

Conversion of Polyester into Heat-Resistant Polyamide by Reacting with Aromatic Diamine Compound II. Semibatch Reaction by Nitrogen Gas Sweeping Process

Yangsoo Kim,¹ Young-Jin Choi²

¹School of Advanced Materials Engineering, Inje University, Gimhae 621-749, Korea

²Technical Research Institute, Dongnam Silicone Co., Buchun 421-808, Korea

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ABSTRACT: The conversion of poly(ethylene terephthalate) (PET) into heat-resistant polyamide was carried out in the solid state polycondensation by applying a nitrogen gas sweeping process. The reaction product obtained by the catalyzed and uncatalyzed batch reaction with the specified reaction condition was used as the starting material in the semibatch reaction process. Nitrogen gas was introduced into the reactor to remove a volatile reaction byproduct from the reaction mixture. Effect of the semibatch reaction variables such as temperature, time, and nitrogen gas sweeping

rate on the extent of reaction and the heat-resistant property of polyamide obtained was investigated. A comparison of the extent of reaction in the semibatch reaction process was made between the catalyzed starting material and the uncatalyzed one. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2223–2232, 2004

Key words: polyesters; polyamides; thermogravimetric analysis (TGA); ester–amide exchange reaction; semibatch solid-state polymerization

INTRODUCTION

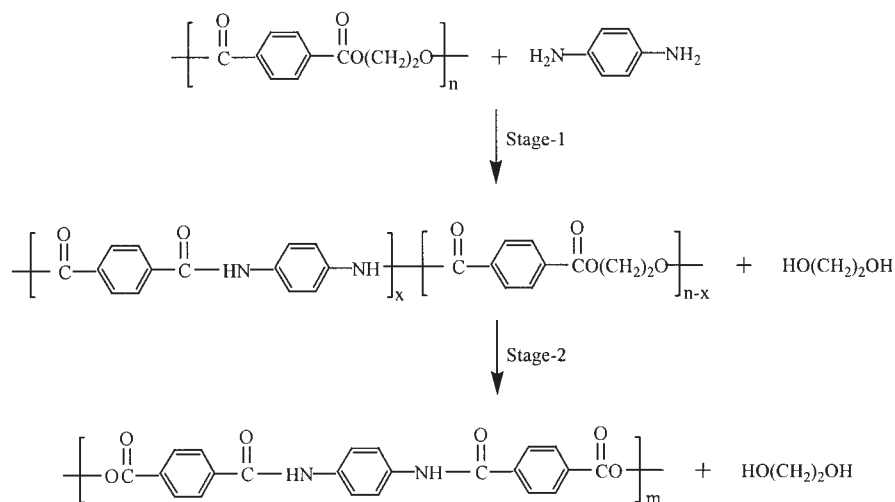
Poly(ethylene terephthalate) (PET) is one of the most rapidly growing thermoplastic polymers, with its balanced mechanical and physicochemical properties. New and diversified application areas for PET resin continue to be broadened showing more than 10% per year growth.¹ As a result, with an increase in demand for PET usage, PET resin shows a large burden on the disposal of used plastics. The growing concern in PET recycling is mainly due to the increased production of soft drink bottles and thus it is necessary to develop a novel technology for the recycling of PET. Paszun and Spychaj² thoroughly reviewed and made comparison of chemical recycling processes of PET, which are methanolysis, glycolysis, hydrolysis, ammonolysis, and aminolysis. They also explained unique recycling methods to obtain valuable products such as coating materials and plasticizers from PET. A couple of chemical recycling methods for PET such as methanolysis and glycolysis are known to be commercially available, however, the feasibility study for the other chemical recycling processes is also highly concerned to alleviate an environmental pollution problem.

Recently, it has been reported that a polymer(I) could be chemically converted into another value-

added polymer(II).^{3–6} Nakano³ claimed that PET could be converted into various polyamides by reacting with aliphatic or aromatic diamines in the presence of organic solvent. A series of batch and semibatch reaction processes was applied to facilitate the extent of reaction and the semibatch reaction was to be applied under the vacuum condition (e.g., ≤ 3 Torr).³ Nakano and Kato⁴ also reported a novel batch reaction process used to obtain poly(hexamethylene terephthalamide) (polyamide 6T) from PET by reacting PET with hexamethylenediamine in the presence of organic solvent. In our previous report,^{5,6} we reported that the ester–amide exchange reaction between PET and *p*-phenylenediamine (PDA) produced a heat-resistant polyamide in the batch reactor and also the reaction could be expedited with the addition of lead(IV) acetate as a catalyst without losing the heat-resistant property of the product. Effects of batch reaction variables such as time, temperature, and the amount of PDA used upon the extent of reaction and the heat-resistant property of polyamide were reported.⁶

The ester–amide exchange reaction between PET and PDA in organic solvent could produce poly(*p*-phenylene terephthalamide) in the complete conversion according to the following reaction route^{5,6} and thus the increase of reaction conversion during the whole reaction process is desirable to obtain the more heat-resistant polyamide product. Since the ester–amide exchange reaction is reversible, it is necessary to

Correspondence to: Y. Kim (cheykim@inje.ac.kr).



Scheme 1

remove a low molecular weight reaction byproduct (e.g., ethylene glycol) from the reaction mixture to promote the forward reaction, which highly increases the extent of reaction relative to the batch reaction (Scheme 1).

