Solid-State Polymerization of Poly(ethylene Terephthalate)

SHUYA CHANG, MING-FA SHEU, and SHU-MAY CHEN, *Union Industrial Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan, Republic of China*

Synopsis

Solid-state polymerization of poly(ethylene terephthalate) (PET) is carried out by heating the low molecular weight prepolymer at temperatures below its melting point but above its glass transition temperature. Postcondensation occurs and the condensation byproducts can be removed by applying vacuum or inert gas. Polymers obtained usually have high molecular weight, low carboxyl and acetaldehyde content, and can be used for beverage bottle or industrial yarns. Polyesters for textile purposes are manufactured by a melt process. Chemical reactions involved in the solid state polymerization are transesterification, esterification, as well as the diffusion of byproducts. Overall reaction rate was governed by the molecular weight, carboxyl content of prepolymer, crystallinity, particle size, reaction temperature, and time. Prepolymer for solid state polymerization should have intrinsic viscosity 0.4 dL/g or more, density 1.38 g/mL, and minimum dimension 3 mm or less. The reaction temperature could be 200–250°C. When textile grade PET is used as prepolymer, crystallization at 180–190°C for 1–2 h increases the density to 1.38 g/mL. Polymerization at 240–245°C for 3–5 h can raise the intrinsic viscosity to 0.72 dL/g and carboxyl content less than 20 meq/kg. Appropriate reaction conditions are subject to the properties of prepolymers and the design of reactors. Reactor used for solid state polymerization could be vacuum dryer type or stationary bed. The former is suitable for a small capacity and is run batchwise. The latter is a continuous process and is economically feasible for large-scale production.

INTRODUCTION

It is well known that most of the physical and mechanical properties of polymers improve as molecular weight increases. Poly(ethylene terephthalate) (PET) follows this same trend. End uses dictate the molecular weight of the polyester. For example, PET for fiber application usually has an intrinsic viscosity (IV) of 0.6 or number average molecular weight of 18,600. As the requirements of mechanical properties become more stringent, higher molecular weight becomes necessary. The PET soft drink bottle has an IV of 0.72 and the industrial tire cord requires an IV of 0.85 or more. Various methods have been used to produce high molecular weight PET, namely,

(1) continuation of the melt polymerization of PET,
(2) chemical coupling (interlinking) reaction,
(3) solid state polymerization of PET.

The first method requires a longer polymerization time. As IV of PET increases, the melt viscosity increases exponentially to the point where it will be difficult to handle.[1] The power consumption of the agitator is very high, and the thermal degradation at the end of the prolonged process is also excessive. This method is only attractive for a continuous process.

Some difunctional chemicals that readily react with hydroxyl or carboxyl end groups can couple the polyester molecules. The reaction time is short; however,
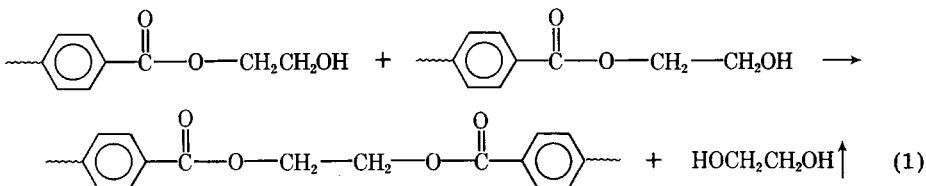
these highly reactive coupling agents usually are thermally unstable: they will cause side reactions or produce undesired byproducts. High molecular weight PET with good quality can be obtained by solid-state polymerization.

