

Thermal Profile of Polypropylene and Polyethylene. I. A Novel Look at a Traditional Technique

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ABSTRACT: A new look at a traditional method of thermal characterization is offered. Oxidative induction temperature method is modified and revised to give a thermal profile of the polymer instead of a single-point measurement. This article is an effort to not only describe a portion of the thermal behavior of polymers, but also to identify some thermal parameters. These parameters; thermal stability, strength, and stiffness, are proposed to be used like tensile properties to differentiate between the behavior of

polymers under controlled conditions. The thermal parameters were successfully used to differentiate between two grades of polypropylene (PP), to study reprocessed PP, and to identify an injection molding problem for a client. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1545–1549, 2008

Key words: PP; DSC; thermal; OIT; profile; novel; technique; stability; degradation

INTRODUCTION

Thermal properties of polymers (resin + additives + other fillers) have influential effect on their performance either during processing or during service.^{1–4} The methods available to determine the thermal properties vary depending on the measuring method, testing conditions, and the used apparatus. For example oxidative induction time^{5,6} (OIT) measures the time needed to initiate “degradation” in a polymer specimen under specific experimental conditions. This is a “static” test as the specimen is heated first to a specific temperature under an inert atmosphere using differential scanning calorimetry (DSC) apparatus. Then the specimen is kept at this specific, or “static,” temperature under oxygen or air flow until “degradation” is initiated. This initiation manifests itself as an exothermic deviation of the DSCs thermograph. The time needed to initiate this “degradation” is considered the OIT of the specimen. OIT is widely used to characterize the thermal properties and to study the degradation kinetics of polymers.^{7–12} Another alternative to OIT is the measurement of the oxidative induction temperature. Conversely, this is a “dynamic” test where a polymer is heated continuously until “degradation” begins. The temperature at which “degradation” started is taken as the oxidative induction tempera-

ture. As far as thermal characterization is concerned, the dynamic method is faster than the static one, but the former is less used due to the thought of being less sensitive.¹³ As reckoned from the preceding explanation, both the static and the dynamic tests only measure one parameter, namely oxidative induction time (OIT) or oxidative induction temperature. Despite OIT being a one-point measurement, some professionals of the polymer industry attempt to characterize the whole thermal performance of a polymer by this single point, which is not advisable. This is similar to trying to characterize the rheological properties of a polymer by a single melt flow index (MFI) value, or attempting to describe the mechanical performance of a polymer by its yield strength only. Simply, we could not and should not attempt to characterize a whole spectrum of polymer properties, either thermal or rheological, or mechanical, by a single parameter. For this reason, the mechanical properties could be partially characterized by the stress–strain curve, and the rheological properties could be better described by the viscosity versus shear–strain curves. Similar to that, the thermal properties need a curve or a profile that describes its performance, at least partially. This article is proposing a method of generating a thermal profile which could be looked at like the stress–strain curve.

The sequence of thermal profile used here is to subject the polymer to an external thermal influence and to record its response for further analysis. This is similar to strain and stress in mechanical testing. Here, the external influence is the continuous increase of the specimen temperature with time. The measured response is the heat release, or the heat flow, as schematically illustrated in Figure 1.

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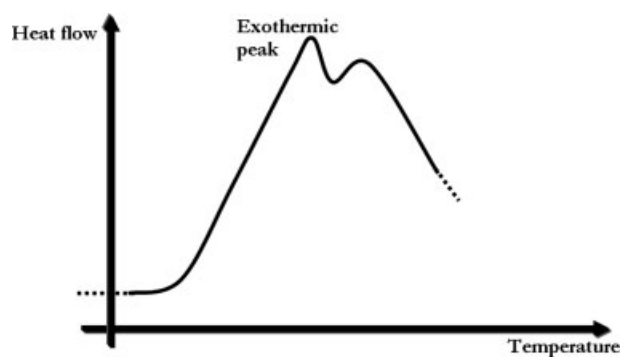


Figure 1 Typical thermal profile of polymers tested here.

