooling rate of 20°C/min.

powder, 0.3 wt % 2Na-*p*-PS, and 2 wt % Na-EMAA, respectively. Table II lists the data for  $T_m$ ,  $\Delta H^{endo}$ ,  $T_c$ ,  $\Delta T_c$ , and  $\Delta H^{exo}$  for those compound samples in which fine talc powder, Na stearate, Na benzoate, 2Na-*p*-PS, 2Na-*p*-HB, and Na-EMAA were included. These results were obtained in DSC measurements under melting conditions of 280°C for 3 min. For comparison, the data of kneaded PTT92 (already shown in Table I) are again listed in Table II. Compared with kneaded PTT92, the changes caused by the addition of fine talc powder were limited. A sample that incorporated 2 wt % talc powder had a  $T_c$  value of

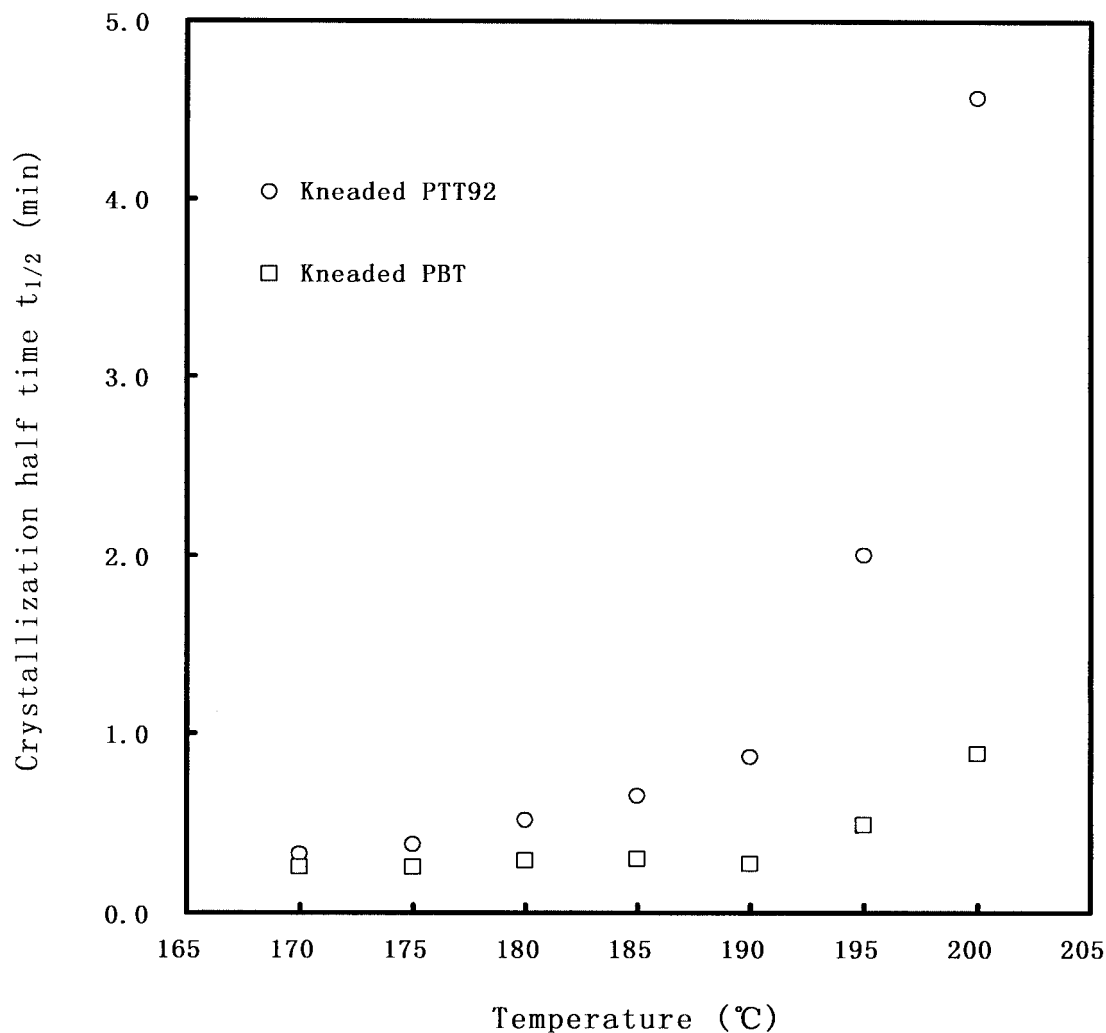
181.4°C and a  $\Delta T_c$  value of 7.0°C. In contrast, the cases added with Na salts were quite different. Samples that included 0.3 and 0.6 wt % Na stearate (with Na contents of 225 and 450 ppm, respectively) showed  $T_c$  values of 179.4 and 186.1°C, respectively, and  $\Delta T_c$  values of 5.4 and 6.2°C, respectively. Those introduced separately with 0.3 and 0.6 wt % Na benzoate (with Na contents of 184.1 and 958 ppm, respectively) had  $T_c$  values of 184.1 and 188.8°C, respectively, and  $\Delta T_c$  values of 6.6 and 4.1°C, respectively. Adding 0.3 and 0.6 wt % 2Na-*p*-PS (with Na contents of 217 and 434 ppm, respectively) raised the  $T_c$  value to 180.7 and

**TABLE I**  
DSC Measurement Results of Raw and Kneaded Polymer Samples

Material	$T_m$ (°C)	$\Delta H^{endo}$ (mJ/mg)	$X^{endo}$ (%)	$T_c$ (°C)	$\Delta T_c$ (°C)	$\Delta H^{exo}$ (mJ/mg)	$X^{exo}$ (%)
PTT92 raw polymer	223.1	84.1	57.7	156.0	23.2	48.1	33.0
3GT raw polymer	230.3	86.5	59.4	154.9	24.8	47.9	32.9
PBT raw polymer	224.2	50.3	34.6	167.1	14.5	45.9	31.6
Kneaded PTT92	226.9	53.5	36.8	177.3	7.5	49.9	34.3
Kneaded 3GT	229.4	55.2	37.9	178.0	7.9	49.3	33.9
Kneaded PBT	225.5	49.7	34.2	194.2	4.5	49.4	33.9

Measurements were carried out at heating and cooling rates of 20°C/min and melting conditions of 280°C for 3 min.