Solid-state polymerization is carried out by heating the low molecular weight polymer (prepolymer) at a temperature above the polymer's glass transition temperature, yet below its melting point. The polymer is then further condensed, and the molecular weight increases. The reaction temperature here is usually much lower than that of the melt process and thermal degradation can be greatly reduced. Byproducts, such as ethylene glycol and water, can be removed by applying vacuum or flushing with an inert gas.
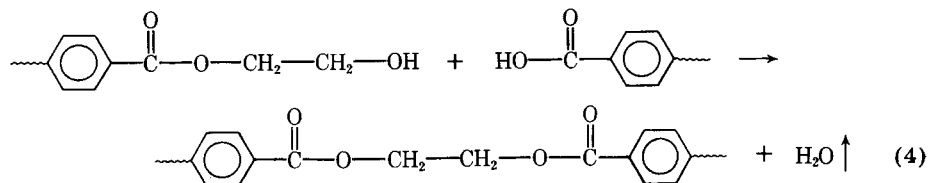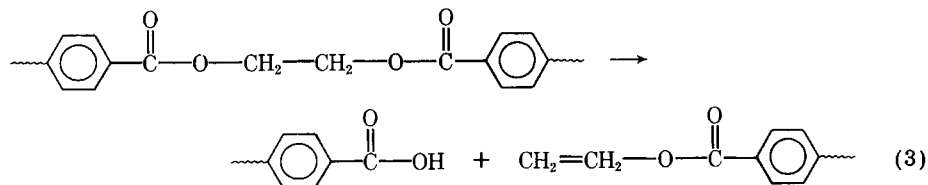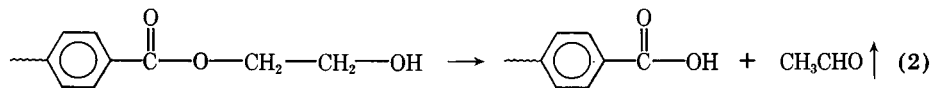
In principle, solid-state polymerization of PET is very straightforward. However, some background information should be considered prior to the preparation studies.

Propagation and Degradation

Chain extension (polycondensation) of PET is accomplished by the transesterification between prepolymers:

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!O\!\!-\!\!CH_2CH_2OH \;+\; \sim\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!O\!\!-\!\!CH_2\!\!-\!\!CH_2OH \;\longrightarrow$$

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!O\!\!-\!\!CH_2\!\!-\!\!CH_2\!\!-\!\!O\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!\langle\bigcirc\rangle\!\!\sim \;+\; HOCH_2CH_2OH\!\uparrow \quad (1)$$

Since the prepolymer is prepared by high temperature melt process, it usually contains degradation products. PET can be degraded by heat, oxygen, moisture, or radiation. Mechanisms for these degradation reactions are very complicated. Degradation products include cyclic oligomer,[2] derivatives of substituted benzoic acids,[3] and more. Carboxyl end group (—COOH) is found in all cases. The simplified main reactions are[4]

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!O\!\!-\!\!CH_2\!\!-\!\!CH_2\!\!-\!\!OH \;\longrightarrow\; \sim\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!OH \;+\; CH_3CHO\!\uparrow \quad (2)$$

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!O\!\!-\!\!CH_2\!\!-\!\!CH_2\!\!-\!\!O\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!\langle\bigcirc\rangle\!\!\sim \;\longrightarrow$$

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!OH \;+\; CH_2\!\!=\!\!CH_2\!\!-\!\!O\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!\langle\bigcirc\rangle\!\!\sim \quad (3)$$

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!O\!\!-\!\!CH_2\!\!-\!\!CH_2\!\!-\!\!OH \;+\; HO\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!\langle\bigcirc\rangle\!\!\sim \;\longrightarrow$$

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!O\!\!-\!\!CH_2\!\!-\!\!CH_2\!\!-\!\!O\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!\langle\bigcirc\rangle\!\!\sim \;+\; H_2O\!\uparrow \quad (4)$$

<div align="center">esterification</div>

where eq. (4) is propagation.

Factors Affecting the Rate

Balance of Carboxyl and Hydroxyl End Groups. Two main chemical reactions, esterification and transesterification, occur simultaneously during solid-state polymerization. In order for them to occur at appreciable rates, the concentrations of carboxyl and hydroxyl ends are critical. In powdered PET prepolymer, a high hydroxyl concentration results in faster reaction. With larger chip size, while EG diffusion is more difficult, esterification becomes more significant and a high carboxyl concentration is preferred. The carboxyl concentration of prepolymer can be controlled by varying the original EG and TPA charge ratio (TPA process) or by changing the polycondensation temperature and time.

A particular manufacturer may produce PET chips with fixed size, shape, and carboxyl content. Optimized polymerization conditions can only be obtained by experiments with this particular prepolymer.

