A Real-Time Study on the Evolution of the Degradation of Polypropylene During Mixing Process

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ABSTRACT: A real-time study to the evolution of the mechanisms of degradation of both PP powder and PP granular during the mixing process was achieved. A quantitative analysis of combination of the rheological torque-time curves obtained by a Haake rheometer with FTIR spectra was made. The construction of a series of the characteristic functions of the torque-time curve and the FTIR characteristic functions for polypropylene (PP) made the real time and quantitative analysis relatively profound. By means of these characteristic functions, the characters of the mechanisms of thermooxidative degradation, and the mechanism of mechanochemical degradation for PP were investigated. Two criterions for the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation were obtained. In the thermooxidative treatment process and the mixing process, the necessary condition for the significant occurrence of thermooxidative degradation of PP is $\Delta h_r (i) > 0.05$, whereas the sufficient condition for the significant occurrence of mechanochemical degradation is $\Delta h_r (i) \leq 0.05$ ($D_l (i) < 0$, and $i > 1$). A detailed description of the evolutions of the degradations for both the PP granules in which an antideteriorant was added and the PP powder without any antideteriorant was made. The roles and the evolutions of both the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation were discussed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1220–1243, 2011

Key words: poly(propylene); real time; mixing; degradation; rheology; FT-IR

INTRODUCTION

Mixing process is one of the most important polymer processing technology widely used.[1–4] The problem of the effects of the mixing process on the structures of the molecules and the mechanical properties of the polymers was paid great attention to in the literature for a long time. Using the Haake or the Brabander rheometer, the quantitative study of the rheological behavior of the mixing process, its effect on the structures of the molecules and the mechanical properties of the polymer processed can be made.[3,4]

Early in the initial stage of the research of the polymer processing, the action of mechanochemical degradation of the polymer caused by the shear effect during mixing or extrusion processing was found and then paid closed attention to for a long time.[5–27] The mechanochemical degradation may give a remarkable influence on the molecular structure, the molecular weight, and the mechanical properties of the polymer processed. Usually, disadvantageous influences may take place. For example, the manufacturers are often afflicted with the decease of the mechanical properties of the fabricate products. Hence, the study of the mechanochemical degradation may give a way to overcome the difficulties. Moreover, mechanochemical degradation may have also advantageous influence on the polymer. The variation of the structure of the molecular and the produce of the radicals can open up possibilities for the reactions of graft, crosslinking, or controlling degradation in the polymer processed by adding some ingredient agents during mixing to obtain modified polymers. It follows that it is very important to study the mechanochemical degradation of polymers during mixing process.

Polypropylene (PP) is rather easy to lead to thermooxidative degradation caused by the tertiary Carbon-Hydrogen bonds on its main chains.[28–32] The effect of thermooxidative degradation might cause a

complicated situation in the mixing process of PP. It is considered that both the thermooxidative degradation and mechanochemical degradation might appear simultaneously during the mixing process of PP.[10,13,14,16–19,24,33–35]

Although a variety of respective studies of thermooxidative degradation and mechanochemical degradation of PP were made, few reports about the research of the relationship between the two degradations were found. Machado et al.[23] studied the evolution of peroxide-induced thermomechanical degradation of PP along the extruder. However, the real time study of the two degradations during mixing process has not been reported so far.

The aim of our work presented in this article is to realize a real time study to the evolution of the mechanisms of both the thermooxidative degradation and mechanochemical degradation of both PP powder and PP granular during the mixing process. For this purpose, a quantitative analysis of combination of the rheological torque-time curves obtained by a Haake rheometer with FTIR spectra was made. FTIR analysis is a very important method to study the degradation of PP.[24,29,36–38] The advantages of FTIR analysis is that the variation of structure of the macromolecular could be determined directly, whereas its disadvantage is the lack of real time. This is because that, it needs to stop mixing process to take out the test samples from the chamber to prepare a sample sheet for the measurement of FTIR. The rheological study by using a Haake rheometer can determine or evaluate the degradation of PP with high sensitivity compared with FTIR analysis.[39] Especially, a real time study can be obtained by the use of a Haake rheometer.[39] However, the disadvantage of the rheological method is the lack of direct evidence of the variation of the structure of macromolecular. The combination of the rheological study with FTIR analysis can overcome each disadvantage of the individual method to obtain a real time study of the degradation of PP during mixing with the evidence of the variation of the structure of the macromolecular. For this purpose, a test design was given in the work presented in this article, which can be outlined as follows: A series of tests were carried out in the chamber of a Haake rheometer by mixing PP powder or PP granules. Each test had different ending mixing time (EM time), whereas their other processing conditions, such as the species of the feeding material, the feeding amount, the rotor speed, and the processing temperature, etc, were kept the same. The longest EM time of the tests was 30 min. A series of rheological torque-time curves were obtained after mix. If all of these torque-time curves were overlapped well, it could be concluded that a good repetitiveness of all the tests was achieved. Hence, both the rheological data and FTIR data of the test sample for every EM time could be used as the

real time data of the test sample for the EM time of 30 min, the longest EM time. Consequently, the real time evidence of the FTIR data, that is, the real time evidence of the variation of the structure of the macromolecular could be obtained. In addition, the real time rheological characteristic of the test sample for the EM time of 30 min was already given by its torque-time curve as usual.

In this work, PP powder and PP granules were studied respectively to compare their characteristics for their significant differences of the morphology and the composition.[39]

EXPERIMENTAL

Materials

The isotactic PP granules employed in this study was a commercial grade (CLS700) of Guangzhou Yinzhu Chemical Engineering Plant (Guangzhou, China). The PP granules contains Antideteriorant 1010 (500 ppm). The value of MFR of the PP granules is 12 (g/min). The isotactic PP powder (F401) used, which was taken directly from the reactor during production, was supplied by Sinopec Guangzhou Petrochemical Complex (Guangzhou, China). The PP powder does not contain any antideteriorant. The value of MFR of the PP powder is 3 (g/min).

Mixing process of PP powder and PP granules and determinations of the torque-time curves

A Haake Rheocord Polylab 300p rheometer (equipped with a Rheomix 600p mixer for mixing or blending, Gebr. HAAKE GmBH, Karlsruhe, Germany) was used for the mix of the materials and the measurement of their rheological properties, especially, for the determination of the torque-time curves. All the processing conditions, except the ending processing time, were kept constant, with a feeding amount of 45 g, a processing temperature of 190°C and a rotor speed of 60 rpm. The ending processing time varied 5, 10, 15, 20, 30 min, respectively.

Real time characteristic of the torque during mixing

The real time value of the torque during mixing process can be characterized by the torque-time curve, which was obtained by using a Haake rheometer. The real time situation of degradation of PP during mixing could be characterized by the torque-time curve.[39]

Characteristics of infrared spectroscopy

FTIR spectra were recorded on a Nexus 670 FT-IR Analyzer (GMI, Inc., Ramsey, MN) with a resolution of 2 cm^{-1}. The test samples taken from the chamber

of mixer after process were thermopressed to pre-pare sample films for the determination of FTIR spectra. The sample films were made by a XLB-D press (Hongtu Machinery Co. Ltd., Huzhou, Zhe-jiang, China) at a pressing temperature of 190°C, for a pressing time of 2 min and at a pressing pressure of 10 MPa. The thickness of the films was controlled to be about 80 μm.

To study the degradation of PP, the main charac-teristic band of FTIR are the stretching band of the carbonyl groups (C=O) in the range of 1659−1815 cm^{-1} and the stretching band of the hydroxyl groups (O—H) in the ranges of 3248−3662 cm^{-1}.[24,29,36−38] Both the carbonyl index and the hydroxyl index are the characteristic indexes of FTIR spectra to evaluate the degradation of PP.[24,29,36,37] The stretching band in the range of 2752−2698 cm^{-1} with a peak value of 2722 cm^{-1}, which characterized the flexural vibration of the bonds of carbon-hydrogen, was used as a reference band to calculate the characteristic indexes.[36,39,40]

The calculation of carbonyl index is made as follows:

$$C = \frac{A_C}{A_{2722}}, \qquad (1)$$

where C is carbonyl index, A_C is the area of the stretching band in the range of 1659−1815 cm^{-1} and A_{2722} is the area of the stretching band in the range of 2752–2696 cm^{-1} with a peak value of 2722 cm^{-1}.

Four test sample films was prepare to obtained FTIR spectra respectively, the value of carbonyl index for each test was the mean of the values obtained from the four sample films.

Similarly, the calculation of hydroxyl index is carried out according to the following formula:

$$H = \frac{A_H}{A_{2722}}, \qquad (2)$$

where H is hydroxyl index, A_H is the area of the stretching band in the range of 3248−3662 cm^{-1}.

The value of hydroxyl index for each test was the mean of the values obtained from the four sample films.

To obtain high calculating precisions of the values of the FTIR characteristic indexes, the calculation was carried out by computer entirely, not simply determined by measuring the absorption bands in Figure 7 and 8 graphically. The FTIR data were exported form the Nexus 670 FTIR Analyzer in the form of Excel documentaries. Then the Excel data were imported into the Origin 6.0 software to obtain digital FTIR spectra. The calculation of the areas of the stretching bands of FTIR spectra was carried out digitally by the Origin 6.0 software. Hence high calculating precisions of the values of the FTIR char-acteristic indexes were achieved.

Real time rheological characteristics of the degradation of PP during mixing

A real time rheological characteristics or evaluation of the evolution of the degradation of PP during mixing can be made by giving the torque-time curve from a Haake rheometer.[39]

Real time evidence for the characteristic indexes of FTIR spectra during mixing

As mentioned in the introduction above, if a good overlap of a series of the torque-time curves having different EM time is achieved, the data of both the carbonyl index and hydroxyl index for different EM time could be used as the real time evidences for the characteristic indexes of FTIR spectra of the test sample with EM time of 30 min at the corresponding same value of the mixing time (M time) during mixing. A detail description and analysis will be made in the following paragraph.

Rheological and FTIR characteristics of the thermooxidative degradation of PP

In our previous work, the rheological properties, the FTIR spectra and the carbonyl index of the ther-mooxidative degradation of PP were studied.[39] Some data about the thermooxidative degradation of PP in the discussion of this article were referred to Ref. 39. Furthermore, the hydroxyl index of the thermooxidative degradation of PP presented in this article was calculated according to the above data of Ref. 39.

RESULTS AND DISCUSSIONS

The purpose of our work presented in this article was the real time study of the evolution of the degradation of PP during mixing with an EM time of 30 min.

PP powder and PP granules were studied, res-pectively. PP powder is easier to degrade than PP granules because the former was taken from the polymerization reactor directly without any additives while the later was a commercial product manu-factured by granulating with extrusion to add an antideteriorant. The comparison of the two kinds of samples of PP is advantageous to the study of the action of the antideteriorant and the degradation of PP during mixing.

Torque-time curves of PP for various EM times

To obtain a real time study of the evolution of the degradation of PP during mixing, a series of tests with same processing conditions, such as the species of PP, the processing temperature, the feeding
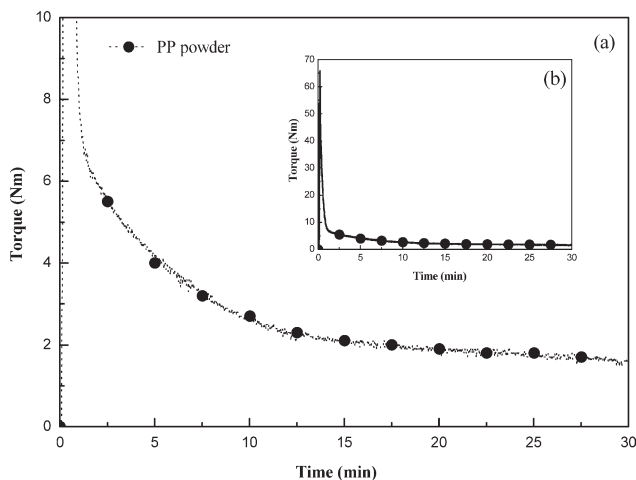
Figure 1 Graph of the rheological torque-time curve of PP powder for EM time of 30 min (mixing conditions: feeding amount: 45g; processing temperature: 190°C; rotor speed: 60 rpm).

amount and the rotor speed, except the EM time were made to achieve both the rheological and FTIR data for discussion.

