

Effects of Carbonate Salts on Crystallization Kinetics and Properties of Recycled Poly(ethylene terephthalate)

M. XANTHOS,* B. C. BALTZIS, P. P. HSU†

Department of Chemical Engineering, Chemistry and Environmental Science, New Jersey Institute of Technology, University Heights, Newark, New Jersey 07102

Received 20 April 1996; accepted 8 November 1996

ABSTRACT: In this study, thermal and microscopic analyses were used to evaluate a variety of carbonate and bicarbonate salts (alkali, alkaline-earth, and other metals), having different thermal stability within the range of poly(ethylene terephthalate) (PET) processing temperatures, as nucleating agents for recycled bottle PET. In addition, the effects of the salts on the melt viscosity and MW of the resin after melt processing were investigated in attempts to determine their overall relative performance as potential nucleating agents during injection molding. It was found that among the additives tried sodium salts are the most effective nucleating agents for recycled PET crystallization with a concomitant relatively small reduction in molecular weight. All other salts were less effective nucleating agents and, in some cases, caused also significant resin degradation. Mechanisms explaining the behavior of the different salts are proposed. With regard to processability of recycled PET in injection molding, it was found that for certain additives temperatures below 100°C could be effectively used, resulting in short cycles that produced crystalline products with satisfactory mechanical properties. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1423–1435, 1997

INTRODUCTION

Poly(ethylene terephthalate) (PET) has a low crystallization rate compared to polymers such as polypropylene (PP) and polyethylene (PE); ultimate degrees of crystallinity are also low. It has been reported^{1,2} that the maximum radial growth of PET crystals is 10 $\mu\text{m}/\text{min}$, a growth rate which is, indeed, very slow when compared, as an example, to that of PE (5,000 $\mu\text{m}/\text{min}$). Crystallization kinetics of unmodified, reactor PET depend primarily on temperature, MW, catalyst residue, and the presence of diethylene glycol formed during industrial synthesis.³ The low crystallization rate

and the slow nuclei formation offer advantages in the manufacture of transparent, partly crystalline containers. However, the development of an injection-molding-grade PET from recycled rigid containers needs to address its slow crystallization at normal mold temperatures.⁴ The crystallization rate can be increased by using high mold temperatures (at least 130°C) attained by oil or electrical heating and longer mold cycles; these techniques present economic disadvantages⁵ and often yield finished parts of low crystallinity that are difficult to remove from the mold or brittle products with a coarse spherulitic structure. A variety of inorganic or organic substances, known as nucleating agents, are commonly added at small concentrations (often <1 wt %) to produce (a) high degrees of crystallinity and (b) a fine spherulitic structure with concomitant improvements in mechanical properties and a faster overall rate of crystallization. Increased rates resulting from the higher nucleus density yield

Correspondence to: M. Xanthos.

* Also at Polymer Processing Institute, Castle Point, Hoboken, NJ 07030.

† Present address: Plastics Industry Development Center, Taichung Industrial Park, Taichung, Taiwan, Republic of China.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/071423-13

shorter cycles with corresponding economic advantages.

To determine the overall crystallization rate and the activity of a nucleating agent, in addition to microscopic examination for spherulitic size, useful parameters obtained from differential thermal analysis⁶ include

- (a) The time needed to achieve a 50% crystallinity at a constant crystallization temperature;
- (b) The overall crystallization rate constant (depending on growth and nucleation rates); and
- (c) The temperature at which the maximum of the exothermic peak occurs when crystallization is achieved while cooling the polymer from the melt state.

Most studies on PET nucleating agents have been conducted on virgin resins with relatively little information available on differences between virgin and recycled PET (e.g., Ref. 7). Due to the particular type of processing, the thermal and mechanical history of PET in finished containers is drastically different from that of PET in the original pellets; thus, the response of the recycled material to nucleating agents could differ from that of the virgin resin.

In this study, thermal and microscopic analyses were used to evaluate a variety of carbonate salts (alkali, alkaline-earth, and other metals) with different thermal stability within the range of PET processing temperatures, as nucleating agents for recycled bottle PET. In addition, the effects of the carbonate salts on the viscosity and MW of the resin after melt processing were investigated in attempts to determine their overall relative performance as potential nucleating agents during injection molding.

MODIFICATION OF PET CRYSTALLIZATION CHARACTERISTICS

A wide variety of additives including plasticizers and nucleating agents have been suggested in the patent literature as crystallization modifiers.⁶ They include low MW inorganic and organic substances, inorganic minerals, and organic polymers. The use of plasticizers increases the growth rate of spherulites, while nucleating agents are additives which induce heterogeneous nucleation

by increasing the density of sites where PET can nucleate.

In addition to moisture that has a plasticizing effect,^{8,9} substances such as epoxidized soybean oil, neopentyl glycol dibenzoate,¹⁰ aliphatic glycol phthalate,¹¹ and carbon dioxide at elevated pressures¹² have been suggested as plasticizers for PET. Addition of plasticizers results in an increased mobility of the polymer chains and a reduced glass transition temperature. As a result, the overall crystallization rate increases. Thermoplastic polyesters crystallize in the presence of high CO₂ concentration (above a critical concentration) to a degree which is controlled by saturation time and pressure, as shown in studies on microcellular foam formation.^{13,14} Crystallization in the presence of other gases has also been studied.¹⁵

The mechanism of heterogeneous nucleation is not well understood. It is believed, though, that nucleation occurs more easily in the presence of foreign particles which reduce the free-energy barrier which needs to be overcome in order to form nuclei having the required critical size. In general, the nucleating effect of an additive can be qualitatively judged by the decrease in size and increase in number of spherulites.⁶

PET synthesis requires the presence of a catalyst commonly based on Mn, Zn, Pb, Cd, Mg, Ca, Ce, Co, Li, Na, and Sb. Catalyst remnants, which are impurities in the PET resin, can act as nucleating agents for PET crystallization.¹⁶ As an example, Lawton¹⁷ demonstrated that an antimony-based catalyst increases the PET crystallization rate. This rate is also known to decrease proportionally to the concentration of diethylene glycol,¹⁸ a side product from the synthesis of PET.

Inorganic compounds are widely used as nucleating agents for PET. A variety of inorganic oxides and salts, such as antimony oxide, sodium borohydride, sodium nitrite, carbonate, phosphate, sulfate, silicate, and chloride salts and even talc, have been patented as promoters of fast PET crystallization.¹⁹⁻²² Various references, e.g., Ref. 23, reported crystallization from the glassy state of PET mixed with 0.2–0.3 vol % of talc, kaolin, silicon dioxide, or titanium dioxide. According to Groeninckx et al.,²⁴ talc and titanium dioxide particles of about 1 μm were the most effective nucleating agents when used at 0.2–0.3 vol %, whereas Dobрева et al.²⁵ reported the high efficiency of fine ZnO.

