Crystallization of Poly(ethylene terephthalate) and Poly(butylene terephthalate) Modified by Diamides

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Poly(ethylene terephthalate) (PET) and poly (butylene terephthalate) have been modified by diamide units (0.1–1 mol%) in an extrusion process and the crystallization behavior studied. The diamides used were: for PET, T2T-dimethyl (N,N′-bis(*p*-carbomethoxybenzoyl)ethanediamine) and for PBT, T4T-dimethyl (N,N′-bis(*p*-carbomethoxybenzoyl)butanediamine). The above materials were compared to talc (0.5 wt%), this being a standard heterogeneous nucleator, and to diamide modified copolymers obtained by a reactor process. Two PET materials were used: a slowly crystallizing recycled grade obtained from soft drink bottles and a rapidly crystallizing injection molding grade. The crystallization was studied by differential scanning calometry (DSC) and under injection molding conditions using wedge shaped specimens; the thermal properties were studied by dynamic mechanical analysis. T2T-dimethyl is effective in increasing the crystallization of PET in both of the extrusion compounds as well as in the reactor materials. It was also found that the crystallization temperature of poly(butylene terephthalate) could be slightly increased by the addition of nucleators.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is the most important polyester, having a relatively high glass transition temperature (T_g) of 85°C and a melting temperature (T_m) of 255°C. Compared with poly(butylene terephthalate) (PBT), PET generally exhibits better properties in that it has a higher dimensional stability, modulus, and yield stress, but a lower impact strength. Its major drawback is its slow rate of crystallization. For the application of PET as an engineering plastic, the polymer must be easily processable by injection molding. For the success of this process, it is important that polymers crystallize rapidly so that the crystallization is complete. It is known that the molecular weight of the polymer influences the crystallization rate (1, 2) and that the level of crystallinity has an effect on the glass transition (T_g) (3) and the melting (T_m) temperatures as well as the dimensional stability. The ease of crystallization of PET also depends on the polymerization catalyst used (4); for instance, it is known that when using Zn-acetate, PET crystallizes more rapidly than polymers prepared using titanates. Given that the crystallization rate of PET is too low to permit reasonable cycle times for injection molding, nucleators are often added to the polymer, and the mold temperatures are maintained at a high level, well over 100°C. However, the addition of these nucleators does decrease the impact strength of the polymer (1, 5).

In general, the polymer crystallization process takes place in two stages—nucleation and growth. Nucleation is the formation of a new phase, and in homogeneous nucleation, the nuclei are created by the random statistical thermodynamic fluctuations of the local polymer structure. In heterogeneous nucleation, the nuclei are created on the surfaces of randomly distributed microscopic insoluble particles that are present in the melt. As the thermodynamic fluctuations are very small in magnitude, and given that significant amounts of impurities are almost always present in a polymer, heterogeneous nucleation normally dominates. The growth step is a secondary nucleation process on a previously crystallized polymer.

Heterogeneities (nucleators) are often purposefully added to PET in order to increase the crystallization rate, and previous research has shown that the crystallization rate of PET (5–7) and PBT (6, 7) can also be enhanced by copolymerization with diamide segments. These diamide segments are considered to be homogeneous nucleators, as they form part of the polymer chain. Given that they are homogeneous nucleators, their effect on the impact strength of the polymer might be different from that of heterogeneous

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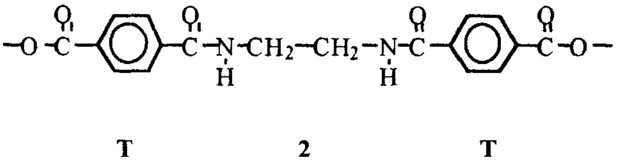
nucleators. The diamide segments used are able to form hydrogen bonds and are therefore expected to self-assemble in the melt, thus inducing the adjacent ordering of the ester segments and thereby increasing the crystallization rate of PET. The nucleating ability of several of these diamide segments has been tested (4) and it has been found that the diamide segment T2T (see formula 1 below) is the most efficient nucleator of PET, with the undercooling (T_m-T_c) in a DSC cycle at 20°C/min being decreased from 74°C to 54°C.

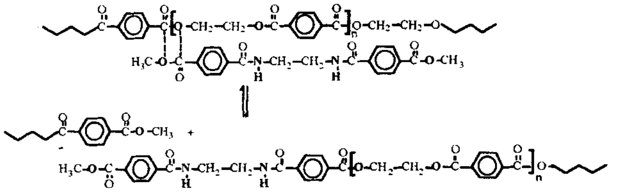


(1)

The diamide segment, T2T, is of approximately the same length as the repeating unit of PET, the only difference being that the ester bond is replaced by an amide bond. The ability of T2T to nucleate by copolymerization is already quite effective at low concentrations (0.01 and 0.1 mol%), with higher concentrations being only slightly more effective (4). The question is whether PET can also be effectively modified by T2T in an extrusion process. Extrusion compounding is a very simple process, and the feedstock can be recycled material; for example, a considerable amount of PET is available as recycled soft drink bottles.