**Figure 2** Temperature dependences of  $t_{1/2}$  of kneaded PTT92 and PBT obtained with isothermal measurements under melting conditions of 280°C for 3 min and at a quenching rate of 150°C/min.

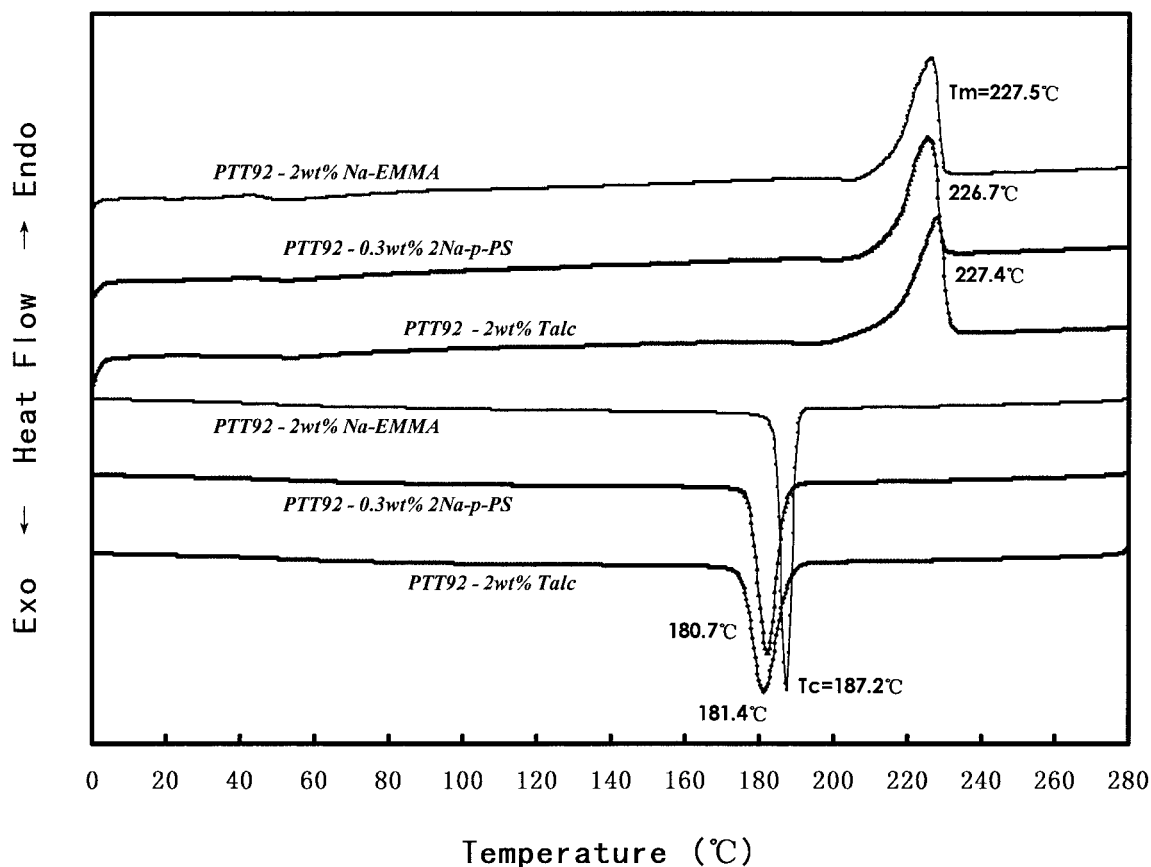
188.5°C and reduced  $\Delta T_c$  to 5.5 and 4.3°C, respectively. Incorporating 0.1 or 3 wt % 2Na-*p*-HB (with Na contents of 126 and 377 ppm, respectively) yielded  $T_c$  values of 183.6 and 187.1°C, respectively, and  $\Delta T_c$  values of 6.6 and 4.1°C, respectively. Introducing 2 wt % Na-EMAA gave values of 187.2°C for  $T_c$  and 2.9°C for  $\Delta T_c$ .

To overcome shortcomings that one single chemical nucleating agent might bring up, which is discussed later, a combination of Na-EMAA and 2Na-*p*-HB was also investigated. As shown in Table II, the coadjutant addition of 1 wt % Na-EMAA and 0.1 wt % 2Na-*p*-HB increased  $T_c$  to 189.4°C and decreased  $\Delta T_c$  to 3.7°C.

Generally, Na salts were more effective than fine talc powder in the acceleration of the crystallization rate of PTT. In addition, within the addition limits investigated,  $T_c$  increased with Na content, and  $\Delta T_c$  diminished with Na content (with the exception of Na stearate). Further, for the addition amount by weight percentage, Na salts showed an efficacious order of

2Na-*p*-HB, Na benzoate, Na stearate, 2Na-*p*-PS, and Na-EMAA. However, if the efficiency of Na content was taken into consideration, the order changed to 2Na-*p*-HB, 2Na-*p*-PS, Na stearate, Na benzoate, and Na-EMAA.