Diffusivity. In the solid-state polymerization process, at temperatures lower than 200°C, esterification is the rate-determining step and the particle size of PET has little or no effect in overall reaction rate.[5] At temperatures higher than 210°C and particle size greater than 100 mesh, reaction becomes diffusion-controlled,[6] and the rate depends on the diffusion of byproduct from the interior of PET chip to the surface. The diffusion of byproducts from the surface of PET into air is relatively fast and can be neglected.[7] Chang[6] has indicated that the activation energy of diffusion, E_a, is 30 kcal/mol at a temperature range of 220–250°C and is independent of the particle size. Rate of diffusion almost doubles with every 10°C temperature increment. High reaction temperature is, therefore, preferred for fast reaction.

Catalyst. Prepolymers prepared from the melt process contain polycondensation catalysts such as Sb_2O_3. These catalysts will also catalyze the solid-state polymerization. However, their poor mobilities in the solid phase make them less active than in the molten state.

Sticking Point

In principle, high reaction temperature is required for high reaction rate. Practically, it is not always possible. When the prepolymer PET chips are heated to 230°C, they stick together. If a mechanical force is applied properly, sticking will be released. However, it will take place again whenever the mechanical force is removed. Sticking becomes more significant when temperature increases. Possible reasons for this are:

Polydispersity. The reported sticking point for PET is 230–240°C.[8] Differential scanning calorimeter (DSC) study of PET indicates a maximum endotherm at temperature 258°C, the melting point of crystalline PET. However, the true melting occurs prior to this temperature. In general, initial endothermic reactions start around 225–230°C.[9] The low molecular weight components in PET start to melt at lower temperatures and cause the chips to stick together. If the PET contains less oligomer, the sticking point will be higher.

Diethylene Glycol (DEG) Content and Melting Point. The melting point of PET is greatly affected by DEG content. As DEG content increases, melting point decreases. In order to increase the sticking point, DEG content of the prepolymer should be kept low.[10,11]

Miscellaneous. We have observed that the shape and size of PET chips also affect the sticking. For cylindrical shaped chips, the shorter they are, the closer they are to a sphere, and they have less opportunity to stick. Cubic chips usually have very smooth upper and bottom surfaces. These two surfaces stick together easily. The side surfaces are cut surfaces and are usually rough and sometimes contain points and ends. Sticking rarely occurs at these surfaces. Chips with small particle size (less than 10 mesh) are fluffy in nature and less sticky even at temperatures up to 250°C. In addition, uneven heating also causes the chips to stick.

The best way to avoid sticking is to polymerize the prepolymers at temperatures below the sticking point for a period of time.[13] This preheat process promotes the molecular weight of low melt oligomers and, therefore, raises the sticking point.

Crystallinity. The preheat process not only promotes the molecular weight of prepolymer, but, more importantly, it increases the crystallinity of prepolymer. Higher crystallinity materials have sharper melting points and higher sticking points.

Crystallization of PET includes two processes: (1) nucleation-formation of nuclei; (2) growth of nuclei. Below melting temperature, low temperature favors the rate of nucleation, but limits the rate of growth.[14] The overall rate of crystallization is fastest at temperatures from 180 to 190°C.[15] In order to avoid the sticking phenomenon, the density of PET should be greater than 1.38 g/mL, or crystallinity greater than 40%. Since different authors reported different density data for amorphous and crystalline PET,[13,15,16] the crystallinity is best described by density. Although increasing crystallinity increases the sticking point and the reaction can occur at higher temperatures, the reaction rate is not always increased; this is because the high crystallinity inhibits the diffusion of byproducts. We have replotted Chang's data[6] and observed that, at fixed reaction time, the polycondensation product from high density prepolymer has a lower molecular weight. Molecular weight changes rather slowly when density increases. A sudden drop is observed when density gets higher than 1.38 g/mL (Fig. 1).

Previous statements have suggested that, at the beginning of the solid state polymerization, the prepolymer should be preheated (crystallized) up to, but
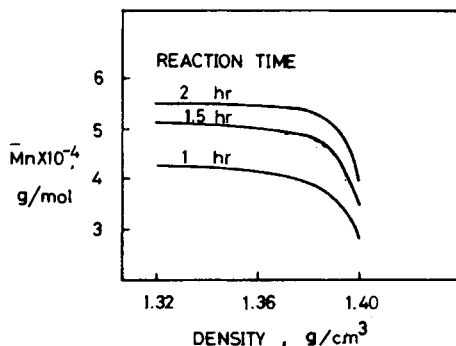