This is similar to the dynamic oxidative induction temperature scheme, but with continuous heating until the first exothermic peak is completed or near completion as seen in Figure 1. The proposed test in this article is analogous to the tensile or instrumented impact tests; however, it is not similar to creep or fatigue tests. Thermal techniques that are similar to the latter tests are the subject of the sequel to this article. Another resemblance of the proposed thermal profile method to mechanical testing of polymers is failure mechanism. Some authors¹⁴ indicated that mechanical fracture of semicrystalline polymers, especially oriented ones, is mainly controlled by chain scission. It is known that thermal degradation of polypropylene (PP) and polyethylene (PE) commences by chain scission as well. Hence some mechanisms that control the mechanical fracture and thermal degradation of PP and PE are thought to be comparable to each other.

As straining rate and specimen geometry would affect the results of tensile testing, there are similar testing conditions that could affect the results of the thermal profile method. Heating rate and sample shape are the two common factors that could alter the apparent results of the thermal properties measurements¹³ and hence of thermal profile curve.

This article is an effort not only to characterize a portion of the thermal behavior of the polymers, but also to identify some thermal parameters. These parameters are proposed to be used to differentiate between the thermal behaviors of polymers under controlled testing conditions.

MATERIAL AND EXPERIMENTAL

Table I lists the samples that were used in this study. Two commercially available homopolymer PPs were used. PP-0 has MFI of 8 and PP-5 has an MFI of 11. Both PPs were thermally stabilized with the same package at the same concentration. Additionally, HDPE was tested.

Processed and then reprocessed samples of PP-0 were prepared as follows. About 2 g of PP-0 pellets

TABLE I
A List of the Samples Used in This Work.

Sample name	Description
PP-0	Virgin homopolymer PP, MFI = 8
PP-5	Virgin homopolymer PP, MFI = 11
#1	PP-0 with 1 processing scheme
#2	PP-0 with 2 processing scheme
#3	PP-0 with 3 processing scheme
#4	PP-0 with 4 processing scheme
#5	PP-0 with 5 processing scheme
HDPE	Virgin HDPE
RC	Reclaimed pellets from client

were put in the cup of the Laboratory Mixing Molder (LMM) made by Dynisco. LMM consists of a cup equipped with electrical heater and a rotating spindle that could be lowered into the cup to induce mixing. The temperature of the cup was set at 250°C and allowed to stabilize before each process. The spindle speed was set at 85 rpm. The 2 g of PP-0 pellets were loaded into the cup in about 20 s. Then the spindle was manually lowered and pressed lightly against the pellets for about 90 s to allow mixing. After that, a manual pressure was applied on the spindle for about 10 s to extrude the polymer melt out of the orifice at the bottom of the cup. The extrudate was allowed to cool down in air for 300 s. These steps constituted one processing scheme. Sample no. 1 was exposed only to one processing scheme. The extrudate of sample no. 1 was cut into small pieces and the previous processing scheme was repeated to extrude another sample, which was labeled no. 2. This process was repeated three more times to produce extrudates no. 3, no. 4, and no. 5. Therefore, sample no. 5 had experienced five processing schemes during its five consecutive extrusions.

Reclaimed, RC, pellets from a client who complained that RC pellets do not process as the virgin PP he buys. The client uses these RC pellets at about 25% loading with virgin PP-0 to reduce cost. The client also complained that the properties of the final product made of RC pellets do not look the same like parts made of virgin PP-0.

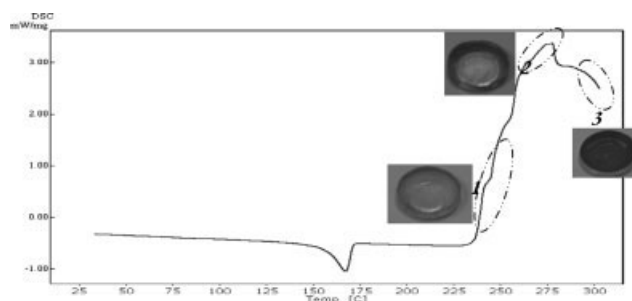


Figure 2 Thermal profile of PP-0 at heating rate of 5°C/min.

