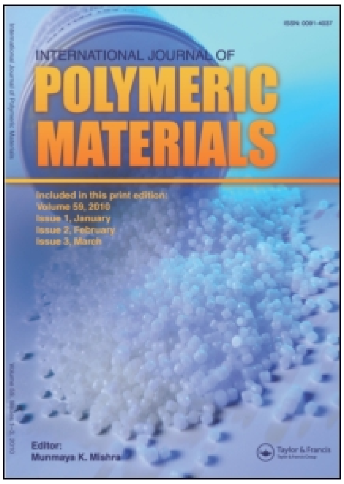

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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Shaul M. Aharoni[a]
[a] Aharoni Associates, Inc., NJ, USA

To cite this Article Aharoni, Shaul M.(2001) 'Physics of Injection-moldable PET', International Journal of Polymeric Materials, 50: 3, 301 — 319

To link to this Article: DOI: 10.1080/00914030108035109

URL: http://dx.doi.org/10.1080/00914030108035109

Intern. J. Polymeric Mater., 2001, Vol. 50, pp. 301–319
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Physics of Injection-moldable PET*

SHAUL M. AHARONI[†]

Aharoni Associates, Inc., 36 Averell drive, Morris Plains, NJ 07950-1959, USA

(Received 12 September 2000; In final form 1 January 2001)

In this article it is shown that in order to render poly(ethylene terephthalate) (PET) injection moldable, the PET resin must contain together at least one of each kind of the following additives: A plasticizer, a crystallization nucleation agent, an impact modifying agent, and a chain extending agent. Additional components, such as fiberglass, are usually added. Only the combined presence of the plasticizer and nucleating agent creates the conditions whereby the crystallization upon heating at the exterior surfaces of the molded parts may occur at sufficiently fast rates at the temperatures deliverable by water-cooled molds and the crystallization upon cooling at the interior of the molded parts will occur fast enough for the parts to solidify and not sag or deform upon ejection from the mold. For the surfaces of the molded parts to be acceptable, and for the parts to exhibit good mechanical properties, highly effective crystallization nucleation is required, resulting in a multitude of spherulitic fragments filling the interior and exterior surfaces of the molded parts, instead of separately grown, large individual spherulites substantially separated from one another by amorphous PET. To counteract the brittleness of the crystalline PET, slightly compatible impact modifying additives are added, serving as rubbery inclusions at ambient temperatures. To mitigate against molecular weight degradation, small amounts of multi-functional chain extension additives are added. The above four kinds of additives are compounded together into the PET with or without reinforcements or fillers to produce acceptable grades of injection moldable PET.

Keywords: PET; Poly(ethylene terephthalate); Crystallization temperature; Impact test; Nucleating agents; Plasticizers; Impact modifiers; Chain-extenders; Injection molding

INTRODUCTION

Although Carothers had patented [1–4] and described [5, 6] in the 1930's a group of polyesters as capable of forming useful fibers with

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* Dedicated to Professor Stoyko Fakirov on the occasion of his 65th birthday.

[†] e-mail: smaharoni@aol.com

some interesting technological properties, the prize discovery, that of poly(ethylene terephthalate)(PET) eluded him and was made by Whinfield and Dickson in England [7, 8] during World War II. The commercial potential of PET was recognized and exploited in the late 1940's [9–11]. The first laboratory-scale PET *fiber* production secretly took place in the laboratories of Imperial Chemical Industries (ICI) in 1944 and pilot plant scale production was launched by ICI in 1946, right after the war. Only in 1953 did E.I. duPont start the commercial production of PET *fibers,* using the Whinfield-Dickson [7, 9] and ICI spinning technologies. Despite the great economical success and a manifold of very appealing physical properties of PET fibers, the creation of *injection-moldable PET* grades of commercial viability had to wait about 25 additional years, and burst onto the US market in the late 1970's and early 1980's. The first commercial products of prominence were the 30% fiberglass reinforced injection-moldable PET grades marketed by E.I. duPont Corp. under the trade name Rinite^{R}-530 and by Allied Chemical Corp. under the trade name Petra^{R}-130. Since then, many other grades of reinforced and unreinforced injection-moldable PET have been introduced in the market.

The common denominator of the successful grades is the presence in each of a total additives package containing nucleating agents, plasticizers, impact-modifying ingredients, chain-extending compounds and, when desired, fiber reinforcement, fillers, coloring agents, *etc.* Many patents were issued for each of these ingredients to be present alone in PET, but the PET products containing each additive alone have always suffered from some detrimental performance characteristic and have failed in the market. Only when all the additives together were present in the PET matrix, did injection-moldable PET succeed. This is because each component of the additives package contributes one or more positive performance characteristic that countermands some negative side-effects imparted to the composite by one or more of the other additives. Independently of whether the injection-moldable PET package is reinforced or not, due to the presence of so many constituents in it, we may call the injection-moldable resin a composite material. Below, we shall use the terms composite, resin and plastic interchangeably, in order to describe the whole package of materials existing together in injection-moldable PET.

