

Applications of Rheological Torque–Time Curves to the Study of Thermooxidative Degradation of Polypropylene Powder

Xiao Wang, Xiaoyun Chen, Wencan Yu, Yaodong Ji, Xiaobo Hu, Jiarui Xu

Key Laboratory for Polymeric Composite and Functional Materials of the Ministry of Education, Materials Science Institute, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China

Received 24 August 2006; accepted 24 August 2006

DOI 10.1002/app.26015

Published online 23 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The torque–time curves of polypropylene (PP) powder treated under various thermooxidative degradation conditions were obtained through processing in the mixing chamber of a rheometer. Meanwhile, the Fourier transform infrared (FTIR) spectra of the corresponding samples were determined, and the quantitative analysis of the carbonyl indices of the FTIR spectra of the samples of the PP powder was carried out to provide evidence for the rheological characterization. PP granules, to which an antideteriorant was added before they were commercially supplied so good antidegradation could be achieved, was investigated for the sake of contrast. The analysis of the experimental results showed that the height of the torque–time curve of the PP powder and the corresponding value of the equilibrium torque could be used to characterize or evaluate the variations of the thermooxidative degradation of the PP powder. Under the same processing conditions, the heights of the torque–time curves of the PP powder and the corresponding values of the equilibrium torque decreased with the enhancement of the thermooxidative degradation treatment before mixing; on the contrary, the heights and areas of the characteristic bands of the carbonyl groups in the FTIR spectra of the PP powder and the corresponding values of the carbonyl index increased. The quantitative analysis of the FTIR spectra provided evidence for the conclusion that the heights of the torque–time curves of the PP powder and the corresponding values of the equilibrium torque could be used to charac-

terize or evaluate the thermooxidative degradation of the PP powder. If the treatment under thermooxidative degradation conditions weakened or the degradation of the PP powder just began (i.e., in the viscosity range for processability), the evaluation method using the heights of the torque–time curves of the PP powder or the corresponding values of the equilibrium torque could provide more sensitivity than the method using the values of the carbonyl index. Consequently, the method using the heights of the torque–time curves to evaluate the thermooxidative degradation of the PP powder had its advantages. The application of the torque–time curves could be used to evaluate not only the variation of the thermooxidative degradation of the PP powder treated under aging conditions before mixing but also the variation of the degradation, including the mechanochemical degradation, of the PP powder during the period of mixing. The dependence of the variation of the degradation of the polymer on the processing time during mixing could be evaluated by the study of the variation of the torque–time curves. It can be concluded that the application of torque–time curves to the evaluation of degradation of PP powder has the advantages of being convenient, real-time, *in situ*, online, and production-oriented. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1316–1330, 2007

Key words: degradation; FT-IR; poly(propylene) (PP); rheology

INTRODUCTION

It is well known that polypropylene (PP) resin just produced directly out from polymerization reactors is in the form of a powder without any additives, including any antideteriorants. However, PP powder is rather easy to degrade because there are many tertiary C–H bonds in the main chain of the polymer.^{1–6}

Therefore, PP powder may age in several months in an ordinary environment and experience significant reductions in its mechanical properties.⁷ This means that it is rather difficult to store PP powder for a long period. For this reason, the commercial grades of PP resins are usually supplied as granules, which are manufactured with extrusion processing to add some antideteriorants as soon as the PP resins come out from the polymerization reactors.

The use of PP powder has some advantages in the research and industrial exploration of PP composites. For instances, using PP powder can lead to better dispersion of fibers or powdered fillers in the resin base than using PP granules in the extrusion technique for

Correspondence to: X. Wang (ceswx@zsu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50073030.

the preparation of short-glass-fiber- or powdered-filler-reinforced PP composites to obtain better mechanical properties.

Because the supply of PP powder is limited, ordinary plastic molding techniques, such as the extrusion technique and the injection-molding technique, use PP granules as raw materials in most cases, but some other plastic molding techniques need PP powder to manufacture PP composites. Long-glass-fiber-reinforced PP composites are ordinarily prepared by a press-molding technique. It is very difficult to use PP granules with this technique to achieve the necessary dispersion in the composite system. PP powder is also needed for manufacturing rotational-molding PP products.^{8,9}

This discussion shows that the study of the behavior of the degradation of PP powder in natural environments and in processing has great practical importance because this is the foundation of the research of methods for the antidegradation of PP powder. The study of the characteristics of the degree of degradation of PP powder is one of the important aspects of the study of the behavior of degradation of PP powder. To find a simple, easy, and processing-suitable method for the evaluation of the degree of degradation of PP powder is the essential requirement of this study.

The study of the degradation of PP is still a problem to be discussed, despite a lot of research.^{1-8,10-17} In this study, some new contributions are described. At the beginning, PP powder was used as the main kind of polymer studied, whereas PP granules were used as reference samples for the research. In previous studies of PP as a raw material, PP granules were often used, and some antideteriorants were added during the granulation process by extrusion before they were supplied as commercial products. Studies of the aging properties of the mechanical behavior of test samples prepared with injection-molding or other plastic-molding techniques have been reported in many publications. Comparatively, one of the characteristics of our work is the use of PP powder, to which no addition of antideteriorants or other additives was made. This is advantageous for avoiding the influence of antideteriorants for the investigation of the thermooxidative degradation of virgin PP.

Furthermore, rheological torque–time curves, which were obtained with a Haake Rheocord PolyLab (Gebr. HAAKE GmbH, Karlsruhe, Germany) 300p (RC300p) rheometer, were used for the study of the behavior of the thermooxidative degradation of PP powder for characterization and evaluation. Meanwhile, the quantitative analysis of the carbonyl index of the Fourier transform infrared (FTIR) spectra of PP powder under different thermooxidative degradation conditions gave further evidence for the rheological characterization. One of the purposes of the torque–

time curves of the Haake rheometer is to characterize the variations of the torque of the materials mixed in the chamber with respect to the processing time.^{18,19} If the mixing conditions, including the processing temperature, rotor speed, and loading amount, are kept stable, the torque is proportional to the apparent viscosity of the melting polymer.^{20,21} For this reason, the torque–time curve of the polymer is characteristic of its apparent-viscosity/time curve during the mixing period. According to the well-known rheology theory for a molten polymer, although the flow of the melting materials in the chamber is non-Newtonian, stable processing conditions may keep the shear rate of the flow constant so there exists a good increasingly progressive dependence of the apparent viscosity on the zero shear viscosity of the polymer. Under these conditions, the apparent viscosity can be used for the characterization or evaluation of the inherent viscosity of the polymer. In other words, the equilibrium torque can be used to evaluate the molecular weight of the polymer or to study the variation of the degradation, grafting, or crosslinking of the polymer. Although there have been some reports about this application, a quantitative analysis has not been performed.²⁰⁻²⁶ In our work, this principle was used to study the variation of the degradation of PP powder, along with a discussion of the quantitative analysis of the carbonyl index of the FTIR spectra.

Finally, the rheological evaluation method of this study, which was used for the characterization of the thermooxidative degradation of PP powder, has the advantages of being simple and easy to operate, convenient, real-time, *in situ*, online, and production-oriented and is especially suitable for testing a large number of samples and for industrial applications.

There have been many methods developed for the measurement, characterization, or evaluation of the degradation of PP, such as gel permeation chromatography (GPC),²⁷⁻³⁰ size exclusion chromatography (SEC),³¹⁻³⁶ capillary rheometry,^{30,37,38} Ubbelohde dilution viscosimetry,^{39,40} FTIR spectroscopy,^{22,27-29,31-36,39-41} FTIR emission spectroscopy,⁴² chemiluminescence (CL) measurements,^{27,39,43,44} differential scanning calorimetry (DSC),^{40,45,46} thermogravimetric analysis (TGA),^{22,41,43} and mechanical property determination.^{31,32,34} Every individual method has its own characteristics and is used for different research purposes.

GPC and SEC are the methods used to measure the number-average molecular weight and weight-average molecular weight of the polymer directly. Ubbelohde dilution viscosimetry is used to measure the viscometric average molecular weight of the polymer directly. All of them are basic, essential, and very important methods for measuring the changes in the molecular weight of PP with degradation. This is their advantage. Unfortunately, PP is a kind of polymer

difficult to dissolve. It is very difficult to find a suitable solvent to dissolve a PP resin at room temperature. To measure the molecular weight of PP by these methods, a high operating temperature above 130°C is needed, and a special solvent rather disadvantageous to human health must be used that leads to hard operating conditions and a relatively high cost. These measurement methods are probably unsuitable for situations that require a fast and convenient operation, a simple and easy-to-operate treatment, and a great number of test samples.