Similar to the modification of PET using T2T, poly(butylene terephthalate) (PBT) can be modified using the diamide T4T (based on 1,4 diaminobutane) (6, 7). PBT is a rapidly crystallizing polymer, and properties such as T_m and T_g can also be enhanced by the incorporation of diamides (7). For example, the crystallization rate of this rapidly crystallizing PBT can be further enhanced by incorporating 2–10 mol% of T4T; however, it is not known if lower T4T concentrations are also effective and whether the incorporation of T4T by extrusion is possible.

In an extrusion process, the bisesterdiamides react with the polyester by ester-ester interchange:



(2)

In the reaction between the bisesterdiamide and polyester, chain scission occurs, thus forming two shortened polymer chains with methyl ester endgroups. The lowering of the molecular weight of PET is expected to be minimal when small quantities of bisesterdiamides (less than 1 mol%) are added.

The aim of this study was to examine the crystallization of PET (slow crystallizing recycled bottle grade material and a rapidly crystallizing grade) and PBT by the use of diamide segments incorporated by an extrusion process. The crystallization behavior was studied by DSC and, in addition, under injection molding conditions using a newly developed method. The modification with diamides was compared with that of talc, a standard heterogeneous nucleator, and of the nucleated materials, a number of mechanical properties were studied. In addition, the modification of PBT with T4T by extrusion was also examined.

EXPERIMENTAL

Materials

Talc (Finn talc M15), with an average particle size of 4.8 μm, was used as a standard nucleator. T2T-dimethyl was synthesized and purified as previously described (8). The commercial PETs used were provided by Eastman Chemicals and Arena Recycling VOF, the Netherlands; Eastman PET is a rapidly crystallizing injection molding grade PET, and RECO PET (obtained from Arena Recycling) is a slowly crystallizing PET recycled from soft drink bottles. PBT and $PBTA_1$ (PBT modified with 1 mol% T4T by copolymerization) were obtained from GE Plastics, Bergen op Zoom, The Netherlands. Eastman and RECO PET both contain approximately 4 mol% of diethylene glycol; in addition, RECO PET contains 3 mol% of isophthalic acid. The PET-T2T copolymers were synthesized as previously described (9).

T4T-dimethyl

T4T-dimethyl was synthesized and purified according to route II for T2T-dimethyl as previously described (8), except that 1,2-diaminoethane was replaced by 1,4-diaminobutane. The product was recrystallized from NMP (50 g/l, 160°C) following synthesis and washing.

Extrusion Compounding

The polyester and nucleators were blended in two steps using a co-rotating twin screw Berstorff ZE 25 extruder (D = 25 mm, L/D = 33) with a barrel temperature of 270°C for PET and 240°C for PBT. The polymers were dried before extrusion in a vacuum oven at 70°C overnight.

Viscometry

The inherent viscosity of the polymers at a concentration of 0.1 g/dl in para-chlorophenol at 45°C was determined using a capillary Ubbelohde 1B.

DSC

DSC spectra were recorded on a Perkin Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. The polymers were dried in a vacuum oven at 70°C overnight. Two to five milligrams of the polymer sample was measured at a cooling and heating rate of 20°C/min; the samples were first heated to 320°C, and, after 2 minutes, cooled to 20°C with the maximum of the cooling scan being taken as the crystallization temperature. The sample was then reheated to 290°C with the maximum of the second heating scan being taken as the melting temperature. DSC measurements were also performed at different cooling rates, for these, the sample was heated to 320°C, and, after 2 minutes, cooled to 100°C using a number of different rates. For PBT based polymers, the maximum temperature used in the DSC was 280°C.

DMA

Samples for the DMA test (70×9×2 mm) were prepared on an Arburg H manual injection molding machine. Prior to injection molding, the polymers were pre-melted in a mini-extruder, quenched in a water bath, and then dried. The barrel temperature of the injection molding machine was set at approximately 50°C above the melting temperature of the polymer; the mold temperature was set at 150°C, with the mold being opened after 2 minutes. The storage modulus G′ and the loss modulus G″ were measured as a function of the temperature using a Myrenne ATM3 torsion pendulum at a frequency of approximately 1 Hz. Dried samples were first cooled to −100°C and subsequently heated at a rate of 1°C/min, with the maximum of the loss modulus being taken as the glass transition temperature. The flow temperature (T_{fl}) was defined as the temperature at which the storage modulus reached 15 MPa.