Besides cost considerations, the main reasons for the long delay in creating injection-moldable PET were the facts that certain performance characteristics of the finished products must be met and, more importantly, that the physical transformations that must occur in PET during the molding cycle proceed at a rate far too slow relative to the short molding cycles employed when common injection molding machines having water-cooled dies are being used.

Below, the physical transformations during injection molding will be discussed first, followed by a brief discussion of certain important performance characteristics. The consequences of the transformations will be highlighted and the approaches taken by technologists to remedy the deficiencies will be elaborated upon.

NON-ISOTHERMAL CRYSTALLIZATION PROCESSES OF PET DURING INJECTION MOLDING

Bulk PET has two crystallization temperatures. The lower, T_{ch}, is the temperature of crystallization upon heating. In initially amorphous PET it is observed above the glass transition temperature, T_g, when the amorphous phase is sufficiently softened to allow polymer chains the mobility necessary for the process of crystallization to proceed at a reasonable rate. The second, higher, crystallization temperature is T_{cc}, the temperature of crystallization upon cooling from the melt. Except for possibly one point where $T_{ch} = T_{cc}$, T_{cc} is always higher than T_{ch}. In Figure 1, the values in °C of T_{ch}, T_{cc} and T_m, the melting point, are shown as function of the intrinsic viscosity (I.V.) and weight average molecular weight, M_w, of PET. The actual data points were all obtained by this author in the same DSC instrument operating at heating and cooling rates of 20 K/min from over 100 samples of PET whose intrinsic viscosities were actually measured and covered the whole range indicated in the Figure. The data points exhibited very narrow scatter. The straight line of each thermal transition was obtained from the respective data points by the least squares method. Then, the data points themselves were removed from the Figure in order to avoid clutter. The important conclusion to be drawn from Figure 1 is that T_{ch}, T_{cc}, and to a lesser degree T_m, are all affected by the molecular weight, M, of the test sample: T_{ch} increases with M while T_{cc} and T_m decrease. This point is

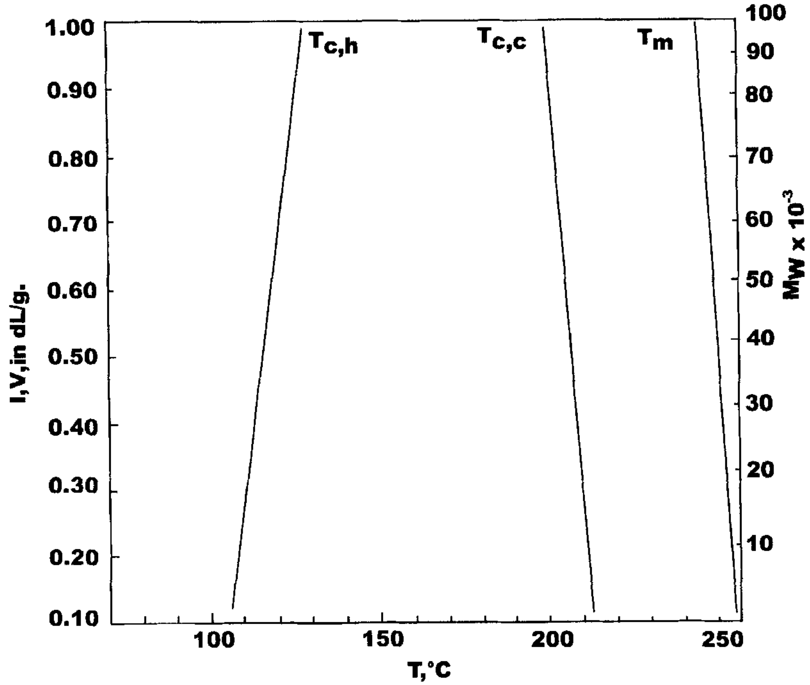


FIGURE 1 T_{ch}, T_{cc} and T_m thermal transitions of PET as function of intrinsic viscosity (I.V.) and weight average molecular weight.

extremely important since it may cloud the experimental observations: During melt processing the presence of even small amount of moisture in PET dramatically reduces its average M and with it affects T_{cc}, T_m and, after quenching, T_{ch}. Thus, for example, the presence in PET of only 20 ppm water may reduce its I.V. by about 10% during each melt processing cycle. Since M_w reduction leads to a decrease in T_{ch} and increase in T_{cc}, these changes, brought about by undesirable molecular weight loss, may be confused with the desirable decrease in T_{ch} and increase in T_{cc} technologists are striving to achieve in order to render PET injection moldable. It is therefore imperative to thoroughly dry the PET pellets or powder to a moisture content of less than 10 ppm prior to melt processing and/or to any study on the effects of any additive on shifts in T_{ch} and/or T_{cc}.