$T_c$  and  $\Delta T_c$  varied largely with melting condition for PTT92 compounds in which Na salts were added, in contrast to kneaded PTT92 and the compound that contained fine talc powder. Table III shows the results measured under different melting conditions: (1) 280°C for 3 min, (2) 280°C for 1 min, and (3) 260°C for 5 min. PTT92 compounds containing Na stearate, Na benzoate, or 2Na-*p*-HB had much higher  $T_c$  values and narrower  $\Delta T_c$  widths when measured under melting conditions of 280°C for 1 min or 260°C for 5 min than those obtained under melting conditions of 280°C for 3 min. For all of the Na salts, decreasing the melting temperatures or shortening the melting time led to higher  $T_c$  values and smaller  $\Delta T_c$  values. This indicated that the chemical agents were not stable in PTT,



**Figure 3** Typical DSC traces of PTT92 compounds containing fine talc powder, 2Na-*p*-PS, Na-EMAA, and 2Na-*p*-HB. Measurements were carried out at heating and cooling rates of 20°C/min and under melting conditions of 280°C for 3 min.

similar to cases for PET.<sup>28–33</sup> Table IV presents the data for 3GT when talc powder and 2Na-*p*-HB were added. These results were consistent with those obtained for PTT92 and shown in Tables II and III.

In this study, the standard melting condition was strictly selected at 280°C for 3 min, which was regarded as rigorous enough to meet practical requirements. Under this melting condition, Na-EMAA

**TABLE II**  
DSC Measurement Results of Kneaded PTT92 and PTT92 Compounds Containing Fine Talc Powder or Na Salts, Including Na Stearate, Na Benzoate, 2Na-*p*-PS, 2Na-*p*-HB, Na-EMAA, and Na-EMAA plus 2Na-*p*-HB

Material	Na (ppm)	$T_m$ (°C)	$\Delta H^{endo}$ (mJ/mg)	$T_c$ (°C)	$\Delta T_c$ (°C)	$T_c$ increase (°C)	$\Delta H^{exo}$ (mJ/mg)
Kneaded PTT92	—	226.9	53.5	177.3	7.5	—	49.9
PTT92 + 2 wt % talc	—	227.4	52.9	181.4	7.0	4.1	48.1
PTT92 + 0.3 wt % Na stearate	225	227.9	51.1	179.4	5.4	2.1	51.7
PTT92 + 0.6 wt % Na stearate	450	225.8	52.3	186.1	6.2	8.8	52.8
PTT92 + 0.3 wt % Na benzoate	479	225.7	50.4	184.1	6.6	6.8	51.2
PTT92 + 0.6 wt % Na benzoate	958	225.4	57.8	188.8	4.1	11.5	55.4
PTT92 + 0.3 wt % 2Na- <i>p</i> -PS	217	226.7	52.6	180.7	5.5	3.5	51.1
PTT92 + 0.6 wt % 2Na- <i>p</i> -PS	434	227.0	48.4	188.5	4.3	11.2	49.8
PTT92 + 0.1 wt % 2Na- <i>p</i> -HB	126	227.7	52.4	183.6	6.6	6.3	50.7
PTT92 + 0.3 wt % 2Na- <i>p</i> -HB	377	226.5	53.7	187.1	4.3	9.9	52.9
PTT92 + 2 wt % Na-EMAA	908	227.5	51.5	187.2	2.9	9.9	50.5
PTT92 + 1 wt % Na-EMAA + 0.1 wt % 2Na- <i>p</i> -HB	580	226.2	52.6	189.4	3.7	12.1	53.2

Data were obtained under melting conditions of 280°C for 3 min and at heating and cooling rates of 20°C/min

**TABLE III**  
Melting Condition Dependences of Kneaded PTT92 and PTT92 Compounds containing Either Fine Talc Powder or Na Salts

Material	Na (ppm)	280°C for 3 min			280°C for 1 min			260°C for 5 min				
		$T_c$ (°C)	$\Delta T_c$ (°C)	$\Delta H^{\text{exo}}$ (mJ/mg)	$T_c$ (°C)	$\Delta T_c$ (°C)	$\Delta H^{\text{exo}}$ (mJ/mg)	$T_c$ change (°C)	$T_c$ (°C)	$\Delta T_c$ (°C)	$\Delta H^{\text{exo}}$ (mJ/mg)	$T_c$ change (°C)
Kneaded PTT92	—	177.3	7.5	49.9	177.3	7.8	49.1	0.1	177.4	7.7	49.2	0.1
PTT92 + 2 wt % talc	—	181.4	7.0	48.1	182.4	7.0	49.2	1.0	181.8	7.3	50.6	0.4
PTT92 + 0.3 wt % Na stearate	225	179.4	5.4	51.7	190.5	3.6	51.3	11.1	192.6	4.4	53.0	13.2
PTT92 + 0.3 wt % Na benzoate	479	184.1	6.6	51.2	190.8	3.5	52.7	6.7	194.6	4.7	52.6	10.5
PTT92 + 0.3 wt % 2Na- <i>p</i> -PS	217	180.7	5.5	51.1	185.8	5.2	50.7	5.0	185.8	4.8	53.0	5.1
PTT92 + 0.6 wt % 2Na- <i>p</i> -PS	434	188.5	4.3	49.8	189.1	3.7	50.2	0.7	191.1	4.2	50.0	2.7
PTT92 + 0.1 wt % 2Na- <i>p</i> -HB	126	183.6	6.6	50.7	187.3	4.5	49.3	3.7	187.5	4.3	52.1	3.9
PTT92 + 0.3 wt % 2Na- <i>p</i> -HB	377	187.1	4.3	52.9	192.9	3.4	53.7	5.8	195.0	4.0	52.2	7.8
PTT92 + 2 wt % Na-EMAA	908	187.2	2.9	50.5	188.6	3.3	50.8	1.4	188.9	4.5	51.1	1.7
PTT92 + 1 wt % Na-EMAA + 0.1 wt % 2Na- <i>p</i> -HB	580	189.4	3.7	53.2	191.8	3.3	48.9	2.4	194.8	4.1	49.2	5.4