The rheological torque-time curve of PP powder

Figure 1 shows that the torque-time curve of PP powder for the EM time of 30 min.

Figure 2 gives the torque-time curves of PP powder for various EM times, 5, 10, 15, 20, and 30 min, respectively. For the convenience of statement, the individual curve in Figure 2 was named after the alphabet of the individual inset. For example, the curve in Figure 2(a) was named after Curve (a), the curve in Figure 2(b) was named after Curve (b), etc. Especially, the curve in Figure 2(e) was named after Curve (e). To investigate the situation of overlap of the curves, all of the curves are shown together in Figure 3. It can be seen from Figure 3 that good overlap of all the curves was achieved. It follows that the torque-time curve with the EM time of 5 min can be looked as a part of the one with the EM time of 30 min. In other words, the torque-time curve with the EM time of 5 min can be looked as a part of Curve (e). By analogy, the torque-time curve with the EM time of 10 min can be looked as a part of Curve (e) as well, etc.

The fact of the good repeatability of the tests and the good overlap of the torque-time curves shown in Figure 3 suggest that the properties, such as the value of the torque, the FTIR spectrum and the corresponding FTIR characteristic index, etc, of the polymer processed with the EM time of 5 min should be equal to the properties of the test sample with the EM time of 30 min at the M time of 5 min. In other words, the value of torque of the torque-time curve with EM time of 5 min at the M time of 5 min could be used for indicating the value of tor-

que of Curve (e) at the M time of 5 min. Similarly, the FTIR spectrum, the carbonyl index and hydroxyl index of the test sample taken from the processing material after mixing with the EM time of 5 min, which is easy to obtain, could be used for indicating those of the test sample of Curve (e) at the M time of 5 min which is difficult to measure. This is because it needs to stop the mixing test at the M time of 5 min to obtain the test sample for the determination of FTIR data, whereas if it were to do so the EM time would not be 30 min. Consequently, a real time evidence of FTIR data including the spectrum, the carbonyl index and the hydroxyl index of the test sample of Curve (e) at the M time of 5 min could be obtained.

Similarly, each of the FTIR spectra, the carbonyl index and hydroxyl index of the test sample taken from the processing material after mixing with the EM time of j ($j = 10, 15, 20, 30$) min respectively, which is easy to obtain, could be used for indicating those of the test sample of Curve (e) at the corresponding M time of j ($j = 10, 15, 20, 30$) min, which is difficult to measure as well.

The rheological torque-time curve of PP granules

The torque-time curve of PP granules for the EM time of 30 min is showed in Figure 4. For the sake of contrast, the torque-time curve of PP powder for the EM time of 30 min is also showed in Figure 4.

The torque-time curves of PP granules with various EM times, 5, 10, 15, 20, 30 min are shown in Figure 5, respectively. They are similar to the cases of PP powder. Figure 6 shows that good overlap of all the curves was obtained.

FTIR spectra of PP for various EM times

The FTIR spectra of both the PP powder and PP granules for various EM time were obtained by taking out the test samples of the polymer materials, which were characterized by various EM times showed in Figure 2 or 5, respectively, from the chamber of the Haake rheometer to carry out the FTIR determination.

Figure 7 and 8 show that the FTIR spectra of the test samples of PP powder and PP granules after mixing with the EM time of j ($j = 5, 10, 15, 20, 30$) min respectively. As discussed above, the respective Spectrum i ($i = 2, 3, 4, 5$) in Figure 7 and 8 could be considered as the real time characteristic of the spectrum of the test sample with the EM time of 30 min at the corresponding M time of j ($j = 5, 10, 25, 20$) min of which the spectrum determined after mixing was the respective Spectrum 6.

To carry out a detailed discussion, the respective calculation of the values of both the carbonyl index
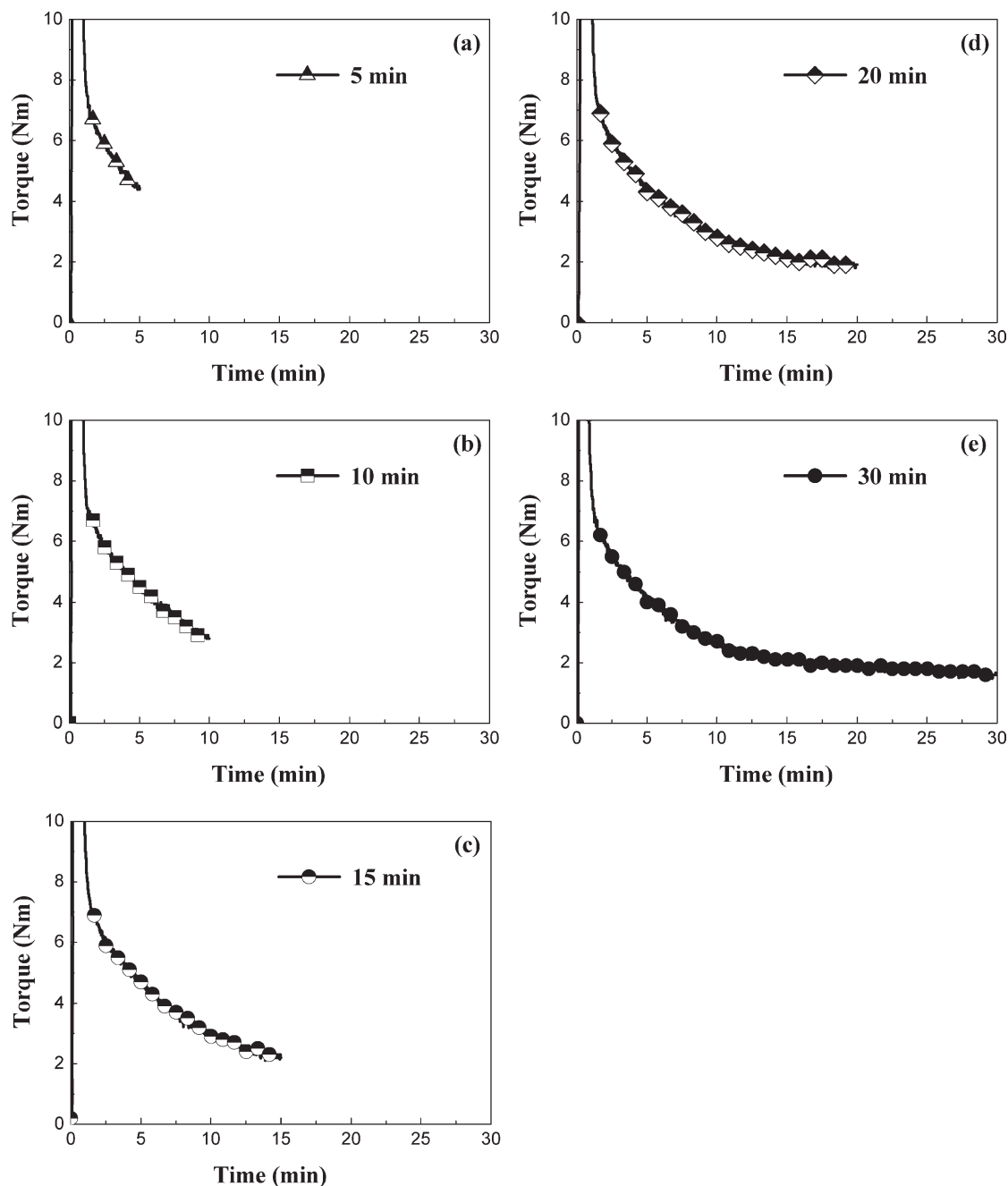
Figure 2 Graphs of the individual rheological torque-time curve of PP powder for EM time of 5, 10, 15, 20, and 30 min. EM time: (a) −5 min; (b) −10 min; (c) −15 min; (d) −20 min; (e) −30 min (mixing conditions: feeding amount: 45 g; processing temperature: 190°C; rotor speed: 60 rpm).

and the hydroxyl index of the spectra in Figure 7 and 8 was made, as shown in Table I.[24,29,36,37]

Discussions of the mechanism of the evolution of the degradation of PP during mixing process

Analysis of the rheological torque-time curve of PP

The values of the torque for various M time for PP powder can be obtained from the torque-time curve of PP powder with the EM time of 30 min shown in Figure 1. The torque values obtained was given in Table I.

To discuss the descending tendency of the torque-time quantitatively, the concept of the torque ratio of the torque-time curve is proposed. The torque ratio of the torque-time curve is defined by the following formula:

$$r_T(t) = \frac{M_t}{M_5} \qquad (5 \leq t \leq 30), \qquad (3)$$

where M_5 is the torque value of the torque-time curve at the M time of 5 min, M_t is the torque value
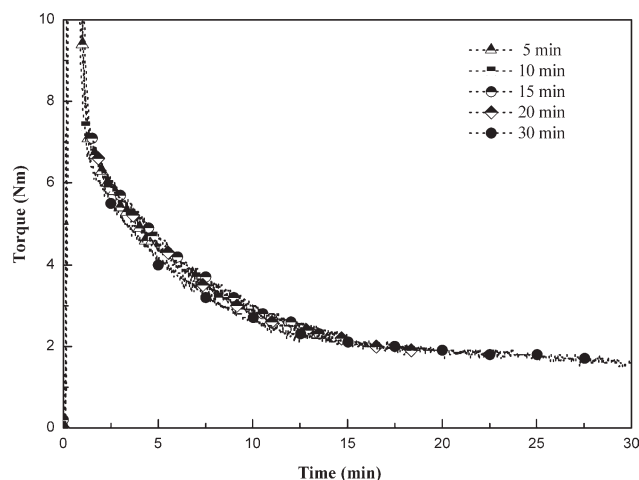
Figure 3 Repitibility of the rheological torque-time curves of PP powder for EM time of 5, 10, 15, 20, and 30 min (mixing conditions: feeding amount: 45 g; processing temperature: 190°C; rotor speed: 60 rpm).

of the same curve at the M time of t min. r_T (t) is called the torque ratio function of the torque-time curve, or the torque ratio, or RTT for short as well. Furthermore, let $r_{T,P}$ (t) denote the torque ratio function of the torque-time curve of PP powder.

The values of the torque ratio function of the torque-time curve of PP powder r_T (t) at the M time of t min are shown in Table II.

The independent variable of the function r_T (t) is the M time t, which is a continuous variable ranging from 5 to 30 min. For the convenience of the following discussion of the comparison of the results of the equilibrium torque to those of FTIR, a new function R_T (i) depending upon an discrete independent variable i, which is the ordinal number of the individual value of the M time t appeared in Table I, was constructed to denote the torque ratio function of the torque-time curve in another expression. If the torque value of the torque-time curve at the M time of t ($t = 5, 10, 15, 20, 30$) min, which could be found in the ith ($i = 2, 3, 4, 5, 6$) row in Table I, is denote by $M(i)$, then R_T (i) can be expressed as follows:

$$R_T(i) = \frac{M(i)}{M(2)} \qquad (i = 2, 3, 4, 5, 6). \qquad (4)$$

Particularly, $M(2)$ is the torque value of the torque-time curve in the second row in Table I, which is M_5, in fact, the torque value of the torque-time curve at the M time of 5 min, as denoted in Formula (3). The general relationship between $M(i)$ and M_t is shown in Table I.

R_T (i) is called the discrete torque ratio function of the torque-time curve.

The function R_T (i) can be consider as a special expression of the function r_T (t) only at several values of M time ($t = 5, 10, 15, 20, 30$). It is advantageous to the comparison with the corresponding experimental FTIR results.

Furthermore, let $R_{T,P}$ (i) denote another expression of the torque ratio function of the torque-time curve of PP powder.

The values of the torque ratio function of the torque-time curve of PP powder $R_{T,P}$ (i) ($i = 2, 3, 4, 5, 6$) are shown in Table II.

The descending of the torque-time curve of PP powder with the increase of the M time can be clearly seen From Table II. The value of the torque ratio at the M time of 15 min was only 0.45. This means that the torque value at the M time of 15 min is only 45 percent of the one at the M time of 5 min, giving a significant decrease. When M time reached at 30 min, the torque ratio went down to 0.34.