During fabrication, when molten PET is injected into the mold, its solidification and crystallization processes are very strongly affected by whether the polymer is in contact with the mold surface or is deep inside the molded element. The polymer in contact with the cold mold surface (by cold we mean significantly less than 110°C) may rapidly quench and vitrify into a solid amorphous layer while the rest of the polymer may remain momentarily liquid. As the mold surface heats, due to heat flow from the hotter polymer, so does the quenched amorphous layer. Crystallization of the PET in that layer, close to the surface, may thus ensue. This crystallization takes place at T_{ch}. While the warming of the PET surface layer continues, cooling down of its molten interior takes place and crystallization may occur once the polymer supercooling is sufficiently large. This crystallization takes place at T_{cc}. In both processes, the crystallization continues at a faster rate once the transition temperature is traversed: faster crystallization near the surface at temperatures higher than T_{ch}, and in the interior at temperatures lower than T_{cc}. The two crystallization processes are shown schematically in Figure 2.

The problem with the processes described in the previous paragraph is that they occur too slowly. An injection molding cycle consists of the following sequence of events: (1) An open die is closed tight. (2) A metered amount of molten polymer is injected through the nozzle of

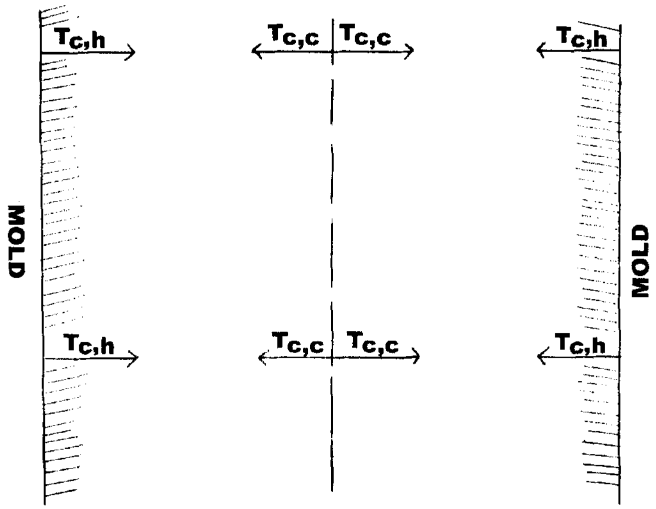


FIGURE 2 Crystallization processes in injection molded PET as function of location: T_{ch} at the colder exterior near the mold surface, and T_{cc} in the hot interior.

the injection molding machine, and flows through runners and gates into the mold cavities to completely fill them. (3) The polymer in the die is maintained under pressure which is applied by the screw of the machine. Concomitantly, the coolant (usually water) in the cooling tubes in the body of the die cools the polymer to solidify it. (4) After a predetermined duration, the injection molding machine screw reverses its rotation direction and reverts back, the pressure on the polymer in the cavities stops, and the die is then opened. (5) Ejection pins now protrude from the surfaces of the mold cavities, pushing the molded parts away, and causing them to fall out of the die. At the same time, the barrel of the injection molding machine fills up with molten polymer. (6) The die closes and the cycle starts afresh. For the process to be economically viable, the whole molding cycle should take less than 20 seconds, preferably closer to 10 seconds. This happens in the case of amorphous polymers that solidify and harden very rapidly, such as polystyrene, and in the case of crystalline polymers that crystallize rapidly, such as Nylon-6,6 or Nylon-6. PET, however, crystallizes relatively slowly and when injection-molded in the absence of plasticizers and crystallization nucleation agents, practically everything that can go wrong – does. All the evident problems may be divided into two categories: problems associated with too high T_{ch}, and problems associated with too low T_{cc}. Among the former, the following injection molding problems are the most important: (a) Upon contact with the cold mold, the polymer vitrifies into an amorphous layer of substantial thickness that does not crystallize sufficiently during the cooling of the polymer in the mold. The fully or mostly amorphous layer adheres to the metal surface of the mold and can not be separated from the mold surface by the ejection pins and ejected from the die. When this happens, the injection molding process must be interrupted and the molded elements pried out manually. (b) Even if ejection from the mold is successful, the appearance of the surfaces of the molded parts is often unacceptable. Instead of the desired highly uniform, glossy and smooth surface, one observes on surfaces of injection molded pure PET patchy areas of non-uniformity, occasional ripples, and generally mottled appearance. Besides requiring unacceptably long residence time in the mold, the two most important injection molding problems associated with low T_{cc} are: (a) Parts of the molded element, especially in its thickest regions, start sagging and bulging when the die is opened and the element ejected. It is obvious that in these regions the molten polymer in the interior have not solidified yet, but solidification of these regions may require such long molding cycles that the whole molding process is rendered non-viable. (b) The areas of the molded elements subjected to the pressure of the ejection pins during the ejection process may be substantially depressed into the elements, leaving behind permanent, deep indentations that make the element unacceptable.

