Effectiveness of High Frequency Heating on Drying and Intrinsic Viscosity Enhancement of Recycled Poly(ethylene Terephthalate)

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ABSTRACT: The effectiveness of a high radio frequency (HF) heating technique as a tool for drying and for enhancement of intrinsic viscosity (IV) in recycled poly(ethylene terephthalate) (R-PET) pellets is described. R-PET that was sourced mainly from postconsumer drinking bottles would generally attain lower molecular weight due to hydrolytic degradation when exposed to repeated thermal processing cycles and also the presence of impurities. Hence, the IV of R-PET would be significantly lower as compared to virgin PET (V-PET), which could affect its processability and significantly limit its application. In this study, R-PET pellets were exposed to HF and their IV and moisture content were monitored with time. HF was found to be a less time consuming method to enhance the IV of R-PET although it was not reliable to be used for drying purposes. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: activation energy; recycling; solid-state polymerization

INTRODUCTION

Poly(ethylene terephthalate) (PET) is widely used in fibers, beverage bottles, and food packaging applications. Recently, studies on recycling of postconsumer PET have mostly focused on the chemical alteration or solid-state polymerization processes to improve the processability and mechanical performance of recycled PET (R-PET). It is known that PET undergoes hydrolysis when heated in the presence of moisture above its glass transition temperature (T_g) and near the melting temperature (T_m) resulting in formation of oligomers with unsatured olefinic and carboxylic end groups.[1–12] Therefore, the presence of acidic compounds at the processing temperature catalyzes the hydrolysis of ester bonds leading to the formation of low molar mass fragments with higher amount of carboxylic end groups. The thermal and hydrolytic degradation of R-PET caused by moisture retention in the pellets could also generate some problems associated with the loss of molecular weight, which leads to a decrease in the intrinsic viscosity (IV). The decrease in both the molecular weight and IV affects the mechanical properties of

the recycled material. The reduction in the chain length of PET caused by hydrolytic chain scission can, in part, be compensated by the use of various heat treatments.[13,14] Mallon and Ray[14] have reported on the enhancement of polycondensation reactions in both PET and Polyamide 66 by the use of microwave technology. They have concluded that the microwaves could selectively excite the condensate in the polymer to cause higher diffusion rates and subsequently promoting fusion of the end groups. Moreover, they have also noted that high field strengths would yield runaway melting of the polymers, especially when high moisture content was present in the bulk. There was, however, no indication whether the presence of moisture could be a barrier for reducing the effectiveness of the solid-state polymerization (SSP) process.

In this work, high radio frequency (HF) was used as the source of energy to promote polycondensation to enhance the molecular weight and subsequently the IV of R-PET. The frequency of HF used was 40 MHz, unlike microwaves that are typically tuned to the frequency of 2450 MHz. The penetration depths, d_p, of HF and microwaves are governed by the following equation[15]:

$$d_p = c \times \left\{ 2\pi f \sqrt{2\varepsilon' \left[\sqrt{1 + (\varepsilon''/\varepsilon')^2} - 1 \right]} \right\}^{-1} \quad (1)$$

where c is the speed of light (3×10^8 m/s), ε' is the material dielectric constant, ε'' is the dielectric loss factor, and f is the frequency.

From eq. (1), it is clear that HF has a much greater penetration depth (to the order of 500–600 cm) as compared to microwaves (about 2–3 cm) and, therefore, is more practical for large scale bulk SSP applications.

The moisture content, molecular weight, and IV of R-PET during HF treatment were monitored and the efficiency and effectiveness of this technique in promoting solid-state polymerization were later compared to other SSP techniques as described in the literature.[16–18] The presence of moisture in the pellets would significantly affect the efficiency of SSP since the polymer would likely undergo hydrolytic degradation rather than polymerization. Thus the pellets would have to be dried at various durations either by using a dehumidifying dryer or HF and their moisture contents accurately monitored prior to transferring them for further HF treatment to induce SSP. The optimum HF treatment parameters such as temperature and time were determined based on the increments in R-PET IV.