Fig. 1. Molecular weight of PET as a function of prepolymer density. The reactions were carried out in the solid state.[6]

not over a density of 1.38 g/mL. A suitable crystallization temperature is 180–190°C because, at this temperature range, the rate of crystallization is fastest and the limiting density is 1.38 g/mL.[15]

EXPERIMENTAL

Materials

All the PET prepolymers used were supplied by local polyester manufacturers and were prepared by melt processes. Bright and semidull chips with different sizes and shapes were studied. Phenol, 1,1,2,2-tetrachloroethane, benzyl alcohol, and chloroform were reagent grade and were supplied by Wako Pure Chemical Industries of Japan. They were used without further purification. m-Cresol was technical grade and was distilled under reduced pressure prior to use. The 99.99% nitrogen was supplied by San Fu Chemical Co., and was used as received.

Apparatus and Procedure

Preparation of Samples. PET chips were ground in a high-speed grinder before passing through a set of ASTM standard sieves. The small particles obtained were irregularly shaped, but close to spheres.

Tube Reactor. Tube reactor was simply equipped and easy to operate (Fig. 2). However, it is only suitable for a small quantity of small particles (less than 20 g/batch, 10 mesh or smaller). The temperature of PET chips inside the reactor was the same as that of the heating block at operation conditions. Vacuum was kept at 0.2 torr.

Rotary Vacuum Reactor. We have borrowed the idea from rotary evaporator in designing this reactor. The rotation of the flask (reactor) (Fig. 3) also provided stirring for the silicone oil bath. As long as the temperature, vacuum, and stirring rate were well controlled, the operation was only to charge and discharge polymer chips. After solid-state polymerization, the product is immediately quenched to room temperature or kept in inert atmosphere for cooling. Contact of hot chips with air or moisture was not suggested.

Stationary Bed Reactor. The stationary bed reactor has an outside diameter of 60 mm (Fig. 4). Nitrogen gas was heated by passing through the heating coil
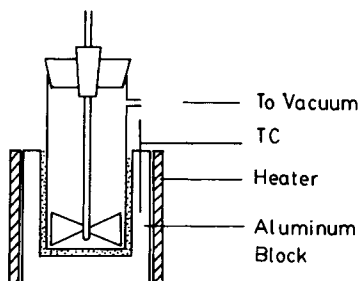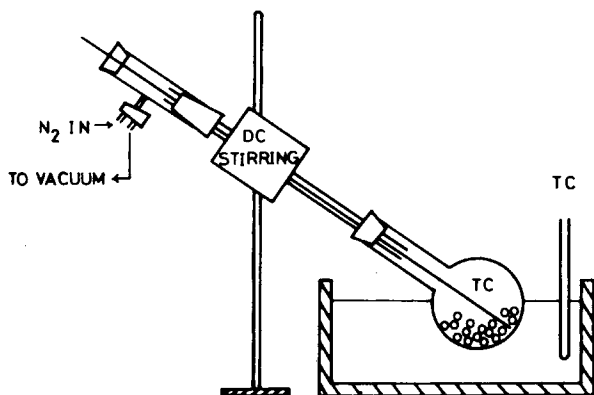

Fig. 2. Tube reactor.

Fig. 3. Rotary vacuum reactor.