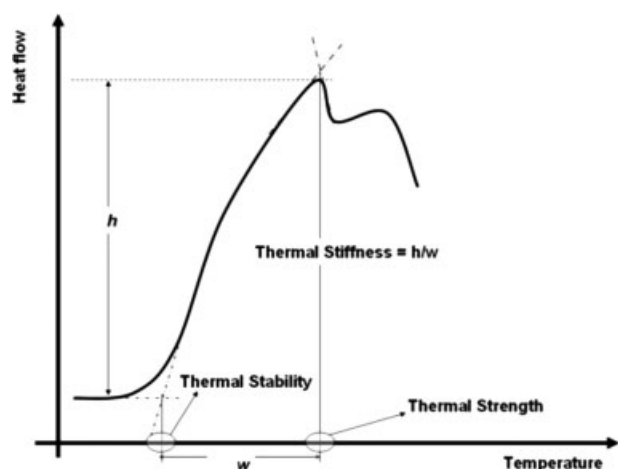


Figure 3 Schematic presentation of the thermal parameters proposed here.

Differential scanning calorimetry (DSC) model DSC-60 made by Shimadzu was used. Specimens of about 4 mg each were prepared out of the samples. Each specimen was prepared by “shaving” off a thin layer, less than 1 mm thickness, of the sample to minimize the thickness effect. Each specimen was put in an aluminum pan without being sealed then placed in the DSCs oven in air at atmospheric pressure. Specimens were heated at a constant heating rate until the 1st exothermic peak was completed, see Figure 1. To illustrate the effect of heating rates on the thermal profile, three heating rates were used, 1, 5, 25°C/min with the virgin PP-0 pellets. However, for the rest of the samples, only a heating rate of 5°C/min was utilized. Most samples were tested more than once. The numbers cited here are representative of the typical values.

RESULTS AND DISCUSSION

A thermal profile of PP-0 at a heating rate of 5°C/min is shown in Figure 2. The first endothermic peak at about 167°C is due to melting. From this endothermic peak valuable information about the polymer and its processing history could be deduced,¹³ but this will not be discussed here because it is out of the focus of this article. Our focus will be on the exothermic peak, which followed the melting peak, see Figure 1.

TABLE II
A Summary of the Thermal Parameters of PP-0 and PP-5

Sample	Thermal stability (K)	Thermal strength (K)	Thermal stiffness (W/g)/K
PP-0	508 ± 2	550 ± 4	90 ± 3
PP-5	506 ± 2	543 ± 3	85 ± 2

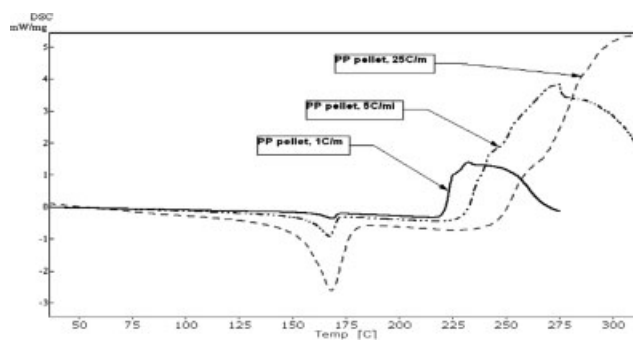


Figure 4 DSC thermographs showing the effect of heating rate.

When we interrupt the test in zones 1, 2, and 3, we noticed the development of polymer degradation in the aluminum pans as seen in Figure 2. The polymer in pan no. 3 is completely charred, whereas, the polymer in pan no. 2 has degraded outer edges, and the polymers in pan no. 1 was just slightly tinted. So, it is assumed that the polymer beyond zone no. 2, or the exothermic peak, is degraded, and considered thermally “failed.”