If the mixing conditions, such as processing temperature, rotor speed, feeding amount, etc., are all kept stable, the torque value is proportional to the apparent viscosity of the melting polymer so the torque-time curve of the polymer is characteristic of its apparent-viscosity/time curve during mixing processing.[41,42] Although the flow of the melting polymer in the mixing chamber is non-Newtonian, stable processing condition might keep the shear rate of the flow constant to give a good increasingly progressive dependence of the apparent viscosity on the zero shear viscosity of the polymer. On the premise of the invariable mixing conditions, the apparent viscosity can be used for the characterization or evaluation of the inherent viscosity of the polymer. As a result, the equilibrium torque can be used for evaluating the molecular weight of the polymer or
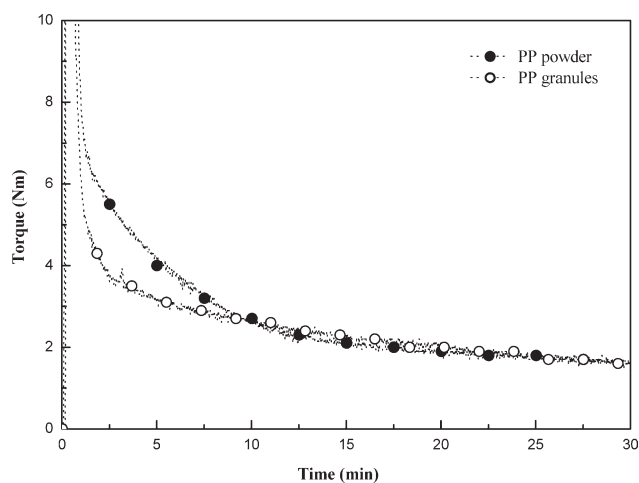

Figure 4 Rheological torque-time curves of PP granules compared with that of PP powder for EM time of 30 min (mixing conditions: feeding amount: 45 g; processing temperature: 190°C; rotor speed: 60 rpm).
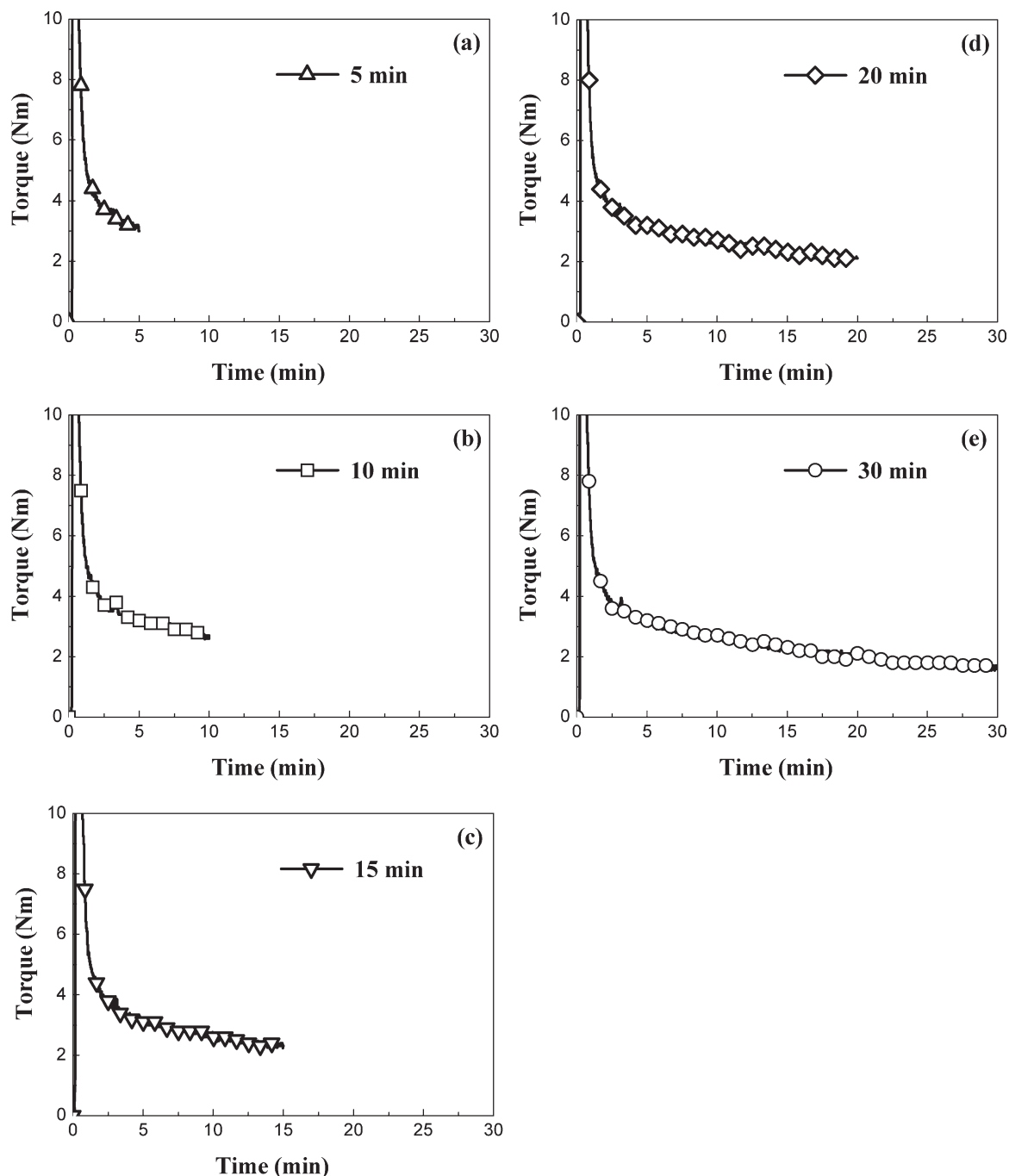
Figure 5 Graphs of the individual rheological torque-time curve of PP granules for EM time of 5, 10, 15, 20, and 30 min EM time: (a) −5 min; (b) −10 min; (c) −15 min; (d) −20 min; (e) −30 min (mixing conditions: feeding amount: 45 g; processing temperature: 190°C; rotor speed: 60 rpm).

for studying of the variation of the degradation, grafting, or crosslinking of the polymer.[24,41–46] A quantitative study of the evaluation of the degradation of PP by using the equilibrium torque and the torque-time curve was made in our previous works.[39]

The decrease of the torque ratio shown in Table II suggests that the degradation of PP should take place with the M time during mixing process. It can

be observed that this degradation was rather significant and became very great at the later stage of the mixing process.

A similar situation can be found to PP granules. The values of the torque for various M time for PP granules can be obtained from the torque-time curve of PP granules with EM time of 30 min shown in Figure 4. The torque values obtained was given in Table I.
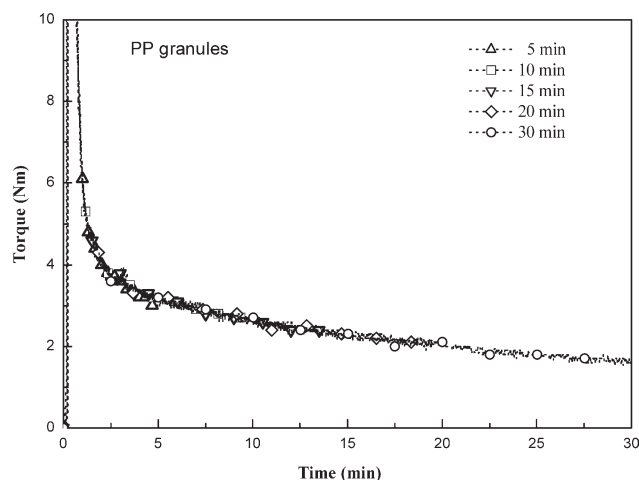
Figure 6 Repitibility of the rheological torque-time curves of PP granules for EM time of 5, 10, 15, 20, and 30 min (mixing conditions: feeding amount: 45 g; processing temperature: 190°C; rotor speed: 60 rpm).

For PP granules, the concept of the torque ratio of the torque-time curve, as expressed by (3) and (4), is also proposed similar to that of PP powder. The values of the torque ratio of the torque-time curve of PP granules are shown in Table II. The torque ratio function of the torque-time curve of PP granules, or the values of RTT of PP granules for short, is denoted by $r_{T,G}$ (t) and the discrete torque ratio function of the torque-time curve of PP granules, is denoted by $R_{T,G}$ (i).

For detailed discussion in the following paragraph, a function to describe the average rate of change of the function of the torque ratio of the torque-time curve is constructed here. Let

$$\Delta r_T(t) = r_T(t) - r_T(t - \Delta t) \qquad (5 \le t \le 30), \quad (5)$$

where Δr_T (t) is the average increment of the function r_T (t) at the M time interval of Δt, then

$$d_l(t) = \frac{\Delta r_T(t)}{\Delta t} = \frac{r_T(t) - r_T(t - \Delta t)}{\Delta t} \quad (5 \le t \le 30) \quad (6)$$

is called the function of the average rate of change of the torque ratio of the torque-time curve in the M time interval of $[t - \Delta t, t]$, or the average rate of change of the torque ratio for short. Particularly, let $d_{l,P}$ (t) denote the function of the average rate of change of the torque ratio of PP powder and $d_{l,G}$ (t) denote the function of the average rate of change of the torque ratio of PP granules. The values of both the function $d_{l,P}$ (t) and $d_{l,G}$ (t) are shown in Table III.

For the convenience of the following discussion of the comparison of the results of the equilibrium torque to those of FTIR, a new function D_l (i) depending upon a discrete independent variable i, which is the ordinal number of the individual value of the M

Figure 7 Graphs of the characteristic bands of both the carbonyl groups and the hydroxyl groups in the FTIR spectra of PP powder for the EM time of 5, 10, 15, 20, and 30 min EM time: 1–0 min; 2–5 min; 3–10 min; 4–15 min; 5–20 min; 6–30 min (mixing conditions: feeding amount: 45 g; processing temperature: 190°C; rotor speed: 60 rpm).

time t appeared in Table III, was constructed to denote the function of the average rate of change of the torque ratio of PP during mixing process in another expression. If the value of the function of the average rate of change of the torque ratio at the M time of t (t = 5, 10, 15, 20, 30) min, which could be found in the ith (i = 2, 3, 4, 5, 6) row in Table II, was expressed in the form of the discrete torque
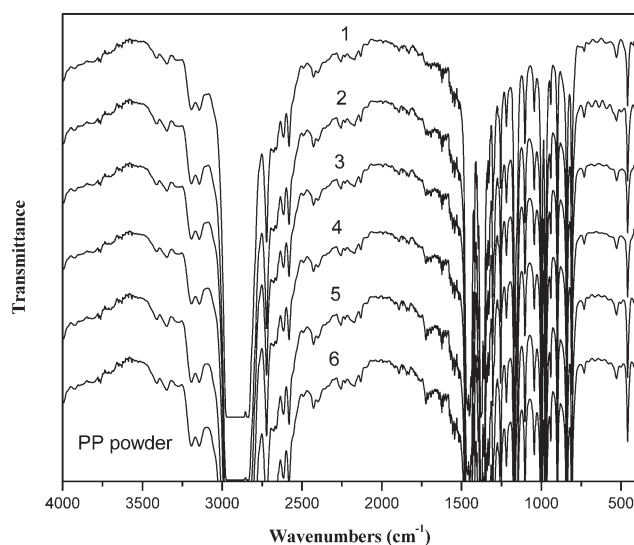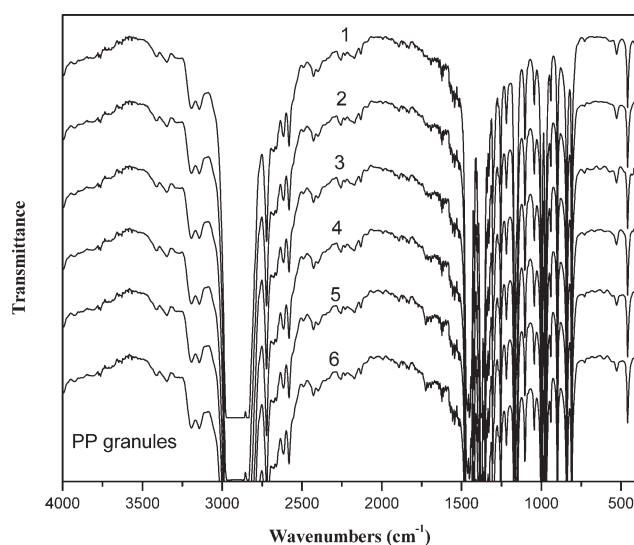

Figure 8 Graphs of the characteristic bands of both the carbonyl groups and the hydroxyl groups in the FTIR spectra of PP granules for the EM time of 5, 10, 15, 20, and 30 min EM time: 1–0 min; 2–5 min; 3–10 min; 4–15 min; 5–20 min; 6–30 min (mixing conditions: feeding amount 45 g; processing temperature 190°C; rotor speed 60 rpm).