From the above, it becomes obvious that the two crystallization processes taking place in the die during injection molding proceed at rates far too slow for the molding cycle to be sufficiently short to render the whole procedure technologically acceptable. To make the injection molding of PET work, the crystallization -solidification processes associated with both T_{ch} and T_{cc} must be accelerated.

T_{ch} Lowering

The T_{ch} of pure PET is far too high for the PET to be injection molded in commonly available injection molding machines equipped with water-cooled dies. The T_{ch} may be lowered by as much as around 20 K as a result of plasticization. Plasticization is brought about by the addition of an appropriate plasticizer and is the condition in which both T_g and T_{ch} are lowered. In general, suitable plasticizers may be solvents, low-M substances compatible with the polymer, or compatible oligomers and even polymers. For PET, it was found early on that certain stable esters, such as neopentylglycoldibenzoate (NPGDB), may admirably serve as plasticizers. Later on it was discovered that NPGDB tends to sublime from the polymer during melt processing and it was replaced by less volatile oligomeric polyesters and polysulfones.

The substantial lowering of T_{ch} by, say, NPGDB facilitated a rapid crystallization of the molten PET in contact with the relatively cold mold surface. This allowed for the molded parts to release better from the molds when the dies were opened and the ejection pins activated. It was found, however, that the release from the mold, even in the presence of mold-release agents, and the appearance of the surfaces of the molded parts were not as good as expected. Analysis of the surfaces revealed that the fraction of surface area which was crystalline was relatively low, comprising rather large crystalline spherulites segregated from one another by large distances of amorphous polymer.

This deficiency was remedied by the addition of crystallization nucleation agents, to be discussed below, which increased the number concentration of crystallization initiation sites at the surfaces, greatly enhancing both the release quality of the molded elements from the mold surfaces and the physical uniformity and optical appearance of these pieces. Analysis of the polymer surfaces have revealed that they were much more crystalline than in the absence of any nucleator. The analysis also revealed that the presence of nucleation agents resulted in the appearance of very many crystallization initiation sites, in the crystalline material existing in many small crystalline fragments of spherulites, and in these fragments covering practically the whole exposed surface of the molded element.

Thus, what was observed is that in order to be acceptable, the injection molded PET surface must at the same time contain two additives that contribute to two concomitant physical processes:

(a) A plasticizer that lowers the T_g of the PET and allows the T_{ch} process to start at substantially lower temperature than in its absence, and
(b) A nucleating agent causing the crystallization to concurrently initiate in very many sites in the surface layer, resulting in high surface crystallinity and the presence of many spherulitic fragments that lead to better release from the mold and higher surface quality.

There are certain limits, however, to the amount of plasticizer that may be used in injection moldable PET. The lower limits are obvious, one may not use such small amounts that their presence will remain unnoticed. The upper limits are dictated by the combination of several properties of the plasticizer, such as (a) cost, (b) compatibility with the PET and the onset of phase separation, (c) deleterious effects of too much plasticizer on the mechanical properties of the molded element, (e) deleterious effects on heat deflection temperature and thermal stability, (f) negative effects on surface uniformity, pitting, and paintability, and (g) health and environmental effects of excess plasticizer during processing, during use, and after use. All these performance variables must be tested and their significance assessed before the concentration of plasticizer in the PET is set and the appropriate compounding instructions issued. In our work [12–15], we have found that amounts of the NPGDB plasticizer in the range of 4–5 weight% of the PET in reinforced and unreinforced injection moldable PET resins serve admirably in lowering the T_{ch} of the composites so that they were easily moldable by common machines using water-cooled dies.

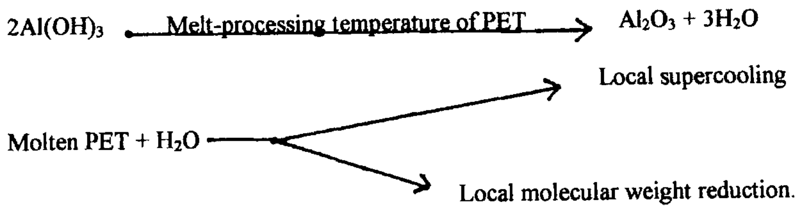
T_{cc} Elevation

The elevation of T_{cc} of PET is not only desirable, but absolutely necessary in order to render its injection molding process technologically sustainable and commercially viable. The interiors of the injection molded elements must crystallize and solidify at a rate commensurate with the molding cycle. This is brought about by the-PET starting, and completing much of, the crystallization process at temperatures as high as possible such that when the mold is opened, the molded part does not sag and deform. The T_{cc} of PET was found to be dramatically elevated by certain unconventional nucleating agents while conventional nucleating agents, such as talc, many metal oxides, and carbon black, among others [16] show very little effect on T_{cc} or none at all. Concomitant with the elevation of T_{cc} the effective nucleating agents may be useful for the acceleration of crystallization in the T_{ch} process. It should be noted at this point that while plasticizing agents have a great effect on T_g and T_{ch}, they have only a small and negative effect on T_{cc}: instead of elevating T_{cc}, the plasticizers tend to lower it slightly.