before entering the reactor.   Thermocouples TC-1 and TC-2 were located 5 mm above and below the wire support, respectively.   The temperature of the inert gas was controlled by TC-1.   TC-3 was located at 100 mm above TC-1.   In order to keep TC-1 and TC-3 at the same temperature, insulation was a must.   The glass reactor was surrounded by a few layers of glassmat, which were heated by a heating plate.   Thermocouple TC-4 was inserted in the glassmat and its temperature was kept the same as TC-1.   Nitrogen flow was 2.5 L/min.
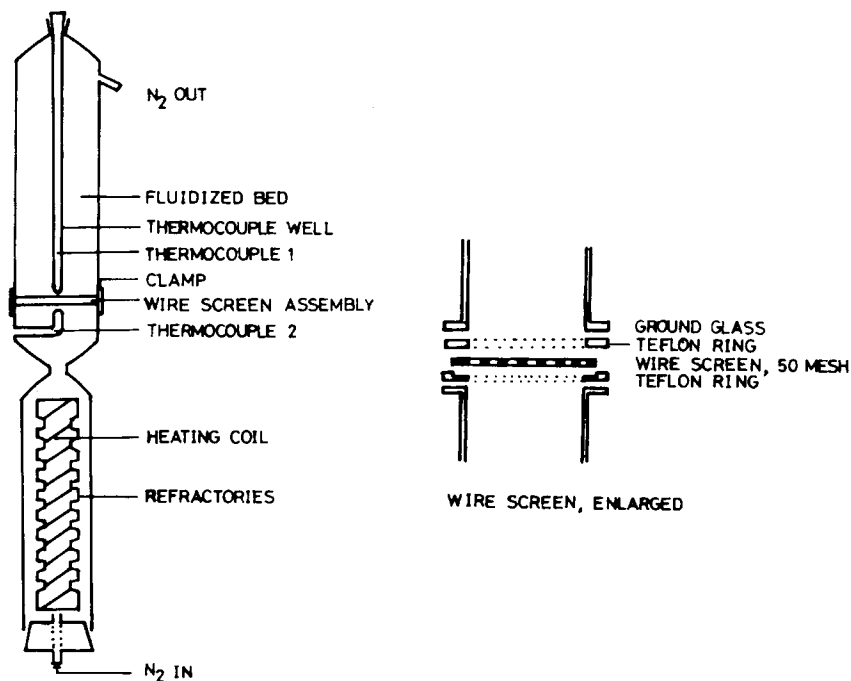

Fig. 4. Stationary bed.

Quantitative Analyses

Determination of the Intrinsic Viscosity. The intrinsic viscosity of PET was measured in a solvent mixture of phenol and 1,1,2,2-tetrachloroethane (1:1, v/v) at 25°C by using a Ubbelohde type viscometer.[17]

Determination of the Carboxyl End Group. Carboxyl end groups were determined by acidicmetric titration in a phenol–chloroform (1:1, v/v) mixture at 80–100°C. The alkaline solution used was $0.1M$ potassium hydroxide in benzyl alcohol and the indicator was bromphenol blue.[18]

Determination of Acetaldehyde Content. Method of analysis was suggested by a local PET bottle manufacturer. A sample was heated in a glass tube with a septum type screw cap. This sample tube was heated at 235°C for 20 min and then allowed to cool. Internal standard propionaldehyde (-30°C) was introduced through the septum and allowed to evaporate at room temperature for 20 min. The tube was then placed in a 50°C oven for complete evaporation and thermal mixing of the gases. A gas sample was injected into a gas chromatograph for acetaldehyde determination at the following operation conditions: column, 6 ft $\times$ 0.125 in. stainless steel packed with 100–120 mesh Poropak Q; carrier gases, helium, 20 mL/min, hydrogen, 25 mL/min, air, 430 mL/min; column temperature, 140°C isothermal, injector temperature, off, FID detector temperature, 200°C.

Determination of Molecular Weight. The molecular weight were measured by size exclusion chromatography (SEC). Waters HPLC 6000 A solvent delivery system was used. Columns chosen were μ-styragel 10^6A, 10^5A, 10^4A, 10^3, 100 from Waters. A mixture of m-cresol and chloroform (1:3, v/v) was eluted at 30°C with a flow rate of 1.0 mL/min.

RESULTS AND DISCUSSION

Overall reaction rate was increased with increasing temperature. As shown in Table I, no polymerization occurred below 180°C. Carboxyl content increased when reacted in the air indicating degradation by moisture and oxygen. The carboxyl content decreased slightly after polycondensation at 180–210°C. A

TABLE I
Effect of Temperature on the Solid-State Polymerization of PET[a]

Temp. (°C)	Intrinsic viscosity (dL/g)	Carboxyl content (meq KOH/kg)
Original	0.720	23
181[b]	0.681	26
181	0.717	9
190	0.726	22
200	0.764	17
210	0.875	20
220	0.910	7

[a] PET–FE, semidull, 20–30 mesh, tube reactor, stirring rate 100 rpm, 10 g/batch, reaction time 2 h, vacuum 0.2 mm Hg.

[b] In air.

TABLE II
Reaction Time as a Function of Solid-State Polymerization of PET[a]

Time (h)	Intrinsic viscosity (dL/g)	Carboxyl content (meq KOH/kg)
Original	0.720	23
2	0.875	21
4	1.23	13
6	1.45	12
6[b]	2.00	9
8	1.98	9

[a] PET–FE, semidull, 20–30 mesh, tube reactor, stirring rate 100 rpm, 10 g/batch, 210°C, vacuum 0.2 mm Hg.
[b] 230°C.

remarkable change was observed at 220°C: esterification was significant at higher temperatures.