A promotion of the forward reaction in the reversible condensation reaction process is achieved in general by applying a vacuum in the reactor to facilitate the removal of reaction byproduct. The ester–amide exchange reaction between PET and PDA was carried out in the batch reactor^{5,6} and the reaction mixture represented the slurry state in the presence of *n*-dodecylbenzene (NDDB). However, the semibatch reaction to remove a reaction byproduct from the reaction mixture needs to be carried out in the solid state. In the solid-state polycondensation process to produce an engineering grade PET with high molecular weight, volatile reaction byproducts are in general removed by applying a vacuum in the reactor for the operation of semibatch fashion.⁷ Recently, Woo et al.⁸ reported that they successfully used the forced gas sweeping process and made a process analysis in the semibatch melt polycondensation of PET.

In this work, the semibatch reaction is carried out for the conversion of PET into heat-resistant polyamide and it is a solid-state polycondensation process with a continuous removal of volatile reaction byproduct by introducing nitrogen (N_2) gas into the reactor, which is here called the N_2 -gas sweeping process. Further we carry out a conversion reaction of PET into polyamide by reacting PET with PDA in the presence of NDDB as a solvent with the addition of lead(IV) acetate as a catalyst by way of a series of batch and semibatch reaction processes. We investigate how the semibatch reaction variables such as temperature, time, and N_2 -gas sweeping rate affect the extent of reaction and the heat-resistant property of polyamide

obtained. And also we study the differences of amidation ratio in the semibatch conversion reaction of PET into polyamide between with the catalyzed starting material and with the uncatalyzed one.

EXPERIMENTAL

Materials

A commercial homopolymer PET resin (Grade A7045; Saehan Co., Korea) having intrinsic viscosity ($[\eta]$) of 0.635 was used after drying in a convection oven prior to the reaction experiment. Lead(IV) acetate and PDA were purchased from Aldrich Chemical Company and used without further purification. NDDB purchased from Kanto Chemical Company, Japan was used as a solvent in the batch reaction. Nitrogen gas of high purity was introduced into the semibatch reactor and the gas flow rate was controlled using the flow meter (Cole-Parmer Co.). A starting material for the semibatch reaction in this study is a reaction product obtained by catalyzed batch reaction at the specified reaction condition (210°C, 1 h, a mole ratio of PDA to PET = 1.0, lead(IV) acetate as catalyst, a mole ratio of catalyst to PET = 0.015, NDDB as solvent).

Series of batch and semibatch conversion reactions of PET into polyamide

Conversion reaction of PET into polyamide was initially carried in the batch reactor pressurized using N_2 gas (about 7 kgf/cm²) for 1 h at 210°C and at the equimolar ratio of PDA to PET (based on the repeating unit of PET). In the batch reaction, NDDB was used as a solvent as much as 10 times by weight of the amount of PDA used. Lead(IV) acetate as a catalyst was added in cases of the catalyzed batch reaction at 0.015 of mole

ratio of catalyst to PET. After a batch reaction process was completed, reaction mixture was precipitated with excess amount of methanol, and solid product was recovered by filtering. Recovered solid reaction product was dried in vacuum for 24 h at 120°C and then it was transferred to the semibatch reactor. Semibatch reaction was then carried out at the specified reaction conditions with the application of the N₂-gas sweeping process to remove reaction byproducts. Nitrogen gas was introduced into the reactor and maintained at the specified flow rate (0.05 ~ 0.25 mL/min/weight of solid reaction mixture) using a flow meter and it passed through the solid reaction mixture going out of the reactor. The reaction mixture in solid state was well agitated at constant speed during the semibatch reaction process. The semibatch reaction conditions such as temperature, time, and N₂-gas sweeping rate were varied in the reaction experiment. After a series of batch and semibatch reaction processes were completed, the reaction product was used for the estimation of amidation ratio by the Fourier transform infrared (FTIR) analysis and for the estimation of heat-resistant property by thermogravimetric analysis (TGA).

Analysis of amidation ratio of polyamide

Amidation ratio (AR) was used as a relative indicator for the extent of reaction and it was estimated using the FTIR spectrum as follows:^{5,6}

$$AR = \frac{\lambda_{1510}}{\lambda_{1510} + \lambda_{1710}}$$

Here λ_{1510} and λ_{1710} are the IR absorbency of the characteristic peaks at 1,510 cm⁻¹ (-CO-NH- group) and 1,710 cm⁻¹ (-COO- group), respectively. Figure 1 shows the FTIR spectrum in the wave number of 1,400 to 2,000 cm⁻¹ for the virgin PET and the semibatch reaction product (210°C, 5 h, 0.25 mL/g/min, catalyzed starting material). Heat-resistant property of polyamide obtained in the reaction experiment was estimated using a TGA method. The reaction product's T_{20} value, which is the temperature at which 20% weight loss has occurred, was determined using the thermogravimetric profile and the relative excellence of heat-resistant property was justified by the comparison of the T_{20} values. Estimation errors of the measured values were $AR \pm 0.005$ and $T_{20} \pm 5^\circ\text{C}$.