We have found 3 different kinds of very effective nucleating agents for PET, all substantially elevated the T_{cc} of the polymer without causing an excessive reduction in its molecular weight. Each kind of these nucleating agents exerts its influence in a completely different way. These will be discussed below.

(a) Metal Hydroxides

We have discovered [15, 17, 18] that if metal hydroxides decompose to oxides or lower hydroxides inside the melt processing temperature interval of PET, with the generation of water, they may elevate the T_{cc} of the polymer by up to 30 K without reducing its molecular weight meaningfully. Metal hydroxides that decompose and release their water at too low temperature, such as barium hydroxide, or at too high temperature, such as lanthanum hydroxide, are ineffective in elevating T_{cc}. Effective metal hydroxides were found to be $Al(OH)_3$, $Cu(OH)_2$, $Ni(OH)_2$ and $In(OH)_3$. All required fine pulverizing in order to maximize their effectiveness. From these, aluminum hydroxide was found to be the best because of its lack of color and low price. We believe that the nucleation process is driven by the following two conditions created together by the nucleating agent:



Because we have repeatedly found that the melt blending of high-M and very low-M PET does not elevate the T_{cc} of the product beyond the value expected from the resulting intermediate-M PET, we know that the effectiveness of the metal hydroxides is due to their *local* effect and not due to gross, long range effects. We also know that the nucleation is not due to the small particle size of the metal hydroxide or residual oxide.

This is because the elevation of T_{cc} vanishes when the nucleated PET is recycled. The nucleation effectiveness is manifested only when water is released locally from the hydroxide particles into the PET in their immediate surrounding.

(b) Elemental Antimony

Usually, about 300–450 ppm of antimony-containing catalysts are used in the polycondensation step of the polymerization of PET. From these, about 30–50 ppm are reduced to elemental antimony during the polymerization, with a concomitant oxidation of most of the CO generated in the system to CO_2 [19]. Electron microscopy studies have revealed to us that the sizes of the primary elemental antimony particles fall in the range of 15–25 nm, but aggregates as large as several microns may occasionally appear. The rest of the antimony ions usually end up in the form of the colorless antimony oxide (some colorless antimony phosphate may also be present in systems where phosphoric acid or its additives were added to the polymerization train). We have found that when the polymer is dissolved in, say, 60:40 Phenol/tetrachloroethane and the solution is treated with trifluoroacetic acid, all the antimony oxide, phosphate and Sb(0) in the system may be dissolved in the acidic medium and remain in the liquid upon precipitation of the PET with, say, methanol. Element analysis of this PET indicated that it contained practically no antimony. The T_{cc} of this purified PET was reduced from about 188°C to about 180°C while the molecular weight remained essentially unaltered. We thought it would be interesting to find what will happen to the T_{cc} if all the antimony ions in the PET would be converted to Sb(0). From previous experience [19, 20], we knew that this is achievable by passing PET containing antimony-catalysts residues with about 1.5–2.5 wt% triphenyl phosphite (TPP) through an extruder at $275°C < T < 305°C$ and allowing a residence time of about 3 minutes:

$$Sb_2O_3 + \text{excess TPP} \longrightarrow 2Sb(0) + 3\ \text{phenol} + \text{diphenyl phosphite}.$$

Concomitant with the reduction of all the antimony trioxide, the TPP reacts with the chain-ends of the PET and its molecular weight is *increased*, such that the T_{cc} elevation is not due to molecular weight reduction of the PET, but to actual nucleation by the minute elemental antimony particles created *in-situ*. When PET prepared with 350 ppm antimony (in the form of antimony trioxide) was subjected to the above procedure, its T_{cc} increased from 188°C to over 225°C. Its intrinsic viscosity have climbed from 0.90 to 1.02 dL/g. This was the highest T_{cc} we have ever obtained from PET with intrinsic viscosity higher than 0.90 dL/g. Electron microscopy studies have revealed that the particle sizes of the elemental antimony fell in the neighborhood of 25 nm with occasional deviations up and down. A typical transmission mode electron micrograph of PET containing many such antimony particles is shown in Figure 3.