Injection Molding

PET specimens were injection molded on an Arburg Allrounder 221-55-250 using a barrel temperature of 270°C and a screw speed of 200 rpm; the mold temperature was varied between 25°C and 138°C and the cooling time was 60 seconds. The polymers were injection molded to dumbbell shaped specimens (ISO R527-1) for tensile testing, whereas rectangular bars (ISO R180/1A) were prepared for impact testing. A wedge mold was used to study the crystallization behavior; the transparency of the wedge samples were measured using a Melles Griot laser beam and a Hameg oscilloscope. Similar conditions were used for PBT, except that the barrel temperatures were set at 250°C.

Izod Impact Test

Notched and unnotched Izod impact tests were carried out at room temperature using a Zwick pendulum equipped with a 4J hammer using rectangular bars (ISO R180/1A). A single-edge 45°V-shaped notch with a tip radius of 0.25 mm and a depth of 2.0 mm was milled into each bar.

Tensile Testing

Tensile tests were carried out on a Zwick Z020 universal tensile testing machine according to DIN 53455 and DIN 53457 at a test speed of 5 mm/min; the resultant strain was recorded by Multisense strain recorders. The tensile tests were performed seven times on dumbbell shaped specimens.

RESULTS AND DISCUSSION

The PET starting materials were either a slowly crystallizing PET (RECO recycled PET from soft drink bottles) (PET_{slow}), a rapidly crystallizing PET (Eastman injection molding grade) (PET_{fast}) or a rapidly crystallizing PBT. The crystallization effect on PET was studied using the nucleators bisesterdiamide T2T-dimethyl, $PETA_{10}$ and talc, a much-used nucleator for PET. $PETA_{10}$ is a PET-T2T copolymer containing 10 mol% of T2T (4).

The effect of the nucleators on the crystallization process was studied by DSC and under injection molding conditions. In addition, the effect of the individual nucleator on the polymers' mechanical properties was investigated. The materials containing nucleators were made by extrusion compounding. During this compounding step, the bisesterdiamide has the potential to react with the polyester by a transesterification reaction; in this way, the diamide can be incorporated into the chain. The effect on the crystallization rate was studied using DSC at cooling rates up to 80°C/min. It is known that under injection molding conditions, the cooling rates are a function of mold temperature and sample thickness and that they are usually very high (> 500°C/min). Therefore, in order to evaluate the crystallization process under injection molding conditions, a new method was developed that involved the injection molding of a wedge shaped specimen in which the crystallization, as function of the sample thickness and mold temperature, could be studied.

Modifying PET_{slow}

RECO PET is a copolymer containing 3 mol% of isophthalic acid; this disturbs the chain order and thereby decreases the rate of crystallization. PET_{slow} was extruded using either 0.1 mol% T2T-dimethyl or 0.5 wt% talc, or both 0.5 wt% talc and 0.1 mol% T2T-dimethyl and then compared with the reactor copolymers synthesized using $Ti(isopropyl)_4$ as a catalyst (*Table 1*). The crystallization temperature (T_c) of PET_{slow} is known to be low and was found to increase considerably with the addition of nucleators. It was also found that the T_c of PET_{slow} nucleated using talc compounds was higher than that of PET_{slow} nucleated with T2T-dimethyl, thus indicating that talc is a more effective nucleator for PET. No further increase in T_c could be observed by using a combination of talc and T2T-dimethyl. The reactor copolymers synthesized using $Ti(i\text{-}OC_3H_7)_4$ were also slowly crystallizing polymers. The copolymerization of this PET with either 0.1% or 1% T2T resulted in a marked increase in the T_m and T_c; however, the T_m and T_c of the copolymer containing 1% T2T were no higher than those obtained

Table 1. DSC and DMA Results of PET_{slow} With Various Different Nucleators.

Nucleator	η_{inh} [dl/g]	T_m [°C]	T_c [°C]	T_g [°C]	T_{fl} [°C]
PET_{slow}	0.82	262	194	84	241
0.1 mol% T2T	0.51	257	206	85	243
0.5 wt% talc	0.56	252	213	85	245
0.1 mol% T2T + 0.5 wt% talc	0.52	251	213	82	245
PET (Ti(isopropyl)$_4$)	0.99*	254	180	88	244
0.1 mol% T2T	1.03*	264	210		
1.0 mol% T2T	1.08*	262	206		

*Post condensed in the solid state during 24 hours at 230°C and 0.1 mbar.

using 0.1% T2T. The T_g of PET was minimally affected by the addition of nucleators; however, the T_{fl} was slightly increased by compounding with nucleators. The T_{fl} value marks the point at which there is a loss of crystalline network structure; this is an indication of the maximum use temperature. In fact, measurement of the T_{fl} by DMA is more accurate than measuring the T_m by DSC.