RESULTS AND DISCUSSION

Effect of semibatch reaction variables (time, temperature, nitrogen gas sweeping rate) on the extent of reaction and the heat-resistant property of polyamide

We have investigated the amidation ratio and the heat-resistant property of reaction product depending

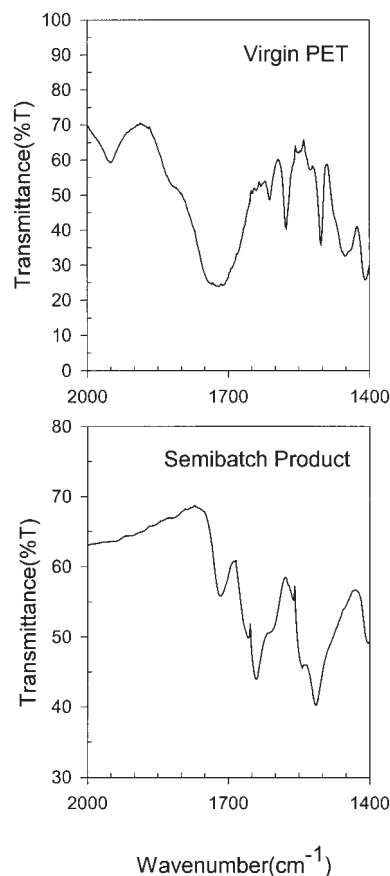


Figure 1 Change of characteristic peak at 1,510 cm⁻¹ (-CO-NH- group) and 1,710 cm⁻¹ (-COO- group) in FTIR spectrum. Semibatch reaction product: 210°C, 5 h, 0.25 mL/g/min, catalyzed starting material.

upon the variation of semibatch reaction time under the specified reaction conditions (210°C, N₂-gas sweeping rate = 0.05 ~ 0.25 mL/min/mass of reaction mixture). Figure 2 shows that the extent of reaction increases with reaction time as far as a sufficient amount of N₂ gas is introduced into the reactor. Note that the extent of reaction is much increased by the application of the semibatch reaction process compared with the starting material obtained by the batch reaction. The increase of amidation ratio from 0.587 to 0.770 has been observed after the semibatch reaction for 10 h at 210°C and 0.25 mL/g/min. The heat-resistant behavior of reaction products obtained by a series of batch and semibatch reaction process was analyzed with the thermal weight reduction plot obtained by TGA and they were compared along with the virgin PET and the commercial poly(*p*-phenylene terephthalamide) resin, which is known as Kevlar (DuPont, Wilmington, DE). Note that poly(*p*-phenylene terephthalamide) is a reaction product that could be obtained at the complete reaction conversion in the ester-amide exchange reaction.

In general, the estimation of the heat-resistant property of polymer using TGA is based on the

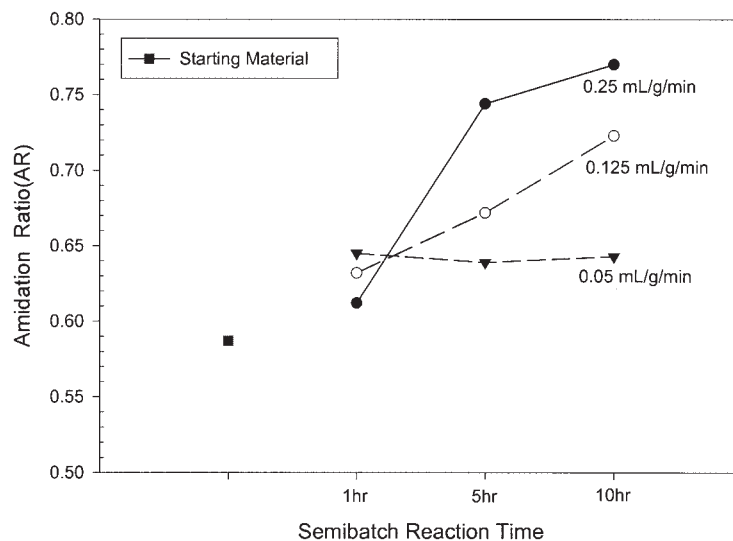


Figure 2 Progress of semibatch reaction with time in the semibatch conversion reaction of PET into polyamide: Variation of N_2 -gas sweeping rate. Semibatch reaction: 210°C , N_2 -gas sweeping process. Starting material for semibatch reaction: reaction product obtained by catalyzed batch reaction at 210°C , 1 h, PDA/PET (mole ratio) = 1.0, lead(IV) acetate, Cat/PET (mole ratio) = 0.015, NDDB (solvent).

value of T_5 corresponding to the 5% weight loss for product. However, the excellent heat-resistant property of polyamide obtained in this study is clearly distinguished in the value of T_{20} in TGA. Table I shows the values of T_{20} for the polyamide obtained in this study along with those for virgin PET and Kevlar resin.

Figure 3 shows that the heat-resistant property of reaction product is clearly increased as long as the semibatch reaction is carried out over a certain reaction time. It shows that the heat-resistant property reaches an upper limit beyond 5 h of reaction time under the specified reaction conditions (210°C , 0.25 mL/g/min). The thermogravimetric behavior of reaction product indicates that its heat-resistant property is much superior to that of virgin PET, but it is inferior to commercial Kevlar resin. Clearly it shows that a series of batch and semibatch operations in the esteramide exchange reaction between PET and PDA is a quite effective process configuration to produce the

reaction product with an excellent heat-resistant property.

How the semibatch reaction temperature affects the extent of reaction and the heat-resistant property of reaction product is another important concern to be studied in designing a semibatch reaction process (Figs. 4 and 5). The amidation ratio and T_{20} value show a peak at around 210°C of the semibatch reaction temperature. Such peak behaviors in both amidation ratio and T_{20} value, depending on the reaction temperature, were also observed in our previous report⁶ regarding the batch reaction process. It reveals that an optimum reaction temperature needs to be applied in the semibatch process to obtain an excellent heat-resistant product whose T_{20} value ($T_{20} = 529^\circ\text{C}$ at 210°C) is much higher relative to that ($T_{20} = 430^\circ\text{C}$) of the virgin PET resin.