DSC measurements were done under three different melting conditions: (1) 280°C for 3 min, (2) 280°C for 1 min, and (3) 280°C for 1 min.

showed the least melting condition dependence; hence, it was the most thermally stable chemical agent among the investigated Na salts, and 2Na-*p*-HB was the most effective with respect to Na efficiency.

To evaluate the state of polymer decomposition caused by the addition of Na salts, melt viscosity curves were measured at 270°C, which was considered to be the approximate temperatures of the melts inside the actual extrusion and injection-molding barrels in this study. Figures 4 and 5 show the melt curves of neat PTT92 and 3GT, respectively, and their compounds. As shown in these figures, the addition of 2 wt % fine talc powder resulted in a slight increase in melt viscosity because the talc powder also acted as a filler in addition to acting as a physical additive. The introduction of Na stearate, Na benzoate, or 2Na-*p*-HB induced large-scale decreases in melt viscosity, whereas the addition of Na-EMAA resulted in an increase in melt viscosity. Interestingly, melt viscosity was nearly unaltered by the incorporation of 2Na-*p*-PS

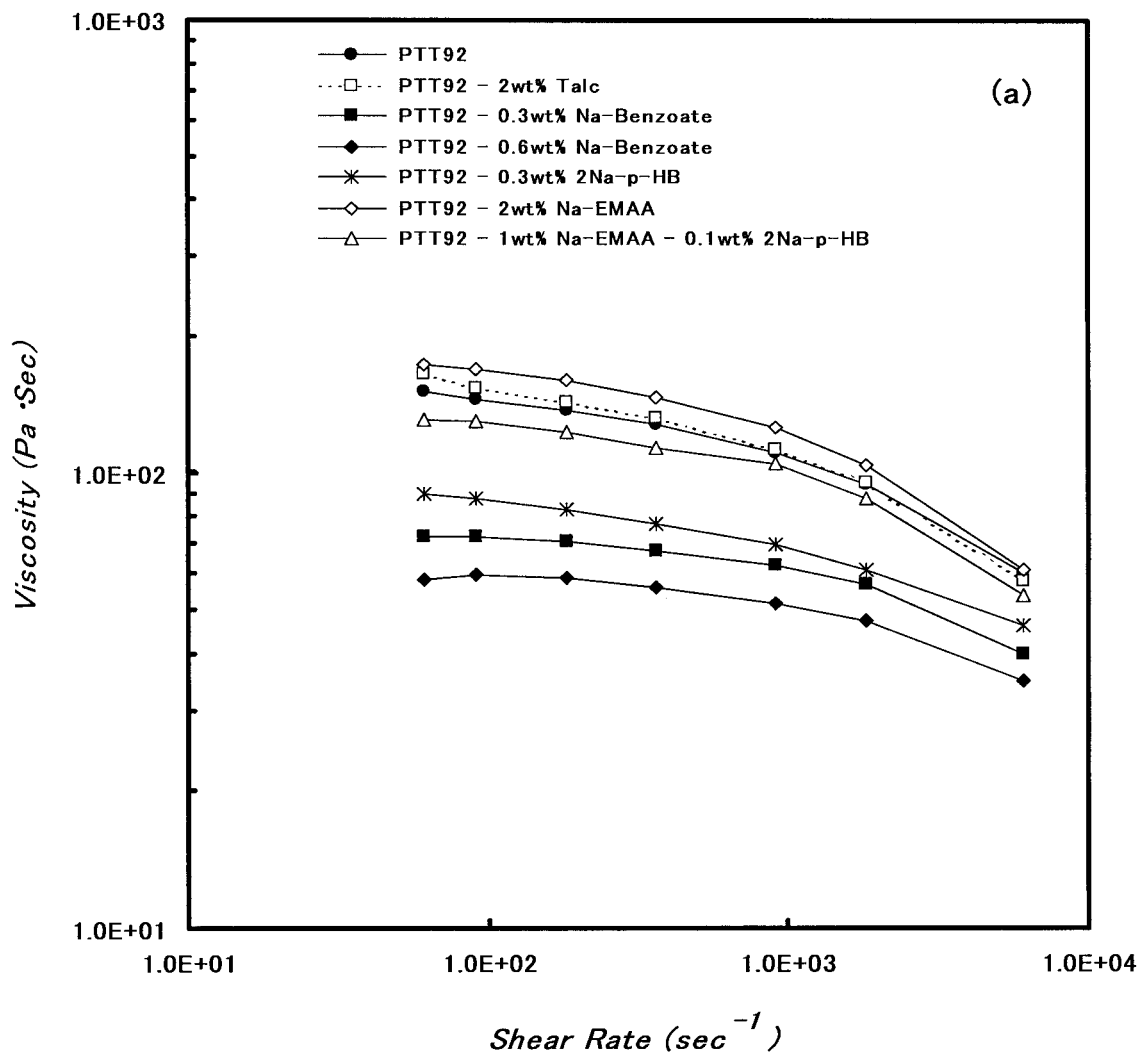
and decreased slightly when the combination of 1 wt % Na-EMAA and 0.1 wt % 2Na-*p*-HB was added.