Hydroxides of aluminum, copper(II), nickel(II), indium, barium, magnesium, cobalt (II), and lan-

thanum were used by Aharoni^{26,27} as nucleating agents for PET. The conclusion from these studies was that nonalkali metal hydroxides capable of releasing water within the range of PET processing temperatures are effective nucleating agents. Aharoni argued that the increased crystallization rates can be attributed to either a localized severe hydrolysis or a localized supercooling of PET in the vicinity of the hydroxide particles. In either case, the effect is from the water released from the hydroxide. In these studies, alkali metal hydroxides were not considered, since they may have induced severe hydrolytic degradation of the polyester.

Use of nucleating agents at high concentrations may decrease rather than increase the PET crystallization rate. This was the case in a study reported by Szekely-pecsi et al.²⁸ where high MgO concentrations yielded a large number of hydroxycarboxylate complexes which reduced the mobility of polyester chains.

Organic salts is another large category of additives used as nucleating agents for PET in industrial applications. This category includes salts of hydrocarbon and polymeric carboxylic acids, alkali metal salts of ethylene terephthalate oligomers, alkali metal salts of benzoic acid,^{11,29–32} and amine carboxylate, which has been reported to act not only as a nucleant, but as a plasticizer as well.³³ Sodium carboxylates based on pyrrole carboxylic acids were found to be effective nucleants without causing reduction of the resin molecular weight.³⁴

Legras et al.^{35–37} studied the crystallization of PET in the presence of additives such as sodium *o*-chlorobenzoate, sodium *p*-chlorobenzoate, sodium benzoate, sodium *p*-hydroxybenzoate, and disodium terephthalate and suggested that a reaction occurs between the salt and the molten polyester. This reaction produces species having ionic end groups which are the actual nucleating agents for PET—more specifically, the sodium–PET salt. More soluble additives lead to an increased probability for reaction and, thus, formation of the actual nucleant. Using IR spectroscopy, Dekoninck et al.³⁸ were able to confirm the suggestions of chemical nucleation by using sodium *o*-chlorobenzoate and identifying chains having sodium carboxylate ends. The authors also showed that these chains precipitate in the PET melt as ionic aggregates which may act as nuclei for crystallization.

If a chemical reaction is involved, one should be thinking along the lines of homogeneous rather than heterogeneous nucleation. Further confir-

mation of the homogeneous nature of PET nucleation with sodium–organic acid salts was given by Garcia³⁹ who concluded that the key factors determining the efficiency of an additive for PET nucleation are the alkalinity of the salt, its solubility and ability to disperse in PET, and, finally, the purity and thermal stability of the additive.

Other substances that have been tried as nucleating agents for PET include some sodium-type ionomers (high and low MW) and various polymers.^{40–43} Recently, Reinsch and Rebenfeld^{3,44,45} demonstrated that crystallization half-times of PET in composites depend on the type of fibrous reinforcement (Kevlar, glass) and its sizing. However, the degree of crystallinity is largely unaffected by the crystallization temperature and the presence of PET additives or reinforcing fibers.

EXPERIMENTAL

Materials

PET Resins

Recycled bottle PET designated as R-PET was obtained from the Center for Plastics Recycling Research, Rutgers University (New Brunswick, NJ); the material was in the form of clear flakes with measured intrinsic viscosity (IV) of 0.715 g/dl. Nominal composition was 99.9% PET, 0.03% PE, 0.01% Al, and 0.06% others. In some experiments, virgin PET designated as V-PET (Kodapak 7352, Eastman) was used in the form of opaque pellets; nominal properties were IV = 0.74 g/dl, $M_n = 23,000$, $M_w = 46,000$, and crystallinity about 50%.

Carbonate Salts

Laboratory grades of the following salts were used: NaHCO₃, Na₂CO₃, K₂CO₃, MgCO₃, ZnCO₃, PbCO₃, BaCO₃, CaCO₃, and SrCO₃. The melting points of Na₂CO₃, K₂CO₃, BaCO₃, CaCO₃, and SrCO₃ were reported⁴⁶ to be well above the estimated maximum processing temperature of PET (300°C) attained in this study, with no decomposition. The following salts were reported⁴⁶ to have decomposition (*d.*) temperatures near, slightly above, or below the 300°C mark: MgCO₃ (*d.* 350°C), ZnCO₃ (*d.* 300°C), PbCO₃ (*d.* 315°C), and NaHCO₃ (*d.* 285°C).

Processing

Materials were dried under a vacuum prior to mixing (PET at 110°C for 15 h, salts at 80°C for

12 h). Samples used for DSC, microscopic examination, and intrinsic viscosity were prepared in a Brabender plasticorder under a nitrogen atmosphere at 280°C and 40 rpm. PET was first melted, and after about 5 min, the additives (0.3–1% by wt) were introduced. Mixing continued for several minutes to prepare samples that were pressed into films for subsequent testing.

A Van Dorn 50 injection-molding machine was used to prepare specimens for melt viscosity measurements, shrinkage, and ASTM mechanical properties from dry blends of PET and inorganic additives. Conditions were as follows: barrel temperature 260–280°C, injection pressure 1100–1350 psi, mold cooling time 10–60 s, and mold temperature up to 90°C.

Characterization

Thermogravimetric Analysis

A Perkin-Elmer thermogravimetric analyzer (TGA-7) was used to determine the thermal stability of the carbonate salts under nitrogen at a scan rate of 20°C/min, from 60 to 300°C.

Differential Scanning Calorimetry (Isothermal, Nonisothermal)

A Perkin-Elmer DSC-2 instrument was used. All measurements were conducted on predried samples under a nitrogen atmosphere to minimize the possibility of moisture regain and consequent hydrolytic degradation. For non-isothermal crystallization studies, the samples underwent two heating/cooling cycles as follows:

- First heating from 60 to 280°C at 20°C/min; keep for at least 5 min to eliminate effects of past thermal/mechanical history.
- First cooling by quenching at 320°C/min to 60°C (20°C/min was used in some runs).
- Second heating from 60 to 280°C at 20°C/min.
- Second cooling at 20°C/min to 60°C.