It has been reported that the flow rate of N_2 gas remarkably affects the kinetics of semibatch solid-state polycondensation process in the synthesis of PET.⁸

TABLE I
Values of T_{20} in TGA for Polyamides Obtained by Semibatch Conversion Reaction of PET into Polyamide

Reference	Virgin poly(ethylene terephthalate) (PET) = 430°C		Starting material for semibatch reaction = 459°C		Poly(<i>p</i> -phenylene terephthalamide) = 664°C	
	N_2 -gas sweeping rate (mL/g/min)	0.05	462°C	Semibatch reaction time (h)	1	453°C
	0.125	531°C		5	520°C	
	0.25	555°C		10	540°C	
Semibatch reaction temperature ($^\circ\text{C}$)	180	452°C	TGA atmosphere	O_2	455°C	
	210	529°C		Air	486°C	
	230	543°C		N_2	536°C	

Starting material for semibatch reaction: reaction product obtained by catalyzed batch reaction at 210°C , 1 h, PDA/PET (mole ratio) = 1.0, lead(IV) acetate, Cat/PET (mole ratio) = 0.015, NDDB (solvent).

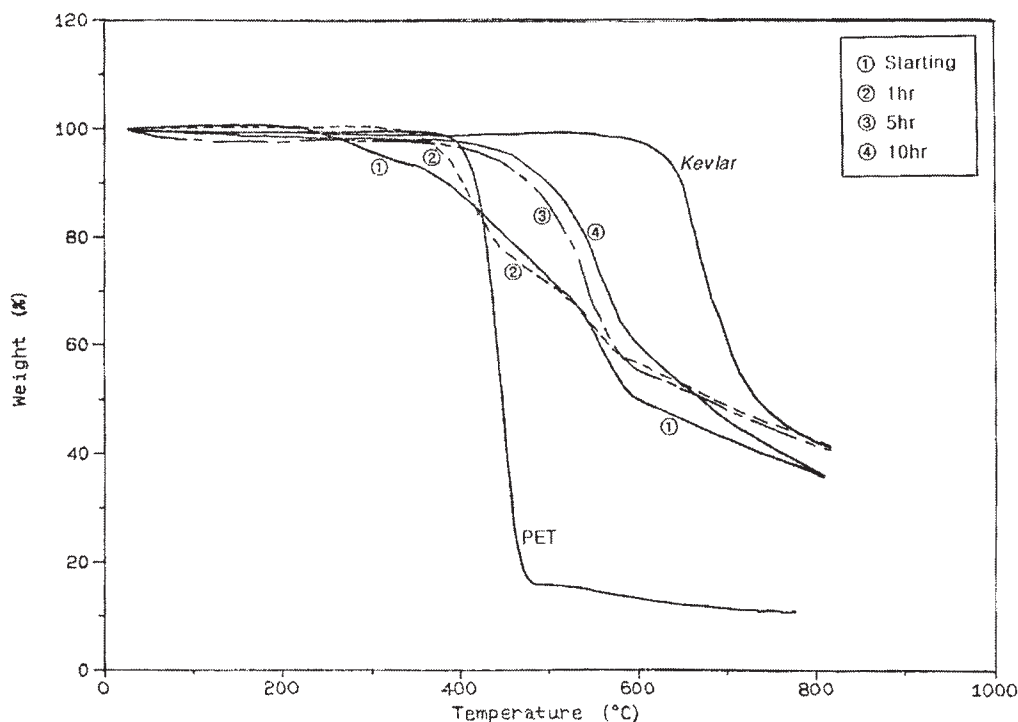


Figure 3 TGA curves for polyamides obtained by semibatch conversion reaction of PET into polyamide: variation of semibatch reaction time (TGA under N₂ atmosphere). Semibatch reaction: 210°C, N₂-gas sweeping process, 0.25 mL/g/min. Starting material for semibatch reaction: reaction product obtained by catalyzed batch reaction at 210°C, 1 h, PDA/PET (mole ratio) = 1.0, lead(IV) acetate, Cat/PET (mole ratio) = 0.015, NDDB (solvent).

Figure 6 shows that the amidation ratio of reaction product highly increases with the N₂-gas sweeping rate as long as the semibatch reaction is carried out for more than 1 h. Figure 7 shows the thermogravimetric behavior depending upon the N₂-gas sweeping rate.

Note that the increase of N₂-gas sweeping rate makes the T₂₀ value of product shift toward higher temperature (Table I). As far as the solid reaction mixture is not swept along with N₂ gas introduced, it needs to be contacted with N₂ gas as much as possible.