EXPERIMENTAL

Materials

Virgin PET (V-PET) pellets were supplied by Kuraray, Japan (KS750RC) while R-PET pellets extruded from crushed postconsumer PET bottles were supplied by Kojima Sangyo (Hyogo, Japan). The initial viscosity average molecular weights for as-received V-PET and R-PET were determined to be 21,548 and 13,131 g/mol, respectively, based on IV values of 0.70 and 0.50 dL/g, respectively.

Sample preparation

Two types of samples from R-PET pellets were prepared by subjecting them to either high radio frequency (HF) heat treatment or conventional dehumidifying drying. The former was conducted within a static bed test batch reactor. The batch reactor (50 cm deep × 90 cm long × 60 cm wide) was constructed from aluminum with a set of parallel electrode plates, one of which is suspended above the pellets and electrically isolated as shown in Figure 1. R-PET pellets were filled in a rectangular frame made from silicone/fiberglass composite laminate (4 cm deep × 40 cm long × 26 cm wide) and positioned on the lower electrode plate. To remove volatile residues and prevent the pellets from degradation during the treatment, nitrogen gas was introduced from the lower one end of the chamber and exits through the opposite upper end of the
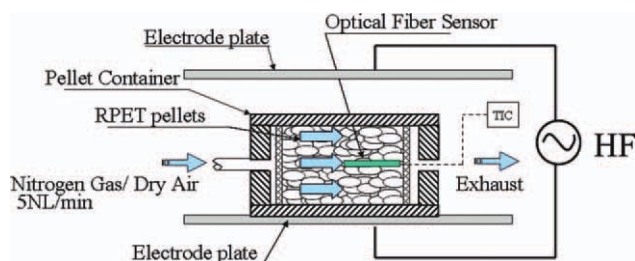

Figure 1 Experimental setup of the high radio frequency (HF) treatment apparatus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chamber. High frequency energy at 40.68 MHz was applied through parallel plate electrodes, which would drastically increase the temperature of the pellets. The temperature of the pellets was constantly monitored by using fiber optic temperature sensing probes and the temperature was controlled by adjusting the distance between the electrode plates; a shorter distance increases the temperature and vice versa. The pellets were exposed to HF treatment at a temperature range between 110 and 240°C while the exposure times were varied between 10 min and 7 h. Specimen designations can be found in Table I.

Figure 2 shows the schematic representation of a conventional dehumidifying dryer (SPMH10, ITSWA Co. Ltd.) wherein R-PET pellets were dried under −30°C dew point atmosphere. The pellets were exposed to similar temperatures as in HF treatment. However, since the pellet heating rates during HF treatment and the dehumidifying dryer were significantly different, as shown in Figure 3, the exposure times allocated for these treatments were different. As such, the pellets were subjected to dehumidified drying at longer time intervals, i.e., 1 to 7 h.

The treated pellets were immediately contained in aluminum bags, filled with dry nitrogen gas and then heat-sealed to preserve the thermal history and moisture content in the pellets. About 2.5 ± 0.1 kg of pellets was produced at each treatment condition

TABLE I

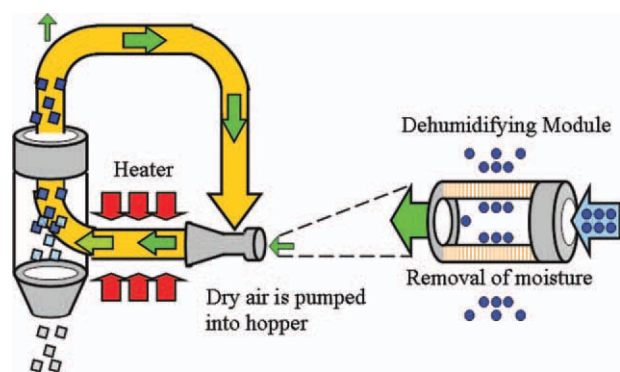| Temperature (°C)	Specimen Designation	
	HF Treatment	Dehumidifying Dryer
110	HF110	DA110
120	HF120	DA120
130	HF130	DA130
140	HF140	DA140
150	HF150	DA150
160	HF160	DA160
200	HF200	DA200
220	HF220	DA220
230	HF230	DA230
240	HF240	DA240

Figure 2 Schematic diagram of the dehumidifying dryer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and about 100 g of these pellets was reserved for various thermal, morphological, molecular weight, and moisture content analyses.