The following data in °C, usually referring to first heating or second heating/cooling, are reported:

T_g glass transition temperature of polymer
 T_{ch} temperature at which the maximum of the crystallization exotherm peak occurs in a heating scan (cold crystallization)

T_{cc} temperature at which the maximum of the crystallization exotherm peak occurs in a cooling scan
 T_m temperature at which the minimum of the melting endotherm peak occurs in a heating scan
 ΔT_{ch} temperature span between T_{cc} and T_{ch}

The procedure for isothermal crystallization was as follows:

- First heating from 60 to 280°C at 20°C/min; keep for 5 min.
- Quench at 320°C/min to the desired temperature (between 170 and 240°C); measure area under the peak as a function of time and fit data into the Avrami equation

$$1 - x(t) = \exp[-kt^n]$$

where $x(t)$ is the fraction of the material which is in crystallized form at time t , also known as reduced crystallinity; k , the rate constant containing nucleation and growth parameters; and n , the Avrami exponent related to the mechanism of crystallization (geometry growth, nucleation mode, rate-determining step).

- Quench to 100°C and heat to 280°C at 20°C/min; determine melting temperature and enthalpy; calculate crystallinity by dividing by 120 J/g (ΔH_m for 100% crystalline PET). The crystallization half-time, $t_{1/2}$, i.e., the time span between starting time and the time needed to achieve a 50% crystallinity is also reported.

Intrinsic Viscosity Measurements

A mixture of phenol (60 wt %) and 1,1,2,2 tetrachloroethane (40 wt %) was used as a solvent and its kinematic viscosity (η_s) was measured by a Cannon-Ubbelohde dilution viscometer (Model T5) at 25°C. The predried polymer samples were accurately weighed, dissolved at concentrations, C , up to 1 g/dl, and filtered before measuring their kinematic viscosity (η_p). The intrinsic viscosity (IV; $[\eta]$) was determined from the average of the two intercepts by using the following standard equations:

$$\eta_{sp}/C = [\eta] + K' [\eta]^2 C \quad (\text{Huggins equation})$$

$$\ln \eta_r/C = [\eta] - K'' [\eta]^2 C \quad (\text{Kraemer equation})$$

where $\eta_r = \eta_p/\eta_s$; $\eta_{sp} = \eta_r - 1$.

Optical Microscopy

Quenched thin films, prepared by predrying followed by compression molding, were examined for texture development by placing on a hot stage mounted to a Bristoline optical microscope electrically heated to about 300°C at 13°C/min. Subsequently, the power supply was cut and the hot stage was allowed to cool down to about 200°C before heating started again. The cooling rate was found to be about 12°C/min from 300 to 260°C and 8.5°C/min from 260 to 200°C. Typically, each sample underwent two heating and two cooling scans. The process of heating and cooling was monitored under the microscope. It should be added that the heating and cooling rates are comparable to the controlled rate (20°C/min) used in the DSC studies and, thus, the results from the two studies can be easily compared.

Melt Viscosity

Melt viscosity was measured in a Kayness capillary Rheometer at 260–280°C and shear rates ranging from 10 to 3000 s⁻¹ on predried samples. Thus, viscosity effects could only be attributed to the presence of the particular nucleating agent.

Mechanical Properties/Shrinkage

Mechanical properties were measured according to ASTM methods; linear shrinkage was measured on injection-molded bars after annealing in a vacuum oven at 130°C for at least 40 h.

RESULTS AND DISCUSSION

Thermogravimetric Analysis of Carbonate Salts

Table I summarizes the weight losses of the carbonate salts under nitrogen within the 60–300°C temperature range. Weight losses up to 125°C can be associated with moisture; losses up to 225°C, with losses of water of hydration or partial decomposition to CO₂ and water (e.g., for NaHCO₃); and losses up to 300°C, with the onset of possible further decomposition to basic oxide and CO₂ (MgCO₃), amphoteric oxides and CO₂ (ZnCO₃, PbCO₃) or complete stoichiometric decomposition (NaHCO₃). The results indicate an excellent ther-

mal stability for the barium, calcium, and strontium salts, a substantial stability for the lead salt, but a lower stability for all other salts. Similar stability trends would be expected during mixing with molten PET.

Effects of Nucleating Agents on PET Molecular Weight/Viscosity

Intrinsic Viscosity

Values for the intrinsic viscosity (IV) of R-PET, with or without nucleating agents, are listed in Table II. Since all values are lower than that of the unprocessed, as-received resin, % retention values after processing are also reported. As shown in the table, melt-processed R-PET as well as R-PET containing 0.5% K₂CO₃, SrCO₃, CaCO₃, MgCO₃, and BaCO₃ have IV retention values higher than 90%. Retention values for R-PET containing 0.5% ZnCO₃ and PbCO₃ are below 75%, whereas R-PET containing 0.5% Na₂CO₃ or NaHCO₃ have intermediate retention values at about 80%. In general, increasing salt concentration is shown to result in lower IV retention values.

To some extent, the reduction in intrinsic viscosity as a result of shear processing can be correlated with the thermal stability of the carbonate salts, (Table I) and their water content which could lead to hydrolytic degradation and reduction in MW. The thermally stable CaCO₃, SrCO₃, and BaCO₃ result in the highest IV retention, whereas the least thermally stable Na₂CO₃ and NaHCO₃ result in the lower IV retention.

From Table I, the weight losses of ZnCO₃ and PbCO₃ are low overall; however, their possible partial decomposition during mixing to form amphoteric oxides appears to have catalyzed a serious molecular breakdown. This is not the case for MgCO₃ and K₂CO₃, which, in spite of their higher weight loss (7.5–9.0% at 300°C), do not cause a significant IV reduction during melt processing. This may be dispersion-related, since it was shown by microscopic examination⁴⁷ that these materials could not be easily dispersed in the molten polymer matrix; the resulting inhomogeneities may have led to localized activity that could have also affected uniform sampling.

It is of interest to note⁴⁷ that similar trends were observed with V-PET (IV of 0.625): 1% CaCO₃ resulted in the highest IV after processing (0.605) or 96.8% retention; 1% Na₂CO₃ resulted in an intermediate IV (0.530) or 84.8% retention;

Table I Weight Loss of Carbonate Salts by TGA, (60–300°C)

Salt	% Wt Loss at 125°C	% Wt Loss at 225°C	% Wt Loss at 300°C	Comments
NaHCO ₃	0.34	29.7	35.8	Decomposition
Na ₂ CO ₃	1.82	14.1	14.3	Moisture, H ₂ O of hydration
K ₂ CO ₃	0.40	8.2	8.8	Moisture, H ₂ O of hydration
MgCO ₃	1.2	3.0	7.4	Moisture, H ₂ O of hydration, decomposition to oxide (onset)
ZnCO ₃	0.45	1.02	4.64	Moisture, decomposition to oxide (onset)
PbCO ₃	0.08	0.34	0.98	Moisture, decomposition to oxide (onset)
BaCO ₃	0.24	0.26	0.26	Moisture
CaCO ₃	0.01	0.02	0.03	Moisture
SrCO ₃	0.03	0.05	0.05	Moisture

and 1% PbCO₃ resulted in the lowest IV (0.380) or 60.8% retention.