TABLE I
Variations of the Carbonyl Index, the Hydroxyl Index, and the Equilibrium Torque Values of the Samples of Both PP Powder and PP Granules for Different M Times

No. (i)	Mixing time t (min)	PP powder			PP granules		
		Torque value (Nm)	Carbonyl index	Hydroxyl index	Torque value (Nm)	Carbonyl index	Hydroxyl index
1	0	–	0.20	0.30	–	0.17	0.31
2	5	4.7	0.23	0.35	3.2	0.19	0.35
3	10	2.6	0.24	0.35	2.7	0.20	0.36
4	15	2.1	0.26	0.35	2.3	0.22	0.36
5	20	1.8	0.28	0.35	2.1	0.25	0.36
6	30	1.6	0.29	0.35	1.7	0.26	0.36

ratio function of the torque-time curve $R_T(i)$, then $D_l(i)$ can be expressed as follows:

$$D_l(i) = \frac{R_T(i) - R_T(i-1)}{\Delta t} \qquad (i > 2). \qquad (7)$$

$D_l(i)$ is called the discrete function of the average rate of change of the torque ratio of PP. Notice that Δt is changeable, not merely 5 min. Particularly, in Table II Δt is 5 min when $i < 5$, while 10 min when $i = 6$. $D_l(i)$ is characteristic of its discrete independent variable so it needs to be determined by finding in Table II. It follows that $D_l(i)$ is a special case of $d_l(t)$. $D_l(i)$ is advantageous to the later discussion.

Particularly, $D_{l,P}(i)$ and $D_{l,G}(i)$ is used for the case of PP powder and PP granules, respectively.

The values of the discrete function of the average rate of change of the torque ratio of both PP powder and PP granules $D_l(i)$ ($i = 2, 3, 4, 5, 6$) are shown in Table III.

From Table III, we have

$$d_l(t) < 0 \qquad (t > 5), \qquad (8)$$

and

$$D_l(i) < 0 \qquad (i > 2). \qquad (9)$$

The fact that both functions are negative suggests that the torque ratio of the processing materials decrease with the increase of the M time.

For the convenient of the following discussion, the functions $r_T(t)$, $R_T(i)$, $d_l(t)$, and $D_l(i)$ are all called the characteristic functions of the torque-time curve of PP, or the characteristic functions of the torque-time curve, or the characteristic functions of the torque curve for short.

It can be seen from Figure 4 that although the values of the equilibrium torque of the torque-time curve of PP powder is rather higher than those of PP granules before the M time of 10 min, the decreasing tendency of the torque-time curve of PP powder is very significant. The torque-time curve of PP powder merely crossed over the one of PP granules a little at the M time of 10 min. After that, the two curves overlapped basically.

The difference between PP powder and PP granules in composition is that some antideteriorant was added in PP granules as soon as the PP resin went out from the reactor by extrusion processing. This may be the cause of the differences of the two kinds of PP resin in rheological behavior mentioned above. In fact, the cause of the gentle slope of the torque-time curve of PP granules and the little decrease of the variation of its torque ratio is that the effective resistance to the degradation by antideteriorant during mixing processing. On the contrary, no addition of antideteriorants in PP powder gave a significant decreasing rate of its torque value. In spite of high torque value in the initial stage of the mixing processing, the torque value of PP powder went down as much as the corresponding level of PP granules

TABLE II
Variation of RTT of the Samples of Both PP Powder and PP Granules for Different M Times

No. (i)	Mixing time t (min)	Expressions of $R_T(i)$	Expressions of $r_T(t)$	Values of RTT of PP powder ($R_{T,P}(i)$)	Values of RTT of PP granules ($R_{T,G}(i)$]
1	0	–	–	–	–
2	5	$R_T(2)$	$r_T(5)$	1	1
3	10	$R_T(3)$	$r_T(10)$	0.55	0.84
4	15	$R_T(4)$	$r_T(15)$	0.45	0.72
5	20	$R_T(5)$	$r_T(20)$	0.38	0.66
6	30	$R_T(6)$	$r_T(30)$	0.34	0.53

RTT indicates the ratio of the torque at the tth minute to the torque of the 5th minute of the torque-time curve.

TABLE III
Variations of the Function of the Average Rate of Change of the Torque Ratio of the Samples of
Both PP Powder and PP Granules for Different M times

No. (i)	Mixing time t (min)	Δt (min)	Expressions of D_l (i) (min^{-1})	Expressions of d_l (t) (min^{-1})	Values of the average relative rate functions of PP powder ($D_{l,P}$ (i)) (min^{-1})	Values of the average relative rate functions of PP granules ($D_{l,G}$ (i)) (min^{-1})
1	0	–	–	–	–	–
2	5	5	D_l (2)	d_l (5)	0	0
3	10	5	D_l (3)	d_l (10)	−0.090	−0.032
4	15	5	D_l (4)	d_l (15)	−0.020	−0.024
5	20	5	D_l (5)	d_l (20)	−0.014	−0.012
6	30	10	D_l (6)	d_l (30)	−0.004	−0.013

in a rather short time. However, although effective resistance to the degradation was given the antideteriorant could not avoid the degradation of PP entirely. This can be seen that no matter how the raw material was PP powder or PP granules, all of their torque-time curves as well as the corresponding values of torque ratio decreased with the increase of M time. Naturally, this suggests that there should be another degradation mechanism, which was not the thermooxidative degradation mechanism, during the mixing processing and there should be a difference of the mechanism of degradation between the initial stage and the later stage of the mixing processing. It seems that no importance of addition of an antideteriorant in the middle and later stage of the mixing processing for the resistance to the degradation. For instance, in spite of a great change of torque value in the initial stage of mixing processing, the variation of the torque value of PP powder, which was not added any antidetertiorant, kept quite similar to that of PP granules after 10 min later.

According to the classical theory of mixing process, mechanochemical degradation of PP may take place in the mixing processing.[5–27] Additionally, thermooxidative degradation of PP may take place simultaneously for the characteristic of the chemical structure of PP.[28–32,47,48] It can be considered that the two mechanisms of degradation of PP cause a compulsive situation during the mixing process of PP.

To achieve a detailed discussion of the degradation mechanisms of PP, a quantitative analysis of FTIR characteristic will be made in the following paragraph of this article.

The carbonyl index and its characteristic functions of the mixed treating PP

Table I and Figure 9 shows the variation of the carbonyl index of PP powder and PP granules for different M times.

To give a detailed discussion, a concept of increasing rate of the carbonyl index of PP during mixing process is proposed similar to the study of the situation of the thermooxidative degradation.[39] It is defined as follows:

$$c_r(i) = \frac{C_i - C_1}{C_1} \qquad (i > 0), \qquad (10)$$

where C_1 is the carbonyl index of spectrum 1 in Figure 7 or 8, which is the one of the test sample of the blank test for PP powder or PP granules, that is, the carbonyl index of the spectrum of the test sample of PP powder or PP granules without any thermooxidative treatment or mixing treatment; C_i is the carbonyl index of spectrum i (i = 1, 2, 3, 4, 5, 6) in Figure 7 or in 8, which is the one of the test sample of PP under various mixing treatment conditions, that is, under various M times with the variation of the order number of the spectra. c_r (i) is called the function of the increasing rate of the carbonyl index of PP during mixing process. For short, c_r (i) is also called the function of the increasing rate of the carbonyl index.
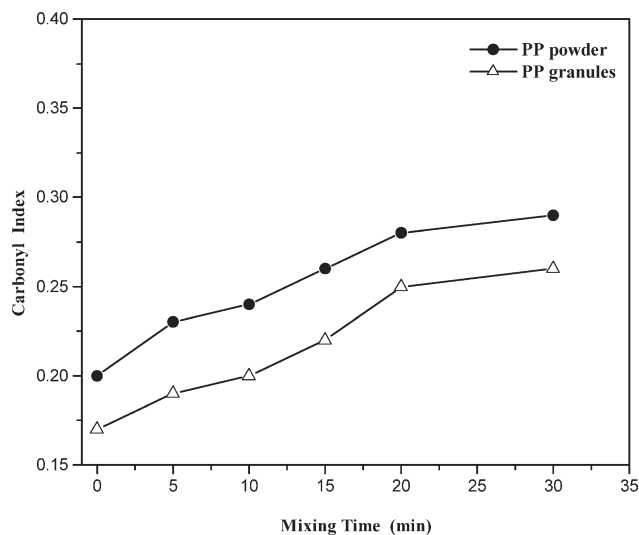

Figure 9 Variations of carbonyl index for both PP powder and PP granule as functions of M time (mixing conditions: feeding amount 45 g; processing temperature 190°C; rotor speed 60 rpm).

TABLE IV
Variations of $c_{r,P}$ (i), $\Delta c_{r,P}$ (i), $h_{r,P}$ (i), and $\Delta h_{r,P}$ (i) of the Samples of PP Powder for Different M times

No. (i)	Mixing time t(min)	$c_{r,P}$ (i)	$\Delta c_{r,P}$ (i)	$h_{r,P}$ (i)	$\Delta h_{r,P}$ (i)
1	0	0	–	0	–
2	5	0.15	0.15	0.17	0.17
3	10	0.20	0.05	0.17	0
4	15	0.30	0.10	0.17	0
5	20	0.40	0.10	0.17	0
6	30	0.45	0.05	0.17	0

TABLE V
Variations of $c_{r,G}$ (i), $\Delta c_{r,G}$ (i), $h_{r,G}$ (i), and $\Delta h_{r,G}$ (i) of the Samples of PP Granules for Different M times

No. (i)	Mixing time t(min)	$c_{r,G}$ (i)	$\Delta c_{r,G}$ (i)	$h_{r,G}$ (i)	$\Delta h_{r,G}$ (i)
1	0	0	–	0	–
2	5	0.12	0.12	0.13	0.13
3	10	0.18	0.06	0.17	0.04
4	15	0.29	0.11	0.17	0
5	20	0.47	0.18	0.17	0
6	30	0.53	0.06	0.17	0

Particularly, let $c_{r,P}$ (i) denote the increasing rate of the carbonyl index of PP powder and $c_{r,G}$ (i) denote the increasing rate of the carbonyl index of PP granules.

The values of the increasing rate of the carbonyl index of PP powder calculated according to (10) are shown in Table IV and the values of the increasing rate of the carbonyl index of PP granules calculated according to (10) are shown in Table V.

In addition, a concept of the increment function of the increasing rate of the carbonyl index of PP during mixing process is proposed. It is defined as follows:

$$\Delta c_r(i) = c_r(i) - c_r(i-1) \qquad (i > 1), \qquad (11)$$

Δc_r (i) is the increment function of the increasing rate of the carbonyl index of spectrum i (i = 2, 3, 4, 5, 6). Δc_r (i) means the increment of the increasing rate of the carbonyl index of spectrum i to that of spectrum i − 1 (i = 2, 3, 4, 5, 6).

Particularly, $\Delta c_{r,P}$ (i) and $\Delta c_{r,P}$ (i) is used for the case of PP powder and PP granules, respectively.

The values of the increment function of the increasing rate of the carbonyl index of PP powder calculated according to (11) are shown in Table IV and the values of the increment function of the increasing rate of the carbonyl index of PP granules calculated according to (11) are shown in Table V.

For the convenience of state, c_r (i) and Δc_r (i) are all called the characteristic functions of the carbonyl index of PP. For short, they are also called the FTIR characteristic functions.

The hydroxyl index and its characteristic functions of the mixed treating PP

The variation of the hydroxyl index of PP powder and PP granules for different M times can be seen from Table I and Figure 10.

Similar to the discussion of the increasing rate of the carbonyl index, a concept of increasing rate of the hydroxyl index of PP during mixing process is proposed to give a detailed discussion. It is defined as follows:

$$h_r(i) = \frac{H_i - H_1}{H_1} \qquad (i > 0) \qquad (12)$$

where H_1 is the hydroxyl index of spectrum 1 in Figure 7 or in 8; H_i is the hydroxyl index of spectrum i (i = 1, 2, 3, 4, 5, 6) in Figure 7 or in 8. h_r (i) is called the function of the increasing rate of the hydroxyl index of PP during mixing process. For short, h_r (i) is also called the function of the increasing rate of the hydroxyl index.