Capillary rheometry is a rheological method by which the melt viscosity of the polymer is measured to calculate the molecular weight based on the principle that there is a good quantitative functional relationship between the melt viscosity and the molecular weight of the polymer. This method can measure the apparent melt viscosity of the polymer over a wide range of shear rates to calculate the zero shear viscosity and furthermore to determine the viscometric average molecular weight. It is a good method for commercial-grade PP granules to which an antioxidant has been added. However, it is rather disadvantageous for PP powder without the addition of any antioxidant. In fact, during the measurement of the capillary rheometry, the test sample must be preheated for a rather long time to achieve an isothermal equilibrium. It should not be ignored that the thermooxidative degradation of PP powder may take place during this rather long preheating time. This may significantly reduce the precision of the measurement. In addition, it needs a number of test samples to obtain a series of data to calculate a single value of the zero shear viscosity and of the molecular weight. Therefore, this measurement method is probably unsuitable for situations that need a fast and convenient operation, a simple and easy-to-operate treatment, and a great number of test samples, too. For this reason, there are few reports in the literature on using capillary rheometry to measure the molecular weight. For example, although capillary rheometry is reported in ref. 30, it was used to study the processing performance of the polymer, whereas the method used for measuring the molecular weight was still GPC.³⁰

FTIR, CL measurements, and TGA determine the pyrolysis products to characterize and evaluate the degradation of PP. The advantage of these methods is that the variation of the side groups and the end groups of the main chain of the polymer can be studied through the measurement of the pyrolysis products of degraded PP. FTIR can provide the increases in both the carbonyl groups and hydroxyl groups in the aged polymer. CL measurements can determine the product of the radicals during oxidation. TGA can measure the tiny variation of gravity of the sample caused by the reactions with oxygen. In particular,

FTIR emission spectroscopy, a new measuring method developed in recent years, is characteristic of real time by strongly heating the test sample, such as PP powder, which is generated under this condition to produce an infrared emission itself, not to reflect or to absorb from the outer infrared radiation as ordinary FTIR spectroscopy does, to avoid the preparation step of test films.⁴² All these methods have been widely used, especially for studies of the whole degradation process of PP. In addition, FTIR spectroscopy can also give a half-quantitative measurement. Moreover, the disadvantage of these methods is that they are poorly sensitive at the beginning of the oxidation degradation. This is because a considerable number of the pyrolysis chemical groups must be produced to obtain sufficient precision of the individual method, but a tiny number of the pyrolysis chemical groups produced in the beginning might cause a considerable reduction of the molecular weight of the polymer. For instance, in the determination of FTIR, the carbonyl groups, the increase of which is characteristic of the appearance of the oxidative degradation of the main chains of PP, decrease at the moment of rupture of the main chains, but one rupture of a main chain merely produces one carbonyl group so the increase in the percentage of the carbonyl groups is less than 1% for the degree of polymerization of an ordinary polymer, which is far more than 100, whereas at this moment, the number-average molecular weight of the polymeric chain discussed may be reduced to 50% because one chain of the polymer has become two chains. Correspondently, the viscosity of the polymer may significantly decrease. It can be deduced from this that the processing performances and mechanical properties of PP powder without any antioxidant might significantly be reduced in the initial stage of oxidative degradation with a tiny corresponding increase in the carbonyl groups.

Both CL measurement and TGA are similar to FTIR. In fact, CL measurement determines the oxidative degradation by detecting the radicals produced during the oxidation, but one radical may generate a number of rupture reactions, so oxidative degradation reactions are chain reactions. The measurement of the variation of the amount of oxygen by TGA, which is used to characterize the oxidative degradation, is just an indirect detection of the radicals produced during the oxidation. It can be seen from this that all these methods have their disadvantages for the study of the initial stage of degradation of PP. Additionally, no advantages of being convenient, *in situ*, online, and production-oriented can be obtained with these methods.

DSC has been widely used to study the variation of the crystallization of PP during pyrolysis.⁴⁰ It is also used for the measurement of the oxidation induction time to characterize and evaluate the efficiency of

antioxidants added.⁴⁵ Even a typical testing method is described in the ASTM D 3895 standard.⁴⁶ However, this method is significantly different from the weathering process because oxygen flow is used and the treatment temperature is close to the melting point for the purpose of shortening the testing time.

Mechanical properties can be used to evaluate the degradation of PP films, too. For example, the ultimate tensile elongation can be used to characterize the embrittlement of PP films caused by oxidation, but this method is indirect.

There is no doubt that all these methods have been widely used in scientific study and practical production. Each has its own advantages and disadvantages. The application of torque–time curves for the characterization and evaluation of the degradation of PP is used only in addition and for improvement, not as a replacement for these conventional methods. This method is based on the principle of rheology, using the equilibrium torque to characterize the melt viscosity of the polymer and furthermore to evaluate the magnitude of the molecular weight. As mentioned previously, the use of the viscosity can provide relatively high sensitivity for the determination in the initial stage of the degradation of the polymer. Therefore, this method is especially suitable for PP powder without the addition of any antioxidant, resulting in easy degradation. Additionally, real-time and online measurement is carried out during the mixing process. Furthermore, the RC300p rheometer can simulate the main plastic-molding processes, such as press molding, extrusion, and injection, through the study of the rheological parameters, so this method has the advantage of being production-oriented. Also, it has the advantages of a fast and convenient operation, a simple and easy-to-operate treatment, and suitability for a great number of test samples.

Some qualitative rheological analysis has been reported to describe the variation of the degradation of polymers and their blends.²² Our study provided a quantitative and detailed analysis of the application of torque–time curves to the characterization and evaluation of the degradation of PP by bringing FTIR analysis into evidence.

The study presented in this article is characterized by the use of PP powder as a raw material to which no additives, especially antideteriorants, were added and by the application of the torque–time curve to evaluate the variation of the thermooxidative degradation of PP powder. The natural environmental degradation of PP powder at room temperature was simulated with experimental treatments under the conditions of thermooxidative degradation at various temperatures and for various times according to the time–temperature equivalent principle. Samples of PP powder under different treatment conditions of thermooxidative degradation were processed in the

mixing chamber of a RC300p rheometer to obtain the torque–time curves. Additionally, tests of FTIR spectra of the corresponding samples of PP powder were carried out, and the values of their carbonyl indices were calculated. The dependence of the heights of the torque–time curves on the values of the carbonyl index was examined to develop a quantitative method for the characterization or evaluation of the degradation of PP powder. PP granules, to which an antideteriorant was added before it was commercially supplied so good antidegradation would be achieved, was investigated for the sake of contrast.

EXPERIMENTAL

Materials

The PP powder (F401), which was isotactic PP taken directly from the reactor during production, was supplied by the Sinopec Guangzhou Petrochemical Complex (Guangzhou, China). The PP granules employed in this study, which were also isotactic PP, were a commercial grade (CLS700) from the Guangzhou Yinzhu Chemical Engineering Plant (Guangzhou, China).

Thermooxidative degradation of PP powder and PP granules

The thermooxidative degradation of PP powder and PP granules was performed in a DHG-9146A thermooxidative aging oven (Jinghong Experimental Apparatus Co. Ltd., Shanghai, China) at a definite treatment temperature and for a definite treatment time; these values are mentioned in the following discussion.

Determination of the torque–time curve

An RC300p system (equipped with a Rheomix 600p mixer for mixing or blending, Gebr. HAAKE GmbH, Karlsruhe, Germany) was used for the mix of materials and the measurement of their rheological properties and especially for the determination of the torque–time curves. All the processing conditions were kept constant, with a feed amount of 45 g, a processing temperature of 190°C, a rotor speed of 60 rpm, and a processing time of 20 min.

Characteristics of the infrared spectroscopy

FTIR spectra were recorded on a Nexus 670 FTIR analyzer (GMI, Inc., Ramsey, MN) with a resolution of 2 cm⁻¹. PP powder or PP granules treated under various conditions of thermooxidative degradation were thermopressed to prepare sample films for the determination of FTIR spectra. The sample films were

made with an XLB-D press (Hongtu Machinery Co. Ltd., Huzhou, Zhejiang, China) at a pressing temperature of 190°C, for a pressing time 2 min, and at a pressure of 10 MPa. The thickness of the films was controlled to be about 80 μm .