Melt Viscosity

Melt viscosity plots as a function of shear rate of R-PET, containing 0.5% or no nucleating agents, are shown in Figures 1–3. In all graphs, the data for the “as-received” resin are shown to be somewhat higher than those of the melt-processed control. The PET/salt compositions may be classified into three categories:

- Those with the smallest melt viscosity reduction relative to the melt-processed PET resin (CaCO₃, SrCO₃, and BaCO₃, see Fig. 1).
- Those with an intermediate melt viscosity reduction relative to the melt-processed PET resin (K₂CO₃, NaHCO₃, and Na₂CO₃, see Fig. 2).
- Those with the largest melt viscosity reduction relative to the melt-processed PET resin (MgCO₃, ZnCO₃, and PbCO₃, see Fig. 3).

Table II Intrinsic Viscosity (IV) of R-PET with Various Nucleating Agents

Nucleating Agent (%, by Wt)	IV (dl/g) (% Retention)
None; as-received resin	0.715 (100)
None; melt-processed resin	0.705 (98.6)
NaHCO ₃ (0.5)	0.567 (79.3)
Na ₂ CO ₃ (0.3)	0.687 (96.1)
(0.5)	0.595 (83.2)
(1.0)	0.525 (73.4)
K ₂ CO ₃ (0.5)	0.657 (91.9)
MgCO ₃ (0.5)	0.650 (90.9)
ZnCO ₃ (0.5)	0.500 (69.9)
PbCO ₃ (0.3)	0.585 (81.8)
(0.5)	0.445 (62.2)
(1.0)	0.390 (54.5)
BaCO ₃ (0.5)	0.645 (90.2)
CaCO ₃ (0.3)	0.700 (97.9)
(0.5)	0.651 (91.0)
(1.0)	0.635 (88.8)
SrCO ₃ (0.5)	0.654 (91.5)

In general, the melt viscosity data show similar trends to those of the IV data discussed earlier; the overall melt viscosity reduction is proportional to the % weight losses of the salts up to 300°C (Table I). By contrast to the IV data, it appears that with respect to melt viscosity K₂CO₃ and MgCO₃ follow also the same trends. The significant melt viscosity reduction through the addition of MgCO₃ is noteworthy. Differences between the IV and the melt viscosity data could be attributed to the different degree of dispersion of the inorganic salts as a result of the different melt mixing equipment used (Brabender mixer vs. injection molder); furthermore, samples used for IV were exposed to only one melt processing step, whereas for melt viscosity samples, decomposition of salts and subsequent resin degradation could continue during the viscosity measurements.

Effects of Nucleating Agents on PET Crystallization Kinetics

DSC Nonisothermal Crystallization

Table III summarizes the information obtained from the nonisothermal DSC scans on quenched

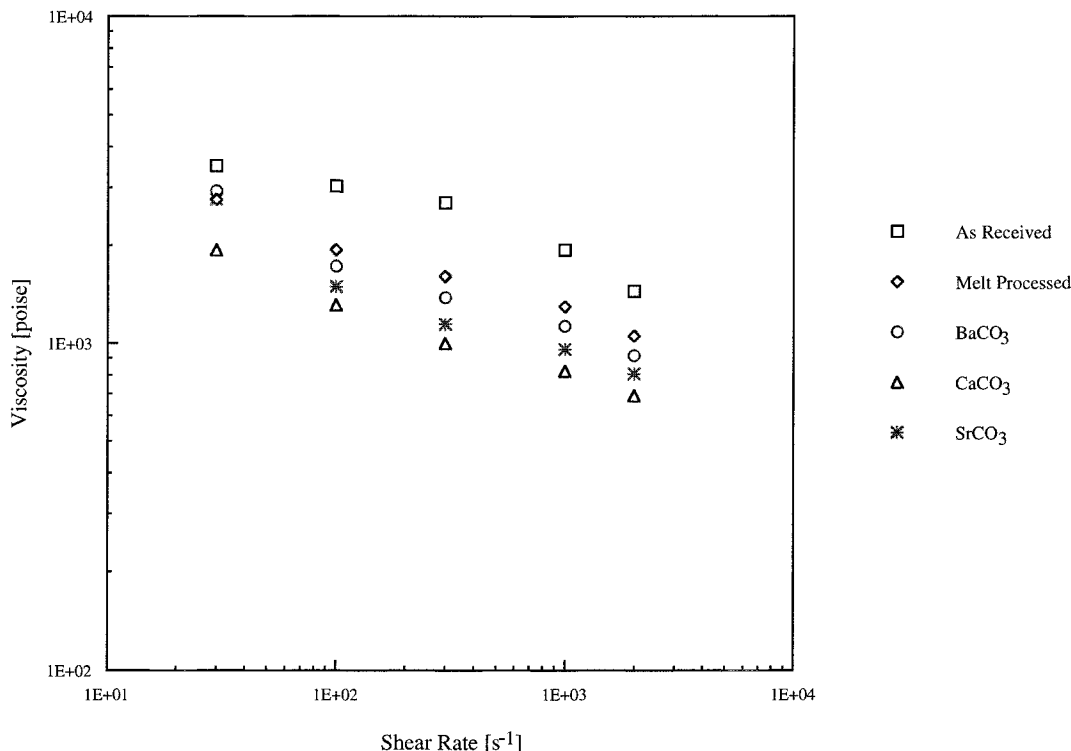


Figure 1 Melt viscosity at 270°C as a function of shear rate for recycled PET containing 0.5 wt % barium, calcium, and strontium carbonate salts; comparison with unmodified, unfilled R-PET (as-received and after melt processing).

samples during the first cooling. In general, T_{ch} , which is mostly affected by molecular mobility, should decrease in the direction of T_g with increasing rate of crystal growth; and T_{cc} , which is mostly affected by the rate of nucleation, should increase in the direction of T_m with increasing nucleation rate. Therefore, efficient nucleating agents would be salts that result in (a) a high value of T_{cc} , as close as possible to T_m , and (b) the largest possible ΔT_{ch} . In general, the crystallization rate should improve with additives which increase the value of T_{cc} or lower the value of T_{ch} .