Molecular weight and moisture content analyses

Measurements of IV in dilute solution were performed by using an Ubbelohde type viscometer in accordance to ASTM D4603. About 0.25 g of pellets was precisely weighed and dissolved in 50 mL solvent at 120–130°C. The solvent consist of a mixture of phenol and 1,1,2,2-tetrachloroethane at 6 : 4 weight ratio. IV was calculated according to the Billmeyer relationship (ISO 1628-1) from the viscosity number dependence on concentration of the polymer solution. Molecular weights of the samples were then determined in accordance to the Mark-Houwink-Sakurada calculation method.

Billmeyer relationship:

$$[\eta] = 0.25(\eta r - 1 + 3 \ln \eta r)/C \tag{2}$$

where ηr is the relative viscosity = t/t_0; t is the average solution flow time (s); t_0 is the average solvent
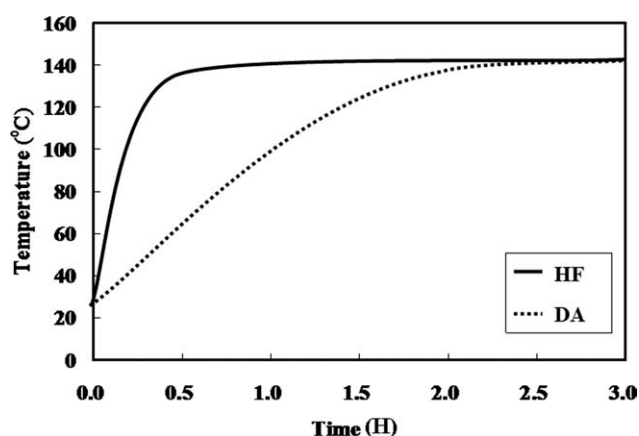

Figure 3 Comparison of heating rates between the HF and dehumidifying dryer (DA) equipment.

flow time (s); and C is the polymer solution concentration (g/dL)

Mark-Houwink-Sakurada relationship:

$$[\eta] = K\mathrm{Mv}^\alpha \tag{3}$$

where Mv is the viscosity average molecular weight; and K and α are Mark-Houwink constants. The K and α values for PET were known to be 7.55×10^{-4} and 0.685, respectively,.[19]

Moisture contents in pellet samples were measured by using a Karl Fischer Moisture Meter (CA-05 and VA05, Mitsubishi Chemical Co. Ltd.) at 230°C. The moisture content was determined when the moisture release rate by the specimen was under 50 μg/s. This technique is known for its ability to detect even minute changes in resistivity of the electrolyte solution as chemical reactions occur due to the presence of moisture, thus the moisture content in the pellets could be accurately determined in the order of parts per million. About 1.5 g of pellets was used for each measurement.

Determination of crystallinity at various cross sections of the R-PET pellets

The effects of different heating techniques on the crystallinity of the R-PET pellets should be analyzed since this would provide information on the heating mechanism as well as to detect the presence of degraded substances, if any. The pellets with typical diameters of about 2 mm were sliced by using a microtome with each slice bearing a thickness of 50 μm. The region from the surface until a depth of 250 μm of the pellets is defined as the skin whereas the core is defined as the area within the 250 μm radius from the center of the pellet. The pellets were mounted on stubs with adhesives prior to being sliced by using a Leica RM2235 manual rotary microtome. The slices were then subjected to differential scanning analysis (DSC) by using a TA Instrument DSC2920 calorimeter to obtain the melting enthalpies that are representative of the crystallinity at a particular region of the pellet. Specimens were heated from 30 to 300°C at a rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Effectiveness of HF as compared to dehumidifying dryer for drying of R-PET