Particularly, let $h_{r,P}$ (i) denote the increasing rate of the hydroxyl index of PP powder and $h_{r,G}$ (i) denote the increasing rate of the hydroxyl index of PP granules.

The values of the increasing rate of the hydroxyl index of PP powder calculated according to (12) are shown in Table IV and the values of the increasing rate of the hydroxyl index of PP granules calculated according to (12) are shown in Table V.

Similar to the construction of the increment function of the increasing rate of the carbonyl index, a concept of the increment function of the increasing
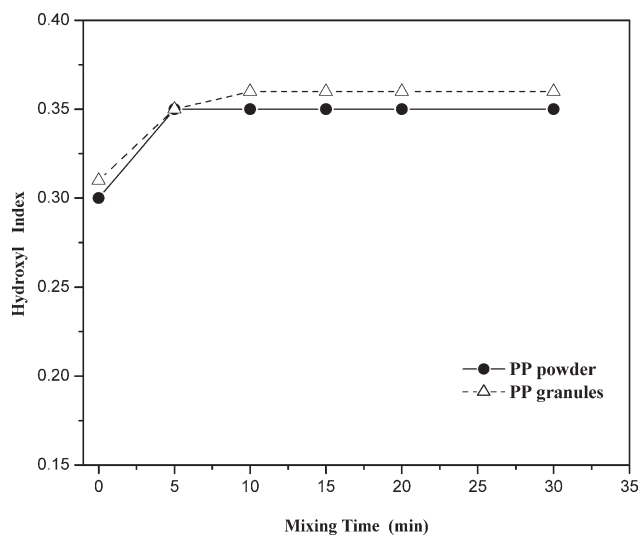

Figure 10 Variations of hydroxyl index for both PP powder and PP granule as functions of M time (mixing conditions: feeding amount 45 g; processing temperature 190°C; rotor speed 60 rpm).

TABLE VI
Variations of the Values of the Carbonyl Index and the Hydroxyl Index of the FTIR Spectra and the
Equilibrium Torques of the Torque-Time Curves of Both PP Powders and PP Granules
Under Different Thermooxidative Treating Conditions

Thermooxidative treating conditions	PP powder			PP granules		
	Carbonyl Index[a]	Hydroxyl Index	Equilibrium torque[b]	Carbonyl Index[c]	Hydroxyl Index	Equilibrium torque[d]
No treatment	0.20	0.30	4.7	0.17	0.31	3.2
120°C for 2.5 h	0.22	0.34	3.0	–	–	–
120°C for 3 h	0.27	0.40	2.1	–	–	–
130°C for 2 h	0.47	0.65	0.6	0.17	0.32	3.1
130°C for 3 h	1.98	2.64	0.1	0.16	0.33	3.0

[a] Obtained from the data in Ref. 39, Table 2.
[b] Obtained from the data in Ref. 39, Table 1.
[c] Obtained from the data in Ref. 39, Table 6.
[d] Obtained from the data in Ref. 39, Table 5.

rate of the hydroxyl index of PP during mixing process is also proposed here. It is defined as follows:

$$\Delta h_r(i) = h_r(i) - h_r(i-1) \qquad (i > 1). \qquad (13)$$

$\Delta h_r (i)$ is called the increment function of the increasing rate of the hydroxyl index of spectrum i ($i = 2, 3, 4, 5, 6$). Particularly, $\Delta h_{r,P} (i)$ and $\Delta h_{r,G} (i)$ is used for the case of PP powder and PP granules, respectively.

The values of the increment function of the increasing rate of the hydroxyl index of PP powder calculated according to (13) are shown in Table IV and the values of the increment function of the increasing rate of the hydroxyl index of PP granules calculated according to (13) are shown in Table V.

For the convenience of state, $h_r (i)$ and $\Delta h_r (i)$ are all called the characteristic functions of the hydroxyl index of PP. For short, they are also called the FTIR characteristic functions.

By comparison of Figure 10 to 9, it can be found that the variation of the hydroxyl index differed significantly from that of carbonyl index during mixing process.

It seems that the ordinary mechanism of thermooxidative degradation of PP could not explain this variation of the hydroxyl index of PP during mixing process. The above four kinds of functions constructed can be used as powerful tools for the detailed analysis of the mechanism of degradation during mixing process.

The carbonyl and hydroxyl indexes and their characteristic functions of the thermooxidative treating PP

In our previous work, the variation of values of the carbonyl index of both PP powder and PP granules under various thermooxidative treatments was studied.[39] Furthermore, this article gave the data of hydroxyl index of the test samples referred in

Ref. 39 for the discussion of the relative action between carbonyl index and hydroxyl index. In Table VI, the values of carbonyl index and the values of the corresponding equilibrium torque were reported in Ref. 39, but the values of hydroxyl index, which were calculated from the FTIR spectra of Ref. 39, were first given in this article.

In Ref. 39, the concept of the increasing rate of the carbonyl index for the thermooxidative treatment of PP $c_r (i)$ was proposed, which was defined by Formula (2) and denoted by c_r there.[39] This can be expressed by Formula (10) here, that is, Formula (10) can be also used for the discussion of thermooxidative treating PP. For this purpose, the phrase "Spectrum i" did not indicate any spectrum reported in this article, while indicated the spectrum discussed in Figure 2 (PP powder) or Figure 4 (PP granules) in Ref. 39. For the convenience of discussion, the thermooxidative treating conditions and their corresponding spectra listed in the following Table VII (PP powder) and Table VIII (PP granules) were numbered correspondingly with those in both the Figure 2 and 4 in Ref. 39. It is evident that $c_r (i)$ is a discrete function here.

It must be noticed that the same expression $c_r (i)$ is used for indicating the increasing rate of the

TABLE VII
Variation of $c_{r,P} (i)$, $\Delta c_{r,P} (i)$, $h_{r,P} (i)$, and $\Delta h_{r,P} (i)$ of PP Powders Under Different Thermooxidative Treating Conditions

No. (i)	Thermooxidative treating conditions	$c_{r,P}$ (i)[a]	$\Delta c_{r,P}$ (i)	$h_{r,P}$ (i)	$\Delta h_{r,P}$ (i)
1	No treatment	0	–	0	–
2	120°C for 2.5 h	0.1	0.1	0.13	0.13
3	120°C for 3 h	0.35	0.25	0.33	0.20
4	130°C for 2 h	1.35	1.00	1.17	0.84
5	130°C for 3 h	8.90	7.55	7.80	6.63

[a] Obtained from the data in Table 4 of Ref. 39. The curve numbers of this table are correspondence to those of the Figure 2 of Ref. 39.

TABLE VIII
Variation of $c_{r,G}$ (i), $\Delta c_{r,G}$ (i), $h_{r,G}$ (i), and $\Delta h_{r,G}$ (i) of PP Granules Under Different Thermooxidative Treating Conditions

No. (i)	Thermooxidative treating conditions	$c_{r,G}$ (i)	$\Delta c_{r,G}$ (i)	$h_{r,G}$ (i)	$\Delta h_{r,G}$ (i)
1	No ageing	0	–	0	–
2	130°C for 2 h	0	0	0.032	0.032
3	130°C for 3 h	−0.059	−0.059	0.064	0.032

The curve numbers of this table are correspondence to those of the Figure 4 of Ref. 39.

carbonyl index of PP either for mixing process or for thermooxidative treating process.

Particularly, $c_{r,P}$ (i) and $c_{r,G}$ (i) is used for the case of PP powder and PP granules in thermooxidative treating process respectively.

Similar to the discussion of the mixing process, the increment function of the increasing rate of the carbonyl index of PP for thermooxidative treating process Δc_r (i) is also constructed here. The functional expression is the same as Formula (11). However, for this purpose the phrase "Spectrum i" did not indicate any spectrum reported in this article, while indicated the spectrum discussed in Figure 2 (PP powder) or 4(PP granules) in Ref. 39.

Particularly, $\Delta c_{r,P}$ (i) and $\Delta c_{r,G}$ (i) is used for the case of PP powder and PP granules in thermooxidative treating process, respectively.

Furthermore, similar to the discussion of the mixing process above, the function of the increasing rate of the hydroxyl index of PP for thermooxidative treating process h_r (i) and the increment function of the increasing rate of the hydroxyl index of PP for thermooxidative treating process Δh_r (i) are also constructed. The expression of the definition of h_r (i) is the same as Formula (12) and the expression of the definition of Δh_r (i) is the same as Formula (13). Apparently, for this purpose the phrase "Spectrum i" did not indicate any spectrum reported in this article, while indicated the spectrum discussed in Figure 2 (PP powder) or 4(PP granules) in Ref. 39.

Particularly, $h_{r,P}$ (i) and $\Delta h_{r,P}$ (i) is not only used for the case of PP powder for mixing process, but also for thermooxidative treating process; $h_{r,G}$ (i) and $\Delta h_{r,G}$ (i) is used for the case of PP granules.

For the convenience of state, c_r (i) and Δc_r (i) are all called the characteristic functions of the carbonyl index of PP for thermooxidative treating process. For short, they are also called the FTIR characteristic functions.

Additionally, h_r (i) and Δh_r (i) are all called the characteristic functions of the hydroxyl index of PP for thermooxidative treating process. For short, they are also called the FTIR characteristic functions.

It is apparent that although each expression of the above functions for thermooxidative treating process is the same as for mixing process formally, all the above functions for thermooxidative treating process are discrete functions.

Discussion of the characteristic indexes and the characteristic functions of the thermooxidative degradation of PP

It is generally considered that there exist four mechanisms of the degradation of PP, the mechanism of thermooxidative degradation, the mechanism of mechanochemical degradation, the mechanism of radiation degradation and the mechanism of photooxidative degradation. In our study, there is not any radiation treatment, so the mechanism of radiation degradation need not consider at all. In mixing process, the feeding material was put in a hermetic chamber in the absence of light so there is not any mechanism of photooxidative degradation in it. Consequently, the mechanisms which might take place during mixing process are the first two mechanisms: the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation. Moreover, which mechanism does take place? Or alternatively, are there the two mechanisms during the mixing process simultaneously? This has been concerned for a long time in the literature and still a problem to be discussed. So this is one of the research aims of this article.

For a detailed research, the thermooxidative aging treating PP, in which no mechanochemical degradation took place, was first studied by investigating its carbonyl index, hydroxyl index and the corresponding FTIR characteristic functions. Then this thermooxidative treating PP was discussed as a blank testing sample against to the mixing treating PP.

Additionally, a detailed and précising distinguish must be made in the exact meaning of the words and phrases for aging, degradation, and treating ways for these purposes to discussed correctly.

The phrase "thermooxidative treatment" or "thermooxidative treating" is used for indicating the way of treatment of the polymer at a certain temperature in a certain time in air. We prefer the phrase "thermooxidative treatment" (or "thermooxidative treating") to "thermooxidative degradation treatment" (thermooxidative degradation treating). This is because that although the thermooxidative treatment may cause age of the polymer, the result of age includes degradation and decomposition. Unlike ordinary polymer, the result of thermooxidative treatment of PP is mainly degradation, but little decomposition might take place accomplishedly. That is, the thermooxidative degradation is the main result of the thermooxidative treatment, but it could not be the only result. So if the

statement is only concerned with the way of treatment, the phrase "thermooxidative treatment" or "thermooxidative treating" is a correct one.

The phrase "mechanism of thermooxidative degradation" indicates the action of "thermooxidative treatment," while the phrase "thermooxidative degradation" means one of the results of "thermooxidative treatment." The action of "thermooxidative treatment" may lead to either "thermooxidative degradation" or "thermooxodative decomposition," especially "thermooxidative degradation" mainly for PP.