Melt-processed resin has a crystallization rate higher than that of the "as-received" flakes, presumably due to the reduction in MW by mechanical shear/degradation which results in higher mobility of the PET segments. As shown in Table III, $BaCO_3$, $CaCO_3$, and $SrCO_3$, regardless of the concentration used, are ineffective nucleating agents, resulting in little or no difference vs. the melt-processed resin control. All other salts are more effective: Na_2CO_3 appears to be the best, resulting in the highest T_{cc} and ΔT_{ch} , followed by $NaHCO_3$. $MgCO_3$, $ZnCO_3$, and $PbCO_3$ also facilitate crystallization, presumably as a result of the

significant reduction in MW, as shown earlier. As shown in Table III, increasing concentrations of these salts result in increased nucleation efficiency. It should be noted that in our experiments all additives resulted in insignificant or no change of the experimentally determined resin T_g (80°C), which also indicates hydrolytic stability during the measurements. Thus, carbon dioxide-induced crystallization that has been observed at significantly higher concentrations and pressures in microcellular PET¹³ does not appear probable; carbon dioxide in our case could be the byproduct of $NaHCO_3$ complete decomposition or possible partial decomposition of the Zn, Pb, and Mg salts.

DSC Isothermal Crystallization

Table IV summarizes crystallization half-time values of PET with and without nucleating agents at different temperatures. $t_{1/2}$ values increase with increasing temperature or, conversely, the inverse of $t_{1/2}$ which can be taken as a crystallization rate decreases with increasing crystallization temperature; this is because undercooling (the driving force for crystallization) is reduced at high

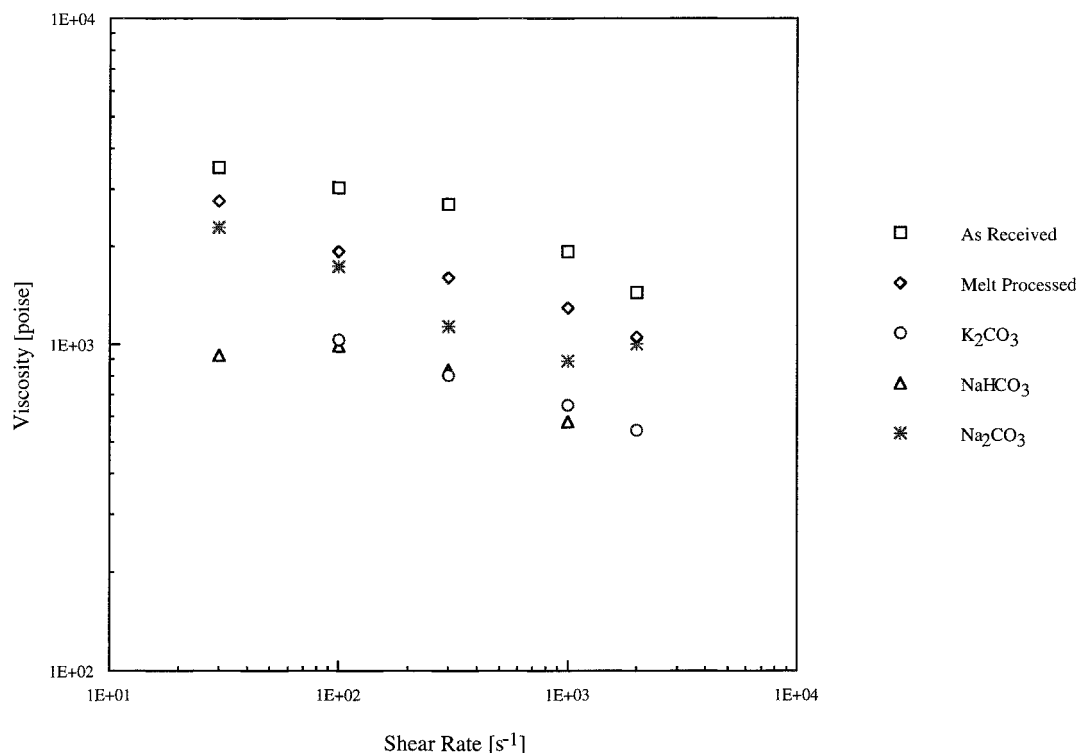


Figure 2 Melt viscosity at 270°C as a function of shear rate for recycled PET containing 0.5 wt % potassium and sodium carbonate and sodium bicarbonate; comparison with unmodified, unfilled R-PET (as-received and after melt processing).

crystallization temperatures. The data confirm our earlier observations, i.e., that in the absence of additives, the melt-processed resin has a higher crystallization rate than has the “as-received” flakes. At 0.5% concentration, the various additives follow similar trends to those observed earlier for non-isothermal crystallization. BaCO_3 , CaCO_3 , and SrCO_3 are the least effective salts, whereas Na_2CO_3 is the best, and NaHCO_3 , the second best. Compositions containing the other salts show intermediate behavior, but are all superior to the melt-processed control.

Similar conclusions may be drawn from the Avrami rate constants shown in Table V which decrease with increasing crystallization temperature. Salts may be rated as before in terms of their efficiency. The Avrami exponents for the Na, K, Mg, Zn, Pb, and Ba salts, at a given temperature and concentration, show small differences but are overall lower than those for the unmodified melt-processed resin and the compounds containing the ineffective Ba, Ca, or Sr salts. Values of the Avrami exponents around 3 at higher temperatures are indicative of heterogeneous, athermally nucleated, spherulitic growth,^{3,18} whereas for the

unprocessed resin, a likely mechanism of crystallization is thermal nucleation, diffusion-controlled.⁴⁸

Optical Microscopy

A summary of texture and thermal transitions from optical microscopy studies is shown in Table VI. From the DSC studies, it could be argued that the higher the T_{cc} value the more effective is the nucleating agent. The analog of T_{cc} in microscopy studies would be T_{mcc} , and, thus, this value could be used as an indicator of the effectiveness of nucleation. Nonetheless, T_{mcc} seems not to be a safe indicator. For example, from Table VI, one could erroneously conclude that 1% Na_2CO_3 is less effective than is 0.3%, in contradiction to the observed texture of patterns. In the present work, T_{mcc} could not be accurately determined, and, in actuality, the recorded value was the temperature where crystallization was completed, especially when the size of the crystals was very small. Thus, if microscopy is to be used for determining the effectiveness of a nucleating agent, it appears that decisions should be based only on the size of the