The values of the carbonyl index of the corresponding samples were calculated according to the characteristic bands of the FTIR spectra.^{2,22,38,39}

To study the thermooxidative degradation of the PP powder, the main characteristic bands of FTIR were the carbonyl group (C=O) stretching band in the range of 1659–1815 cm^{-1} and the hydroxyl group (O–H) stretching band in the range of 3248–3662 cm^{-1} .^{2,22,38–40,47–49} This study used only the carbonyl group (C=O) stretching band as the characteristic band. In the calculation of the values of the carbonyl index in our study, a reference band of the FTIR spectrum of a sample film located at 2722 cm^{-1} was used. Four samples of the films for each degradation condition of the PP powder were examined for the records of the FTIR spectra. Then, the mean of the four values of the carbonyl index of the individual sample film was calculated to indicate the carbonyl index of the PP powder for each thermooxidative degradation condition.

RESULTS AND DISCUSSION

Torque–time curves of PP powder treated under the conditions of thermooxidative degradation

The first goal of our research was to develop a rheological method to characterize or evaluate the variation of the degradation of PP powder through the study of the torque–time curves of PP powder treated under various conditions of thermooxidative degradation and through the quantitative investigation of the relationship between the variations of the torque–time curves and the corresponding equilibrium torques and those of aging degradation.

According to Goodrich and Porter,^{20,21} if all the experimental conditions, including the processing temperature, the rotor speed, and the polymer, are kept constant, the torque of the mixer is proportional to the apparent melt viscosity of the melt fluid in the mixing chamber because under this condition the shear rate may be kept constant, so it can be used to indicate the flowability of the fluid. Under this condition, the variation of the apparent melt viscosity of the melt fluid indicates the variation of the molecular weight of the polymer. The greater the apparent viscosity is of the fluid, the greater the molecular weight is of the polymer.^{20–26} This means that the apparent viscosity of the fluid in the mixing chamber can be used to evaluate the variations of the thermooxidative degradation of the PP powder in our study for aging degradation. If the apparent viscosity decreases, the degree of degradation of the PP powder should increase.

The premise of the aforementioned conclusion is that all the processing conditions, especially the shear rate of the fluid, must be kept quite stable for the non-Newtonian flow of the melt polymer. Even if the samples are the same kind of polymer, the differences of production companies or production standards may cause differences in the rheological behavior of the polymer fluids because the samples may have different molecular weights and different molecular weight distributions.

In this study, PP powder supplied by the same production company using the same production standards and same batches were treated under various thermooxidative degradations to obtain a number of samples with different molecular weights, which were used for the study of the rheological characteristics.

It is evident that there are many tertiary C–H bonds on the main chain of PP, which easily cause degradation through the action of thermooxidation. PP powder has a low ability for antidegradation with no addition of antioxidants, so it is easy to age in a natural environment.

According to the time–temperature equivalent principle, the aging of PP powder in a natural environment can be simulated through experimental tests in an aging oven with an increase in the treatment temperature to shorten the observation time greatly.^{50,51}

Figure 1 shows the graph of the rheological torque–time curves of PP powder under various thermooxidative degradation conditions. Figure 1(a) provides a full-scale image of the curves to show their feeding peaks. However, to distinguish the curves clearly in the range of the equilibrium torque, the scale range of the torque axis of Figure 1(b) had to be limited to 10 N m, whereas the feeding peaks of the curves were out of sight. This means that the images of the parts of the curves in the range of the equilibrium torque were enlarged in Figure 1(b) compared with those in Figure 1(a).

As shown in Figure 1, all the curves had similar shapes. For example, there was a feeding peak in the individual curve, and all the curves sloped gently after the feeding peak to end with a small decrease.

The difference of the curves was that the heights of the curves, which were the values of the equilibrium torques of the curves, apparently after their feeding peaks varied, depending on the different conditions of thermooxidative degradation.

The variations of the heights of the curves, depending on the treatments of the PP powder under different conditions of thermooxidative degradation, are shown in Figure 1. Curve 1 is the torque–time curve of the PP powder without any aging treatment, used as a blank testing curve; it is the highest of all the curves. The other curves are for the PP powder treated under various conditions of thermooxidative degradation. All are below curve 1. The conditions of

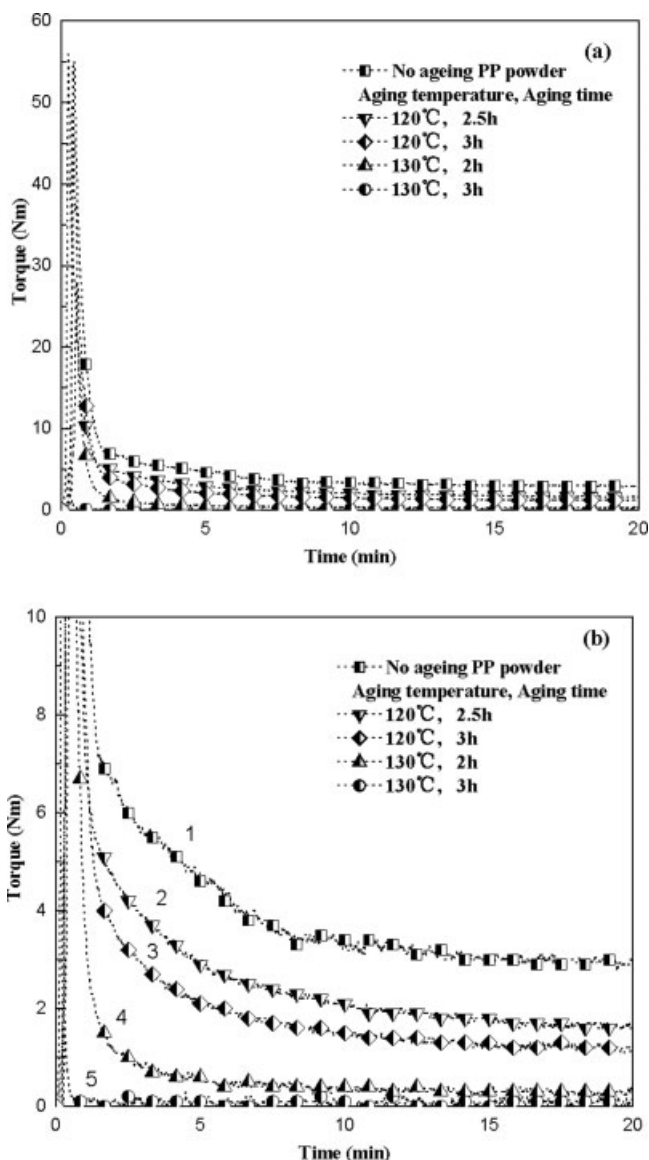


Figure 1 Graph of the rheological torque–time curves of PP powders under various thermooxidative degradation conditions: (1) no aging, (2) 120°C for 2.5 h, (3) 120°C for 3 h, (4) 130°C for 2 h, and (5) 130°C for 3 h.

thermooxidative degradation of curve 2 were 120°C and 2.5 h. These were the weakest conditions of thermooxidative degradation. Curve 3 had somewhat stronger conditions, that is, 120°C and 3 h, than curve 2 because although the treatment temperature was the same, the treatment time increased a little. The condi-

tions of thermooxidative degradation of curve 4 were 120°C and 3 h. Despite the decrease in the treatment time compared with that of curve 3, the treatment temperature rose by 10°C. According to an Arrhenius formula, the reaction rate can usually rise 2–4 times when the reaction temperature increases by 10°C, so the conditions of thermooxidative degradation of curve 4 were stronger than those of curve 3.⁵² Curve 5 had the strongest conditions of thermooxidative degradation of all the curves because its treatment conditions were 130°C and 3 h, that is, the highest treatment temperature and the longest treatment time.

Figure 1 shows that the treatments of the PP powder under the conditions of thermooxidative degradation might cause the entire torque–time curves to decrease. The height of curve 2 was significantly lower than that of curve 1, the blank testing curve, during the whole processing time. Although the conditions of thermooxidative degradation were not too strong, the degree of degradation of the treated PP powder increased significantly because no antideteriorants were added to the polymer before treating.