Three parameters are identified here: thermal stability, thermal strength, and thermal stiffness. Thermal stability is the onset temperature of the exothermic peak. It is comparable to, but not the same as, the oxidative induction temperature.* Thermal strength is the maximum temperature at the exothermic peak. If the exotherm has more than one peak, then the temperature of the 1st peak is considered the thermal strength as illustrated in Figure 3. Thermal stiffness is the virtual slope of the first peak. It is calculated by dividing the heat difference between thermal strength and thermal stability (h) by the temperature difference between thermal strength and thermal stability (w) as schematically shown in Figure 3. Table II lists these three thermal parameters for PP-0 and PP-5 at a heating rate of 5°C/min. This Table indicates, despite the small differences, that PP-0 has higher thermal parameters than PP-5. So, this thermal profile method was able to differentiate between two apparently similar PP products based on the three proposed thermal parameters. This difference in thermal parameters could be attributed to the difference of molecular weight between the PP samples as implied to by the different melt flow index (MFI) of PP-0 and PP-5.

The effect of heating rate on the thermal parameters is seen in the thermal profiles of PP pellets depicted in Figure 4. As the heating rate increased, the thermal stability and strength increased. A simi-

* The term thermal stability and not oxidative induction temperature will be used here to differentiate between both terms as the test procedures for obtaining each are not identical.

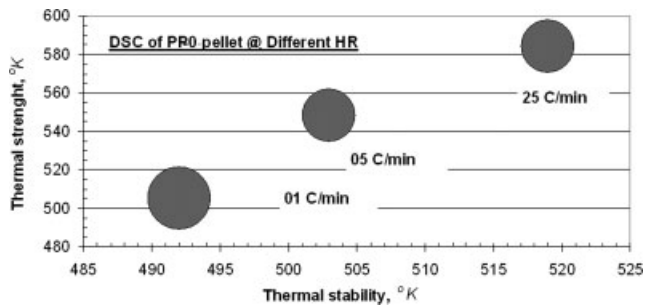


Figure 5 Effect of heating rate on thermal stability, strength, and stiffness of PP-0.

lar effect of straining rate on tensile strength is known. The effect of heating rate is presented schematically in Figure 5 where the bubble size indicates the thermal stiffness. At slower heating rate the specimen has more time to reach a specific thermal condition and it is heated more uniformly. This could explain the direct proportionality between the heating rate and thermal stability or strength. A similar relation between OIT and heating rate was reported in the literature.¹³ However, in the thermal profile method this relation was highlighted by the difference seen in the proposed parameters and by the shape of the curve instead of a single OIT point as traditionally done. This would give the researcher more confidence and a detailed analytical method than OIT to describe and understand the thermal performance of the sample.

Now, we turn our attention to the reprocessed samples. Again, the thermal profile method demonstrated to be effective in illustrating the difference between the thermal properties of PP-0 sample and reprocessed sample no. 5 as seen in Figure 6. The thermal stability, strength, and stiffness of virgin PP-0 are higher than those of sample no. 5. These lower parameters are indication of the thermal “degradation” of sample no. 5 and the depletion of the ther-

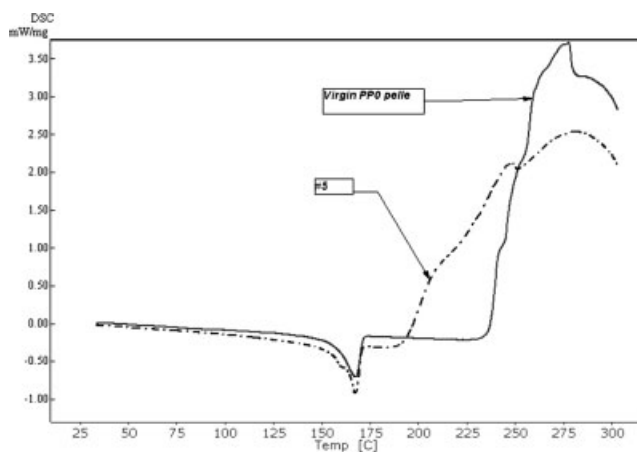


Figure 6 Thermal profile of virgin PP-0 and sample no. 5.

