

Effects of Thermal Aging on Chemical–Physical and Electrical Properties of Poly(propylene terephthalate)

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ABSTRACT: Poly(propylene terephthalate) (PPT) was subjected to aging at high temperatures (150–190°C) in air and some mechanical (impact strength), physical (weight loss), and electrical (dc conductivity and ac electrical strength) properties were determined as a function of aging time and temperature. Some chemical–physical characteristics (such as the average molecular weight, the carboxyl end-group content, and crystallinity degree) were investigated during the degradation process, as well. From the collected data, the thermal endurance parameters (i.e., the

temperature index and the halving interval), which are key parameters in the determination of materials reliability and design of electrical insulating system, were derived according to IEC 216 Standard, and compared with those relevant to other thermoplastic polyesters. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2848–2854, 2004

Key words: poly(propylene terephthalate) (PPT); degradation; temperature index; thermoplastics; thermal endurance parameters

INTRODUCTION

Poly(propylene terephthalate) (PPT) belongs to the family of the engineering thermoplastic polyesters whose monomeric units incorporate a $-(\text{CH}_2)_\gamma-$ segment. Until now, it has been mostly confined to the production of fibers^{1,2} mainly because of its high cost. Recently, a novel, less-expensive method of synthesis of 1,3-propanediol³ has opened new possibilities to the marketing of this polyester.

After having investigated the electrical and thermal behavior of this polymer,^{4,5} it seemed important to study its thermal stability, in view of its possible wider use in the electrical industry; indeed, in analogy to poly(butylene terephthalate) (PBT), the application of the polymer in housing or connectors, particularly in the automotive industry, implies high temperatures in service conditions. Therefore, samples of laboratory-synthesized PPT, free from additives, were subjected to thermooxidative aging in air at high temperatures. The dc electrical conductivity, ac electrical strength, weight loss, impact strength, average molecular weight, carboxyl end-group content, and crystallinity degree were determined as a function of aging time and temperature. The aim of this research was to investigate the degradation processes and estimate the

thermal endurance parameters, that is, the temperature index (TI) and the halving interval (HIC), according to IEC 216 Standard. The parameter TI is defined as the specific temperature at which the material can withstand a continuous thermal stress for 20,000 h, still maintaining a certain performance at the end of such period; HIC is defined as the temperature increase that just halves the endurance time. These parameters are somewhat dependent on the choice of the investigated diagnostic property, as well as on the value that is taken as property limit or end-point value; nevertheless, the TI is a powerful tool for the design of electrical insulating systems, the evaluation of material reliability in service condition, and the selection of materials.⁶

EXPERIMENTAL

Material and samples

The investigated PPT, free from additives and stabilizers and just containing the catalyst $[\text{Ti}(\text{O}i\text{Bu})_4]$ residuals, whose polymerization reaction is described in detail elsewhere,⁵ had the following characteristics: glass-transition temperature $T_g = 45^\circ\text{C}$; melting point $T_m = 226^\circ\text{C}$, measured by differential scanning calorimetry (DSC); number-average molecular weight $M_n = 27,200$; weight-average molecular weight $M_w = 75,000$ determined by gel permeation chromatography (GPC); carboxyl end-group content: 30 meq/kg.⁵

Polymer specimens were molded under vacuum at 250°C for 5 min; under these conditions, neither sig-

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nificant thermal degradation phenomena occur, nor are memory effects of the previous structure present.⁵ Molded specimens were in the form of disks (0.3 to 1.0 mm thick and 60 mm in diameter) for electrical tests, and in the form of prisms (3 × 12.7 × 64 mm) according to the ASTM D256 Standard, for the impact strength and weight loss tests. Before measurements, specimens were vacuum annealed at 150°C for 48 h; after this treatment the polymer exhibited a crystallinity degree of about 40 wt % (determined by DSC and assuming a melting heat of 145.6 J/g for the crystalline PPT⁷).