It is also possible to study the crystallization process as a function of the cooling rate by measuring the T_c. For PET, the temperature at which the maximum crystal growth rate occurs ($T_{c,max}$) is 175°C (2). If the T_c drops below the $T_{c,max}$, then it can be expected that crystallization will be slow. The influence of the cooling rate on the T_c was studied using DSC (*Fig. 1*), and the extrapolation of the lines to a cooling rate of 500°C (injection molding conditions) suggests that PET_{slow} has a T_c near the T_g value and therefore that PET_{slow} has little chance of crystallizing under injection molding conditions. Nucleators are able to considerably improve the crystallization rate, but at 500°C/min, the T_c is still below $T_{c,max}$, thus indicating that the crystallization rate is improved but still low.

The maximum cooling rate of the DSC apparatus used is 80°C/min. To study the nucleating ability of talc and T2T under injection molding conditions, a new method was developed in which a wedge shaped sample was injection molded (*Fig. 2*). The change in the transparency of the wedge sample as a function of the sample thickness was determined using a laser beam, with the loss of transparency being taken as measure of the degree of crystallization. The cooling rates in the core of the wedge were found to decrease with increasing sample thickness and mold temperature. Therefore, at a certain thickness, the cooling rate is low enough in order to allow the polymer to crystallize, thus reducing the transparency. Using this method, we were able to study the influence of nucleators as a function of the temperature of the mold. The transparency of PET_{slow} versus the sample thickness as function of mold temperature is shown in *Fig. 3*. The change in transparency with sample thickness was found to be remarkably sharp, thus suggesting that the mold temperature is critical to crystallization, such that on increasing the mold temperature, the crystallization takes place at a reduced thickness. The

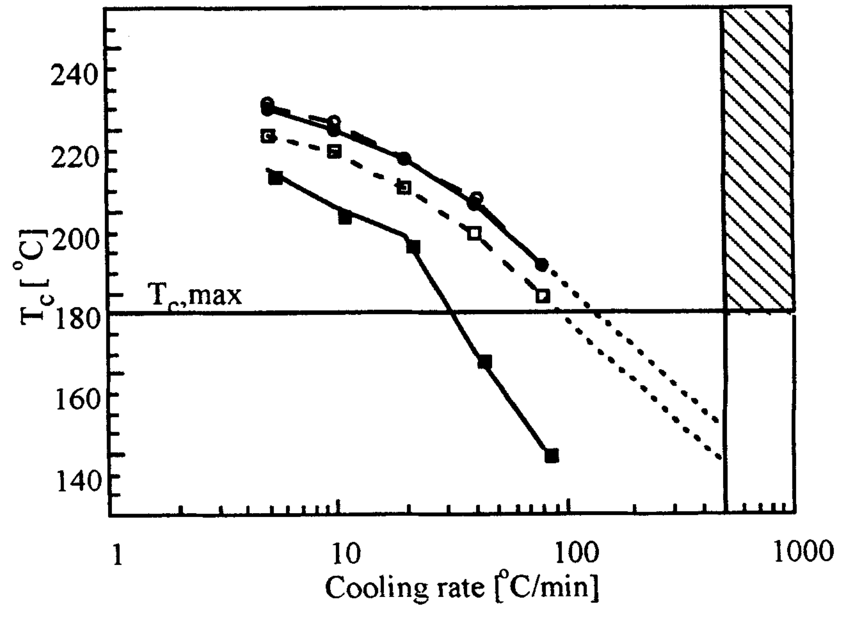


Fig. 1. T_c versus the cooling rate of a slowly crystallizing PET with different nucleators: ■, PET neat; □, 0.1 mol T2T; ●, 0.5 wt % talc; O, 0.5 wt% talc + 0.1 mol% T2T.

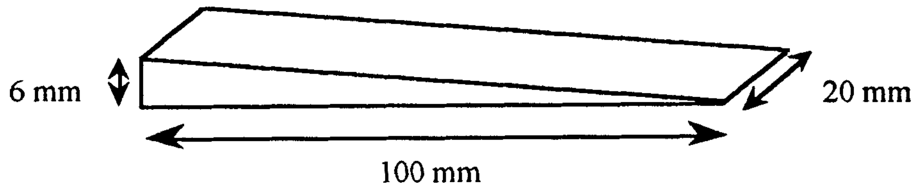


Fig. 2. Schematic representation of the injection molded wedge specimen.

thickness at which a 50% transparency was achieved was taken as a measure of the transition point, which is therefore close to the crystallization point. This value changes with mold temperature (*Fig. 4*), such that a zero mm 50% transparency thickness could be expected to occur at around 175°C; this is termed $T_{c,max}$. For example, a rapidly crystallizing PBT with a mold temperature of 75°C was found to have a 50% transparency at a thickness of 0.3 mm.