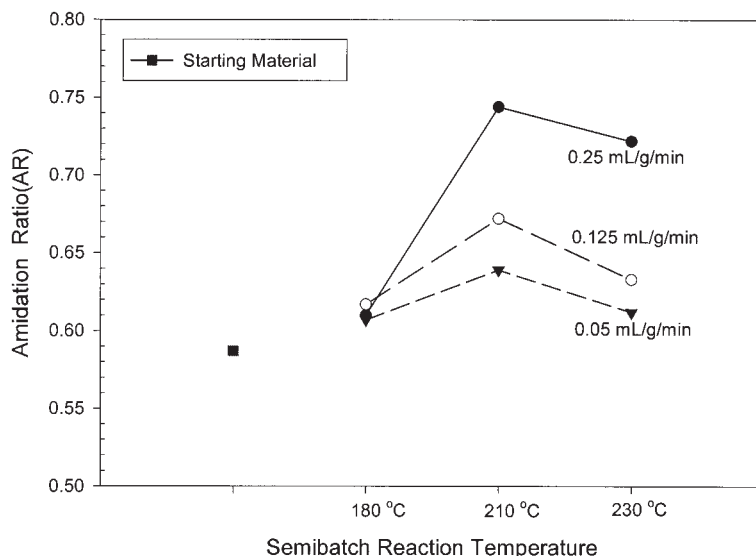


Figure 4 Dependence of semibatch reaction progress on temperature in the semibatch conversion reaction of PET into polyamide: variation of N₂-gas sweeping rate. Semibatch reaction: 5 h, N₂-gas sweeping process. Starting material for semibatch reaction: reaction product obtained by catalyzed batch reaction at 210°C, 1 h, PDA/PET (mole ratio) = 1.0, lead(IV) acetate, Cat/PET (mole ratio) = 0.015, NDDB (solvent).

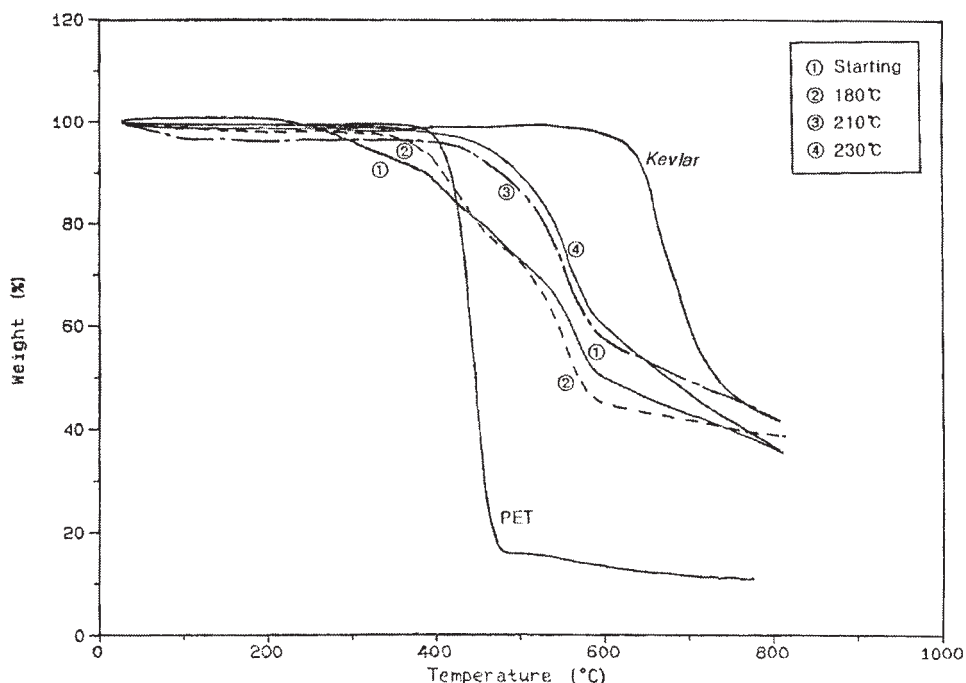


Figure 5 TGA curves for polyamides obtained by semibatch conversion reaction of PET into polyamide: variation of semibatch reaction temperature (TGA under N_2 atmosphere). Semibatch reaction: 5 h, N_2 -gas sweeping process, 0.25 mL/g/min. Starting material for semibatch reaction: reaction product obtained by catalyzed batch reaction at 210°C, 1 h, PDA/PET (mole ratio) = 1.0, lead(IV) acetate, Cat/PET (mole ratio) = 0.015, NDDB (solvent).

Comparison of the catalyzed starting material with the uncatalyzed one for the extent of reaction in the semibatch ester-amide exchange reaction

We have investigated the differences in progress of amidation ratio with reaction time in the semibatch conversion reaction of PET into polyamide between

the catalyzed starting material and the uncatalyzed one. Figure 8 shows that a series of process operations, which is the uncatalyzed batch reaction (1 h, AR = 0.506) followed by the semibatch reaction (5 h, AR = 0.702), remarkably increases the extent of reaction relative to the uncatalyzed batch reaction proceeded

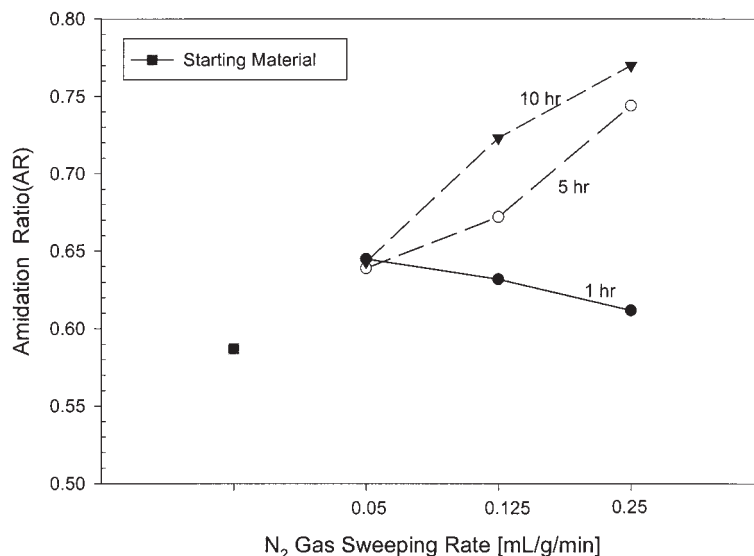


Figure 6 Dependence of semibatch reaction progress on N_2 -gas sweeping rate in the semibatch conversion reaction of PET into polyamide: variation of semibatch reaction time. Semibatch reaction: 210°C, N_2 -gas sweeping process. Starting material for semibatch reaction: reaction product obtained by catalyzed batch reaction at 210°C, 1 h, PDA/PET (mole ratio) = 1.0, lead(IV) acetate, Cat/PET (mole ratio) = 0.015, NDDB(solvent).