Molecular and thermal characterization

Molecular weight data were obtained by gel permeation chromatography using a 1100 HP Series system (Hewlett-Packard, Palo Alto, CA), equipped with a PL gel 5 μ Mixed C column and a UV detector set at 254 nm. A mixture of dichloromethane/chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (CH₂Cl₂/CHCl₃/HFIP) (75/20/5 wt/wt) was employed as eluent. The solution injected had a sample concentration of about 0.1 wt %. The molecular weights were determined using a calibration curve obtained from polystyrene standards. Carboxyl end-groups content was determined by potentiometric titration using a DL 25 automated titration system equipped with a SC-111 combination electrode from Mettler (Greifensee, Switzerland). About 0.5–1 g of polymer was dissolved in a 20 mL of a hot *o*-cresol/dichloromethane solution (25/75 v/v). Once dissolved, the solution was allowed to cool to room temperature and 50 mL of dichloromethane was added. The solution was titrated with a 0.01N tetrabutyl ammonium hydroxide and the carboxyl concentration expressed in milliequivalents per kilogram (meq/kg). The standard deviation of the mea-

TABLE I
Molecular Characterization Data for Unaged and Aged PPT Samples

Specimen	M_n	M_w	-COOH (meq/kg)
Unaged	27,200	75,200	30
150°C			
500 h	26,000	55,000	48
1100 h	16,000	47,500	70
1500 h	17,900	48,000	82
170°C			
500 h	14,200	42,000	60
900 h	8400	25,900	80
1500 h	8000	24,400	96
190°C			
240 h	8600	22,600	189
500 h	9900	25,100	229
900 h	10,300	24,400	257
1500 h	7300	21,600	279

TABLE II
Calorimetric Data of Unaged and Aged PPT Samples

Specimen	T_m I (°C)	T_m II (°C)	ΔH_f (J/g)	T_g (°C)
Unaged	—	226	57	58
150°C				
500 h	190	227	61	56
1100 h	200	226	72	56
1500 h	201	226	74	55
170°C				
500 h	200	227	66	57
900 h	205	226	76	60
1500 h	208	226	77	53
190°C				
240 h	210	226	84	54
500 h	211	225	81	53
900 h	213	225	87	59
1500 h	216	224	89	53

surements was <0.85 meq/kg. Calorimetric measurements were carried out by means of a Perkin-Elmer DSC7 instrument (Perkin Elmer Cetus Instruments, Norwalk, CT) equipped with a liquid subambient accessory and calibrated with high-purity standards (indium and cyclohexane). Weighted samples (about 10 mg) of PPT were heated from 0 to 270°C at a rate of 20°C/min. The glass-transition temperature T_g was taken as the midpoint of the heat capacity increment Δc_p associated with the glass-to-rubber transition. The melting temperature (T_m) was taken as the peak values of the endothermal phenomenon in the DSC curve. The enthalpy of fusion (ΔH_m) was determined from the total area of the DSC endotherms. Repeated measurements on each sample showed excellent reproducibility.

Aging conditions

Specimens were aged in air at 190, 170, and 150°C; at scheduled times, specimens were removed and subjected to destructive or nondestructive tests.

Tests on aged specimens

The dc charging currents (and therefore dc conductivity) were measured as a function of time (up to 3 h) and temperature (from 25 to 130°C), under a constant electrical field of 10 kV cm⁻¹, by the voltmeter-ammeter method according to ASTM D257 Standard and with the three-terminal cells and instrumentation described elsewhere.⁸ Before measurements, specimens were gold coated by vacuum deposition, to obtain the suitable three-terminal electrode configuration. All measurements were made in a dynamic vacuum from the highest to the lowest temperature, to minimize the effects of accidental adsorption of gases or vapors on the samples' surfaces. Electrical strength was mea-

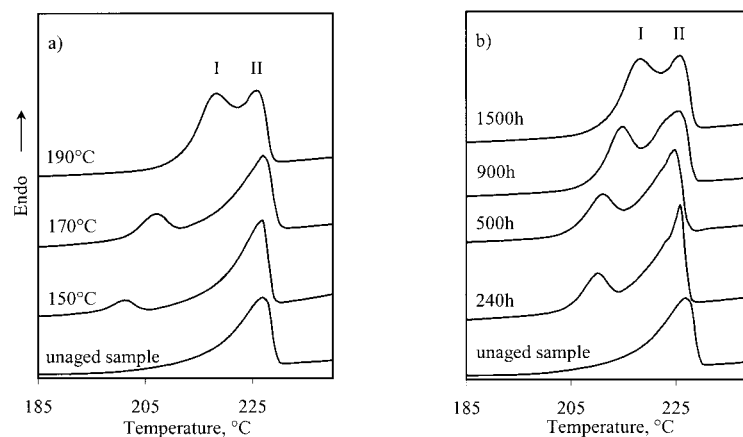


Figure 1 Calorimetric curves of unaged and aged samples of PPT: (a) aged at the indicated temperatures for 1500 h; (b) aged at 190°C for the indicated times.