For nucleated PETs, the 50% transparency thickness can be expected to occur at lower values; however, the dependence on the mold temperature is reduced. Under these injection molding conditions, T2T was found to be the most effective nucleator of PET having a 50% transparency thickness of 1 mm at a mold temperature of 75°C. However, when the mold temperature was increased to 125°C, little difference was found in the 50% transparency values between the nucleators; even PET had a similar value. Therefore, the positive effect of the nucleators can be seen at low mold temperatures, and the use of the nucleators T2T and T2T plus talc seems to have proven more effective than just talc alone. Thus, using the combination of T2T and talc has no advantage. The DSC experiments measuring the T_c values suggest that talc is the most effective nucleator; however, according to the injection molded wedge method, T2T is the most effective.

Modifying PET_{fast}

Slowly crystallizing PET can be effectively nucleated by T2T units incorporated by both reactor and extrusion processes. The question is whether T2T units and talc are also effective when used in a more rapidly crystallizing PET. Using an extrusion process, T2T-dimethyl (0.1 mol%), $PETA_{10}$ (10 mol%) and talc (0.5 wt%) were added to an industrial PET_{fast} (*Table 2*). PET (co)polymers synthesized using the Sb_2O_3/Zn-acetate catalyst system are rapidly crystallizing; unmodified PET was used for comparison (4). The inherent viscosities of the extruded compounds are somewhat lower in value than the pure PET_{fast}. It was found that for the extrusion compounds, the addition of T2T-dimethyl or $PETA_{10}$ had little effect on the melting temperature of the polymer, and that when compared with copolymers prepared by copolymerization, the melting temperatures were somewhat lower. The compound containing talc had a lower T_m and a slightly higher crystallization temperature (T_c). The T_c was also slightly increased in both the T2T modified extrusion and reactor PET, with PET_{fast} having a slightly better T_c value. The flow temperatures (T_{fl}), as measured by DMA, were only partially affected by the presence of nucleators. *Figure 5* illustrates T_c as a function of the cooling rate. It can be seen that over the whole cooling rate range, the T_c of the talc modified polymer is just a

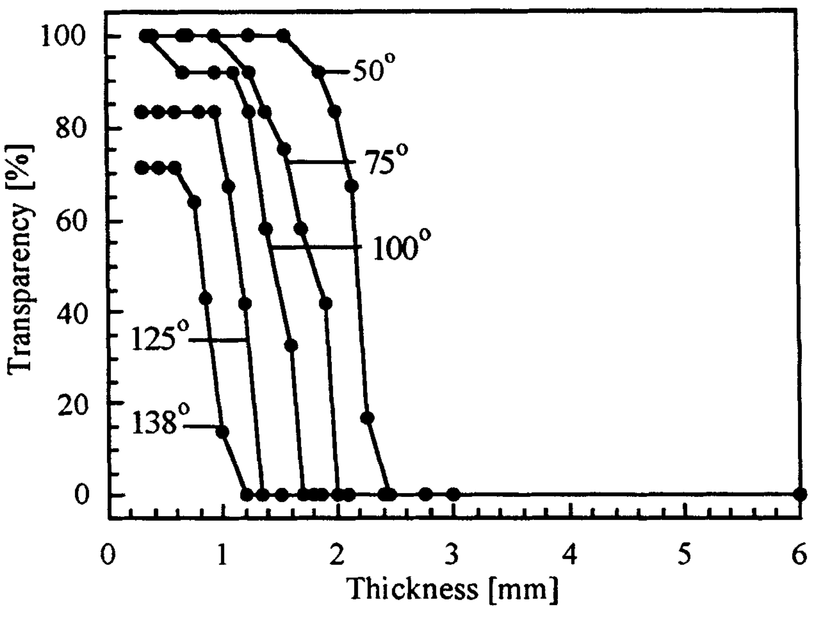


Fig. 3. Transparency versus the sample thickness, of injection molded wedge samples at different mold temperatures, of a slow crystallizing PET.