It can be seen from the above discussion that the distinguishing of the exact meaning in the phrases of "thermooxidative treatment," "thermooxidative degradation," and "mechanism of thermooxidative degradation" is very important. If the way of treatment is merely concerned in statement, the phrase "thermooxidative treatment" is suitable. The phrase "thermooxidative degradation treatment" is not suitable here because the result of the treatment may not be the "thermooxidative degradation" if the polymer treated is not PP. For example, the result of the treatment of PVC may cause "thermooxidative decomposition." If the result or the mechanism is concerned, it is recommended to use the phrase "thermooxidative degradation" or "the mechanism of thermooxidative degradation." This is because that for PP the main aging chemical reaction is degradation, not decomposition, and the main product of the aging reaction is still a polymer.
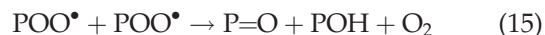
Similarly, the phrase "mixing treatment" or "mixing treating" means a way of treatment of the polymer mixing in a chamber at a certain temperature in a certain time of which the results might include both degradation and decomposition.

The phrase of "mechanism of mechanochemical degradation" usually indicates the action of "mixing treatment," while the phrase "mechanochemical degradation" means one of the results of "mixing treatment." The action of "mixing treatment" may not cause merely one result of "mechanochemical degradation," perhaps may lead to a result of "thermooxidative degradation" accomplishedly, as pointed out as the following paragraph in this article. Hence if the way of treatment is only concerned in statement, the phrase "mixing treatment" is preferred.

It can be seen from Tables VI and VII that for its thermooxidative treatment, the carbonyl index, hydroxyl index, and all the corresponding FTIR characteristic functions of PP increased with the enhancement of the thermooxidative condition. This can be explained by the mechanism of thermooxidative degradation of PP.

According to the mechanism of thermooxidative degradation of PP reported, the reaction of the thermooxidative degradation of PP is a complicated chain-reaction of radical with a series of reactional steps.[27,30,49–59] Before its rupture, some hydroxyl groups on the macromolecular chain of PP may form during the thermooxidative degradation. These hydroxyl groups may be produced by the following step reactions[27,30,49–59]:

$$POO^\bullet + PH \rightarrow P^\bullet + POOH \qquad (14)$$

$$POO^\bullet + POO^\bullet \rightarrow P{=}O + POH + O_2 \qquad (15)$$

$$P^\bullet + OH^\bullet \rightarrow POH \qquad (16)$$

All of the hydroxyl groups are connected on the main chains or the side chains of PP, so the rupture reaction may not carry out immediately as soon as the hydroxyl groups produced. Sorts of hydroxyl groups on them have various molecular structures and various linkage powers. Only a small part of them could form the quite stable radicals of either PO· or POO·with a certain reactivity to lead to further chain-reactions to produce the following rupture reaction finally:

$$PO^\bullet \rightarrow (P{=}O)_{\text{methyl-keone}} + P^\bullet. \qquad (17)$$

The product of the terminus of the rupture macromolecular chain usually forms a carbonyl group.[30,49,50–53,56–59]

In other words, an essential premise for the rupture reaction of PP is to form many hydroxyl groups on the main chains at first during the thermooxidative treatment. After that, one part of the hydroxyl groups could produce the radicals of either PO or POO to lead to further chain-reactions to result in rupture of the main chains finally. This conclusion is in correspondence with the above observation that the enhancement of the condition of thermooxidative treatment may raise the values of the hydroxyl index and the corresponding hydroxyl characteristic functions.

Meanwhile, the increase of the carbonyl groups in the PP during the thermooxodative degradation comes from both the rupture reaction and the chain-end reaction (15) in which hydroxyl groups forms simultaneously. Hence the carbonyl groups increase gradually with the enhancement of the thermooxidative treating condition to lead to the increase of the values of the carbonyl index and the corresponding carbonyl characteristic functions.

It can be seen from the above discussion that the essential premise for the further rupture reaction to form carbonyl groups, or rather, the necessary condition of rupture reaction is the enough formation of hydroxyl groups on the main chains of PP during the process of thermooxidative degradation. Only can the enough quantity of the hydroxyl groups form the rupture reaction carry out. This is because that merely a small part of hydroxyl groups can lead to the rupture of the main chains while the rest

might connect on the main chains to form side groups. It can be seen from Table VII that the significant increase of both $h_{r,P}(i)$ and $\Delta h_{r,P}(i)$ caused a significant raise of the value of the carbonyl index.

Therefore, $\Delta h_{r,P}(i)$ can be used as a quantitative criterion to judge if the thermooxidative degradation of PP powder can take place. In other words, only the value of the function $\Delta h_{r,P}(i)$ is greater significantly than zero can the thermooxidative degradation take place when the thermooxidative treating condition enhances gradually for a set of tests by various treating conditions.

Generally, it can be considered that $\Delta h_r(i)$ can be used as a quantitative criterion to judge whether the thermooxidative degradation of PP can take place when the thermooxidative treating condition enhances gradually for a set of tests by various treating conditions. That is, only $\Delta h_r(i)$ is greater significantly than zero

$$\Delta h_r(i) > 0 \qquad (i > 1) \qquad (18)$$

can the thermooxidative degradation take place when the thermooxidative treating condition enhances gradually.

To consider the precise of the measurement, a formula is used for instead of Formula (18) reasonably:

$$\Delta h_r(i) > 0.05 \qquad (i > 1) \qquad (19)$$

That is, only when the Formula (19) holds can the thermooxidative degradation take place in the thermooxidative treating system. In other words, in order to obtain a significant thermooxidative degradation of PP, the Formula (19) must hold.

PP granules differed greatly from PP powder in the variation of the characteristic functions under the thermooxidative treating conditions listed in Table VI. This can be easily seen from Table VIII.

In fact, from Table VIII we have

$$\Delta h_r(i) = \Delta h_{r,G}(i) = 0.032 < 0.05 \approx 0 \quad (i = 2, 3) \quad (20)$$

Apparently, no significant increase of $\Delta h_r(i)$ for PP granules, so according to the above quantitative criterion it can be concluded that no thermooxidative degradation took place basically in corresponding with the results reported by Ref. 39.

It must be pointed out that the quantitative criterion (19) is the necessary condition of the thermooxidative degradation, but not the sufficient condition mathematically. In other words, the fact that the Formula (19) holds does not mean that the occurrence of the thermooxidative degradation of PP is definitely obtained, while merely can be obtained. This can be clearly seen from the process of the reaction of the thermooxidative degradation.

In fact, the stepped reactions in which hydroxyl groups form from (14) to (16) are not the rupture reactions yet. They are merely the intermediate steps for the rupture reaction. If at these steps there is an antideteriorant in the matrix of the PP, the radicals formed by thermooxidative treatment may be captured by it to stop the rupture reaction (17). As a result, a number of hydroxyl groups connected on the main-chain of PP, while the rupture reaction does not take place. This is caused by the action of the antideteriorant so the thermooxidative degradation does not appeared but the Formula (19) holds.

Therefore, it can be seen from the above discussion that the quantitative criterion (19) can be used for evaluating whether the thermooxidative degradation could take place, but the quantitative criterion can not tell us that the thermooxidative degradation definitely take place. In other words, if the Formula (19) does not hold, the thermooxidative degradation cannot take place.

Discussion of the characteristic indexes and the characteristic functions of the mechanochemical degradation of PP

As stated above, in our study, if the degradation of PP takes place, the mechanism of degradation is either the thermooxidative degradation or the mechanochemical degradation. This means that if the mechanism of degradation is not the mechanism of thermooxidative degradation, then it is nothing but the mechanism of mechanochemical degradation. According to the above discussion about the FTIR characteristic indexes and the FTIR characteristic functions of the thermooxidative degradation of PP, especially the discussion of the necessary condition of the Formula (18) and (19) of the thermooxidative degradation, it is evident that if the equilibrium torque decreased and the function $\Delta h_r(i)$ did not increased significantly, then the mechanism of the degradation is, or mainly is the mechanism of mechanochemical degradation.

A précising description about the above conclusion can be made by a quantitative formula as follows.

The following formula

$$\Delta h_r(i) = 0 \qquad (D_l(i) < 0, \quad \text{and} \quad (i > 1) \qquad (21)$$

can be used as a sufficient condition of the mechanism of mechanochemical degradation and the premise $D_l(i) < 0 \; (i > 1)$ means that the equilibrium torque definitely decreased so the degradation of PP had definitely taken place. Now the problem is that which mechanism of degradation of PP had taken place. This is just a problem of the use of the function $\Delta h_r(i)$ to judge.

A weaker sufficient condition than that of Formula (21) is used for a better description that the function $\Delta h_r(i)$ did not increased significantly:

$$\Delta h_r(i) \leq 0.05 \qquad (D_l(i) < 0, \quad \text{and} \quad i > 1). \qquad (22)$$

Formula (22) means $\Delta h_r(i) \approx 0$. In other words, if Formula (22) holds, the mechanism of degradation of PP is, or mainly is the mechanism of mechanochemical degradation.

A typical example is the PP granules by mixing treatment. In the above discussion for the characteristic functions of the torque-time curve of PP granules, it was seen from Table III that

$$D_{l,G}(i) < 0 \qquad (i > 2), \qquad (23)$$

satisfying Formula (9). Hence, it can be deduced that the degradation of PP granules did took place during the mixing process. In addition, as discussed above for Table II and the function $R_{T,G}(i)$, the degradation is rather significant so it is very different from the case of the thermooxidative treatment of PP granules.

It can be considered that the thermooxidative degradation of PP granules may be restrained for the addition of the antideteriorant by extrusion processing for granulating. Hence if a significant degradation takes place, it is, or mainly is caused by the mechanism of mechanochemical degradation.

In Table V, we have

$$\Delta h_{r,G}(i) = 0 \qquad (i = 4 \sim 6) \qquad (24)$$

and

$$\Delta h_{r,G}(i) = 0.04 < 0.05 \approx 0 \qquad (i = 3). \qquad (25)$$

Apparently, Formula (24) satisfies Formula (21) and Formula (25) satisfies Formula (22), so it can be concluded that after the M time of 10 min later, the mechanism of degradation of PP granules is mainly the mechanism of mechanochemical degradation.

Formula (21) and Formula (22) are all sufficient conditions for mechanochemical degradation. Please notice that the conditions are sufficient in strictly mathematical sense. This means that if the conditions are true, then the mechanism of degradation is, or mainly is definitely mechanochemical degradation. However, if the conditions are not true, it could not tell us whether the mechanochemical degradation had taken place. Sometimes the mechanochemical degradation might still take place. The sufficient conditions cannot be used to judge the case that no mechanochemical degradation took place. In the strictly mathematical sense, more than one sufficient conditions can be obtained and chosen. Formula (22) is a weaker sufficient condition than Formula (21).

$\Delta h_r(i) \leq 0.05$ means $\Delta h_r(i) \approx 0$. In other words, it means that $\Delta h_r(i)$ is very small, or almost equals zero. The use of 0.05 is based on the observation of both Table VII and VIII. Table VII shows that even a very tiny thermooxidative degradation (thermooxidative treating condition No. 2 for PP powder) may cause relatively large value of $\Delta h_r(i)$ (0.13). In addition, Table VIII shows that even without thermooxidative degradation (PP granules), a very little value of $\Delta h_r(i)$ (0.032) could be found, but it was below 0.05. Hence Formula (22) can be used as one of the sufficient conditions for mechanochemical degradation, which was weaker than Formula (21).

The mechanism of mechanochemical degradation can gives a reasonable explanation for Formula (21) and (22).

As reported, the mechanochemical degradation is usually considered being caused by the concentration of shear stress during the mixing process to lead to the rupture of the main chains of macromolecule.[9,25–27] Mechanochemical degradation may cause the decrease of molecule weight and viscosity to lead to a descent of the equilibrium torque. The mechanism of mechanochemical degradation differs significantly from that of thermooxidative degradation. Early Bueche[9] considered that the mechanochemical degradation was entirely caused by the action of shear stress. In recent research, Scott[27] made a further analysis to the mechanism of mechanochemical degradation of the polyvinyl species, such as PP, polyethylene, etc. He considered that the procedure of the rupture of the main chains by mechanochemical degradation can be divided into two steps. The first step is the rupture of the main chains by the action of shear stress. This rupture may cause, however, the reduction of the degree of polymerization of the polymer, and however, the production of the hydroxyl groups on the main chains under the condition of the exposure of the polymer to the air. The hydroxyl groups might cause further rupture reaction generated by the mechanism of thermooxidative degradation as mentioned above as the second step of the rupture. It can be seen from this that the mechanism of mechanochemical degradation is a very complicated procedure of rupture reactions. Besides the rupture reaction generated by shear stress at the first step, the second step of the rupture reaction might appear. It is very interested that the second step of the rupture reaction is actually the mechanism of thermooxidative degradation.