Figure 4 compares the effectiveness of HF treatment and dehumidifying drying on the moisture content in R-PET pellets. Pellets that were dried by using the dehumidifying drier (DA120, DA140, and DA160) contained less than 1000 ppm of moisture
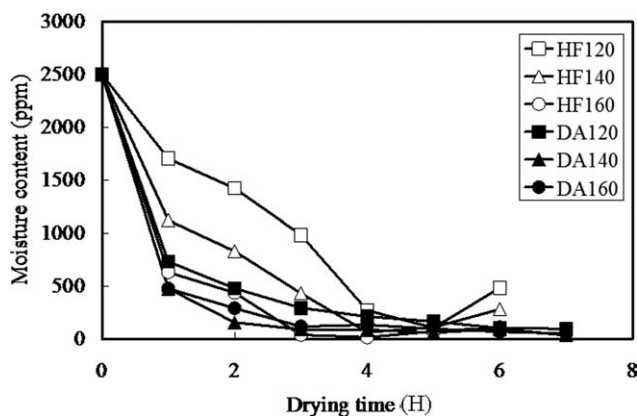
Figure 4 Comparison on the effectiveness of drying by HF-treatment and dehumidifying dryer (DA) at various drying times and temperatures.

after only 1 h of drying whereas those exposed to HF treatment (HF120, HF140, and HF160) contained much higher moisture levels although they were dried at similar times and temperatures. Moreover, despite the higher heating rate during HF treatment, the pellets needed more than 4 h of drying to achieve moisture content levels of less than 200 ppm whereas those dried by the dehumidifying dryer only needed 3 h. It is important to note that the pellets should attain a moisture content of less than 100 ppm to prevent depolymerization during the SSP process. The high heating rate during HF treatment could have induced crystallization especially at the outer surfaces of the pellets. The crystallized surface regions would then act as a barrier that suppresses the diffusion of moisture towards the outside of the pellets, hence the pellets would be more difficult to dry.

The enthalpy ratios between the skin and core regions (E_r) were determined and are shown in Figures 5 and 6 for pellets dried by using a dehumidifying dryer and HF apparatus, respectively. $E_r = 1$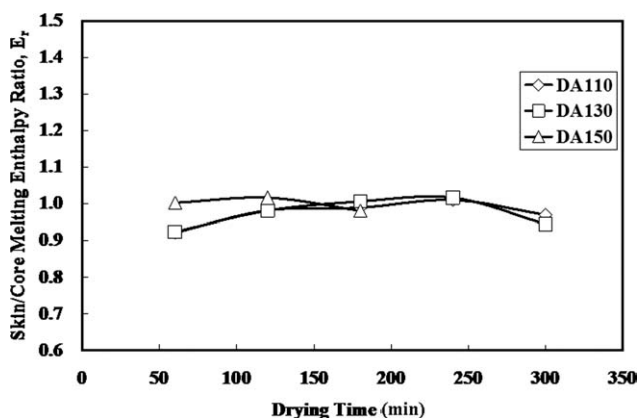 indicates that the crystallinity at the skin and core regions is the same. However, $E_r > 1$ would indicate that the crystallinity at the skin is higher than the core while $E_r < 1$ would mean otherwise. It should be noted that the E_r in RPET pellets before drying is less than 1.
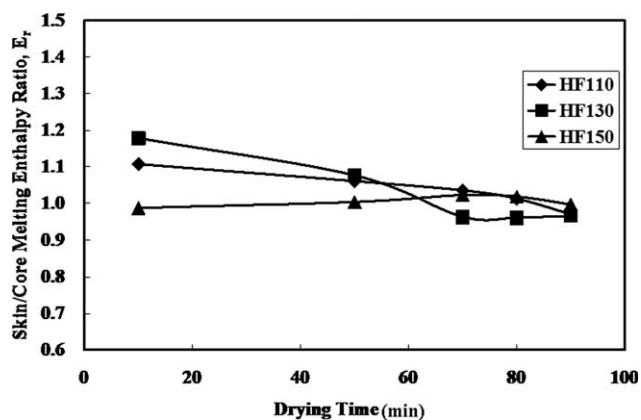
In the case of pellets dried by using a dehumidifying dryer, the E_r values consistently hovered at around 1.0, as indicated in Figure 5. The slow heating rate of the dehumidifying process allowed the pellets to maintain a uniform heat distribution throughout its thickness. Therefore, the skin and core regions in the pellets were able to attain similar crystallinity, which is reflected by the consistent E_r values irrespective of drying time.