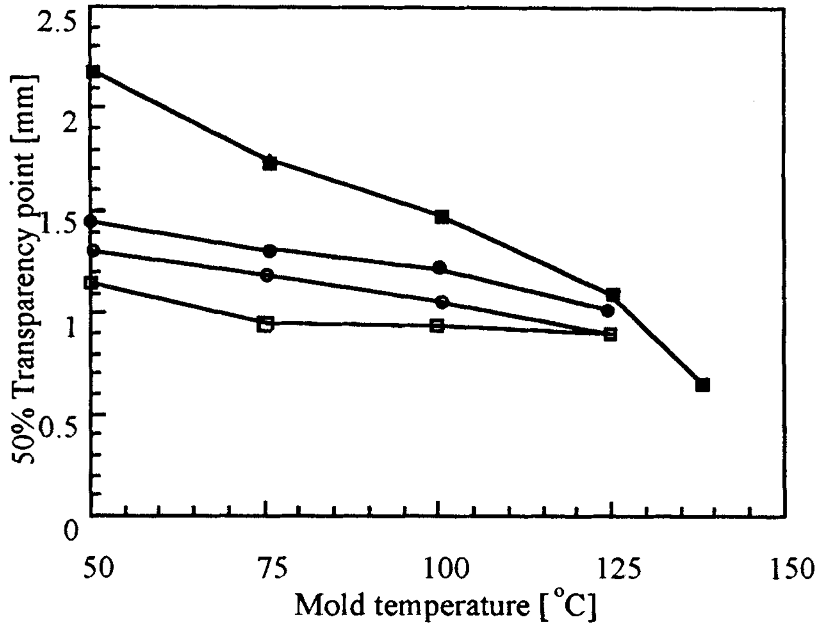


Fig. 4. The 50% transparency point in wedge samples versus the mold temperature of slowly crystallizing PET with different nucleators: ■, PET neat; □, 0.1 mol% T2T; ●, 0.5 wt% talc; ○, 0.5 wt% talc + 0.1 mol% T2T.

few degrees higher than that of the T2T modified PET, and that for injection molded compounds, the T_c of these compounds is still well below the $T_{c,max}$.

It is predicted that T2T-dimethyl is incorporated into the polymer by an interchange reaction, and that as the T2T group is built into the polymer chain, it can then be regarded as a homogeneous nucleator. Talc, which is a standard heterogeneous nucleator for PET, is known to lower the impact strength of the resulting polymer (5); when the material is strained, the heterogeneous talc particles act as stress concentrators and thus decrease the impact strength. The mechanical properties of injection molded PET_{fast} compounds using mold temperatures of 50° and 100°C are shown in *Table 3*.

The PET_{fast} specimens that were injection molded at 50°C were found to be transparent, thus suggesting they were amorphous. In contrast, the PET specimens containing either 0.1 mol% T2T-dimethyl, 1 mol% $PETA_{10}$ or 0.5 wt% talc were found to be translucent and appeared to have crystallized. The incorporation of nucleators was found to slightly increase the E-modulus, the highest E-moduli being obtained for talc nucleated PET. When the mold temperature was increased to 100°C, the moduli were again slightly higher, thus indicating that the polymers were probably more crystalline.

The maximum stress value for PET was found to be increased by the use of nucleators and by increasing the mold temperature; this suggests that there was an increased degree of crystallization under these conditions. The maximum stress values for talc at 100°C were low; this is due to the lower fracture strain of this compound. The strain at maximum stress was not influenced by the use of T2T compounds, but was lowered by the addition of talc as a nucleator.

The unnotched Izod impact fracture energy for PET was found to be decreased by the addition of nucleators; this decrease was greater in the samples that were injection molded at 100°C. PET nucleated with talc was found to have a lower impact strength than PET nucleated with T2T compounds. In addition, all the PET notched Izod specimens were found to fail in a brittle manner when nucleated by T2T compounds, having a similar or a slightly higher fracture energy than PET nucleated by talc; this difference was more pronounced in the samples that were injection molded at 100°C.

Table 2. Extrusion Compounds of PET_{fast} and T2T-dimethyl at 280°C and a Residence Time of 0.5 min, Compared With Reactor Compounds.

Nucleator	η_{inh} [dl/g]	T_m [°C]	T_c [°C]	T_g [°C]	T_{fl} [°C]	G′(150°C) [MPa]
PET_{fast}	0.65	257	207	85	238	73
1 mol% $PETA_{10}$	0.53	260	207	85	241	83
0.1 mol% T2T	0.56	260	212	84	242	87
0.5 wt% talc	0.48	253	215	88	241	73
PET (Zn/Sb)	0.80	264	207	88	247	67
0.1 mol% T2T	0.76	264	209			
1 mol% T2T	0.64	268	217			