Table I lists the corresponding torques of the torque–time curves of the PP powder under different thermooxidative degradation conditions at processing times of 5 and 10 min, which could be used as the equilibrium torques of the torque–time curves of the PP powder because in this range of processing times the curves became quite even. As shown in Table I, the torque of the torque–time curve of the PP powder without any degradation treatment, which was used as a blank testing curve (curve 1), was 4.7 N m at 5 min and 3.3 N m at 10 min. They were higher than those of curve 2, whose treatment conditions of thermooxidative degradation were 120°C and 2.5 h. In fact, the torque of curve 2 at 5 min of processing was 3.0 N m, which was significantly lower than that of curve 1 (the difference was 1.7 N m), whereas the torque of curve 2 at 10 min was 2.1 N m, which was significantly lower than that of curve 1 (the difference was 0.9 N m), too.

As mentioned previously, the same processing conditions were used in the mixing process, so the torque of the fluid in the mixing chamber was related only to the viscosity of the polymer. This suggested that the viscosity of the melt fluid should be related only to the molecular weight of the polymer. In other words, the greater the molecular weight was, the greater the

TABLE I
Variations of the Equilibrium Torques of the Torque–Time Curves of PP Powders Under Different Thermooxidative Degradation Conditions

Curve	1	2	3	4	5	
Conditions of thermooxidative degradation	No ageing	120°C for 2.5 h	120°C for 3 h	130°C for 2 h	130°C for 3 h	
Equilibrium torque (N m)	5 min	4.7	3.0	2.1	0.6	0.1
	10 min	3.3	2.1	1.5	0.4	0.1

viscosity was. Therefore, it could be deduced that the rise of the molecular weight and the rise of the viscosity could increase the equilibrium torques and the heights of the torque–time curves. The decrease in the height of curve 2, shown in Figure 1, and the decrease in the equilibrium torque, shown in Table I, compared with those of curve 1 meant that significant degradation of the PP powder took place with the decrease in the molecular weight after the treatment under the degradation conditions of 120°C and 2.5 h.

Moreover, curve 2 kept a definite value of the equilibrium torque despite a significant decrease in its height. This means that the melt fluid of the treated polymer still demonstrated a definite viscosity, so it kept a relatively large molecular weight. In other words, the PP powder treated under the conditions of thermooxidative degradation was still a polymeric material. This fact supported the generally acknowledged theory of the thermooxidative degradation of PP.^{1–6,10,53} According to the theory, during the process of thermooxidative degradation, the main chains of PP are interrupted into relatively small polymer chains, which still have definite molecular weights, so the degraded product is still a polymer, regardless of the decrease in the molecular weight. This differs from the mechanism of decomposition of poly(vinyl chloride), which decomposes into monomers directly, escaping in a gas state immediately.

The conditions of the thermooxidative degradation of curve 3 were 120°C and 3 h. They were stronger than those of curve 2. Consequently, the degree of degradation of the treated polymer of curve 3 increased and led to a further decrease in the height of the torque–time curve. As can be seen in Figure 1, the height of curve 3 was lower than that of curve 2. Table I provides the same explanation. The torque of curve 3 (120°C and 3 h) at 5 min was 2.1 N m, which was lower than that of curve 2 (the difference was 0.9 N m). In comparison with curve 1 (no aging treatment), the torque of curve 3 (120°C and 3 h) at 5 min was much lower (the difference was 2.6 N m). Similarly, the torque of curve 3 at 5 min was 1.5 N m, which was lower than that of curve 2 (the difference was 0.6 N m) and much lower than that of curve 1 (the difference was 1.8 N m).

Raising the treatment temperature can effectively enforce thermooxidative degradation. The treatment temperature of curve 4 was raised from 120 to 130°C, and then more significant degradation was achieved than that found with curve 3, even though its treatment time (2 h) was shorter than that of curve 3 or curve 2. Figure 1 shows that the height of curve 4 was not only much lower than that of curve 1 but also significantly lower than that of curve 2 or curve 3. As shown in Table I, the height of curve 4 was very low because the torque of curve 4 at 5 min of processing was 0.6 N m and at 10 min was 0.4 N m.

Curve 5 is the torque–time curve of the sample of PP powder treated under the strongest conditions of thermooxidative degradation (120°C and 3 h) of all the samples of PP powder investigated. Therefore, the degree of degradation of the sample of PP powder of curve 5 was the greatest, whereas the height of the torque–time curve was the lowest. Figure 1 shows that the height of curve 5 was very low and nearly at the abscissa. Additionally, Table I shows that the values of the torque of curve 5 both at 5 min and at 10 min were 0.1 N m, being close to zero.

In a word, Figure 1 and Table I show that under the same processing conditions, including the same feed amount, same rotor speed, same processing temperature and same kinds of the materials processed, the height of the torque–time curve and the value of the equilibrium torque at the same processing time gradually decreased according to the enforcement of the conditions of thermooxidative degradation of PP powder treated before mixing.

This discussion means that under definite conditions or, more exactly, under the same processing conditions, including the same feed amount, same rotor speed, same processing temperature, and same kinds of materials processed, the height of the torque–time curve and the equilibrium torque at the same processing time could be used to evaluate the degree of degradation of the polymer mixing in the chamber of the rheometer. The stronger the thermooxidative degradation conditions were for the treatment of the PP powder, the smaller the height of the torque–time curve and the corresponding value of the equilibrium torque were.

It must be pointed out that the premise of the evaluation method, that is, the use of the same processing conditions, is essential.

The fact that all the curves in Figure 1 have definite heights means that although most of the samples of PP powder were degraded, each sample of the treated PP powder still had a definite value of the viscosity, so all of them were still polymers.

The height of the individual curves in Figure 1 gradually decreased during the whole mixing process, whereas the torques were different at different points of the processing time. This can be explained as follows: degradation, including not only the thermooxidative degradation mentioned previously but also the mechanochemical degradation caused by the mechanical action of the rotors during mixing, of PP powder to which no antideteriorants were added still took place during the mixing in the chamber at the melting point.

It can be concluded from the discussions that the torque–time curves of polymers could be used to evaluate the degree of thermooxidative degradation. This method has the advantages of a fast and convenient operation and a simple and easy-to-operate treat-

ment and is especially suitable for industrial production research because the determinations are carried out in a rheometer and also in real time and on line. The real-time degradation of PP powder with the passage of time during the mixing process can be observed by the variation of the torque–time curves. It is difficult to do this with other methods.

Characteristics of FTIR spectra of PP powder treated under the conditions of thermooxidative degradation

To obtain further evidence for the conclusions, the characteristics of the FTIR spectra of samples of PP powder treated under various conditions of thermooxidative degradation were determined, and a quantitative analysis of the values of the carbonyl index of the corresponding FTIR spectra was carried out.

Figure 2 shows that the variations of the characteristic bands of the carbonyl groups in the FTIR spectra of PP powder under different thermooxidative degradation conditions (from 750 to 1900 cm^{-1}).

Spectrum 1 in Figure 2 is the FTIR spectrum of virgin PP powder without any aging treatment for the purpose of a blank test. Spectrum 5 is the FTIR spectrum of PP powder treated under the strongest conditions of thermooxidative degradation of all the samples (130°C and 3 h). Figure 2 shows that there is a strong absorption band ranging from 1659 to 1815 cm^{-1} in spectrum 5, which is the carbonyl group (C=O) stretching band. Comparatively, there is a tiny absorption that is rather difficult to find in the same range of spectrum 1. This means that great degradation of the PP powder treated under the

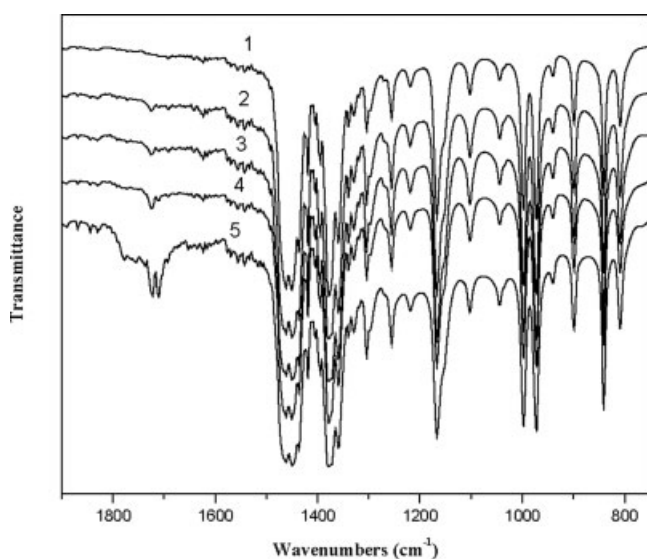


Figure 2 Variations of the characteristic bands of the carbonyl groups in the FTIR spectra of PP powders under different thermooxidative degradation conditions: (1) no aging, (2) 120°C for 2.5 h, (3) 120°C for 3 h, (4) 130°C for 2 h, and (5) 130°C for 3 h.

strong conditions of thermooxidative degradation took place for spectrum 5, whereas little degradation of the virgin PP powder without any aging treatment took place for spectrum 1. As shown in both Figures 1 and 2, the sample with little absorption of the carbonyl group (C=O) stretching band produced a high torque–time curve, whereas the sample with strong absorption of the carbonyl group stretching band gave a low torque–time curve. Therefore, the experimental results of the FTIR spectra supported the conclusion of rheological behavior.