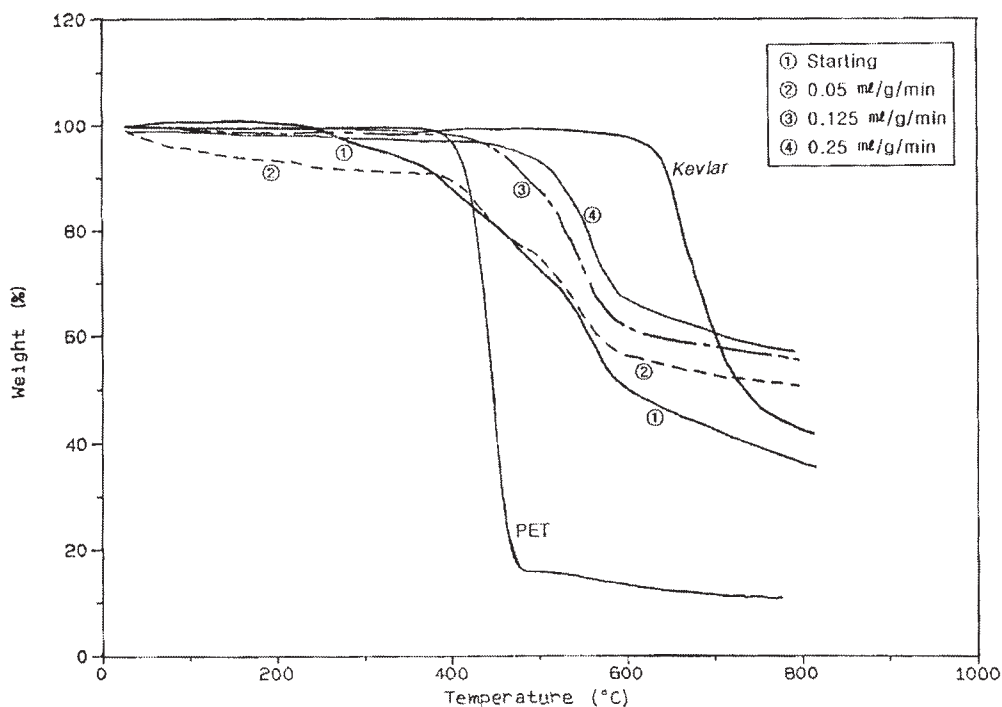


Figure 7 TGA curves for polyamides obtained by semibatch conversion reaction of PET into polyamide: variation of N₂-gas sweeping rate (TGA under N₂ atmosphere). Semibatch reaction: 210°C, 10 h, N₂-gas sweeping process. Starting material for semibatch reaction: reaction product obtained by catalyzed batch reaction at 210°C, 1 h, PDA/PET (mole ratio) = 1.0, lead(IV) acetate, Cat/PET (mole ratio) = 0.015, NDDB (solvent).

for 10 h (AR = 0.589). Also note that the semibatch reaction process with catalyzed starting material produces the reaction product having higher AR values

compared with the semibatch reaction with uncatalyzed starting material. Figures 9 and 10 show comparisons of the extent of reaction as a function of

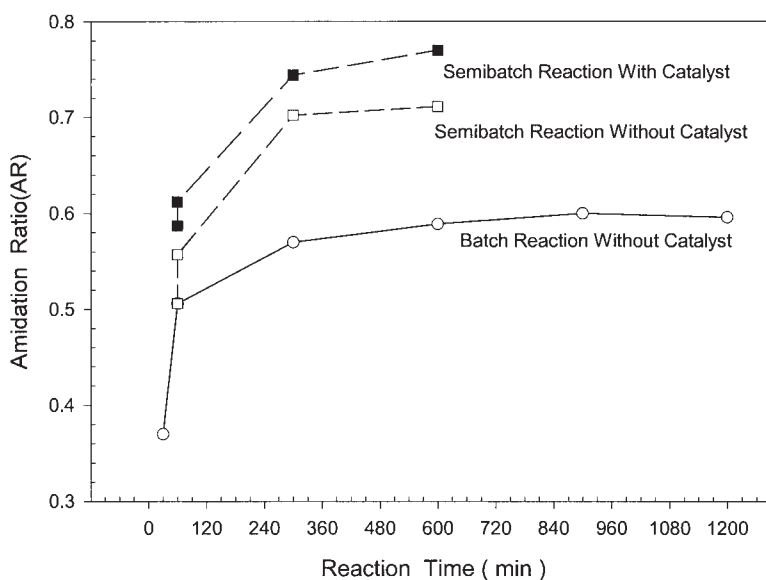


Figure 8 Progress of reaction with time in the uncatalyzed batch reaction, semibatch reaction with uncatalyzed starting material, and semibatch reaction with catalyzed starting material for the conversion reaction of PET into polyamide. Uncatalyzed batch reaction: 210°C, PDA/PET (mole ratio) = 1.0, NDDB (solvent). Uncatalyzed starting material for semibatch reaction: reaction product obtained by batch reaction at 210°C, 1 h. Catalyzed starting material for semibatch reaction: reaction product obtained by batch reaction at 210°C, 1 h, lead(IV) acetate, Cat/PET (mole ratio) = 0.015. Semibatch reaction: 210°C, N₂-gas sweeping process, 0.25 mL/g/min.