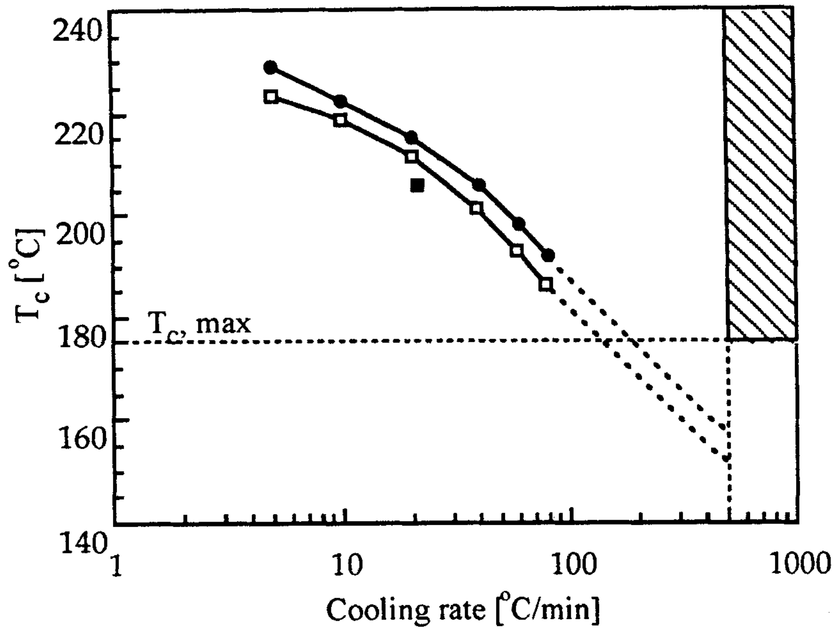


Fig. 5. T_c versus the cooling rate of a fast crystallizing PET with various nucleators: ■, *neat PET;* □, *0.1 mol % T2T;* ●, *0.5 wt% talc.*

The addition of nucleators to PET_{fast} had an effect on the crystallization occurring during injection molding; thus there was a slightly improved E-modulus and a decreased Izod fracture energy. This was particularly true when talc was used as nucleator. Little difference was detected between the mechanical properties of PET nucleated by either form of T2T (T2T-dimethyl or $PETA_{10}$). We therefore conclude that even the crystallization of the PET_{fast} can be improved by the addition of diamide and talc.

Modifying PBT

PBT itself is a rapidly crystallizing polymer (7, 10). However, if the crystallization rate could be increased even further, this would certainly be of commercial interest, as the injection molding cycle time could then be shorted. We therefore studied the effect of modifying PBT by a bisesterdiamide (T4T-dimethyl) and talc using DSC and the injection molded wedge sample method. We also evaluated a PBT copolymer with 1 mol% T4T ($PBTA_1$). Pure PBT itself was also extruded in order to have a control with the same thermal history as the samples containing the nucleators. The addition of nucleators to PBT had no effect on the melting temperature, while the crystallization temperature was only slightly increased. Furthermore, using DSC, no noticeable differences were detected in the crystallization abilities of talc, T4T-dimethyl and T4T-segments incorporated by copolymerization. The glass transition temperature and the modulus level of the rubbery plateau were found to be approximately the same for all the polymers; however, $PBTA_1$ was found to have a 5°C higher flow temperature.

DSC measurements were performed at a number of different cooling rates; *Fig. 6* shows the T_c plotted against the logarithm of the cooling rate. For PBT, $T_{c,max}$ is approximately 150°C/min; the extrapolation of the cooling rates for PBT and the PBT compounds suggest that at 500°C, the modified PBT compounds would approach $T_{c,max}$. This is in agreement with the fact that PBT crystallizes well under conditions of injection molding. Modified PBT appears to have a slightly higher T_c value than that of PBT, and, of the series examined, talc seems to perform the best. Little

Table 3. Mechanical Properties PET_{fast} With Nucleators, Injection Molded at Different Mold Temperatures. Tests Were Performed at Room Temperature.

Nucleator	T_{mold} [°C]	E-Modulus [GPa]	Max. Stress [MPa]	Strain at Max. Stress [%]	Unnotched Izod [kJ/m²]	Notched Izod [kJ/m²]
Pure PET	50	2.4	59	3.6	118	2.4
1 mol% $PETA_{10}$	50	2.5	62	3.7	93	2.3
0.1 mol% T2T	50	2.4	62	3.6	83	2.7
0.5 wt% talc	50	2.6	62	3.5	53	2.3
1 mol% $PETA_{10}$	100	2.5	61	3.5	77	2.7
0.1 mol% T2T	100	2.6	64	3.6	80	2.4
0.5 wt% talc	100	2.9	53	2.2	45	1.9