Commercially available 100-mesh antimony powder was pulverized under nitrogen to further reduce its particle size, and then intensively melt blended into PET. The addition of elemental antimony in this

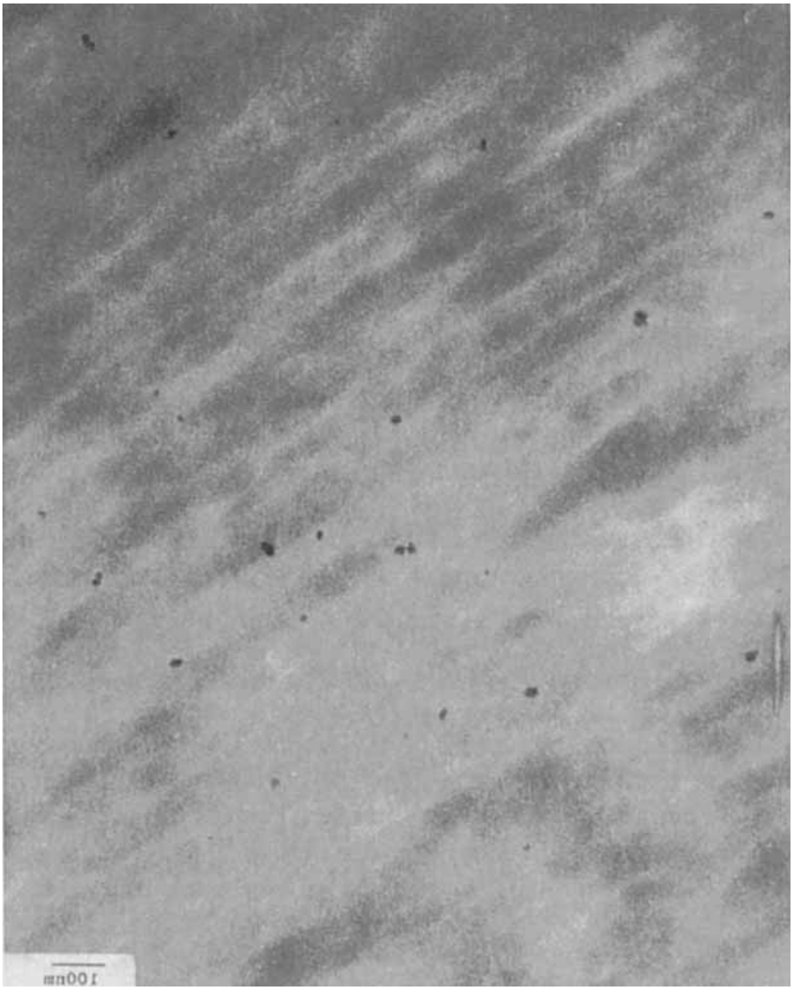


FIGURE 3 Transmission electron micrograph through microtomed injection molded PET containing elemental antimony particles of 10–25 nm size, created *in-situ* by the reduction of antimony-catalyst residues. Original magnification: 70,000 x.

form have failed to significantly elevate the T_{cc} beyond 200°C. Similarly, finely pulverized Sb_2O_3 have failed to elevate T_{cc} beyond 200°C. We have roughly compared the sizes obtained of materials by grinding or milling (about 1 micron and over) with the average of

25 nm of our *in-situ* generated antimony and found that each particle obtained by grinding has the cumulative volume of bout 65000 of the small Sb(0) particles. We thus know that because the elemental antimony was created *in-situ* it is characterized by particles whose size is sufficiently small to create a huge number of them, and sufficiently large to serve as heterogeneous nucleation sites larger than the lamellar thickness of the polymer. It is not surprising, hence, that the presence of a huge number of appropriately-sized heterogeneous nucleating sites greatly affects the crystallization and elevates T_{cc} so much.

(c) Sodium-containing Nucleators

The first sodium-containing nucleating agent to be used in a successfully-launched injection moldable PET was Surlyn^R 1856 ionomer, which is a duPont copolymer derived from ethylene and methacrylic acid containing 0.9 wt% sodium. It was used by duPont in the first injection moldable PET resin successfully introduced in the United States in the late 1970's, *i.e.*, Rinite^R-530. One may obtain similar polymeric nucleating agents by neutralizing copolymers of ethylene and acrylic acid, such as Dow Chemical Corp. Dow EAA^R 455 which has 8% by weight acrylic acid. Neutralization with sodium ions may be achieved by extruding the EAA copolymer at 150°C with sodium carbonate [14]. Otherwise, metal alkoxides may serve as the source for the desired cations [14].

The initial duPont patents covering Rinite^R-530, such as the Dutch patents Nos. 79010605 of 1978 and 79010609 of 1979, did not attempt to claim the mechanism of nucleation, nor did they claim all sodium-containing compounds as nucleating agents. Both these classes of claims were introduced by duPont several years later and were allowed by the US Patent Office even though composition of matter patents describing certain specific sodium-containing compounds as effective PET nucleators were granted and assigned to competing companies. Two such patents were issued to this author [12, 13], the first involves anhydrous sodium citrate (trisodium salt of citric acid) as the nucleating agent, and the second one uses sodium nitrite. Both nucleating agents have elevated the T_{cc} of PET by about 20 K without affecting the molecular weight adversely. The T_{cc} elevation appeared to have been only marginally sensitive to the presence of up to ca. 5 wt % plasticizers.