Spectrum 2 is the one of the PP powder treated under the weakest condition of thermooxidative degradation of all the samples (120°C and 2.5 h). Figure 2 shows that a little absorption of the carbonyl group stretching band took place. Meanwhile, the treatment conditions of the thermooxidative degradation of PP powder for spectrum 3 were rather stronger than those for spectrum 2, so a significant absorption band could be observed. For spectrum 4, the treatment conditions (130°C and 2 h) were stronger than those of spectra 2 and 3, so the absorption area of the corresponding stretching band was greater than those of the two spectra, but it was weaker than that of spectrum 5, so the absorption area was not greater than the area of that one.

In summary, it can be concluded that with the gradual enforcement of the treatment conditions of thermooxidative degradation, the degree of absorption of the carbonyl group stretching band gradually increased and the height of the corresponding torque–time curve gradually decreased.

Furthermore, a quantitative analysis of the carbonyl index of the FTIR spectra of the samples of PP powder was carried out to confirm these conclusions. The variations of the values of the carbonyl index of the FTIR spectra of PP powder under different thermooxidative degradation conditions are shown in Table II.

The carbonyl index for the sample of virgin PP powder, which was not treated under any conditions for degradation, was 0.20, that is, the smallest. The carbonyl index for the sample of PP powder under the conditions of thermooxidative degradation with a processing temperature of 120°C and a processing time of 2.5 h was 0.22, showing a very small increase. This meant that little degradation had taken place. Degradation at 120°C for 3 h gave a carbonyl index for the treated PP powder of 0.27, which showed that a little degradation had taken place but still not much. The sample of PP powder treated at 130°C for 2 h degraded rather seriously because its carbonyl index went up to 0.47. The greatest value of the carbonyl index of all those shown in Table II was that of the PP powder treated at 130°C for 3 h. Table II shows that its carbonyl index jumped to 1.98, indicating very serious degradation.

TABLE II
Variations of the Carbonyl Indices of the FTIR Spectra of PP Powders Under Different Thermooxidative Degradation Conditions

Spectrum	1	2	3	4	5
Conditions of thermooxidative degradation	No aging	120°C for 2.5 h	120°C for 3 h	130°C for 2 h	130°C for 3 h
Carbonyl index	0.20	0.22	0.27	0.47	1.98

The quantitative analysis of the carbonyl index confirmed the rheological conclusions. In fact, the enforcement of the conditions of thermooxidative degradation caused the rise in the degree of degradation of the PP powder, providing for the evidence for the increase in the corresponding value of the carbonyl index. This could explain why both the height of the torque–time curve shown in Figure 1 and the values of the equilibrium torque shown in Table I gradually decreased with the enforcement of the treatment conditions.

Further discussions about the equilibrium torque and carbonyl index

If a careful observation of both Tables I and II is made, we can found that although the increase in the carbonyl index corresponded well to the decrease in the equilibrium torque with the enforcement of the treatment conditions of thermooxidative degradation, their relative rates were not the same. For instance, the difference between the value of the equilibrium torque of curve 1 and that of curve 2 was rather large, reaching 1.7 N m, as shown in Table I; on the contrary, the difference between the carbonyl index of spectrum 1 and that of spectrum 2 was very small because it was only 0.02, as shown in Table II.

To carry out a detailed analysis, the concept of the decreasing rate of the equilibrium torque and the concept of the increasing rate of the carbonyl index are now introduced.

Let M_1 be the equilibrium torque of curve 1 (at 5 or 10 min), which is the torque–time curve of the PP powder without any aging treatment and is used as a blank testing curve, and let M_i be the equilibrium torque of curve i (at 5 or 10 min), which is the one of the PP powders treated under definite conditions of thermooxidative degradation:

$$m_d = \frac{M_1 - M_i}{M_1} \quad (1)$$

where m_d is the decreasing percentage of the equilibrium torque, indicating the decreasing rate of the equilibrium torque of curve i against that of curve 1.

Similarly, let C_1 denote the carbonyl index of spectrum 1, which is the graph of the spectrum of the PP powder without any thermooxidative degradation treatment and is used as a blank testing spectrum graph, and let C_i denote the carbonyl index of spectrum i , which is the one of the PP powder treated under definite conditions of thermooxidative degradations:

$$c_r = \frac{C_i - C_1}{C_1} \quad (2)$$

where c_r is the increasing percentage of the carbonyl index, indicating the increasing relative rate of the carbonyl index of spectrum i against that of spectrum 1.

The decreasing percentages of the equilibrium torques of the torque–time curves of PP powder under different thermooxidative degradation conditions obtained from the calculation with eq. (1) are shown in Table III.

The increasing percentages of the carbonyl index in the FTIR spectra of PP powder under different thermooxidative degradation conditions obtained from the calculation with eq. (2) are shown in Table IV.

It appears from a study of Table III that the value of the decreasing percentage of the equilibrium torque at 5 min of processing was basically the same as that at 10 min for all the curves listed. For example, curve 2 gave a decreasing percentage of the equilibrium torque of 36% at 5 and 10 min of processing. Only curve 4 gave a tiny variation with 87% at 5 min and 88% at 10 min. Apparently, all the curves have the same variation tendency. This means that as long as the

TABLE III
Variations of m_d of the Torque–Time Curves of PP Powders Under Different Thermooxidative Degradation Conditions

Curve	1	2	3	4	5
Conditions of thermooxidative degradation	No aging	120°C for 2.5 h	120°C for 3 h	130°C for 2 h	130°C for 3 h
m_d (%)					
5 min	0	36	55	87	97
10 min	0	36	55	88	97

TABLE IV
Variations of c_r in the FTIR Spectra of PP Powders Under Different Thermooxidative Degradation Conditions

Spectrum	1	2	3	4	5
Conditions of thermooxidative degradation	No aging	120°C for 2.5 h	120°C for 3 h	130°C for 2 h	130°C for 3 h
c_r (%)	0	10	35	135	890

processing conditions are kept stable, the equilibrium torque of the individual curve could be used to characterize the variation of the viscosity of the fluids or to evaluate the molecular weight and the degree of degradation of the polymers.

Table III further reveals that although the conditions of thermooxidative degradation of curve 2 were rather weak (120°C and 2.5 h), the decreasing percentages of the equilibrium torque at 5 and 10 min of processing were rather significant, reaching 36%. In fact, both decreasing values of the equilibrium torque were 1.7 N m, as shown in Figure 1 and Table I. Comparatively, the corresponding increasing percentage of the carbonyl index was rather small, merely 10%, as shown in Table IV.

Similarly, even though the conditions of thermooxidative degradation of curve 3 were still relatively weak (120°C and 3 h), the decreasing percentages of the equilibrium torque at 5 and 10 min of processing were so great that they reached up to 55%, as shown in Table III. Figure 1 and Table I show that both decreasing values of the equilibrium torque were 2.6 N m. However, although the corresponding increasing percentage of the carbonyl index was relatively large (35%), as shown later in Figure 4, it was still rather small in comparison with the situation of the equilibrium torque.

Therefore, when the treatment conditions of thermooxidative degradation were relatively weak or when the action of thermooxidation of the treated PP powder just began with little degradation, the evaluation of the degree of degradation of the polymer with the heights of the torque–time curves or the corresponding values of the equilibrium torques was more sensitive than that using the corresponding values of the carbonyl index. As a result, the method of evaluating the degradation of PP powder with the torque–time curves has the advantage of high sensitivity at a low degree of degradation.

This situation can be explained by the mechanism of the degradation of PP.^{1–6,10,53} When PP powder is degraded, the main chains of PP do not decompose into monomers directly; they are interrupted into relatively small main chains of PP, usually forming carbonyl groups on the terminals. It can be seen from a simple calculation that one interruption of a main chain of PP could produce one carbonyl group at most. This number is much smaller than that of the chain element of the whole main chain, so the increas-

ing percentages of the carbonyl index are small at the beginning of the degradation, giving a small carbonyl group band characteristic of the FTIR spectrum.