For experimental simplicity, the effects of the chemical agents were investigated in nonreinforced systems in this study. However, the results obtained proved applicable to reinforced composites in a subsequent work, which will be reported elsewhere in the future. A reduction in molecular weight is usually undesirable in practical applications. From this viewpoint and also that of thermally stable performance, 2Na-*p*-PS and Na-EMAA were considered good chemical agents for the acceleration of the crystallization rate of PTT. Nevertheless, the addition of Na-EMAA usually worsens the mechanical strength when used with glass-fiber-reinforced composites because it is basically an ethylene-based material. To overcome this problem, an appropriate combination of Na-EMAA with other effective Na salts, such as 2Na-*p*-HB, was thought to be a feasible method. Indeed, as shown in Table II and Figure 4, the example used in this way, with the

**TABLE IV**  
DSC Measurement Results of Kneaded 3GT and 3GT Compounds Containing Fine Talc Powder or 2Na-*p*-HBr

Materials	$T_m$ (°C)	$\Delta H^{\text{endo}}$ (mJ/mg)	280°C for 3 min			260°C for 5 min		
			$T_c$ (°C)	$\Delta T_c$ (°C)	$\Delta H^{\text{exo}}$ (mJ/mg)	$T_c$ (°C)	$\Delta T_c$ (°C)	$\Delta H^{\text{exo}}$ (mJ/mg)
Kneaded 3GT	229.4	55.2	178.0	7.9	49.3	181.1	7.6	50.8
3GT + 2 wt % Talc	229.1	57.4	182.1	7.1	50.0	181.8	7.6	50.7
3GT + 0.3 wt % 2Na- <i>p</i> -HB	228.9	55.0	192.6	4.4	54.0	199.3	4.6	53.1

Measurements were performed under melting conditions of 280°C for 3 min and 260°C for 5 min.



**Figure 4** Melt flow curves for kneaded PTT92 and PTT92 compounds containing fine talc or Na salts, including Na benzoate, Na stearate, 2Na-*p*-PS, 2Na-*p*-HB, Na-EMAA, and both Na-EMAA and 2Na-*p*-HB. Measurements were performed at 270°C. For clarity, the data were plotted in two graphs.

coadjuvant addition of 1 wt % Na-EMAA and 0.1 wt % 2Na-*p*-HB, efficiently promoted the crystallization rate of PTT92 and showed only a mild melt viscosity change.

The temperature dependences of the  $t_{1/2}$  values of the samples that contained 0.6 wt % 2Na-*p*-PS, 1 wt % Na-EMAA, and 0.1 wt % 2Na-*p*-HB were further investigated by isothermal measurement. The results are shown in Figure 6. For comparison purposes, the data of kneaded PBT shown in Figure 2 were plotted together with these results. As shown in Figure 6, the crystallization rate of the sample containing 0.6 wt % 2Na-*p*-PS was largely improved to a level close to that of kneaded PBT, and the crystallization rate of the sample that contained both 1 wt % Na-EMAA and 0.1 wt % 2Na-*p*-hB was completely comparable to that of kneaded PBT.

The results obtained in this study were generally in good agreement with those found in PET studies,

where chemical nucleating agents provided a significant promotion of crystallization rate and also usually caused an undesirable reduction in the molecular weight of the polymer and where nucleating agents that did not significantly lower the molecular weight tended to have little effect on the crystallization behavior. Na stearate and Na benzoate addition resulted in the large-scale decomposition of the PTT polymer. These samples were also thermally unstable at high temperatures; thus, Na stearate and Na benzoate were not good chemical nucleating agents for PTT. 2Na-*p*-PS showed little influence on melt viscosity and was also quite thermally stable and comparatively efficient in the acceleration of the crystallization rate, so it was considered to be quite a good chemical nucleating agent. Although 2Na-*p*-HB was not all that thermally stable, because it was very efficient in the promotion of the crystallization rate and led to only mild decomposition of PTT, it was also thought to be an attractive