Intrinsic viscosity of the product increased when polymerization continued. No degradation was observed at 210°C (Table II). Diffusion can also be neglected for the small particles used. The low carboxyl content at high intrinsic viscosity indicated the importance of esterification.

The diffusion rate was slow at low temperatures. The effect of diffusion on the polycondensation could, therefore, be observed by running the reaction with different sizes of PET particles at low temperatures (Table III). The reaction rate was reversely proportionate to the particle size (Fig. 5). However, the effect was greater than one would expect from diffusion. Other factors might also exist. In a solid-state reaction, the heat transfer was accomplished by the contact between reactor wall and particles and among particles themselves. Small particles had a high specific surface area and received more contact from each other. Good heat transfer should accelerate the reaction rate. When the particle size remained unchanged, increasing the stirring rate improved the heat transfer. If heat transfer was important to reaction rate as predicted previously, the reaction rate, expressed in terms of intrinsic viscosity, should increase with increasing stirring rate. This is actually the case (Fig. 6). However, if stirring rate got too high, centrifugation force made the particles gather around the reactor wall. Stirring became meaningless, and the reaction rate was reduced.

TABLE III
Effect of Particle Size on the Solid-State Polymerization of PET[a]

Particle size	MW (g/mol)	COOH (meq KOH/kg)
10–14	54,800	10
14–20	56,800	—
20–30	59,300	21
30–35	61,600	22
35–50	64,400	13
50 and up	66,400	25

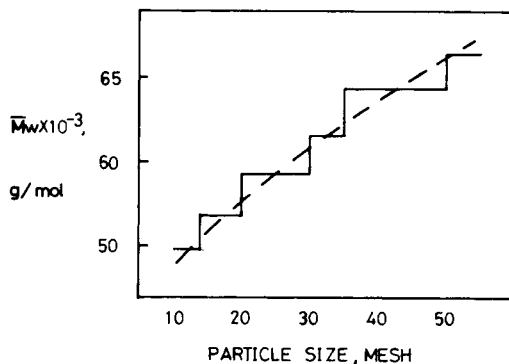[a] Tube reactor, 100 rpm, 10 g/batch, 210°C, 2 h, 0.20 mm Hg, PET–FE, semidull.

Fig. 5. Molecular weight of PET as a function of prepolymer particle size. Prepolymer: PET–YH, tube reactor, 10 g/batch, 210°C, 4 h, 100 rpm, 0.2 mm Hg.

The foregoing results have provided a basic understanding of the solid-state polymerization of PET. In production, granulation of PET chips was not cost- or handling-effective. In the latter part of this study, PET chips used were directly obtained from the PET manufacturer. Although the tube reactor could provide good mechanical force and sticking phenomena need not be considered, it was difficult to handle large particles. A rotary vacuum reactor and a stationary bed reactor would be used instead. Some of the experimental results are shown (Figs. 7 and 8). All the temperatures recorded were the temperatures of polymers. In a rotary vacuum reactor, 2 mm from the wall, the temperature of PET was recorded 3°C lower than that of the silicone oil bath (238°C). While near the center of the reactor, when there were only a few chips around, the temperature was 15°C lower than bath temperature. Continuous rotating of PET granules provided good thermal contact through the reactor.
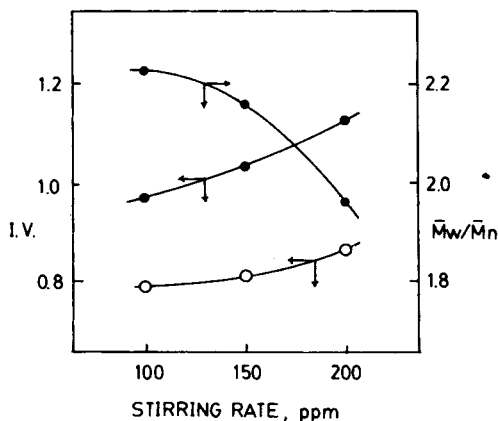