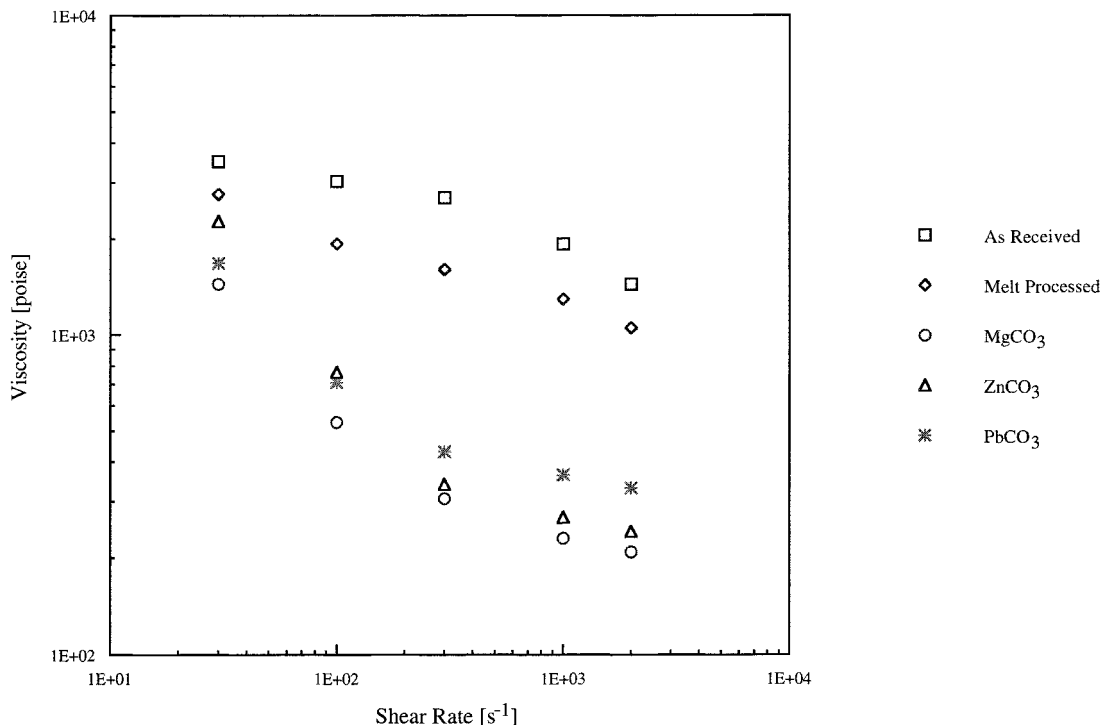


Figure 3 Melt viscosity at 270°C as a function of shear rate for recycled PET containing 0.5 wt % magnesium, zinc, and lead carbonate salts; comparison with unmodified, unfilled R-PET (as-received and after melt processing).

observed patterns, i.e., tiny grainy vs. Maltese cross pattern.

The results in Table VI confirm our previous findings, suggesting that sodium, potassium, and magnesium salts at 0.5% concentration are effective nucleating agents, whereas Ba, Ca, and Sr salts are not. It is also suggested that both DSC and microscopy studies should be used in order to make safe conclusions about the effectiveness of a substance as a nucleating agent. As an example, the T_{cc} value from DSC studies indicates that $PbCO_3$ is a good nucleating agent, which contradicts the findings based on fineness of texture. In this case, the fast crystallization rate determined via DSC studies should really be attributed to the low average molecular weight of PET due to molecular chain breakdown and not to the effectiveness of the nucleating agent as a crystal-size reducer.

Properties of Injection-molded PET

Molded parts were evaluated for apparent crystallinity, surface appearance, thermal stability, mechanical properties, and shrinkage character-

istics. Some results from Ref. 47 are summarized in Table VII and discussed below:

Flexural strength data indicate that at a low mold temperature (40°C), R-PET without nucleating agents was equal or better than was R-PET containing 0.5% $CaCO_3$, but had lower strength than had R-PET containing 0.5% Na_2CO_3 . R-PET and R-PET with $CaCO_3$ were uniformly amorphous, whereas R-PET with Na_2CO_3 had a thin amorphous surface, but otherwise appeared uniformly opaque.

At a higher mold temperature (90°C), samples with 0.5% Na_2CO_3 had higher flexural strength than did those with $CaCO_3$ or $PbCO_3$. Improved crystallinity as a result of an improved nucleation rate in the presence of the effective sodium salts (carbonate and bicarbonate) was also evident from the uniform opacity with no apparent amorphous regions. All other salts resulted in little (Mg, K) or no (Ca, Sr, Ba, Zn, Pb) opacity. It should be mentioned that K_2CO_3 was poorly dispersed as coarse particles in the matrix, while in $PbCO_3$ -containing samples, the presence of black dots was attributed to the salt decomposition and subsequent degradation of the polymer.

The dimensions of injection-molded R-PET

Table III Nonisothermal DSC Transitions of R-PET with Nucleating Agents

Nucleating Agent (% by Wt)	T_{ch} (°C)	T_{cc} (°C)	T_m (°C)	ΔT_{ch} (°C)
None; as-received resin	158	168	248	10
None; melt-processed resin	138	181	248	43
NaHCO ₃				
(0.3)	134	193	249	59
(0.5)	134	194	250	60
(1.0)	130	200	249	70
Na ₂ CO ₃				
(0.3)	134	197	249	63
(0.5)	129	201	248	72
(1.0)	122	203	247	81
K ₂ CO ₃				
(0.3)	136	183	249	47
(0.5)	132	187	249	55
(1.0)	129	198	249	69
MgCO ₃				
(0.3)	135	184	248	49
(0.5)	136	186	248	50
(1.0)	136	189	250	53
ZnCO ₃ (0.5)	140	192	250	52
PbCO ₃				
(0.3)	143	186	249	43
(0.5)	141	192	248	51
(1.0)	143	197	250	54
BaCO ₃				
(0.3)	142	180	248	38
(0.5)	135	181	249	46
(1.0)	145	180	248	35
CaCO ₃				
(0.3)	140	181	247	41
(0.5)	144	181	248	37
(1.0)	142	181	248	39
SrCO ₃				
(0.3)	144	181	247	37
(0.5)	142	182	247	40
(1.0)	142	181	247	39

bars containing effective nucleating agents were lower than those without additives, particularly at a 90°C mold temperature. Reduction in linear shrinkage data (after annealing) can also be correlated with increased crystallinity. With the exception of Na₂CO₃ and NaHCO₃ nucleated R-PET, all bars annealed for 40 h prior to shrinkage measurements were observed to warp, an indication of thermal instability. At a mold temperature of 40°C, the shrinkage of R-PET was high and equal to that of R-PET containing 0.5% CaCO₃; addition of 0.5% Na₂CO₃ resulted in a much lower shrinkage. At a mold temperature of 90°C, Na₂CO₃ resulted in the lowest shrinkage at 0.5% concentration with the three salts ranked in the following shrinkage order: Na₂CO₃ < CaCO₃ < PbCO₃.