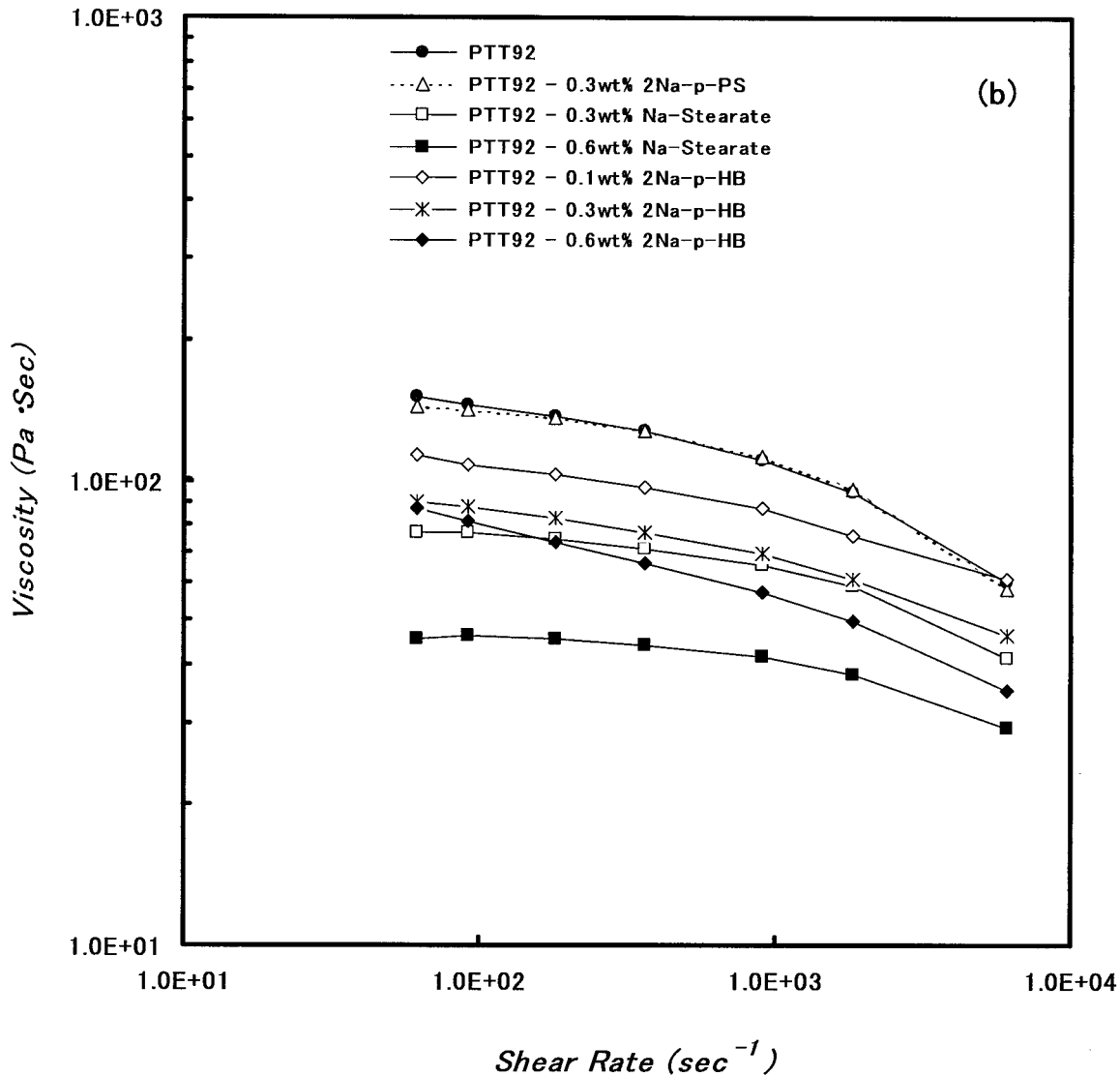
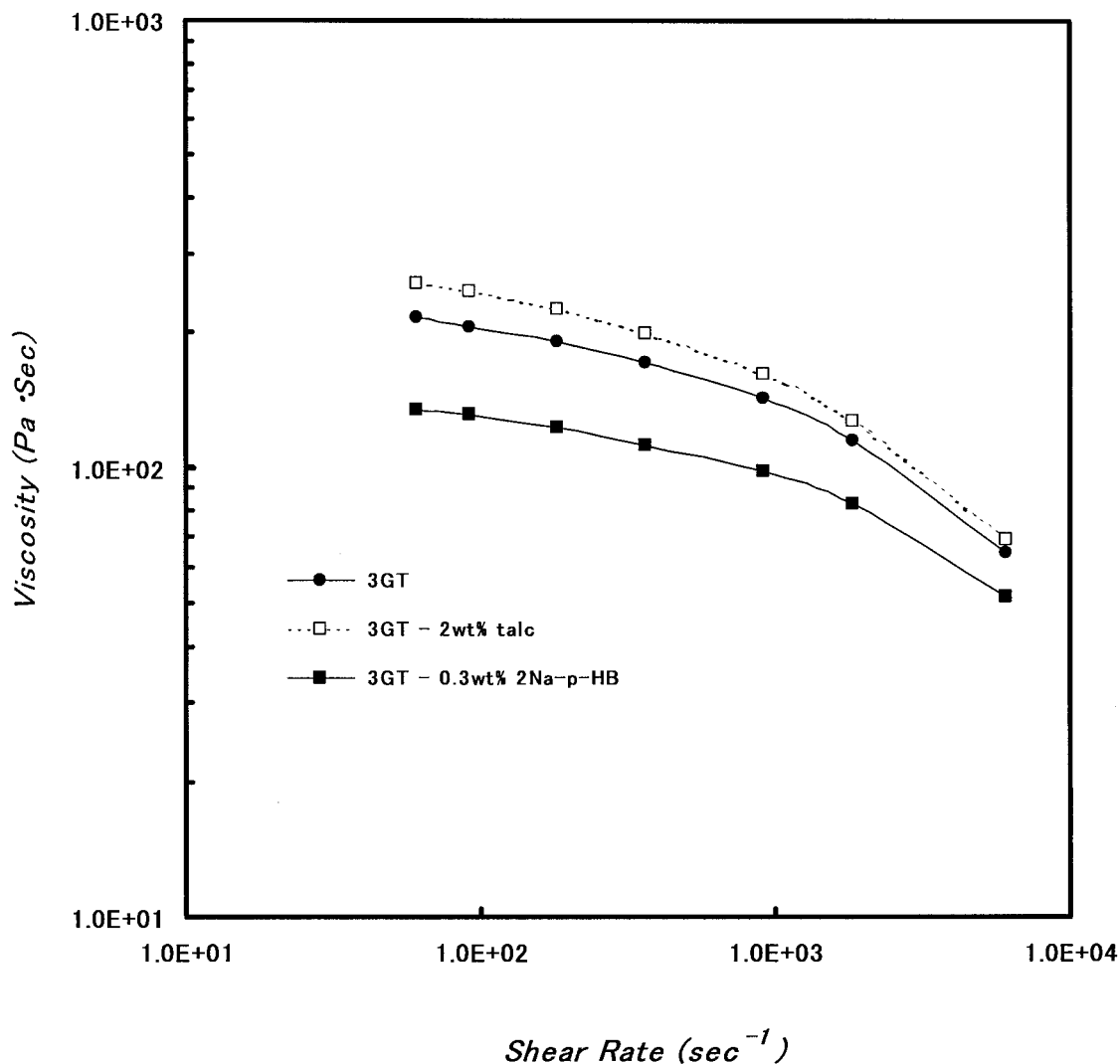