On the other hand, the rupture of a main chain of the polymer might cause a great variation of its molecular weight. In fact, the average molecular weight of the main chain after rupture might decrease to 50%. In other words, if the number of carbonyl groups merely increases by less than 1% of the number of chain elements of the whole main chain, the average molecular weight of the main chain ruptured might fall down by half. This is a big change. It can be concluded that a tiny variation of the carbonyl index might cause a great variation of the molecular weight at the beginning of the degradation.

Consequently, it is rather difficult to use the carbonyl index to characterize the beginning of thermooxidative degradation because of its poor sensitivity. Moreover, the method of using the torque–time curve has its advantages at this time. If the processing conditions are kept stable, the variation of the height of the torque–time curve (or the value of the equilibrium torque) depends merely on the variation of the viscosity and, furthermore, the molecular weight of the polymer. When the treatment conditions of the thermooxidative degradation are rather weak, or the degradation just begins, despite a tiny variation of the carbonyl index, the molecular weight of the polymer may decrease significantly and cause a decrease in the viscosity of the fluid, producing a significant decrease in the height of the torque–time curve and in the equilibrium torque.

When the treatment conditions of the degradation of PP powder are rather strong, or the degradation continues to reach a definite degree, the sensitivity of the method using the carbonyl index may be improved to give a significant variation. At this time, this method can be used to evaluate the degree of degradation. This can be seen in Table IV. The relatively strong treatment conditions of the degradation of PP powder could give rather large values of the increasing percentage of the carbonyl index. For instance, the increasing percentage of the carbonyl index of spectrum 4 (130°C and 2 h) reached 135%, whereas that of spectrum 5 (130°C and 3 h) jumped up to 890%. Meanwhile, the corresponding torque–time curves decreased so much that both curve 4 and curve 5 got close to the abscissa because the molecular weights of the treated PP powder decreased

greatly and led to the values of the melt viscosity of the fluids becoming very small.

From the perspective of polymer processing, the fact that the equilibrium torques of both curve 4 and curve 5 got close to zero means that at this time the processing properties of the polymers had become poor. In a mixing process, a very low equilibrium torque of the polymer might cause poor mixing efficiency because a definite viscosity is needed. Similarly, the extrusion process and injection process need a definite viscosity for normal processing. Therefore, the processing properties of the degraded polymers indicated by both curve 4 and curve 5 were poor for these conventional plastic processing methods.

It can be seen from this discussion that within the range of viscosities of processability, using the equilibrium torque of the torque–time curve to evaluate the thermooxidative degradation of PP powder is more sensitive than using the carbonyl index of FTIR. As soon as the carbonyl groups propagate to such a high level that they can be significantly detected by FTIR spectroscopy, the processing properties of the degraded polymer become rather poor for ordinary plastic processing methods. Tables III and IV show the functional relationship between m_d for the torque–time curves of varieties of PP powder under different thermooxidative degradation conditions and c_r in the FTIR spectra of the corresponding ones. Also, the two tables show the functional relationship between the viscosity of varieties of PP powder under different thermooxidative degradation conditions and c_r , too. In the view of the kinetics of the formation of the carbonyl groups, the range of viscosities of the polymer needed for mixing, extrusion, or injection is limited in the initial stage. Consequently, in this stage, the increase in the rate of the carbonyl groups is rather small, so instead of the carbonyl index, the application of torque–time curves may have relatively high sensitivity. This is exactly the advantage of the method using the torque–time curve to study the thermooxidative degradation of PP powder.

Torque–time curves of PP granules treated under the conditions of thermooxidative degradation

To obtain further evidence of the aforementioned conclusions, a study of the torque–time curves of the samples of PP granules, which were produced by a different production company than the PP powder and to which was added Antideteriorant 1010 during granulation, under a series of treatment conditions was carried out, as shown in Figure 3.

Figure 3 shows that the graph of the torque–time curves of PP granules treated under various conditions of thermooxidative degradation is similar to that of the PP powder shown in Figure 1. In fact, there is a feeding peak in the individual curve, and all the

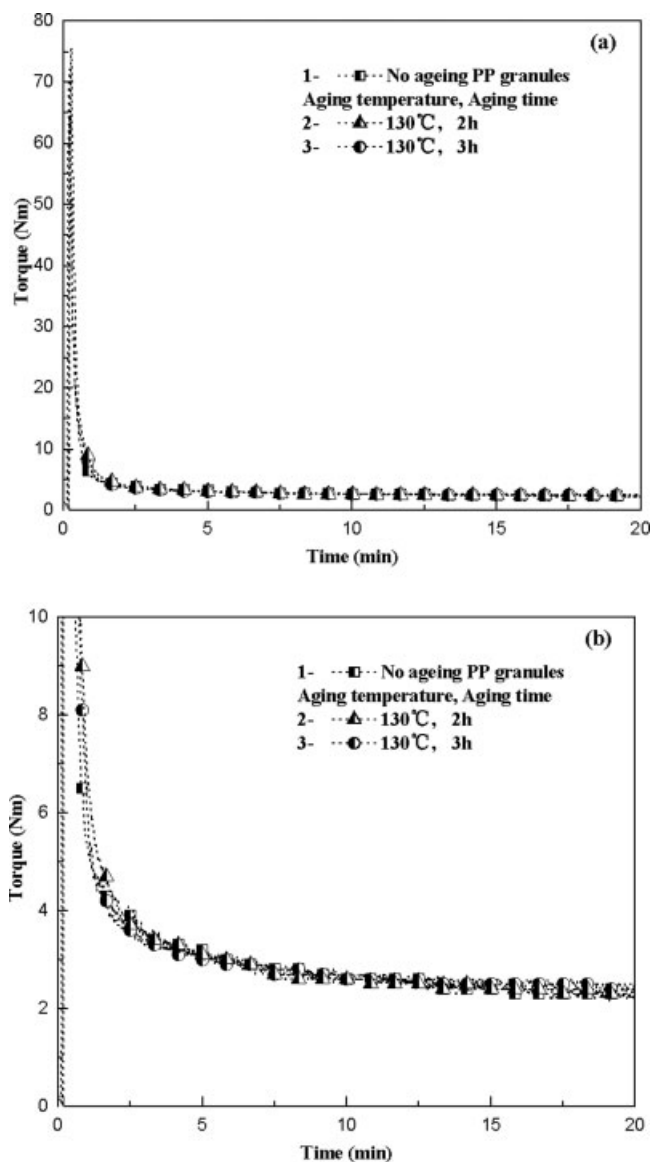


Figure 3 Graph of the rheological torque–time curves of PP granules under various thermooxidative degradation conditions: (1) no aging, (2) 130°C for 2 h, and (3) 130°C for 3 h.

curves slope gently after the feeding peak to the end with a small decrease.

However, there are many differences between the curves of Figure 3 and those of Figure 1.

First, the feeding peaks of the torque–time curves of PP granules treated under a series of conditions of thermooxidative degradation were higher than those of PP powder. All the values of the feeding peaks of the curves of PP granules were about 75 N m, whereas the ones of the PP powder were about 55 N m. This can be explained as follows: the pressure needed to push the grains of PP granules into the processing chamber was quite large because the diameters of the grains of the PP granules were much larger than those of the PP powder, so the transfer of

TABLE V
Variations of the Equilibrium Torques of the Torque–Time Curves of PP Granules Under Different Thermooxidative Degradation Conditions

Curve		1	2	3
Conditions of thermooxidative degradation		No aging	130°C for 2 h	130°C for 3 h
Equilibrium torque (N m)	5 min	3.2	3.1	3.0
	10 min	2.6	2.6	2.6

heat was rather difficult and the melting time needed was relatively long.

Second, the equilibrium torques of both blank testing curves, that is, the one of the sample of PP powder and the one of the sample of PP granules without any aging treatment, differed greatly from each other. As shown in Tables I and V, at 5 min of processing, the value of the equilibrium torque of the PP powder was 4.7 N m, whereas that of the PP granules was 3.2 N m, and at 10 min of processing, that of the PP powder was 3.3 N m, whereas that of the PP granules was 2.6 N m. In other words, the heights of the torque–time curves of the PP granules were lower than those of the PP powder. This cannot be explained by the fact that the PP granules were degraded before mixing. This was caused because the PP powder and PP granules were produced by different production companies, so their average molecular weights, their molecular weight distributions, and their viscosities were greatly different, leading to the significant differences in the heights of the curves.