Additional Comments on the Role of Additives

The experimental results indicate that among the studied salts sodium carbonate and sodium bicarbonate were the best nucleating agents in terms of increased crystallization temperature and rates, fine crystalline microstructure, minimum reduction in MW, and satisfactory molding characteristics. A common characteristic of both salts is their relative high weight losses (carbon dioxide and/or water) at processing temperatures; the observed MW reduction could be related to chain scission from hydrolytic degradation, possibly catalyzed by sodium ions. Gilmer et al.³⁴ suggested that if the mechanism of chemical nucleation is applicable any sodium salt that is effective as a nucleat-

Table IV Isothermal DSC Crystallization Half-time, $t_{1/2}$, of R-PET with Nucleating Agents at Different Temperatures

Nucleating Agent (% by Wt)	$t_{1/2}$ (min) at 170°C	$t_{1/2}$ (min) at 190°C	$t_{1/2}$ (min) at 210°C	$t_{1/2}$ (min) at 220°C
None; as-received resin	0.71	1.14	4.57	—
None; melt-processed resin	—	—	2.55	—
NaHCO ₃ (0.5%)	—	0.18	0.84	2.61
Na ₂ CO ₃				
(0.3)	—	—	0.67	2.96
(0.5)	—	—	0.62	1.98
(1.0)	—	0.15	0.57	1.87
K ₂ CO ₃ (0.5)	—	0.45	1.52	4.07
MgCO ₃ (0.5)	0.24	0.39	1.36	3.65
ZnCO ₃ (0.5)	0.22	0.34	1.18	2.93
PbCO ₃ (0.5)	0.22	0.56	1.94	5.37
BaCO ₃ (0.5)	0.36	0.57	2.13	5.78
CaCO ₃				
(0.3)	—	0.6	2.48	6.64
(0.5)	0.25	0.28	2.14	5.81
(1.0)	—	0.56	1.88	—
SrCO ₃ (0.5)	0.37	0.57	2.10	5.49

ing agent for PET must cause a reduction in MW. By contrast to the other carbonate salts evaluated in this study, the sodium salts are characterized by both water solubility and, reportedly,⁴⁶ a certain alcohol solubility. Solubility may be correlated with enhanced dispersion/miscibility of the carbonate salts or any resultant PET sodium salts

in the resin after reaction; the resin could also contain other polar components at small concentrations (e.g., ethylene glycol from hydrolytic degradation or residual diethylene glycol) that could enhance solubility or affect nucleation. It should be noted that solubility or ease of dispersion of the salts in the melt, although not investigated in

Table V Isothermal DSC Calculated Avrami Constants for Crystallization of R-PET with Nucleating Agents at Different Temperatures

Nucleating Agent (% by Wt)	$n-k$ at 170°C	$n-k$ at 190°C	$n-k$ at 210°C	$n-k$ at 220°C
None; as-received resin	1.8–1.266	2.3–0.516	2.4–0.018	—
None; melt-processed resin	—	—	3.0–0.042	—
NaHCO ₃ (0.5)	—	2.0–21.6	2.8–1.11	3.2–0.033
Na ₂ CO ₃				
(0.3)	—	—	3.2–1.44	4.0–0.009
(0.5)	—	—	2.2–1.97	2.2–0.16
(1.0)	—	1.6–13.87	2.3–2.602	2.5–0.005
K ₂ CO ₃ (0.5)	—	2.1–3.744	2.3–0.264	2.3–0.027
MgCO ₃ (0.5)	1.7–7.948	2.0–4.474	2.5–0.32	2.4–0.031
ZnCO ₃ (0.5)	1.5–6.782	1.8–4.896	2.6–0.451	2.5–0.046
PbCO ₃ (0.5)	1.6–8.017	1.8–9.518	2.6–0.725	2.5–0.048
BaCO ₃ (0.5)	1.8–4.459	2.2–2.341	3.2–0.064	2.5–0.008
CaCO ₃				
(0.3)	—	2.1–2.06	3.4–0.031	3.0–0.002
(0.5)	1.9–10.348	2.2–2.212	3.4–0.053	3.2–0.002
(1.0)	—	1.8–1.946	2.5–0.143	—
SrCO ₃ (0.5)	1.9–4.386	2.2–2.341	3.2–0.064	2.5–0.008

this study, should be of paramount importance for either nucleation or chain scission catalytic reactions as shown in earlier publications.³⁹

By contrast to the sodium salts, common characteristics of the barium, calcium, and strontium salts that were shown to be totally ineffective nucleating agents without also affecting molecular weight are high thermal stability and insignificant moisture losses at processing temperatures. This supports the mechanism presented earlier in this article by Aharoni^{26,27} emphasizing the importance of released water in increasing the crystallization rate. Although lead, zinc, and magnesium salts could be considered as effective nucleating agents according to the criteria set in this study, these metals cause a significant MW reduction. Common characteristics of these salts are intermediate moisture losses that could be responsible for hydrolytic degradation and the possibility of decomposition to oxides at/or near processing temperatures; the oxides may act catalytically in promoting further chain scission reactions.

Table VI Texture Characteristics and Thermal Transitions of R-PET With and Without Nucleating Agents from Microscopy Studies

Nucleating Agent (% by Wt)	T_{mch} (°C)	T_{mcc} (°C)	T_{mm} (°C)
None; as-received resin	144 MC	222 RM	260
None; melt-processed resin	138 MC	221 RM	257
NaHCO ₃ (0.5)	137	223 TG	250
Na ₂ CO ₃ (0.3)	135	215 MG	250
(0.5)	130	220 TG	255
(1.0)	135	217 TG	254
K ₂ CO ₃ (0.5)	140	219 TG	250
MgCO ₃ (0.5)	144	233 TG	267
ZnCO ₃ (0.5)	134	223 RM	255
PbCO ₃ (0.5)	—	223 RM	254
BaCO ₃ (0.5)	148	223 RM	260
CaCO ₃ (0.3)	141	219 MC	252
(0.5)	141	217 MC	254
(1.0)	140	216 MC	250
SrCO ₃ (0.5)	140	217 RM	259

^a T_{mch} : temperature at which texture was first observed during the heating scan. T_{mcc} : temperature at which texture was first observed during the cooling scan. T_{mm} : temperature at which birefringence was observed to totally disappear. RM: ring Maltese cross pattern; MC: Maltese cross pattern; TG: tony grainy.

Table VII Flexural Strength and Shrinkage of Injection-molded Samples

	Flexural Strength, (MPa)	Shrinkage (%)
Mold temperature, 40°C		
As-received resin	88.2	5.5
+0.5% Na ₂ CO ₃	91.3	1.8
+0.5% CaCO ₃	85.5	5.5
Mold temperature, 90°C		
+0.5% CaCO ₃	95.7	1.2
+0.5% PbCO ₃	86.2	3.3
+0.5% Na ₂ CO ₃	108	0.2

CONCLUSIONS

Crystallization kinetics of recycled PET were studied in the presence of Na₂CO₃, NaHCO₃, K₂CO₃, MgCO₃, CaCO₃, SrCO₃, BaCO₃, ZnCO₃, and PbCO₃ as nucleating agents. Based on results from differential scanning calorimetry, optical microscopy, and resin hydrolytic/thermal stability studies, it is shown that among the additives tried Na₂CO₃ and NaHCO₃ are the most effective nucleating agents for recycled PET crystallization with a concomitant relatively small reduction in molecular weight. All other salts were less effective nucleating agents and, in some cases, caused significant resin degradation.