Figure 4 (Continued from the previous page)

nucleating agent. A fast crystallization rate was gained by the addition of a suitable amount of either 2Na-*p*-PS or 2Na-*p*-HB, where the least loss of molecular weight occurred. With regard to chemical structure, both of these chemical agents own the soluble —ONa group but differ in that 2Na-*p*-HB has the —COONa group and 2Na-*p*-PS has the —SO<sub>3</sub>Na group; therefore, their different behaviors as nucleating chemical agents are considered closely related to this difference in chemical structure.

Because Na-EMAA was the most thermally stable and caused an increase in the melt viscosity of the PTT92, it was considered a useful chemical nucleating agent, although the introduction of Na-EMAA alone might worsen the mechanical properties of glass-fiber-reinforced composites because of its ethylene-based properties. Morphology analyses of PTT92 that con-

tained 2 wt % Na-EMAA were performed with transmission electron microscopy in this study. These analyses revealed that small isolated Na-EMAA islands (with an average diameter of about 0.5 μm) were distributed in the matrix of the PTT polymer and that fibril-like PTT lamellas grew from the surfaces of these isolated islands. The morphology of Na-EMAA itself has been reported to be rather complicated, and some fundamental issues about it remain unsolved.<sup>47,48</sup> This ionomer consists of hydrophobic organic backbone chains and a small amount of pendant carboxylic acid and metal carboxylate. The hydrophilic ionic groups (ionic clusters) are separated from the hydrophobic backbone chains. Ion pairs aggregate to form multiplets (also called clusters), which play a role in physical crosslinking. Thus, Na-EMAA is composed of three phases of crystalline and amorphous phases and clus-



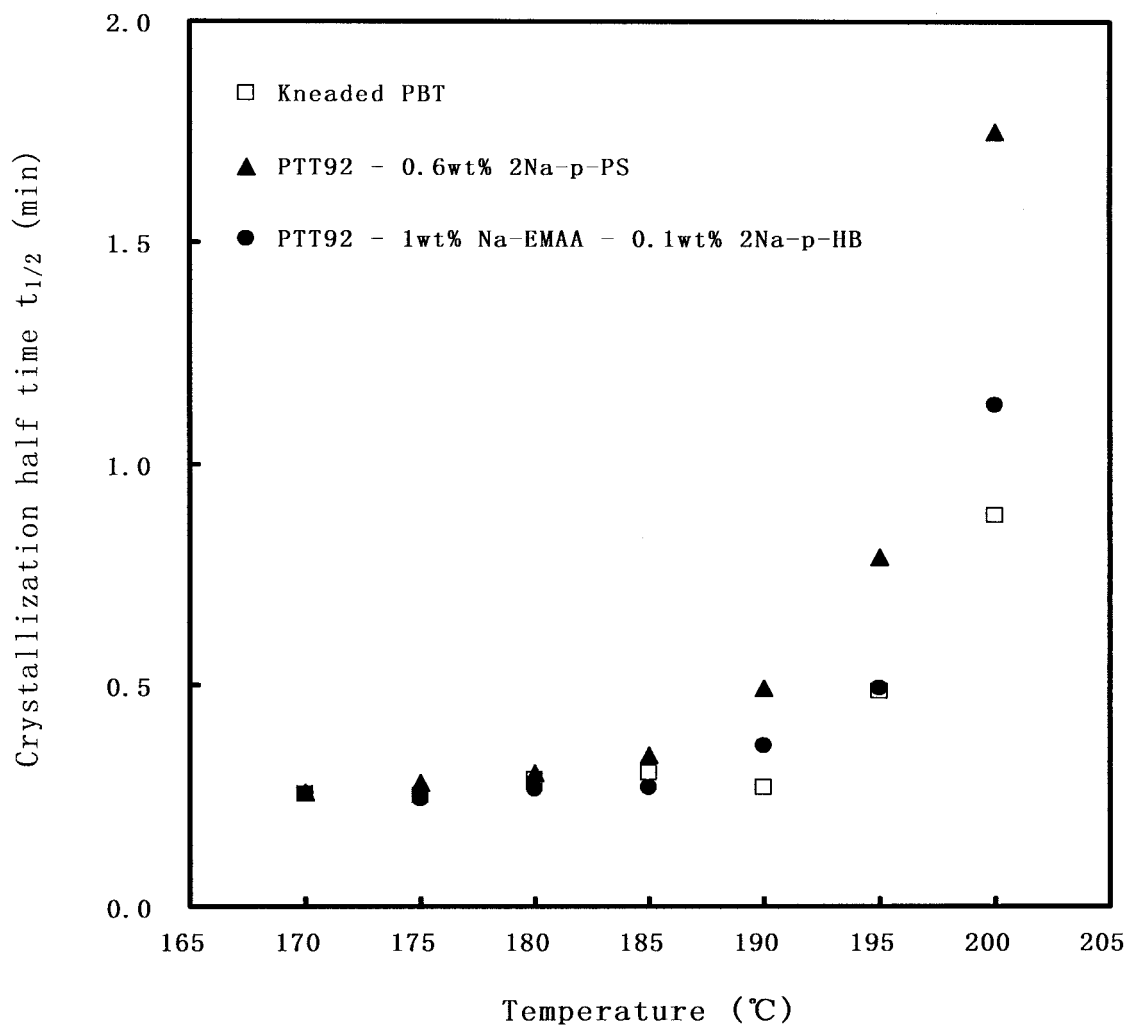
**Figure 5** Melt flow curves for kneaded 3GT and 3GT compounds containing fine talc powder or 2Na-*p*-HB. Measurements were performed at 270°C.