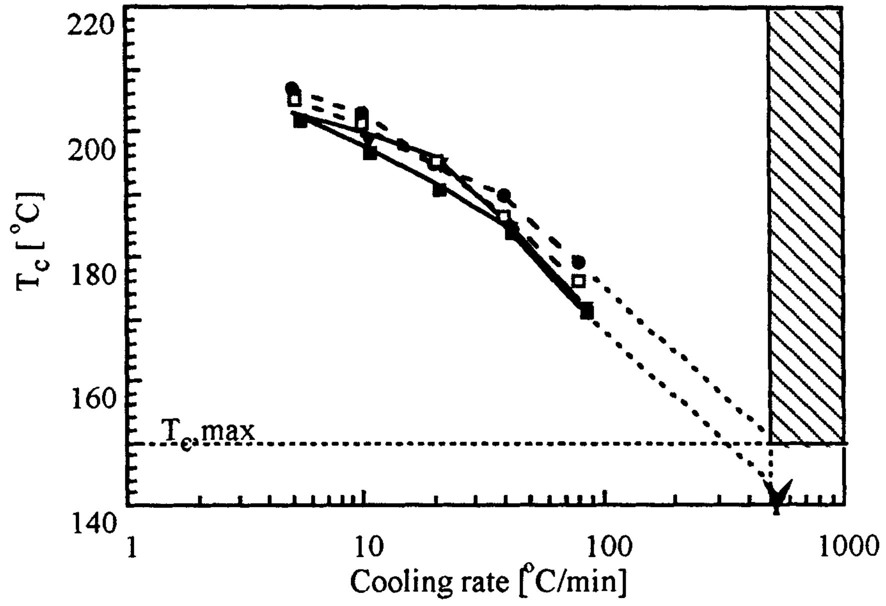


Fig. 6. T_c versus the cooling rate of PBT with different nucleators: ■, PBT neat; □, 0.1 mol % T4T; ▼, copolymer PBTA0.1; ●, 0.5 wt% talc.

difference was observed between the use of T4T as a nucleator in a reactor compound compared with an extruder compound.

Injection molding experiments were performed using a wedge mold (see *Fig. 1*) at various mold temperatures ranging from 25°C to 100°C with a cooling time of 60 seconds in order to determine the transition point between transparency and non-transparency. Again, the differences detected were very small, with the transition point occurring between 0.3 and 0.4 mm in all specimens. Under the injection molding conditions used, all samples were found to crystallize well. However, this method, which employs a 60 second cooling time, was apparently not sensitive enough to observe any influence of mold temperature or any differences in the crystallization ability of talc, T4T-dimethyl and incorporated T4T segments in PBT. A shortening of the cooling cycle might show bigger differences.

A comparison was made of the wedge method using PBT and PET_{slow} and a number of different nucleators at a mold temperature of 75°C (*Fig. 7*). The 50% transparency thickness values of PET were found to decrease with modification by diamide or talc, but the low values that were obtained for PBT were not reached. However, it should be remembered that for PET, a mold temperature of 75°C is just below the glass transition temperature, whereas for PBT, it is above the glass transition temperature.

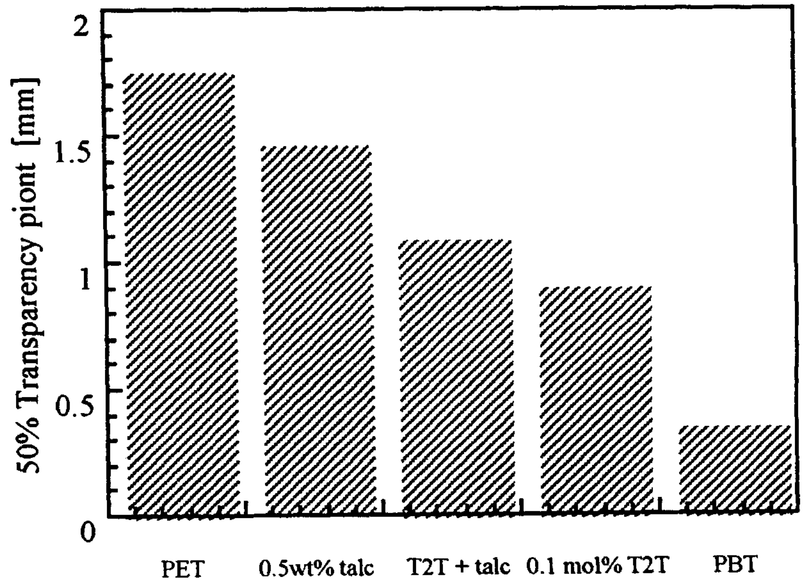


Fig. 7. 50% Transparency point on wedge samples at a mold temperature of 75°C of slowly crystallizing PET with different nucleators and PBT.

CONCLUSIONS

The diamide segment T2T has been shown to be capable of nucleating PET, even at very low diamide concentrations (< 0.1 mol%); in addition, we have shown that the diamide can be incorporated in an extrusion process as effectively as in a reactor process. The rate of crystallization of the nucleated PET was found to be independent of whether the original PET was a slowly or rapidly crystallizing grade polymer. Therefore, the greatest improvements were obtained using slowly crystallizing PET, although the crystallization of rapidly crystallizing PBT could also be slightly enhanced by the presence of talc and diamides. The crystallization temperature of PET, as studied by DSC using talc as nucleator, was found to be even better than with T2T; however, the material was found to be more brittle.

A new method was also developed for the study of crystallization under injection molding conditions. In this method, a wedge shaped sample was injection molded and the transparency of the wedge as function of the thickness then determined. The wedge method demonstrated that for PET, the mold temperature had a strong effect on the degree of crystallinity and that a fully crystallized sample could be reached only at high molding temperatures. The addition of nucleators did increase the degree of crystallization, in particular at low mold temperatures, and therefore when this method was used, diamide appeared to be more effective than talc. However, nucleated PET was still unable to crystallize as rapidly as PBT.

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