These T_{cc} elevations are similar in magnitude to those obtained using Surlyn^{R}-1856 or neutralized EAA^{R}-455 carrying comparable amounts of sodium ions. Test trials of a large number of sodium-containing compounds, conducted by this author at Allied Chemical Laboratories about 25 years ago, have revealed that in order to become an efficient nucleating agent, the compound must be dispersible on a molecular level in the molten PET. This is consistent with the observations of Legras *et al.* [21] which were published several years after our trials. Thus, $NaNO_2$ melts at 271°C, in the middle of the melt-processing temperature window, while NaCl does not melt and is not an effective nucleator even when very finely pulverized. Sodium thiocyanate (NaSCN) which melts at 287°C also was found by us to be a good nucleating agent, but tended to badly discolor the PET. Anhydrous sodium citrate is conveniently melt blended with PET at 275–280°C [12] to produce a single-phase, homogeneous clear melt. It is an excellent nucleator. Conversely, sodium salts of fatty acids, such as sodium stearate or sodium palmitate, seemed not to function well as nucleating agents. We believe that this is due to the fact that these high-M salts necessitate the addition of rather large wt% in order for the effects of sodium to become noticed, and at these concentrations the compounds tended to phase separate out of the molten PET.

Thus, we have satisfied ourselves, and it later became well accepted, that in order to be an effective nucleating agent a compound must contain sodium ions in a molecular level dispersible form. We have also ascertained that whenever effective sodium ion-induced crystallization took place, the molecular weight of the PET in the system was measurably lower than that of the starting PET. These two observations have a direct bearing on the crystallization-initiation mechanism. Do the sodium ions remain associated with their original anionic counterparts, and the reduction in PET molecular eight in merely a secondary effect, or did the sodium ions migrate from their original counter-ions, and cleaved PET chains to create new and shorter PET chains ending with monosodium terephthalate groups? Legras *et al.* [21] has demonstrated that the sodium ions in the system do cleave some of the original chains. They remain associated with the ends of the newly formed shorter chains and with terephthalate residues at the end of the original chains. By so doing, they arrest or restrict the PET chain mobility and crystallization may ensue. What is not yet known is whether the sodium ions are present as individual entities existing far apart from one another, or must they agglomerate in smaller or larger multi-ion entities in order to exert their effect and initiate the PET crystallization. Legras *et al.* [21] believe that the sodium ions associate in small aggregates and this is what initiates crystal nucleation. They also mention that the melt viscosity of the PET is markedly decreased after the addition of the appropriate organic Na-salts. The question we have in mind is: wouldn't the ionic aggregates arrest chain mobility and enhance the viscosity of the molten PET instead of lowering it?

Another interesting question to which we have not found yet a satisfactory answer is why are sodium or potassium ions so effective in PET nucleation while lithium and cesium are ineffective? During our trial tests we have prepared organic salts of both these alkali metals and attempted to nucleate by them PET, but with no success. Since Cs and Li belong to the same alkali metals family as Na and K, are there additional factors, such as ionic diameter or ionic charge distribution, that play a hitherto unconsidered role in the nucleation of PET crystals?

We conclude this section by mentioning two important observations. (a) Economically viable injection molding machines use water-cooled dies. These operate at temperatures not lower than about 77°C during the molding cycle, and may not operate at temperatures higher than 110°C. It was found that although the presence of nucleating agents may significantly lower the T_{ch} of PET, they were by themselves insufficient and the T_{ch} of PET having technologically acceptable molecular weight was too high for the mold cycles to be of acceptable duration, so that plasticizers *must* be added to further depress T_{ch} and achieve short enough mold cycles in common injection molding machines. (b) We have found that the addition of ever increasing amounts of effective nucleators does not increase the T_{cc} of PET above 220–225°C. What we did find is that with increased amounts of Na-containing nucleating agents the T_{cc} finally settles at around 220–225°C and further addition of the nucleating agent contributes to more pronounced molecular weight reduction and not to any measurably increase of T_{cc}.

PERFORMANCE CHARACTERISTICS OF INJECTION MOLDED PET PARTS

In the discussion above, it was already mentioned that an important performance characteristic of the finished injection molded PET parts is the appearance of their surfaces. It was mentioned that the surface must be very uniform and have high gloss. The surfaces must not appear blotchy or mottled, may not have pits, and must be easily and uniformly dyeable. All the desired surface characteristics are achieved by creating highly crystalline surfaces, in which the amount of amorphous polymer and the size of amorphous regions are minimized. At the same time, the appearance on the surface of large, well-developed crystalline spherulites is not desirable, and these are broken down by appropriate nucleation to many more crystalline fragments. So the surface quality of the finished product may be controlled by the addition of appropriate amounts of both plasticizer and nucleation agent.

Among the mechanical properties of the finished products, we have to differentiate between those noticeable only in unreinforced products and those noticeable in both reinforced and unreinforced ones. A problematic property particularly noticeable in unreinforced finished parts is their tendency to fail in a highly brittle manner under tensile stress. Keeping the total crystallinity level constant, we have found that minimizing the presence of well-developed spherulites in the PET, and replacing them by a multitude of crystalline fragments, greatly decreases the tendency toward brittle fracture and increased the strain at failure substantially. Effective nucleation agents helped in solving this problem. The addition of reinforcing agents, most common among them being chopped glass fibers, masked the brittle failure deficiency to a large extent by allowing for only very small strains at failure.