In mechanochemical degradation, the first step at which the rupture reaction is caused by shear stress is a chain-initiating reaction for the second step at which the rupture reaction is generated by the mechanism of thermooxidative degradation. The first step is the necessary condition of the production of hydroxyl

groups. The chain-initiating reaction of the mechanism of mechanochemical degradation causes rupture of the main chains immediately, unlike the case of the chain-initiating reaction of the mechanism of thermooxidative degradation in which the chain rupture does not take place yet. In the lack of oxygen or the present of the antideteriorant, the production of hydroxyl groups might be restrained. Then the second step might be restrained as well. However, it must be notice that the cause of the generation of the chain rupture at the first step of the mechanochemical degradation is shear stress without the generation of the radicals by the hydroxyl groups. Hence the existence of the hydroxyl groups is not the necessary condition of the mechanochemical degradation. As stated above, Formula (22) can be used as a sufficient condition of the mechanism of mechanochemical degradation. It must be notice that this criterion is "sufficient," not "necessary." In other words, when the equilibrium torque of PP during mixing reduced, the fact that Formula (22) holds means that the mechanism of mechanochemical degradation is the dominant mechanism, but if Formula (22) does not hold to show hydroxyl groups having produced, it cannot be sure that there is no action of the mechanism of mechanochemical degradation.

Additionally, it cannot be affirmed from the result of the FTIR analysis that there is no thermooxidative degradation at all, even the mechanism of mechanochemical degradation is the dominant mechenism. It can be merely said that the thermooxidative degradation might take place, but not the dominant mechanism.

It can be considered that the cause of the low level of the hydroxyl index of the PP granules during mixing process is the lack of oxygen in the mixing chamber totally. In the mixing process, most of main chains of PP were surrounded by the melting feeding material itself with high viscosity. This might lead to a low diffusing rate of the gaseous oxygen molecule to the inner of the melt PP phase. The low diffusing rate of the gaseous oxygen might cause very lack of oxygen near the reactional location. This might cause the low level of the hydroxyl index as well. This is very different from the case of the thermooxidative treatment of PP granules. In that case, the treating temperature was lower than that of melting point of PP so the polymer treated was in the form of solid granule. This ensured a sufficient contact between the surfaces of the gains of PP granules. The gaseous oxygen in the treating oven in whole time kept sufficient air convection. Therefore, the lack of oxygen cannot take place in the case of thermooxidative treatment but can do in the case of mixing treatment.

Even in the sufficient present of oxygen, the thermooxidative degradation does not always take place for PP granules as mentioned above. In fact, even in the treating oven, the thermooxidative degradation of PP granules did not take place under the treating condition stated in this article caused apparently by the action of the antideteriorant.

However, in the mixing process of PP granules the antideterioriant could not stop the degradation. This can be seen from the variation of the torque and its characteristic functions of the torque curve and the carbonyl index of the mixing treating PP granules.

A detailed discussion of the FTIR characteristic index and the corresponding characteristic functions of the mixing treating PP will be made compared with those of the thermooxidative treating PP granules in the following.

The increasing rate of the carbonyl index of mixing treating PP granules is greater than that of thermooxidative treating PP granules. For example, the value of the carbonyl index of mixing treating PP granules at the mixing ending time of 30 min was 0.26 (Table I), while the value of he carbonyl index of the thermooxidative treating PP granules under the condition of treating temperature at 130°C and the treating time for 3 h was just 0.16 (Table VI). The corresponding characteristic functions had similar variation as well (Table V and VI).

The analysis of the carbonyl index and the corresponding characteristic functions of PP granules showed that a definite degradation took place during mixing process, but nor did it during thermooxidative treatment. This is basically in correspondence with the conclusion of Ref. 39.

The above conclusion from the analysis of the carbonyl index of PP granules is in correspondence with the analysis of the equilibrium torque. In fact, the value of the equilibrium torque of mixing treating PP granules was 1.7 Nm at the EM time of 30 min (Table I), while the one of thermooxidative treating PP granules was 3.0 Nm at 130°C for 3 h (Table VI), basically equating to that of the blank testing sample.

It is noted that the function $\Delta c_{r,G}$ (i) of the mixing treating PP granules did not equate to zero in the whole mixing process (Table V) with a significant difference to the function $\Delta h_{r,G}$ (i), which equated to or got closed to zero shown in Formula (24) and (25). This means that $c_{r,G}$ (i) increased successively.

As mentioned above, the character of PP granules is the addition of a definite amount of an antideterionant. It is evident that the antideteriorant can effectively restrain the thermooxidative degradation of PP granules during the thermooxidative treatment. Moreover, the antideterionant could not effectively restrain the degradation of PP granules entirely during mixing process. The degree of degradation in mixing process is rather great compared significantly with the case of the thermooxidative treatment of PP

granules in which little degradation is observed. It follows that there exists a mechanism of degradation, which differs from the thermooxidative degradation, during the mixing process in which the antideteriorant could not restrain the degradation. This is nothing but the mechanism of mechanochemical degradation because only using it can explain why the antideteriorant could not entirely restrain the degradation.

It is well-known that the action of the antideteriorant for restraining the degradation of PP is that the antideteriorant is an agent of capture of radicals, eliminating the radicals such as "POO·," "PO·," "P·," and "OH·," which may cause the further reaction to lead to the rupture reaction (17). The mechanism of the restraint of the antiderteriorant is that the radicals are already eliminated before the rupture reaction takes place.

However, in the mechanochemical degradation, the action of shear stress may cause directly the rupture of the main chains so the first step, chain-initiating reaction, can lead to rupture even the radicals do not produced before.

The mechanism of mechanochemical degradation can explains why the carbonyl index of the mixing treating PP still increases gradually in spite of low hydroxyl index during the mixing process. In the thermooxidative degradation, only a small part of hydroxyl groups can produce radicals for the initiation of the chain rupture reaction, while most of them connected on the main chains of the polymer as side groups, so it needs enough gaseous oxygen to produce hydroxyl groups. In mixing process, the lack of oxygen may restrain the rate of the production of hydroxyl groups to reduce thermooxidative degradation. On the contrary, the formation of carbonyl groups is different from that of hydroxyl groups. No matter how the thermooxidative degradation or mechanochemical degradation it is, the degrading product of PP is still a product of macromolecule, so the number of the carbonyl groups on the terminals of the main chains is far smaller than the number of the chain elements. Consequently, the formation of the carbonyl groups does not require high level of gaseous oxygen. The lack of oxygen may restrain the formation of hydroxyl groups but nor the formation of carbonyl groups. Hence in mixing process, although the increasing rate of hydroxyl index is restrained to cause the mechanochemical degradation to become the dominant mechanism of degradation, the carbonyl index still increases significantly. It is noticed that the mechanism of mechanochemical degradation needs no oxygen to initiate the chain rupture reaction. Under the condition of the lack of oxygen, a part of the terminals of the ruptured main chains produced by the action of shear stress can form double bond groups at first. After the mixing process, when the test sample is taken out from the chamber to be exposed in the air, the contact surface of the sample with the air may increases significantly. This may lead to subsequent reactions at the double bond groups at the terminals of the ruptured main chains. In this case the double bond groups might react with oxygen to form carbonyl groups finally. Both the variations of carbonyl index and hydroxyl index can be seen from Table I. Table V further shows that $c_{r,G}$ (i) still increased compared with the invariance of $h_{r,G}$ (i).

It can be seen from the above discussion that during the mixing treating process of PP granules the dominant mechanism of degradation is the mechanism of mechanochemical degradation.

It must be emphasized that we do not deny the action of the mechanism of thermooxidative degradation in this mixing treating process at all. The mechanism of thermooxidative degradation is just considered as a subordinate mechanism in this case because that in spite of little action of it, the thermooxidative degradation is not entirely eliminated under the treating condition investigated.

It follows from the above analysis that Formula (22) can be used as a sufficient condition for the judgment of the dominant mechanism for the mechanism of mechanochemical degradation. In addition, if the dominant mechanism of degradation is the one of mechanochemical degradation during the treating process, both the carbonyl index and c_r (i) may increase gradually with the enhance of the treating condition compared with the basically invariance of both the hydroxyl index and h_r (i).

A real time study of the evolution of the degradation of PP granules during mixing process

By means of the characteristic functions constructed, a real time study of the evolution of the degradation of PP granules during mixing process can be carried out. If a careful analysis of Table V is made, it can be found that at the M time of 5min (i = 2), $\Delta h_{r,G}$ (i) does not satisfy the sufficient condition (22). At this time, we have

$$\Delta h_{r,G}(i) = 0.13 \geq 0.05 \neq 0 \qquad (i = 2). \qquad (26)$$

This means that at the M time of 5 min, the hydroxyl index increased significantly. It can be seen from Table I that the value of hydroxyl index varies from 0.31 for the blank test sample to 0.35 at the M time of 5 min. Hence a question is naturally propounded here: does this mean that at the initial stage of the mixing process the increase of hydroxyl groups lead to the mechanism of thermooxidative degradation as the dominant one?

It should be said that, if we consider the thermooxidative degradation is the dominant mechanism at the

initial stage merely according to Formula (22), then the reason is not enough. In fact, Formula (22) is merely a sufficient condition for the mechanism of mechanochemical degradation. This means that when Formula (22) does not hold, that is, when the hydroxyl groups produced, it can not be concluded that no action of the mechanochemical degradation took place at this time. In addition, Formula (26) is satisfied Formula (19), but it is merely the necessary condition of the mechanism of thermooxidative degradation. The "necessary condition" merely suggests the possibility of the generation of the thermooxidative degradation, could not affirm the definition of it. Hence it is not sufficient to merely use the Formula (22) and (19) to study the mechanism of degradation of PP granules at the initial stage of mixing process. It needs more criterions to study for obtaining an exact conclusion.

As stated above, the feeding material was put in a closed chamber away from light, so the mechanism of photooxidative degradation is out of consider. According to the above two criterion, there may be one of the following cases of degradation of PP in the initial stage of the mixing process. One is the case that the mechanochemical degradation is still a dominant mechanism. The other is the case that the two mechanisms, that is, the mechanism of mechanochemical degradation and the mechanism of thermooxidative degradation, act simultaneously and compete with each other. It can be seen from Table I that the carbonyl index increased rather significantly varying from 0.17 for the blank test sample to 0.19 for the M time of 5 min to show a valid evidence of the action of the degradation.

During the whole mixing process, the rotor speed and the feeding load kept constant so the feeding material was acted upon by a constant shear stress. Since in the middle stage and the later stage, the mechanochemical degradation took place and in the initial stage, the cause that generated the mechanochemical degradation is the same as in the middle stage and the later stage, then it can be deduced from this that in the initial stage the mechanochemical degradation still took place.

Moreover, in the initial stage of mixing, the feeding material just to be put into the chamber may contact with fresh air. The stack of PP granules before melt gave greater area of contact surface with the air than that after melt. Hence the concentration of oxygen near the reaction location in the initial stage was greater than that after the initial stage. It can be speculated from this that in the initial stage greater action of the thermooxidative degradation may took place than that in other stages. One of the characters of the mixing condition is the high processing temperature (190°C) compared with the thermooxidative treating temperature adopted by this article as listed in Table VI and VIII. This may

lead to a significant raise of the possibility of the thermooxidative degradation compared with the absence of thermooxidative degradation of PP granules under the condition in Table VI and VIII. Table VIII shows that the function $\Delta h_{r,G}$ (i) for thermooxidative treatment satisfies Formula (20), but Table V shows that the function $\Delta h_{r,G}$ (i) for mixing process satisfies Formula (26). Hence, it can be seen that the action of the thermooxidative degradation arose. Certainly, the antideteriorant in the PP granules may still restrain the thermooxidative degradation so the action of mechanochemical degradation should not be neglected yet.

It can be concluded from the above discussion that the mechanism of degradation of PP granules in the initial stage of the mixing process is the second case mentioned above that the two mechanisms, the mechanism of mechanochemical degradation and the mechanism of thermooxidative degradation, act simultaneously and compete with each other.