ters. One previous study<sup>34</sup> reported that metal salts of organic-polymer-containing pendant carboxyl groups play the role of a nucleating agent and, at the same time, induce the molecular motion of PET because of their flexible chains; the addition of Na-EMAA led to a smaller reduction in the molecular weight of PET. However, the detailed mechanism of how Na-EMAA acts as an effective chemical agent in both PET and PTT is still not clear enough at present and needs to be studied further. The origin of the high melt viscosity of PTT92 is considered to be the comparatively high melt viscosity of Na-EMAA itself and possible ion and molecular crosslinkings between Na carboxylate, carboxylic acid groups of Na-EMAA, and residual hydroxyl groups of PTT92.

In summary, I succeeded in finding effective nucleating chemical agents for PTT that produced polymers characterized by (1) relatively rapid crystallization rates and (2) relatively slight reductions in molecular

weight versus the neat PTT polymer. Remarkable improvements in the crystallization rate of PTT were attained by the proper addition of 2Na-*p*-PS, 2Na-*p*-HB, and Na-EMAA and by the addition of a combination of 2Na-*p*-HB and Na-EMAA with a small sacrifice in polymer molecular weight.

The crystallization promotion mechanism of Na salts has been studied in PET by many researchers.<sup>28-33</sup> These studies have revealed that the high nucleation efficiency of Na salts is due to the created products of Na carboxylate chain ends by chemical reactions that occur during the mixing process between the Na salts and ester linkages; Na carboxylate chain ends ( $-\text{COONa}$ ) precipitate in the polymer melts as ionic aggregates, which act as seeds for the subsequent crystallization of the PET polymer. Chain scissions occur during the chemical reactions, which result in the molecular weight decrease of the PET polymer. The nucleating efficiency is closely linked to



**Figure 6** Temperature dependences of  $t_{1/2}$  of kneaded PBT and PTT92 compounds containing 0.6 wt % 2Na-*p*-PS and both 1 wt % Na-EMAA and 0.1 wt % 2Na-*p*-HB. The data were obtained by isothermal measurements under melting conditions of 280°C for 3 min and at a quenching rate of 150°C/min.

the presence of ionic end groups, is unstable, and decreases significantly with mixing time. The instability is due to a disproportionate reaction. The —COONa chain ends react to give disodium terephthalate (DST), and their concentration decreases with the production of DST, which is directly linked to the loss in nucleation efficiency. The molecular weight decrease is of minor importance to the crystallization kinetics. In contrast to physical additives, the most effective nucleating chemical agents are those that are the most soluble in the polymer melt because the reaction between nucleating chemical agents and the polymer occur in the liquid phase. Thus, solubility and reactivity are important parameters in the control of PET–salt mixtures. In a typical example, DST, which is completely insoluble in PET, has no effect on the crystallization rate, even in a very dispersed state.<sup>32</sup> Because PTT has a similar chemical structure as PET, it seems reasonable to suggest that the mechanisms

described previously also apply to the mixture systems of PTT and Na salts, by which Na salts effectively increase nucleus density and, hence, promote the crystallization of PTT.

## CONCLUSIONS

Two commercial PTT polymers, PTT92 and 3GT, were used in this study. The two raw polymers had  $T_c$  values much lower than that of the PBT raw polymer, and their crystallization rates were largely improved through an extrusion process. Nevertheless, a large difference in the crystallization rates between kneaded PBT and kneaded PTT92 and 3GT still remained. Thus, it was desirable to find an effective means to promote the crystallization rates of PTT for the purpose of applications in engineering thermoplastics.

Crystallization of the PTT polymers was investigated in the presence of nucleating chemical agents.

Na stearate, Na benzoate, 2Na-*p*-PS, 2Na-*p*-HB, and Na-EMAA were chosen as candidates for nucleating chemical agents. For comparison purposes, fine talc powder addition was also tested. The effects of nucleating chemical agents and fine talc powder were investigated with DSC and capillary viscometry.

By and large, Na salts were more effective than fine talc powder. Na stearate and Na benzoate resulted in large-scale decompositions of PTT. 2Na-*p*-PS was a thermally quite stable nucleating agent and caused little decomposition. 2Na-*p*-HB was the most efficacious one; it was thermally comparatively stable and had comparatively little negative decomposition effect. Na-EMAA was the most thermally stable and led to a melt viscosity increase. A remarkable improvement in the crystallization rate of PTT was successfully attained with a minimum sacrifice of polymer decomposition by the addition of 2Na-*p*-PS, 2Na-*p*-HB, or Na-EMAA or by the coadjutant addition of the latter two. Therefore, 2Na-*p*-PS, 2Na-*p*-HB, and Na-EMAA were considered effective chemical agents for the crystallization promotion of PTT.

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