sured according to ASTM D3755 Standard, on samples stored on silicon oil and by applying the electrical field at an increasing rate of 10 kV/min. Before measurements, specimens were gold coated by vacuum deposition. Impact strength tests were performed according to ASTM D256 Standard (Izod configuration), on unnotched samples at room temperature, by means of a Resil 5.5 instrument (Ceast, Forino, Italy).

RESULTS AND DISCUSSION

A preliminary investigation of the aged specimens from the molecular perspective was performed to evaluate the influence of aging on average molecular weight and carboxyl end-group content. In Table I, the

average molecular weight (numerical M_n , and weight M_w) and the concentration of carboxylic end groups of unaged and aged specimens are reported. Molecular weight reduction (more evident considering M_w) and an increment of the $-COOH$ content are the main effects of the aging process. It must be underlined that at 190°C, after a first significant molecular weight reduction, M_w tends to slightly increase: this trend can be explained considering that, under these particular conditions, the postpolymerization process⁹ may become competitive with the degradation reactions. At the longest times (1500 h), however, M_w again decreases. The increase in the $-COOH$ content exhibits a linear trend as a function of aging time at 150 and 170°C but not at 190°C. Again the results at 190°C can

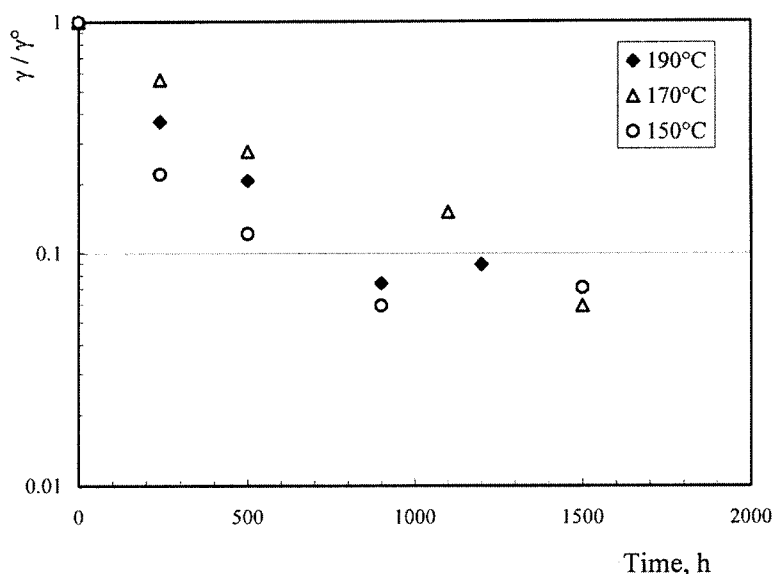


Figure 2 Electrical conductivity (after 3600 s) at 130°C of aged samples of PPT as a function of aging time versus that of the unaged material.

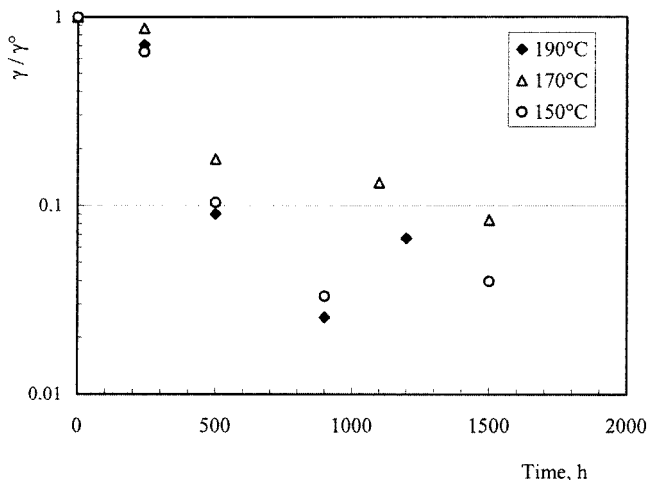


Figure 3 Electrical conductivity (after 3600 s) at 90°C of aged samples of PPT as a function of aging time versus that of the unaged material.