Fig. 6. Effect of stirring on the solid-state polymerization of PET. Prepolymer: PET–YH, tube reactor, 10 g/batch, 210°C, 4 h, 100 rpm, 0.2 mm Hg. (●) Less than 20 mesh; (○) 10–20 mesh.
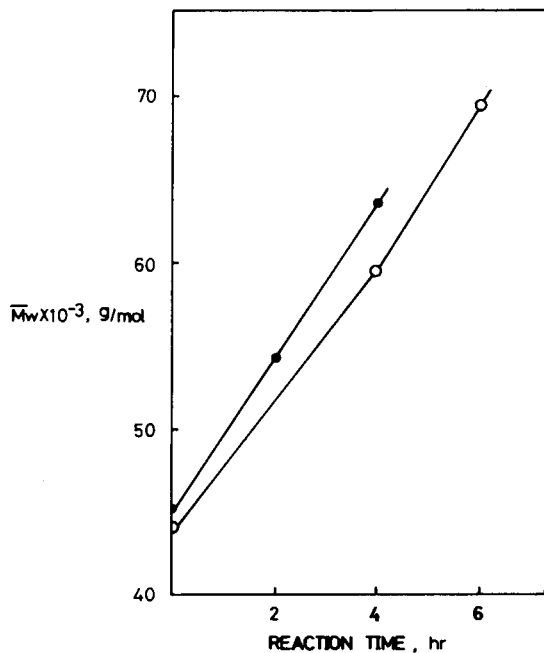
Fig. 7. Effect of crystallization temperature on the solid-state polymerization of PET. Prepolymer: PET–YH, 8–10 mesh, rotary vacuum reactor, 20 g/batch, 40 rpm, 0.2 mm Hg, postcondensation temperature 240°C, crystallization time 1 h: (●) crystallized at 220°C, (O) crystallized at 190°C.
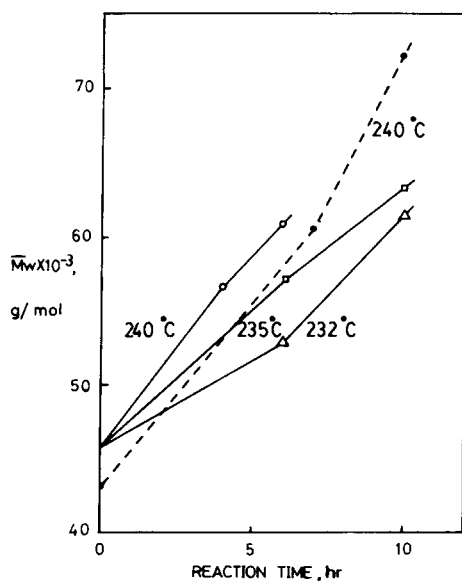

Fig. 8. Effect of reaction temperature on the solid-state polymerization of PET. Prepolymer PET–HL, 20 g/batch, 40 rpm, rotary vacuum reactor (——), PET–HLD, 100 g/batch, stationary bed reactor (---), all prepolymers have dimensions 5 × 5 × (2.2–2.5) mm, all crystallized at 190°C for 1 h.

Figure 7 indicated that crystallization at 190°C yielded a product with higher molecular weight than at 220°C. This confirmed our prediction that byproduct diffusion was inhibited by the crystalline region of polymer. Figure 8 illustrated the postcondensation of different PET chips at various temperatures and processes. Crystallization conditions were the same and particle sizes were similar in all cases. No difference in reaction rate was observed between vacuum rotary reactor and stationary bed. These had demonstrated that under the conditions where byproducts could be removed efficiently, the rate of reaction was governed by temperature.

It was also observed that, for PET–HL, the original sample contained 172 ppm of acetaldehyde. After solid-state polymerization for 6 and 10 h, the acetaldehyde content dropped to 2 and 1 ppm, respectively. Oligomers, especially cyclic oligomers, could also be removed by inert gas or vacuum. The polydispersity of the product was always slightly better than its prepolymers.

CONCLUSIONS AND SUGGESTIONS

In order to obtain high molecular weight poly(ethylene terephthalate) with good quality, polymerization in the solid state is preferred. The low reaction temperature excludes the possibility of thermal degration. Factors affecting the solid-state polymerization of PET include:

(1) particle size: heat transfer and rate of byproduct diffusion,

(2) carboxyl content: overall reaction rate,

(3) crystallinity of PET: sticking point, diffusion of byproducts,

(4) reaction temperature: reaction rate,

(5) reaction time: extent of polymerization,

(6) purity of inert gas: moisture and oxygen degrade the polymer while ethylene glycol and acetaldehyde reduce the reaction rate,

(7) stirring rate or inert gas flow rate: heat transfer.