It can be seen from Figure 6 that the E_r values were higher than 1 even after only 10 min of HF treatment at 110 and 130°C. This indicates that the skin region of the pellets would undergo crystallization earlier than the core region, which is caused by the conductive heating mechanism during HF treatment. During conductive heating, the outer surface temperature of the pellets would rise significantly before the heat is transferred towards the core. The E_r values would decrease towards unity with time as the core region crystallizes to a similar degree as the skin. At high HF temperatures (150°C), the crystallization rate at both the skin and core was high and the difference in enthalpies could not be seen after 10 min of drying.

In the case of pellets dried in the dehumidifying dryer, low E_r values were observed in the early stages of drying while these values would gradually increase towards unity with time. The heating mechanism in the dehumidifying dryer is mostly convective, which would allow the temperature in the pellets to slowly rise. This allowed the pellets to gradually crystallize from the core towards the skin. It can, therefore, be concluded that the dehumidifying dryer is more preferable for drying of R-PET due to its high efficiency despite its low heating

Figure 6 Skin/core melting enthalpy ratios of R-PET pellets dried by HF.

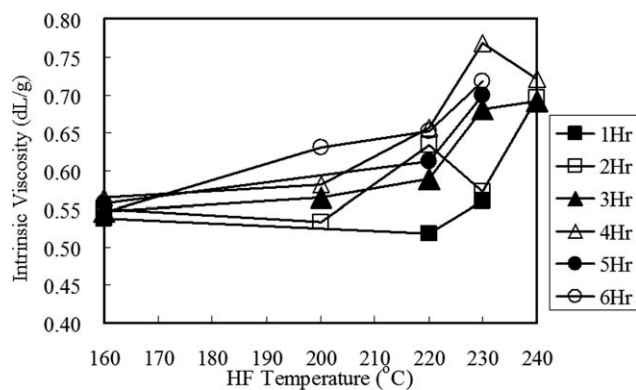**Figure 5** Skin/core melting enthalpy ratios of R-PET pellets dried by dehumidifying dryer.

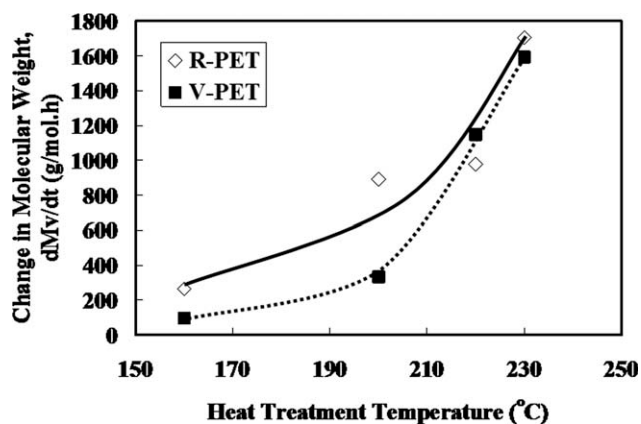**Figure 7** Dependence of intrinsic viscosity on HF treatment temperature and time.

Figure 8 Comparison between the intrinsic viscosity increment ratios of R-PET and V-PET at various HF treatment times.

rate. Henceforth, all R-PET pellets were predried with the dehumidifying dryer until the moisture content in the pellets were less than 100 ppm prior to subsequent HF treatment for solid-state polymerization.

Effect of HF treatment conditions on the IV of R-PET

Solid-state polymerization is typically performed at a temperature range of 200–240°C, which is above the limit of the dehumidifying dryer. Furthermore, an inert gas (in this case nitrogen) would have to be used for purging to reduce the amount of condensates so that high molecular weights could be achieved. The molecular weight of the specimens could be estimated by measuring the IV through procedures described in the methodology. The effect of HF temperature and time on the IV of R-PET is illustrated in Figure 7. It can be seen that the highest IV of 0.77 dL/g could be achieved when the specimens were HF-treated at 230°C for 4 h. It should be noted that this treatment time is significantly shorter than most solid-state polymerization methods, which typically requires at least 6 h of reaction time to achieve similar IV.[17,18,20,21] Moreover, notable improvements in IV could also be seen even after HF-treatment for only 2 h. It was also found that the usage of temperatures higher than 230°C yield little difference in terms of IV increments.