be ascribed to the competition between postpolymerization and degradation reactions. All samples under investigation were afterward examined by differential scanning calorimetry (DSC). The results obtained are reported in Table II. To evaluate the effect of aging temperature and time on the aging process, the thermograms of samples aged at the three temperatures, for a fixed time, are reported in Figure 1(a) and compared with that of unaged PPT. In Figure 1(b), the DSC curves of samples aged at 190°C for different times are shown with that of unaged PPT. Two endothermic peaks, marked by (I) and (II) in order of increasing

temperature, can be observed: only the unaged specimen exhibits a single peak. A trend of the position and intensity of the endotherms on temperature and aging time can be observed. In particular, the position of melting peak (I) shifts to higher temperature and its magnitude increases with aging temperature and time. On the contrary, the location of the highest melting endotherm (II) does not change with aging condition.

With respect to the total heat of fusion, a marked increment of ΔH_m of the aged samples, with respect to the unaged one is found (Table II). Moreover, the heat of fusion increases both with increasing the aging temperature, at constant aging time, and increasing the aging time at constant aging temperature. The increment of crystallinity degree during the degradation process was previously found for poly(ethylene terephthalate) (PET),¹⁰ as well as in other thermoplastics.¹¹ A possible explanation of this behavior is that the macromolecular chain breakages, which take place mainly in the amorphous regions, reduce the concentration of entanglements, and allow the chain fragments thus generated to become part of the crystalline domains. In our case, this hypothesis seems to be supported by both the appearance of the melting peak (I) at temperatures lower than 226°C in the aged samples and the dependency of endotherm (I) on aging conditions. Therefore, on the basis of the observed trend, endotherm (I) can be ascribed to the fusion of crystals grown by normal primary crystallization during the aging process. Its dependency on the temperature and time of aging, in terms of both peak position

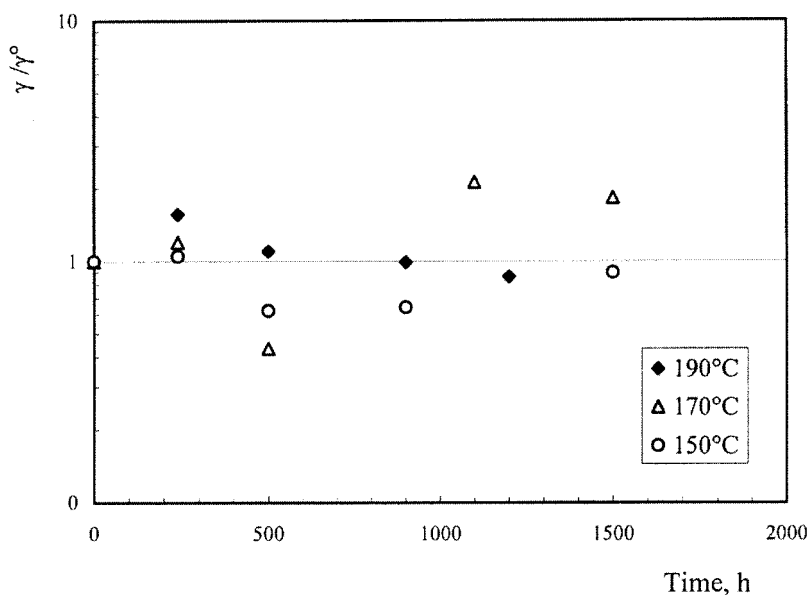


Figure 4 Electrical conductivity (after 3600 s) at 25°C of aged samples of PPT as a function of aging time versus that of the unaged material.