Consequently, the cause of the variations of the heights of the two blank testing torque–time curves differed from the causes of the decreases in the heights of the curves of the PP powder treated under various conditions of thermooxidative degradation; that is, there may be many causes of the variations of the heights of the curves and of the decreases in the viscosities of the polymers used. One is the thermooxidative degradation, and another is the differences in the products made by different production companies. Therefore, the premise of the evaluation method of the thermooxidative degradation using the torque–time curves is that the samples of the polymer must be manufactured by the same production company under the same production standards for comparison.

Third, the most significant difference between Figures 1 and 3 is the difference in the effects of the treatment conditions of thermooxidative degradation on the variations of the heights of the torque–time curves between the PP powder and PP granules. The treatment conditions of thermooxidative degradation caused significant decreases in the heights of the torque–time curves of the PP powder, as shown in Figure 1. On the contrary, invariance of the heights of the curves of the PP granules was obtained under the same treatment conditions, as shown in Figure 3.

Because the antideteriorant had been added to the PP granules, it was concluded that the addition of the antideteriorant could effectively eliminate the degradation of the PP resin. This explained why the commercial-grade PP granules had good antidegradation and why the PP powder obtained directly from the reactors without the addition of antideteriorants was easy to degrade. From the discussion, it follows that the variation of the heights of the torque–time curves can be used to effectively evaluate or characterize the degree of thermooxidative degradation of PP resin.

Finally, further quantitative analysis could support these conclusions. As shown in Table V, at 5 min of processing, the values of the equilibrium torque of the PP granules before and after treatment under the conditions of degradation were almost equal to each other with a tiny difference. This difference was caused by a random unstable flow that might have taken place in the chamber during mixing. Meanwhile, at 10 min of processing, the values of the equilibrium torque of the PP granules before and after treatment under the conditions of degradation were entirely equal to each other. These observations mean that no thermooxidative degradation of PP granules took place under the conditions of 130°C and 3 h, which were the strongest conditions used. Therefore, it can be concluded that all the treatment conditions of thermooxidative degradation used in this study could not cause any degradation of PP granules.

It must be pointed out that the so-called treatment under the conditions of thermooxidative degradation mentioned previously was the one that was carried out before mixing. However, the degradation of the PP resin still took place during mixing. This was caused by two mechanisms of degradation. One was still the mechanism of thermooxidative degradation, but at this time, the treatment conditions were rather different from those of the previous mixing because the processing temperature was as high as 190°C and the processing time was merely 20 min. Although the processing temperature was higher than that of the treatment temperatures mentioned previously, the processing time was greatly shorter, so the effect of the degradation of the PP resin was not serious compared with the treatment before mixing.

The other was the mechanism of mechanochemical degradation. This was caused by the mechanical

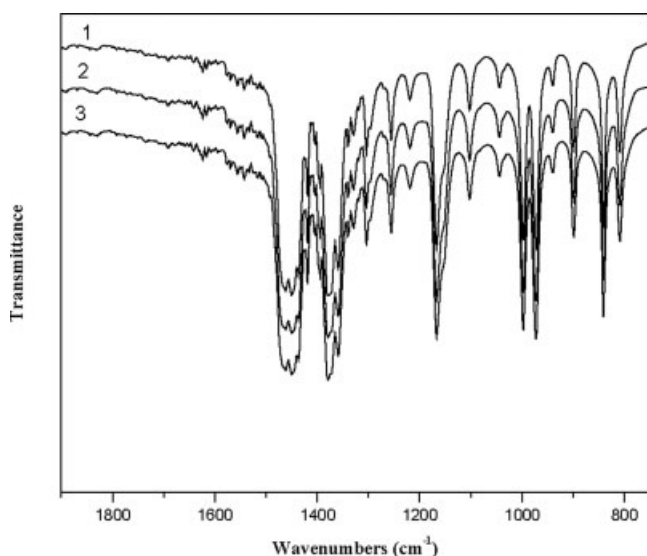


Figure 4 Graph of the characteristic bands of the carbonyl groups in the FTIR spectra of PP granules under different thermooxidative degradation conditions: (1) no aging, (2) 130°C for 2 h, and (3) 130°C for 3 h.

action of the rotors during mixing. Figure 3 shows that although invariance of the heights of the torque–time curves of PP granules before and after treatment under the conditions of thermooxidative degradation was found, the equilibrium torque still gradually decreased little by little with the variation of the processing time after the feeding peak for each of the curves. This can be explained by the action of the mechanism of mechanochemical degradation. Table V gave more evidence. At 5 min of processing, the equilibrium torque of PP granules without any degradation treatment was 3.2 N m, whereas at 10 min, it was 2.6 N m. The difference was 0.6 N m. This was so large a difference that it could not be neglected to show significant mechanochemical degradation during mixing. It was the same for the samples of PP granules treated under thermooxidative degradation conditions before mixing with a little variation of the differences, as shown in Table V.

Therefore, it can be concluded that there was a significant action of mechanochemical degradation even for PP granules during mixing, which can be characterized by the torque–time curve of the melt fluid, which is real-time, online, and production-oriented. This is exactly the advantage of the method using torque–time curves to study the variation of the degradation of PP.

Characteristics of FTIR spectra of PP granules treated under the conditions of thermooxidative degradation

Figure 4 shows the graph of the characteristic bands of the carbonyl groups in the FTIR spectra of PP gran-

ules under different thermooxidative degradation conditions (from 750 to 1900 cm^{-1}). Spectrum 1 is the FTIR spectrum of the virgin PP granules, that is, PP granules without any aging treatment for the purpose of a blank test. Spectrum 2 is the FTIR spectrum of PP granules treated under the strong conditions of thermooxidative degradation (130°C and 2 h), and spectrum 3 is the spectrum under the strongest conditions of all the samples (130°C and 3 h). The individual treatment conditions of thermooxidative degradation for spectra 2 and 3 for PP granules in Figure 4 were entirely the same as those for spectra 4 and 5 for PP powder in Figure 2. These two treatment conditions were relatively strong and the strongest conditions of all the treatment conditions shown in Figure 2 for PP powder. Because these two treatment conditions could not cause any degradation of PP granules, the other relatively weak treatment conditions for spectra 2 and 3 shown in Figure 2 for PP powder (120°C and 2.5 h and 120°C and 3 h, respectively) were certainly not going to cause any thermooxidative degradation of PP granules.

Figure 4 shows that all three spectra presented no changes in the carbonyl group (C=O) stretching band in the range of 1659–1815 cm^{-1} , so no thermooxidative degradation of PP granules took place under the treatment conditions of thermooxidative degradation used in this work, including the strongest (120°C and 3 h).

A further quantitative analysis of the carbonyl index provided more evidence supporting this conclusion. The variations of the values of the carbonyl index of the FTIR spectra of PP granules under different conditions of thermooxidative degradation are shown in Table VI. The carbonyl index of the spectrum of PP granules without the degradation treatment was 0.17, smaller than that of the PP powder without the treatment under the conditions of degradation, as shown in Table II (0.20). This can be explained as follows: the addition of the antideteriorant could effectively reduce the degradation of PP granules during the period of storage. In addition, the carbonyl index of the spectra of the samples of PP granules before and after the treatment under the conditions of degradation was quite stable, showing quantitatively that there was basically no thermooxi-

TABLE VI
Variations of the Carbonyl Indices of the FTIR Spectra of PP Granules Under Different Thermooxidative Degradation Conditions

Spectrum	1	2	3
Conditions of thermooxidative degradation	No aging	130°C for 2 h	130°C for 3 h
Carbonyl index	0.17	0.17	0.16

degradative degradation of the PP granules, to which the antideteriorant was added in the granulation process, under the treatment conditions used in this study.

The fact of no degradation of PP granules under the conditions of thermooxidative degradation might cause the invariance of the heights of the corresponding torque–time curves. This was exactly the observation found in both Figure 3 and Table V. On the other hand, the PP powder was different from the PP granules, as shown in the previous discussion: the heights of the torque–time curves decreased with the enforcement of the corresponding treatment conditions of thermooxidative degradation used in this work.

From the discussion, it follows that under the same mixing conditions, if no degradation of PP resin took place, then invariance of the heights of the torque–time curves was given; on the contrary, if the degradation of PP resin took place, then a reduction of the heights of the corresponding curves was achieved.