TABLE II

Temperature (°C)	Viscosity Average Molecular Weight, Mv(g/mol)	
	VPET	RPET
160	22997	15660
200	23594	18415
220	29971	19551
230	29722	24549

The highest achievable viscosity average molecular weights (Mv), as calculated from eq. (3), for samples heat-treated at various HF temperatures are compiled in Table II. With increasing HF temperatures, higher Mv values could be achieved in both R-PET and V-PET. However, it is important to note that the highest Mv achievable for R-PET after HF treatment at 230°C even exceeded the Mv of untreated V-PET, which reiterates the ability of HF treatment in upgrading the properties of R-PET to match that of neat materials.

The rates of Mv increment (dMv/dt) or polymerization rate at various HF temperatures for R-PET and V-PET are compared in Figure 8. As can be seen, the polymerization rate increases exponentially with increasing HF temperature for both materials. However, it is obvious that the polymerization rate in R-PET was higher than that of V-PET even at low HF temperatures. This could be due to the presence of more free volume and activation sites that allow for faster polycondensation to take place in R-PET. Moreover, given the high polymerization rate, significant increment in Mv of R-PET can be achieved by HF treatment at relatively shorter times (≈4 h) as compared to conventional SSP processes, which typically require at least 6 h to attain equivalent Mv values even under vacuum conditions.[17]

The Mv increment rate could also be described through the following Arrhenius equation:

$$\ln(k) = \frac{-E}{R}\frac{1}{T} + \ln(A) \qquad (4)$$

where k is the reaction rate given by dMv/dt while E is the activation energy at a given temperature T, A is the frequency factor for the reaction, and R is the gas constant. The plots of $\ln(k)$ versus $1/T$ are compared in Figure 9 for V-PET and R-PET. A smaller gradient for the R-PET curve could be
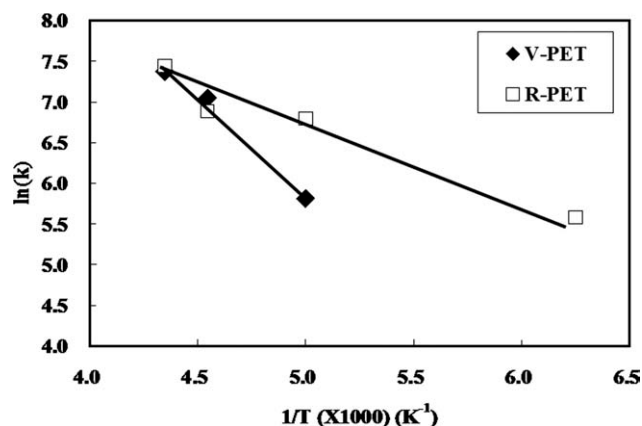
Figure 9 Comparison between Arrhenius derivative curves of R-PET and V-PET.

observed, which gives an activation energy, $E_{\text{R-PET}} = 2.53$ kcal/mol whereas the activation energy for V-PET, $E_{\text{V-PET}} = 4.77$ was almost twice that of R-PET. The lower activation energy for R-PET indicates that HF was more effective in enhancing the IV of R-PET and this can be done even at lower HF temperatures. Therefore, it is thought that the HF-treatment method can be a cost effective and energy saving alternative for solid-state polymerization of PET.

CONCLUSIONS

The effectiveness of high radio frequency (HF) heating for drying recycled PET pellets was compared to that of conventional dehumidifying dryers at a temperature range between 110 and 160°C. Although the heating rate of HF was comparatively high, the dehumidifying dryers were more effective in removing moisture from the pellets. The HF-treatment was then used as a method for inducing solid-state polymerization by increasing the temperature range between 200 and 240°C, which is beyond the range of the dehumidifying dryer. The HF-treatment was found to be a very effective method for enhancing the IV of R-PET, judging from the shorter reaction time and lower temperature as compared to the conditions used in the literature. Therefore, HF-treatment can be considered as an alternative method to upgrade R-PET materials so that they attain mechanical and thermal properties that are comparable to that of virgin materials.

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