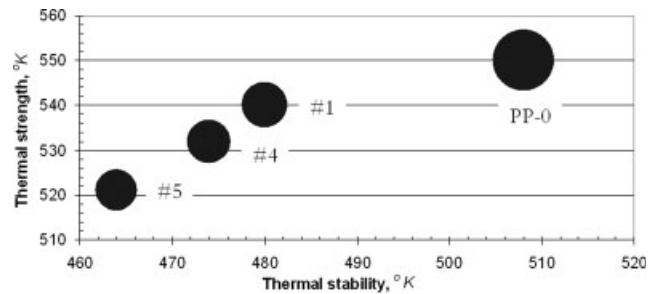


Figure 7 Thermal parameters of the reprocessed samples as compared to PP-0.

mal stabilizer due to multiple reprocessing. The reprocessing effect of samples nos. 1, 4, 5 and virgin PP-0 is compared in Figure 7. An immediate reduction in all of the thermal parameters of the reprocessed samples is readily noticed from Figure 7. The thermal stiffness of samples nos. 1, 4, and 5 were comparable to each other, but they were lower than that of PP-0. This could indicate that there is an initial depletion of the thermal stabilizer during the first processing scheme.

Finally, the thermal profile method was used to investigate a client complaint about the reclaimed pellets, sample RC. Recall that the client complained that RC pellets were processing like virgin PP and are giving the client problems during molding. The thermal profile of RC is shown in Figure 8. The first noticeable feature is that it has two melting peaks. The first melting peak was associated with HDPE melting and the second one was attributed to PP. Thus, sample RC is not reclaimed PP, but rather a blend of reclaimed PP and HDPE. Comparing the thermal stability, strength, and stiffness of RC to PP-0 showed other striking differences. Table III summarizes the thermal parameters of PP-0, RC, and HPDE. As Table III shows, all of the thermal parameters of RC are lower than those of PP-0 and even lower than those of virgin HDPE. The thermal profile of RC would suggest that the client would face

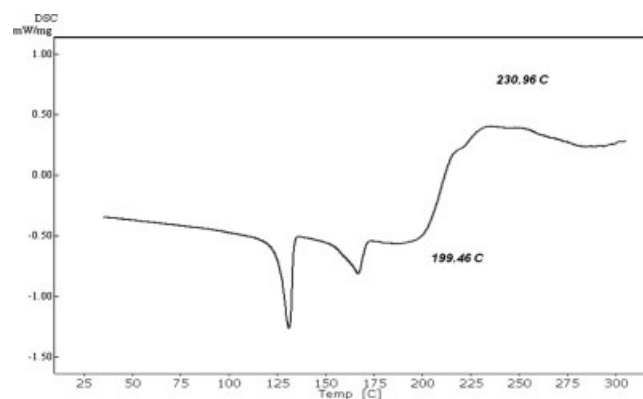


Figure 8 Thermal profile of reclaimed (RC) pellet.

TABLE III
A Summary of the Thermal Parameters of PP-0 and PP-5

Sample	Thermal stability (K)	Thermal strength (K)	Thermal stiffness (W/g)/K
PP-0	508 ± 2	550 ± 4	90 ± 3
RC	427 ± 2	489 ± 3	39 ± 3
HDPE	490 ± 1	510 ± 2	48 ± 2

three major problems during processing; (1) dealing with an inhomogeneous “blend,” (2) early melting of the HDPE portion of the RC pellets, and (3) lower thermal strength of RC, which is much lower than virgin PP-0 or HDPE. All these factors contributed to the problems that the customer was complaining about.

CONCLUSIONS

A novel look at a tradition method was proposed here to identify unique thermal parameters of polymers. This method is analogous to tensile test in that it generates a thermal profile of the polymer under investigation. From this thermal profile three parameters were identified; thermal stability, thermal strength, and thermal stiffness.

The proposed thermal parameters proved to be effective in differentiating between apparently similar polypropylenes. Thermal parameters were also used with success to study the reprocessing effects on PP, and to identify the source of an injection molding problem.

The proposed thermal profile and the deduced thermal parameters gave a fuller picture of the polymer thermal behavior than the traditional single-point tests, e.g., OIT, which are currently in use. It is proposed to use thermal stability, thermal strength,

and thermal stiffness to thermally differentiate between polymers. After standardizing this thermal profile method and the proposed thermal parameters, it is recommended to include these thermal parameters in datasheets similar to tensile strength and modulus of elasticity.

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