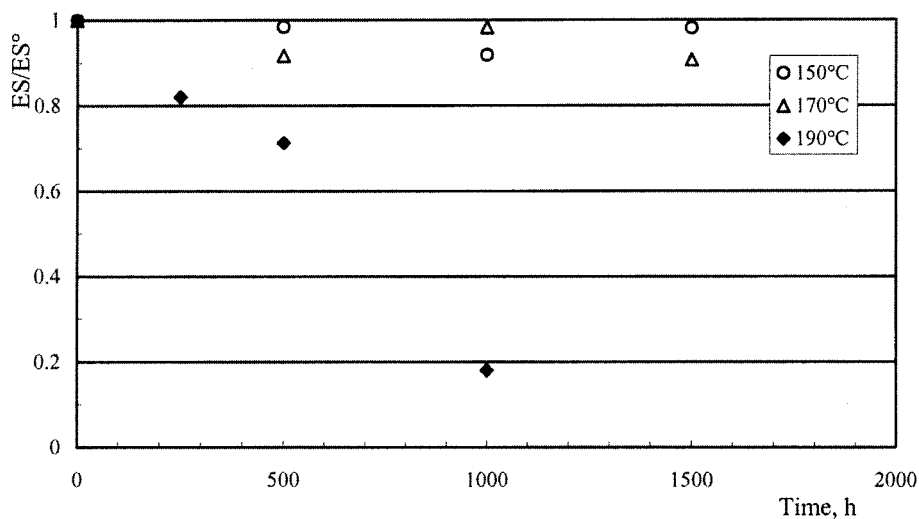


Figure 5 Electrical strength as a function of aging time at different aging temperatures versus the value of unaged material.

and area, suggests that thicker crystalline lamellae develop with increasing temperature and time of aging. The higher-temperature peak (II) can be ascribed to the melting of crystals of higher stability and perfection possibly grown during the heating run as a consequence of recrystallization or reorganization of crystals initially formed. Concerning the glass-transition temperature, no significant differences were found between unaged and aged samples even though the latter are characterized by a higher degree of crystallinity.

The dc electrical conductivity at 25, 90, and 130°C is reported in Figures 2, 3, and 4 respectively, as a function of aging time. Values obtained after 3600 s from the voltage setting are reported.

The conductivity of the polymer was previously related,⁴ particularly at temperatures higher than 70°C (i.e., above the glass-transition temperature), to the motion of protons arising from the dissociation of carboxyl end groups: the electronic contribution to the conduction becomes significant only at lower temperatures. A continuous decrease of conductivity can be observed (Figs. 2 and 3) at the higher temperatures investigated. This effect is noteworthy, given that from Table I we can observe that the concentration of carboxyl end groups (and thus the concentration of possible charge carriers) increases steadily during the aging process. It can be postulated that the increase in charge carriers is counterbalanced and even overcome by the reduction of their mobility inside the material. The reduction of mobility can be ascribed to the crystallinity increase, which should reduce the extent and, perhaps, the flexibility of the amorphous domains, where ions can diffuse more easily, even though this effect is not confirmed by T_g temperatures derived by DSC. On the other hand, at the lowest temperature

(Fig. 4) conductivity tends to remain almost constant or even to increase, although a clear trend cannot be distinguished. In this case, an increase in the carbonyl groups or double bonds content inside the polymer can promote the electronic mechanism of conduction.

Figures 5–7 show the variation of electrical strength, impact strength, and weight as a function of aging time, respectively. Contrarily to the electrical conductivity behavior, all these investigated properties tend to decrease as degradation proceeds, more and more as the aging temperature increases: the only exception

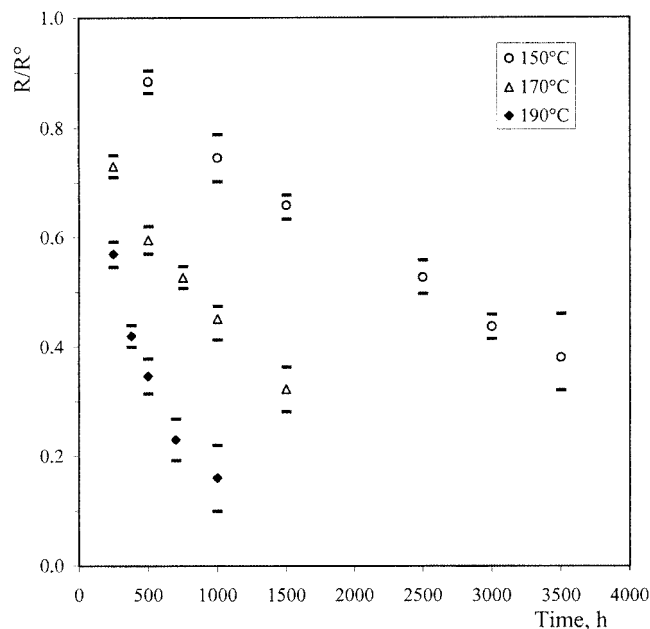


Figure 6 Impact resilience as a function of aging time at different aging temperatures versus the value of unaged material.