CONCLUSIONS

It can be concluded that under the same processing conditions, the heights of the torque–time curves of PP powder and the corresponding values of the equilibrium torque decrease with the enhancement of the conditions of thermooxidative degradation before mixing; on the contrary, the heights and areas of the characteristic bands of the carbonyl groups in the FTIR spectra of PP powder and the corresponding values of the carbonyl index increase. The quantitative analysis of FTIR spectra provides evidence for the conclusion that the heights of the torque–time curves of PP powder and the corresponding values of the equilibrium torque can be used to characterize or evaluate the thermooxidative degradation of PP powder.

If the thermooxidative degradation conditions are weakened or the degradation of the PP powder has just begun, the evaluation using the heights of the torque–time curves of the PP powder or the corresponding values of the equilibrium torque can provide more sensitivity than that using the carbonyl index.

For conventional plastic processing methods, such as mixing, extrusion, and injection molding, in the range of viscosities for processability, the evaluation method using the heights of the torque–time curves of PP powder or the corresponding values of the equilibrium torque can give more sensitivity than that using the carbonyl index. Consequently, the method using the heights of the torque–time curves to evaluate the thermooxidative degradation of PP powder has its advantages.

The application of torque–time curves can be used to evaluate not only the variation of the thermooxidative degradation of PP powder treated under aging conditions before mixing but also the variation of the

degradation, including the mechanochemical degradation, of PP powder during the period of mixing. The dependence of the variations of degradation of the polymer on the processing time during mixing can be evaluated by the study of the variation of the torque–time curves.

It can be concluded that the application of torque–time curves to the evaluation of the degradation of PP powder has the advantages of a fast and convenient operation and a simple and easy-to-operate treatment and of being real-time, *in situ*, online, and production-oriented.

References

1. Bolland, J. L.; Gee, G. *Trans Faraday Soc* 1946, 42, 236.
2. Allen, N. S. *Degradation and Stabilization of Polyolefins*; Applied Science: London, 1983.
3. Livanova, N. M.; Zaikov, G. E. *Polym Degrad Stab* 1997, 57, 1.
4. Zhou, D.; Xie, G. *Aging of Plastics and the Technology of Anti-Aging*; China Light Industry: Beijing, 1998; p 12.
5. Xu, J. *Materials of Plastics*; China Light Industry: Beijing, 1999; p 85.
6. Zhong, S.; Xu, Q.; Wang, G. *Degradation and Anti-Degradation of Polymers*; Chemical Industry: Beijing, 2002; p 63.
7. Zhu, S. *The Application and Composition of Polypropylene*; China Light Industry: Beijing, 1988; p 61.
8. Wang, X.; Ji, Y.; Xu, J. *China Plast* 2003, 17, 63.
9. Wang, X.; Nie, Q.; Xu, J. *China Plast* 2003, 17, 54.
10. James, C.; Chien, W.; Boss, C. R. *J Polym Sci Part A: Polym Chem* 1967, 5, 3091.
11. James, C. W.; Vandenberg, E. J.; Jabloner, H. J. *J Polym Sci Part A: Polym Chem* 1968, 6, 381.
12. Carlsson, D. J.; Wiles, D. M. *Macromolecules* 1969, 2, 587.
13. Gugumus, F. *Polym Degrad Stab* 2001, 74, 327.
14. Tobolsky, A. V.; Norling, P. M.; Frick, N. H.; Yu, H. *J Am Chem Soc* 1964, 86, 3925.
15. Carlsson, D. J.; Dobbin, C. J. B.; Wiles, D. M. *Macromolecules* 1985, 18, 2092.
16. Gugumus, F. *Polym Degrad Stab* 2002, 77, 147.
17. Gijsman, P.; Kroon, M.; van Oorschot, M. *Polym Degrad Stab* 1996, 51, 3.
18. Zhou, Y. *Foundations of Rheology of Polymer Processing*; Xi'an Transportation University: Xi'an, China, 1988.
19. Wang, X.; Zhang, M.; Xu, J. *Guangdong Rubber* 2001, 6, 150.
20. Goodrich, J. E.; Porter, R. S. *Polym Eng Sci* 1967, 7, 45.
21. Maity, A. K.; Xavier, S. F. *Eur Polym J* 1999, 35, 173.
22. Waldman, W. R.; De Paoli, M. A. *Polym Degrad Stab* 1998, 60, 301.
23. Song, C.; Zhang, J. *Shenyang Chem Eng* 1998, 27, 26.
24. Kim, J. K.; Lee, H. *Polymer* 1996, 37, 305.
25. Chandra, R.; Rustgi, R. *Polym Degrad Stab* 1997, 56, 185.
26. Kumar, M. S. C.; Alagar, M. *Eur Polym J* 2002, 38, 2023.
27. Kato, M.; Osawa, Z. *Polym Degrad Stab* 1999, 65, 457.
28. Kato, M.; Tsuruta, A.; Kuroda, S.; Osawa, Z. *Polym Degrad Stab* 2000, 67, 1.
29. Gensler, R.; Plummer, C. J. G.; Kausch, H. H.; Kramer, E.; Pauquet, J. R.; Zweifel, H. *Polym Degrad Stab* 2000, 67, 195.
30. Ramirez-Vatgas, E.; Navarro-Rodriguez, D.; Blanqueto-Menchaca, A. I.; Huerta-Martinez, B. M.; Palacios-Mezta, M. *Polym Degrad Stab* 2004, 86, 301.
31. Fayolle, B.; Audouin, L.; Verdu, J. *Polym Degrad Stab* 2002, 75, 123.
32. Fayolle, B.; Audouin, L.; George, G. A.; Verdu, J. *Polym Degrad Stab* 2002, 77, 515.

33. Fayolle, B.; Audouin, L.; Verdu, J. *Polym Degrad Stab* 2000, 70, 333.
34. Fayolle, B.; Audouin, L.; Verdu, J. *Polymer* 2004, 45, 4323.
35. Girois, S.; Audouin, L.; Verdu, J.; Delprat, P.; Marot, G. *Polym Degrad Stab* 1996, 51, 125.
36. Rincon-Rubio, L. M.; Fayolle, B.; Audouin, L.; Verdu, J. *Polym Degrad Stab* 2001, 74, 177.
37. Godshall, D.; White, C.; Wilkes, G. L. *J Appl Polym Sci* 2001, 80, 130.
38. Liang, J. Z.; Ness, J. N. *Polym Test* 1998, 17, 179.
39. Tiemblo, P.; Gomez-Elvira, J. M.; Teyssedre, G.; Massines, F.; Laurent, C. *Polym Degrad Stab* 1999, 65, 113.
40. Elvira, M.; Tiemblo, P.; Gomez-Elvira, J. M. *Polym Degrad Stab* 2004, 83, 509.
41. Achimsky, L.; Audouin, L.; Verdu, J. *Polym Degrad Stab* 1996, 57, 231.
42. George, G. A.; Celina, M.; Vassallo, A. M.; Cole-Clarke, P. A. *Polym Degrad Stab* 1995, 48, 199.
43. Matisova-Rychia, L.; Rychly, J.; Verdu, J.; Audouin, L.; Csomorova, K. *Polym Degrad Stab* 1995, 49, 51.
44. Kron, A.; Stenberg, B.; Reitberger, T. *Polym Degrad Stab* 1996, 54, 89.
45. Volponi, J. E.; Mei, L. H. I.; Rosa, D. S. *J Polym Environ* 2004, 12, 231.
46. American Society for Testing and Materials. ASTM D3895-98; American Society for Testing and Materials. Easton: MD, 1998.
47. Sheng, D. *Application of the Infra-Red Spectra in the Study of Polymers*; Science: Beijing, 1982.
48. Subowo Wiwik, S.; Barmawi, M.; Liang, O. B. *J Polym Sci Part A: Polym Chem* 1986, 24, 1351.
49. Allen, N. S.; Robinson, P. J.; White, N. G.; Skelhorne, G. G. *Eur Polym J* 1984, 20, 13.
50. Zhang, K. *Polymer Physics*; Chemical Industry: Beijing, 1981; p 127.
51. He, M.; Chen, W.; Dong, X. *Polymer Physics*; Fudan University Press: Shanghai, 1998; p 357.
52. Jilin University. *Principles of Physical Chemistry*; People's Education: Beijing, 1975; p 327.
53. Huang, R.; Zeng, B. *Technology of Plastic Processing*; China Light Industry: Beijing, 1997; p 41.