The presence of fiberglass did not, however, resolve the other major problem, a problem noticeable in both reinforced and unreinforced injection molded PET parts, namely, poor resistance against impact, especially in notched specimens. When test-bars of injection molded PET containing 30 wt% chopped fiberglass and, of course, both plasticizer and nucleating agent, were notched and then subjected to room temperature Izod-type impact tests, they have usually fractured in a highly brittle manner under impacts as low as about 1 foot-pound. Such a poor performance was, and still is, unacceptable. Its resolution required the addition of an impact modifying additive. Effective amounts of the impact modifiers generally fell in the range of 8–10 wt% of the PET in the resulting resin, and they succeeded in increasing the impact resistance of the notched test-bars from about it between 2.5 and 3.5 foot-pounds. At these levels, the impact resistance of the material was deemed acceptable.

What were the impact modifiers of chice and how do they work? We have tested 4 impact modifiers with about equal success. They were commercially available as Surlyn^R-1855, Surlyn^R-1856, sodium-neutralized and un-neutralized Dow EAA^R-455. All are copolymers of ethylene and methacrylic acid or acrylic acid. In the form we have used them, they were, respectively neutralized by zinc-, sodium-, and sodium-ions. All were easily compounded into the PET mixture by melt blending in melt blenders or extruders, as were their un-neutralized analogues. It is important to note here that, in addition to their impact modifying function, Surlyn^R-1856 and neutralized Dow EAA^R-455 served as the source of sodium ions for the crystallization nucleation processes of the PET. Surlyn^R-1855 which was neutralized by zinc ions, served well in its capacity of impact modifier but had no effect at all as a nucleating agent. Similar observations were made with respect to un-neutralized Dow EAA^R-455. We are certain that at present there are many other nucleating/impact modifying agents available in the market.

All 4 impact modifying copolymers are slightly crystalline at ambient temperatures, and all have a glass transition temperature substantially lower than normal room temperature. At normal use temperatures, a very large fraction of the total volume of each such material is present in a rubbery state, far above its T_g. Electron microscopy studies of injection molded PET specimens containing 30 wt% fiberglass and impact modifying agent (Na-neutralized EAA^R-455) have revealed that this agent was usually dispersed as very small irregularly-shaped entities of sizes in the order of tens to few hundreds nanometers. The interfaces between the impact modifier and the PET matrix were often blurred and showed no separation, indicating that the impact modifier and PET were well-bonded to one another. The good contact between the impact modifying additives and the PET indicates that thermodynamically they may be slightly compatible, or that chemical bonds were created between the PET and the additive during the melt processing, or both. At present, however, we do not know for sure whether the impact modifying inclusions are chemically grafted to the PET matrix or not.

We believe that when they still maintain their separate identity yet so finely dispersed in and intimately attached to the PET matrix, the impact modifying additives behave as rubbery inclusions, absorbing the energy in crack and/or craze tips and blunting them from propagating and reaching the point where catastrophic failure begins. In this respect, the impact modifiers in PET behave in a fashion similar to the rubbery inclusions in ductile polymers such as high impact polystyrene (HIPS) or acrylonitrile-butadiene-styrene (ABS).

It is interesting to add at this junction that when injection molded PET elements impact modified by both Surlyn^{R}-1856 and Na-neutralized Dow EAA^{R}-455 were studied by means of electron microprobe, we have found that the sodium ions did not remain entirely in the impact modifiers inclusions, but a substantial fraction of the sodium ions have migrated out and were distributed throughout the volume of the PET. At the time of the experiments, we could not determine whether the Na-ions were distributed evenly or were aggregated in the PET matrix.

To maintain the molecular weight of the PET by minimizing its degradation during each heat cycle of melt processing and recycling, and to mitigate against the loss of molecular weight by Na-containing nucleating agents, a small amount of polyfunctional epoxy is usually added to the PET mixture during its compounding. We have found that when epoxy compounds each containing more than 2 functionalities are used, amounts of 0.5 wt% or less are sufficient. At this concentration range, the poly-epoxies neither increase nor measurably decrease the molecular weight of the PET during the injection molding process. Specific examples of some preferred epoxies may be found in Refs. [12] and [13]. Other chain extending agents may, of course, used instead.

In conclusion, a complete package of injection moldable PET must contain: PET, nucleating agent, plasticizer, impact modifier, and chain extending agent. To these, fiber reinforcement and/or particulate fillers as well dyes or pigments may be added as desired. A small amount of process lubricating aid, such as sodium stearate, is usually added. Only when all these are together present in the PET matrix, acceptable injection molded parts, with all the above mentioned desirable properties, are obtained.

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