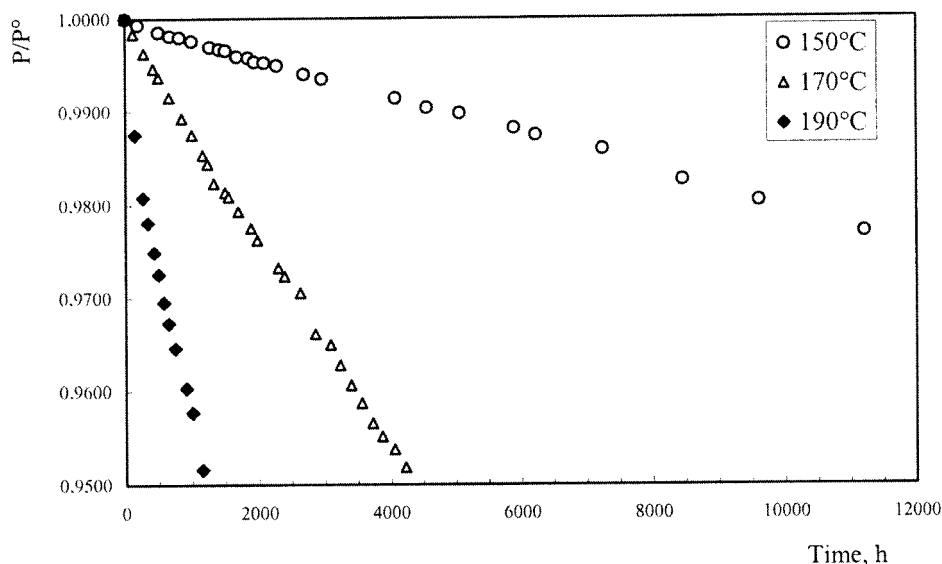


Figure 7 Weight loss as a function of aging time at different aging temperatures versus the value of unaged material.

is found for electrical strength, whose value remains almost constant below 170°C, at least at the investigated degradation times. Impact strength and weight loss exhibit an almost linear trend as a function of time. These two properties can thus be used to calculate the thermal index (TI) and the halving interval (HIC) according to IEC 216, in analogy to what was previously done for polyolefins^{12,13} and polyesters.¹⁴ End-point values of 0.5, 0.4, and 0.3 for impact strength and 0.985, 0.980, and 0.970 for weight loss were selected. Table III reports values of TI and HIC obtained considering the two different diagnostic properties and the relevant end points.

The two properties provide quite different results: TI values derived from impact strength tests are almost unaffected by choice of end points and are lower than those derived by weight loss; HIC values are instead higher and show higher dispersion. TI values calculated by means of impact strength tests are only slightly higher than those for PBT,¹⁴ whereas values of HIC are significantly higher (~ 4–6°C). PET thermal

endurance parameters, obtained by weight loss at close end points,¹⁵ disclosed a higher value of TI and a somewhat lower HIC value (TI = 154°C, HIC = 5.4).

CONCLUSIONS

The main effects of thermal aging in air on poly(propylene terephthalate) can thus be summarized:

- Crystallinity and –COOH concentration increase, whereas molecular weight decrease as a function of time.
- Electrical volume conductivity, measured at temperatures above the glass-transition temperature, continuously decreases as a function of aging time; below T_g , conductivity instead increases. This effect can be related to the different mechanism of conduction; at high temperatures, where the conduction mechanism is mainly ionic, the increase of crystallinity causes a strong decrease in the mobility of charge carriers overcoming the effect relevant to their increase in concentration. At low temperatures, where an electronic mechanism is postulated, degradation favors the conduction mechanism by increasing both mobility and charge carrier concentration.
- The thermal endurance parameters of the polymer are close to those found for similar polyesters.

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TABLE III
Values of Temperature Index (TI) and Halving Interval (HIC) from Impact Strength and Weight Loss Data at Different End Points

Property	End point	TI (°C)	HIC (°C)
Impact strength	0.5	120	9.7
	0.4	119	11.2
	0.3	120	12.0
Weight	0.99	140	6.5
	0.98	142	6.8
	0.97	143	7.0

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