These factors also interrelate to each other. Careful analyses should be done prior to the solid-state polymerization.

A prepolymer prepared by a melt process usually has the following properties:

(1) intrinsic viscosity: 0.60–0.66 dL/g,

(2) carboxyl content: 30–35 meq KOH/kg,

(3) melting point: 257–263°C,

(4) density: depends on thermal history,

(5) dimensions: the minimum dimension is 2–3 mm (too long a reaction time will be required if this value is exceeded).

A suitable procedure to conduct solid-state polymerization of PET chips is: crystallize at 180–190°C for 1–2 h or until density reaches 1.38 g/cm³. Gradually increase the temperature to 230–235°C. After 3–5 h, the intrinsic viscosity will increase to 0.72 and is suitable for soft drink bottle applications. Longer reaction time is required for tire cord applications. Temperature control is very important, and local overheating should be avoided. Because of the difference in reactor design and production capacity, reaction conditions can only be optimized on line.

Considering the various methods for solid-state polymerization, fluidized bed

consumes a great deal of energy and is not economically feasible. Two other methods are compared as follows:

	Stationary bed	Vacuum
Process	Continuous	Batch
Capacity	Large	Small
Nitrogen	Yes	No
Vacuum	No	Yes

A vacuum is preferred for small capacity. The reactor can just be a conical type or rotary type vacuum dryer. When a large capacity is required, the design of the reactor becomes more critical. The balance force on the supporting bearing becomes uneven. A vacuum is also an expansive process. A stationary bed is ideal for continuous process with large capacity. Gravity force makes PET chips travel against the elevated hot, inert gas. The difficulty here is to minimize the temperature gradient across the reactor. This method calls for large amounts of hot nitrogen. The recovery of nitrogen is also an energy consuming process. Increasing capacity averages out the investment and energy cost.

For practical purposes, crystallization (180–190°C) and polymerization (230–240°C) should be performed in separate reactors. The product should be kept in an inert atmosphere while still hot.

References

1. C. J. Heffelfinger and K. L. Knox, "Polymer Films," in *The Science and Technology of Polymer Films*, O. J. Sweeting, Ed., Wiley-Interscience, New York, 1971, Vol. II, p. 587.

2. I. Goodman and B. F. Nesbitt, *Polymer*, **1**, 384 (1960); *J. Polym. Sci.*, **19**, 423 (1960).

3. E. P. Goodings, *Soc. Chem. Ind. (London), Monogr. No. 13*, 211 (1961).

4. L. H. Buxbaum, *Angew. Chem. Int. Ed.*, **7**, 182 (1968).

5. F. C. Chen, Richard G. Griskey, and G. H. Beyer, *AIChE J.*, **15**, 680 (1969).

6. T. M. Chang, *Polym. Eng. Sci.*, **10**, 364 (1970).

7. B. I. Lee and R. G. Griskey, *J. Appl. Polym. Sci.*, **10**, 105 (1965).

8. B. V. Petukhov, *The Technology of Polyester Fibers*, MacMillan, New York, 1963.

9. A. Angelova, S. Woinova, and D. Dimitrov, *Angew. Makromol. Chem.*, **64**, 75–80 (1977).

10. R. Janssen, H. Ruysschaert, and R. Vroom, *Makromol. Chem.*, **77**, 153 (1964).

11. J. R. Kirby, A. J. Baldwin, and R. H. Heidner, *Anal. Chem.*, **37**, 1306 (1965).

12. E. J. Maxion, U.S. Pat. 3,728,309 (1973).

13. A. B. Thompson and D. W. Woods, *Nature*, **176**, 78 (1965).

14. T. Alfrey, *Polym. Bull.*, **1**, 40 (1945).

15. W. H. Cobbs, Jr., and R. L. Burton, *J. Polym. Sci.*, **10**, 275 (1953).

16. R. de P. Danbeny, C. W. Bunn, and C. J. Brown, *Proc. R. Soc. London Ser. A*, **226**, 531 (1954).

17. K. Tomita and I. Hiroaki, *Polymer*, **14**, 55 (1973).

18. W. Griehl and S. Neue, *Faserforsch. Textiltech.*, **5**, 423 (1954).