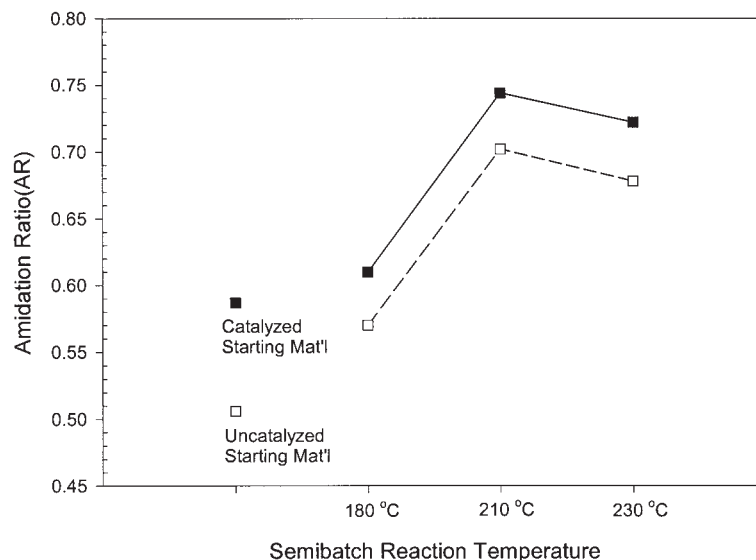


Figure 9 Variation of semibatch reaction progress with temperature in the semibatch conversion reaction of PET into polyamide using a catalyzed starting material and an uncatalyzed one. Semibatch reaction: 5 h, N_2 -gas sweeping process, 0.25 mL/g/min. Starting material for semibatch reaction: reaction product obtained by batch reaction at 210°C, 1 h, PDA/PET (mole ratio) = 1.0, NDDB (solvent), Catalyzed batch reaction using lead(IV) acetate at Cat/PET (mole ratio) = 0.015.

reaction temperature and nitrogen gas sweeping rate, respectively. They clearly indicate that the catalyzed starting material in the semibatch reaction process is favorable to producing a much higher yield of amide content in the product, which means a more pronounced heat-resistant property for the product, compared with the uncatalyzed starting material. The amidation ratio profiles of semibatch reaction product depending on the reaction temperature and the nitro-

gen gas sweeping rate show an identical behavior in both the semibatch reaction process using an uncatalyzed starting material and the semibatch reaction process using a catalyzed one.

The heat-resistant property of polyamide produced by the semibatch reaction process has been analyzed with the thermal weight reduction plot by the TGA method in this study. The thermal analysis has been carried out in the nitrogen environment and their TGA

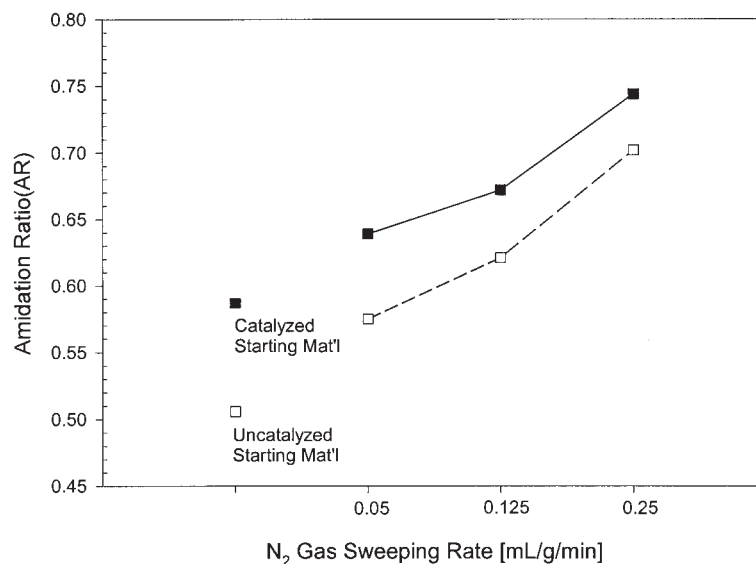


Figure 10 Variation of semibatch reaction progress with N_2 -gas sweeping rate in the semibatch conversion reaction of PET into polyamide using a catalyzed starting material and an uncatalyzed one. Semibatch reaction: 210°C, 5 h. Starting material for semibatch reaction: reaction product obtained by batch reaction at 210°C, 1 h, PDA/PET (mole ratio) = 1.0, NDDB (solvent), catalyzed batch reaction using lead(IV) acetate at Cat/PET (mole ratio) = 0.015.