Processability of recycled PET in injection molding was also investigated. It is shown that temperatures below 100°C can be effectively used with short cycle times. More specifically, a mold temperature of 40°C was used to produce amorphous specimens, while at 90°C and in the presence of either Na₂CO₃ or NaHCO₃, crystalline products with better mechanical properties than specimens containing other carbonate salts were formed.

REFERENCES

1. F. Gallez, R. Legras, and J. P. Mercier, *Polym. Eng. Sci.*, **16**, 276 (1976).
2. L. H. Palys and P. J. Phillips, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 829 (1980).
3. V. E. Reinsch and L. Rebenfeld, *J. Appl. Polym. Sci.*, **52**, 649 (1994).
4. B. A. Mathew, R. E. Nunn, and S. A. Orroth, in

- Proceedings of the Society of Plastics Engineers 47th ANTEC*, 1989, p. 333.
5. J. D. Muzzy, D. G. Bright, and G. H. Hoyos, *Polym. Eng. Sci.*, **18**, 437 (1978).
 6. R. Gächter and H. Müller, Eds., *Plastics Additives*, Hanser, Munich, 1985, Chap. 17, pp. 672–682.
 7. A. J. Muller, J. L. Feijoo, M. E. Alvarez, and A. C. Febles, *Polym. Eng. Sci.*, **27**, 796 (1987).
 8. S. A. Jabarin and E. A. Lofgren, *Polym. Eng. Sci.*, **26**, 620 (1986).
 9. S. A. Jabarin, *J. Appl. Polym. Sci.*, **34**, 103 (1987).
 10. E. A. Coleman, U.S. Pat. 4,368,285 (1983).
 11. S. B. Nelsen, U.S. Pat. 4,539,356 (1985).
 12. K. Mizoguchi, T. Hirose, Y. Naito, and Y. Kamiya, *Polymer*, **28**, 1298 (1987).
 13. D. F. Baldwin, N. P. Suh, and M. Shimbo, *Cellular Polymers*, American Society of Mechanical Engineers, Materials Division, ASME, New York, 1992, Vol. 38, p. 109.
 14. V. Kumar and O. S. Gebizlioglu, in *Proceedings of the Society of Plastics Engineers, 49th ANTEC*, 1991, p. 1297.
 15. K. Mizoguchi, K. Terada, T. Hirose, and Y. Kamiya, *Polym. Commun.*, **31**, 146 (1990).
 16. C. Di Fiore, B. Leone, C. De Rosa, G. Guerra, V. Petraccone, D. Di Dino, R. Bianchi, and R. Vosa, *J. Appl. Polym. Sci.*, **48**, 1997 (1993).
 17. E. L. Lawton, *Polym. Eng. Sci.*, **25**, 348 (1985).
 18. S. M. Patkar and S. A. Jabarin, in *Proceedings of the Society of Plastics Engineers, 49th ANTEC*, 1991, p. 1955.
 19. S. M. Aharoni, U.S. Pat. 4,349,503 (1982).
 20. J. Christiansen and S. J. Lu, U.S. Pat. 4,483,955 (1984).
 21. E. A. Coleman, U.K. Pat. Appl. GB 2108968A (1982).
 22. E. A. Coleman, U.K. Pat. Appl. GB 2108969A (1982).
 23. W. Przygocki and A. Wlochowicz, *J. Appl. Polym. Sci.*, **19**, 2683 (1975).
 24. G. Groeninckx, H. Berghmans, N. Overbegh, and G. Smets, *J. Polym. Sci. Polym. Phys. Ed.*, **12**, 303 (1974).
 25. A. Dobreva, A. Stoyanov, and I. Gutzow, *J. Appl. Polym. Sci.*, **48**, 473 (1991).
 26. S. M. Aharoni, U.S. Pat. 4,390,649 (1983).
 27. S. M. Aharoni, *J. Appl. Polym. Sci.*, **29**, 853 (1984).
 28. Z. Szekely-pesci, I. Vancso-szmercsanyi, and F. Cser, *J. Polym. Sci.*, **19**, 703 (1981).
 29. R. J. Axelrod, F. N. Liberi, and J. Semen, U.S. Pat. 4,401,792 (1983).
 30. E. J. Deyrup, U.S. Pat. 4,352,904 (1982).
 31. D. S. Garcia, U.S. Pat. 4,425,470 (1984).
 32. W. E. Garrison, Jr., U.S. Pat. 4,548,978 (1985).
 33. J. C. Haylock and N. Vanderkooi, Jr., U.S. Pat. 4,551,507 (1985).
 34. J. W. Gilmer, R. P. Neu, Y. J. Liu, and A. K.-Y. Jen, *Polym. Eng. Sci.*, **35**, 1407 (1995).
 35. R. Legras, J. P. Mercier, and E. Nield, *Nature*, **304**, 432 (1983).
 36. R. Legras, C. Bailly, M. Daumerie, J. M. Dekoninck, J. P. Mercier, V. Zichy, and E. Nield, *Polymer*, **25**, 835 (1984).
 37. R. Legras, J. M. Dekoninck, A. Van Zielegheem, J. P. Mercier, and E. Nield, *Polymer*, **27**, 109 (1986).
 38. J. M. Dekoninck, R. Legras, and J. P. Mercier, *Polymer*, **30**, 910 (1989).
 39. D. S. Garcia, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 2063 (1984).
 40. L. Bourland, *Plast. Eng.*, **43**, 39 (1987).
 41. A. Misra and S. N. Garg, *J. Polym. Sci. Part B Polym. Phys.*, **24**, 983 (1986).
 42. K. Nakamura and K. Neki, U.S. Pat. 4,534,191 (1985).
 43. J. J. Zeilstra, *J. Polym. Sci.*, **31**, 1977 (1986).
 44. V. E. Reinsch and L. Rebenfeld, *ACS-PMSE*, **68**, 182 (1993).
 45. V. E. Reinsch and L. Rebenfeld, in *Proceedings of the Society of Plastics Engineers, 49th ANTEC*, 1991, p. 2075.
 46. D. R. Lide, Ed., *Handbook of Chemistry and Physics*, 76th ed., CRC Press, Boca Raton, FL, 1995.
 47. P. P. Hsu, PhD Thesis in Chemical Engineering, New Jersey Institute of Technology, Newark, NJ, 1991.
 48. B. Wunderlich, *Macromolecular Physics*, Academic Press, New York, 1976, Vol. 2.