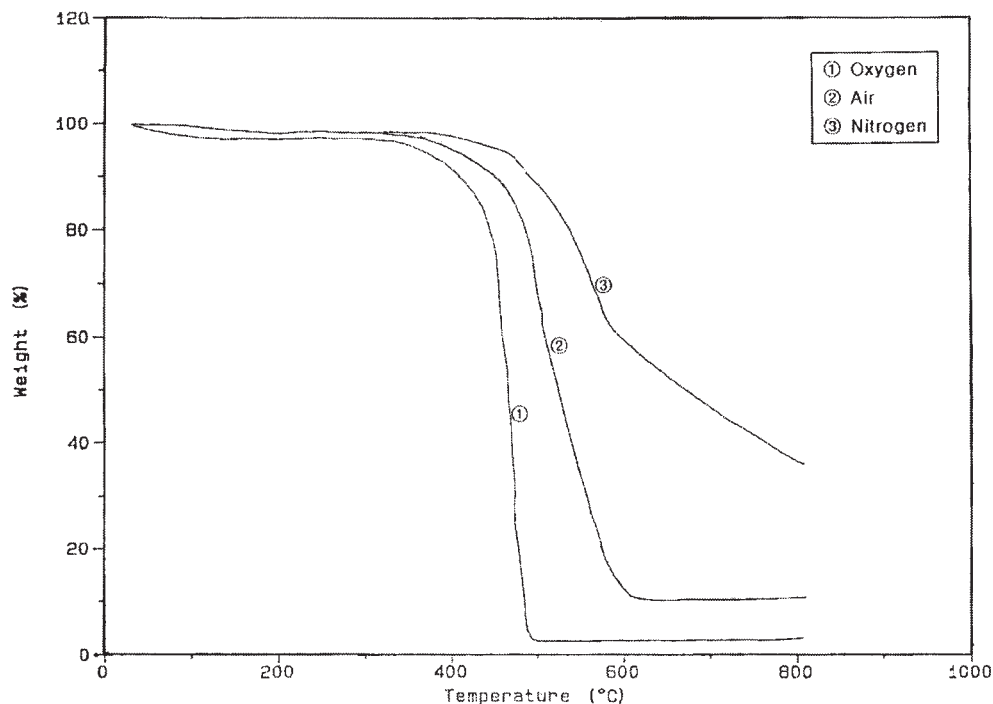


Figure 11 TGA curves for polyamides obtained by semibatch conversion reaction of PET into polyamide: variation of the type of TGA atmosphere. Semibatch reaction: 210°C, 5 h, N₂-gas sweeping process, 0.25 mL/g/min. Starting material for semibatch reaction: reaction product obtained by catalyzed batch reaction at 210°C, 1 h, PDA/PET (mole ratio) = 1.0, lead(IV) acetate, Cat/PET (mole ratio) = 0.015, NDDDB (solvent).

plots are shown in Figures 3, 5, and 7. Here it has been also investigated how the thermal weight reduction behavior is varied with the change of TGA atmosphere. Figure 11 indicates that the heat-resistant behavior of product produced by the semibatch reaction under the specified reaction conditions (210°C, 5 h, 0.25 mL/g/min) is lowered as nitrogen > air > oxygen. The oxygen atmosphere in TGA makes it degrade the reaction product very rapidly relative to the other atmospheres. However, notice that the heat-resistant behavior of the semibatch reaction product analyzed under an oxygen atmosphere ($T_{20} = 455^\circ\text{C}$ under O₂ gas), which is the most severe thermal degradation condition, is still superior to that of the virgin PET analyzed under a nitrogen atmosphere ($T_{20} = 430^\circ\text{C}$ under N₂ gas), which is the mildest condition.

We have observed that the product obtained by the ester–amide exchange reaction between PET and PDA is soluble in sulfuric acid and their intrinsic viscosity is relatively to be compared. In the forthcoming study, the change of molecular weight of the products by the comparison of intrinsic viscosity needs to be estimated.

CONCLUSION

In this study, the conversion of PET into heat-resistant polyamide was successfully carried out in the solid

state by applying a nitrogen gas sweeping process. The reaction products obtained by the catalyzed and uncatalyzed batch reaction under the specified reaction conditions (210°C, 1 h, 1.0 of mole ratio of PDA to PET, 0.015 of mole ratio of lead(IV) acetate to PET in case of the catalyzed reaction) were used as the starting materials in the semibatch reaction process. To obtain the starting materials, the batch reaction was firstly carried out in the presence of *n*-dodecylbenzene as a solvent. Nitrogen gas was introduced into the reactor to eliminate the reaction byproduct produced in a solid-state polycondensation reaction and it proved to be very effective means to promote the forward reaction.

It has been observed that the extent of reaction for the reaction product obtained by the semibatch reaction process increases with reaction time as far as nitrogen gas is introduced into the reactor enough over 0.05 mL/g/min of the flow rate. The heat-resistant property of reaction product obtained was increased in the semibatch reaction carried out for more than 1 h and it reached an upper limit beyond 5 h of reaction time under the specified reaction conditions (210°C, 0.25 mL/g/min). It has shown a maximum value of the amidation ratio at 210°C, which is an optimum semibatch reaction temperature to obtain a more excellent heat-resistant polyamide relative to the virgin PET resin. The N₂-gas sweeping rate needs to

be increased to make the T_{20} value of product shift toward higher temperature. However, it is necessary to be cautious not to sweep away the solid reaction mixture with the N_2 gas introduced. A series of uncatalyzed batch reactions for 1 h and semibatch reactions for 5 h produced a reaction product with a higher value of the extent of reaction than that of the product obtained by the uncatalyzed batch reaction carried out for 10 h. Note that the amidation ratio showed a value of 0.589 in the 10-h batch reaction, however, the amidation ratio was increased to 0.702 by applying a series of 1-h batch and 5-h semibatch reaction processes.

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