It can be observed from Figure 10 that after the M time of 10 min later, the hydroxyl index of PP granules kept quite stable. This is quantitatively expressed by Formula (24) and (25). A concept of "stabilizing time for hydroxyl index" is proposed here to describe this phenomenon. The concept of "stabilizing time for hydroxyl index" is defined that the minimum M time at which Formula (22), the sufficient condition of the mechanochemical degradation, is satisfied, being denoted by t_H. Obviously, t_H is the minimum M time at which the invariance of hydroxyl index begins during the mixing process. Here the case of mixing treating PP granules t_H is 10 min.

According to the above discussion, it can be seen that t_H has its clearly defined meaning. Apparently, t_H is the point of M time at which the behavior of degradation begins from the competition of the two mechanisms, the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation, with each other simultaneously to become one mechanism among them, the mechanism of mehcanochemical degradation, as a dominant mechanism.

Summarily, the evolution of degradation of PP granules during mixing process can be described as follows. During the whole mixing process, the mechanism of mechanochemical degradation acts from the beginning to the end giving a very remarkable degradation of PP granules for the antideteriorant fails to stop the mechanochemial degradation entirely. At the initial stage of mixing process, that is, before the stabilizing time for hydroxyl index t_H, the stack of PP granules before melt gives greater area of contact surface with the air than that after melt, so the concentration of oxygen near the reaction location is greater than other stages to lead to a rather strong action of the mechanism of

thermooxidative degradation. As a result, two mechanisms of degradation, that is, the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation, act simultaneously to compete with each other. However, the antideteriorant may restrain the thermooxidative degradation effectively. Although the action of thermooxidative degradation may carry out easily at the first step to produce many hydroxyl groups as side groups connected on the main chains of the polymer, showing little effect of the antideteriorant for forming hydroxyl groups, it is restrained effectively by the antideteriorant at the second step to decrease the rupture reaction. In the middle and the later stage, that is, after t_H, the envelopment of the melt feeding material reduces greatly the area of the surface of the polymer contacted with the air. In addition, the consumption of gaseous oxygen for the degradation reaction may reduce the concentration of gaseous oxygen in the closed mixing chamber. These may reduce the diffusing rate of gaseous oxygen to the phase of the polymer to lead to a reduction of the concentration of oxygen near the location of the degradation reaction. The thermooxidative degradation is strongly affected by the quantity of the hydroxyl groups, which produce under the strong influence of the concentration of oxygen, so the thermooxidative degradation is strongly affected by the concentration of oxygen. The lack of concentration of oxygen may restrain the production of hydroxyl groups. Hence in the middle and the later stage, little increase of hydroxyl groups can be observed and the hydroxyl index keeps constant basically. This may cause that $\Delta h_{r,G}$ (i) equals or merely equals to zero to show little action of the thermooxidative degradation and the dominant action of the mechanochemical degradation. However, although the formation of the carbonyl groups also needs oxygen, the carbonyl index increases constantly regardless of the lack of oxygen in the chamber during the whole mixing process. This is caused for the reason that the carbonyl groups mainly form at the terminals of the main chains so the ratio of the number of carbonyl groups to the number of the chain elements is rather small, hence little amount of oxygen is needed. Even in the case of free-oxygen the mechanochemical degradation still acts to produce rupture reaction to form double bond groups at the terminals of the main chains, which may further react with oxygen to form carbonyl groups after the end of the mixing process when the feeding material is got out from the chamber to expose in the air.

Discussion of the characteristic indexes and the characteristic functions of the mixing treating PP powder

The increasing rate of the carbonyl index of mixing treating PP powder is smaller than that of thermooxidative treating PP powder under the thermooxidative treating conditions reported in this article. For instances, even the EM time was 30 min, the carbonyl index of mixing treating PP powder was merely 0.29 (Table I). Comparatively, the carbonyl index of thermooxidative treating PP powder went up to 1.98 at 130°C for 3 h (Table VI). The corresponding characteristic functions $c_{r,P}$ (i) and $\Delta c_{r,P}$ (i) had similar trends of variation.

The hydroxyl index of PP powder has similar cases. The increasing rate of the hydroxyl index of mixing treating PP powder is smaller than that of thermooxidative treating PP powder under the thermooxidative treating conditions reported in this article. The values of hydroxyl indexes of the two sorts of treating PP powder are all higher than those of the corresponding carbonyl indexes. For example, even the EM time was 30 min, the hydroxyl index of mixing treating PP powder was merely 0.35 (Table I). Comparatively, the hydroxyl index of thermooxidative treating PP powder jumped up to 2.64 at 130°C for 3 h (Table VI). The corresponding characteristic functions $c_{r,P}$ (i) and $\Delta c_{r,P}$ (i) had similar trends of variation.

These observations reveal that PP powder degraded in the two sorts of treating methods. Under both the mixing treating condition and the thermooxidative treating condition reported in our study, the degradation of mixing treating PP powder is less than that of thermooxidative treating PP powder.

The above conclusion from the analysis of the characteristic indexes and the characteristic functions is consistent with that from the analysis of the values of the equilibrium torque of PP powder. In fact, the equilibrium torque of mixing treating PP powder was 1.6 Nm at the EM time of 30 min (Table I) compared with 0.1 Nm for the equilibrium torque of thermooxidative treating PP powder at 130°C for 3 h (Table VI).

Hence, a question is naturally propounded here: which mechanism of degradation of PP powder does take place in the mixing process?

The answer can be obtained by the above analysis of the characteristic indexes and the characteristic functions of PP powder by comparing the above discussions of the mechanism of degradations of mixing treating PP granules. It can be deduced that, there exist two mechanisms of degradation, the mechanism of thermooxidative degradation, and the mechanism of mechanochemical degradation, during the mixing process of PP powder simultaneously.

However, it needs further discussion to answer, which one the dominant mechanism is and how strong the degradation is.

In the above section "Discussion of the characteristic indexes and the characteristic functions of the

mechanochemical degradation of PP" and Section "A real time study of the evolution of the degradation of PP granules during mixing process," it is pointed that the lack of oxygen in the chamber and the envelopment of the melt feeding material reduce the rate of thermooxidative degradation remarkably. The fact that the degradation of mixing treating PP powder is weaker than that of thermooxidative treating PP powder further gives the evidence to support this conclusion.

This is because that the degradation of mixing treating PP powder includes two parts, one is the thermooxidative degradation and the other is the mechnochemical degradation, so if the total addition of contributions of the two parts of the degradation is lower than that of the thermooxidative treating PP, then the level of thermooxidative degradation generated in the mixing process is definitely lower than that in the thermooxidative treatment.

The mixing processing temperature of the mixing treatment listed in this article is 190°C, while the treating temperature of thermooxidative degradation adopted in our study is 120°C and 130°C. The former is much higher than the later. According to Arrhenius Formula, although the mixing treating time is less than the thermooxidative treating time, the degrading reaction would accelerate significantly for the mixing processing temperature is much higher 30 to 40°C than the thermooxidative treating temperature. However, the exact opposite is true. This means that the degrading reaction was restrained by some causes. It is evident that the restraint of the degradation reaction was caused by the significant reduction of the concentration of oxygen near the location of the degradation reaction and the diffusing rate of gaseous oxygen to the phase of the polymer.

One of the characters of PP powder is the small size of the gains. In the thermooxidative treatment of PP powder, small diameters of the gains make large contact surface of the polymer with the air and good convection of air is achieved in the oven. Hence ordinary concentration of gaseous oxygen and the high diffusing rate of oxygen are obtained to raise the rate of thermooxidative degradation significantly. However, in the mixing process, PP powder melts in a rather short time to bring about a lack of oxygen in the inner of the melt feeding material except its outer surface contacting with the air. The difficulty of the diffuse of oxygen to the inner of the melt feeding material is far greater than that to the inner of the gains of PP powder of which the diameters are merely about tens of microns to hundreds of microns, so the rate of diffuse of oxygen to the inner of the melt feeding material may reduce greatly. All of these restrain the thermooxidative degradation in mixing process greatly.

Now that there exist two mechanisms of degradation in the mixing treatment of PP powder, the ques-

tion that which one of them is the dominant mechanism of degradation is naturally to be discussed.

It can be seen from Table III and IV that for the mixing treating PP powder we have following equation:

$$\Delta h_{r,P}(i) = 0 \qquad (D_l(i) < 0, \quad i = 3\text{--}6). \qquad (27)$$

Obviously, Formula (27) satisfies the sufficient condition (21), so it can be concluded that the dominant mechanism of degradation of mixing treating PP powder is the mechanism of mechanochemical degradation after the M time of 10 min.

Table I shows that the variation of the carbonyl index of PP powder is basically as same as PP granules. This can be also observed from Figure 9. The curve of carbonyl index of PP powder is paralleled to the one of PP granules basically revealing similar varying tendency only with a little difference of the heights of the curves to show a little raise of degradation of PP powder. This means that the variations of degradation of the two sorts of mixing treating PP were rather close. The corresponding values of the equilibrium torque of them shows the same varying tendency. At the end of mixing, the values of the equilibrium torque of the two sorts of mixing treating PP are 1.6 and 1.7 Nm, respectively being very close (Table I).

This same varying tendency shows that the mechanisms of degradation of mixing treating PP powder are as same as PP granules basically. In addition, it can be seen from Table IV to V that both the function $c_{r,P}(i)$ and $c_{r,G}(i)$ arose with the increasing of M time to keep similar magnitude, while both the function $h_{r,P}(i)$ and $h_{r,G}(i)$ kept constant basically. In other words, the variation of the function $c_{r,P}(i)$ for mixing treating PP powder is the same as the function $c_{r,G}(i)$ for mixing treating PP granules basically. The variation of the function $h_{r,P}(i)$ for mixing treating PP powder is also the same as the function $h_{r,G}(i)$ for mixing treating PP granules basically. All of these give further evidences to suppose the conclusion that the dominant mechanism of the mixing treating PP powder is the mechanism of mechnochemical degradation.

Moreover, there are some differences between the behavior of the degradation of mixing treating PP powder and that of PP granules. These will be discussed in the evolution of degradation in the following.

A real time study of the evolution of the degradation of PP powder during mixing process

Similar to the discussion of PP granules, a real time study of the evolution of the degradation of PP powder during mixing process can be also carried out. It

can be found from Table IV that at the M time of 5 min ($i = 2$), $\Delta h_{r,P}$ (i) does not satisfy the sufficient condition (22). At this time we have,

$$\Delta h_{r,P}(i) = 0.17 \geq 0.05 \neq 0 \qquad (i = 2). \qquad (28)$$

This means that at the M time of 5 min the hydroxyl index increased significantly. It can be seen from Table I that the value of hydroxyl index was from 0.30 for the blank test sample to 0.35 at the M time of 5 min. Consequently, similar to the discussion of mixing treating PP granules, it can be deduced that at the initial stage of mixing process of PP powder the two mechanisms of degradation, that is, the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation, take place simultaneously and compete with each other.

From Figure 10 it can be found that after the M time of 10 min later, the hydroxyl index of PP powder kept constant basically. This is expressed algebraically by Formula (27). Therefore, there exists stabilizing time for hydroxyl index t_H of mixing treating PP powder and similar to the case of mixing treating PP granules, it is also at the M time of 10 min.

According to the above discussion, it can be seen that the exact meaning of the stabilizing time for hydroxyl index t_H of mixing treating PP powder is as same as mixing treating PP granules. Both of them are all turning points of the M time. Before t_H, the two mechanisms of degradation, the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation, carry out and compete with simultaneously. After t_H, the mechanochemical degradation becomes the dominant mechanism of degradation.

However, can we consider that before t_H for mixing treating PP powder, that is, during the initial stage, the mechanism of thermooxidative degradation play more important role than that for mixing treating PP granules for the absence of the antideterionant in PP powder? The answer is "yes." This can be explained by both theoretical deduction and experimental observation. However, it is evident that a very significant degradation may take place for the mixing treating PP powder without any antideterionant in theory. However, it can be observed from Figure 4 that the torque-time curve of PP powder is higher than that of PP granules before the mixing ending time of 5 min. This is because that both sorts of PP were made from different producers giving higher molecule weight of PP powder than that of PP granules. Obviously, the significant reduction of the torque-time curve is caused by the action of degradation. Moreover, it can be also observed from Figure 4 that the descent of the height of the torque-time curve of PP powder from 5 min to 10 min was greater

than that of PP granules correspondingly. This can be considered the result of the mechanism of thermooxidative degradation because both sorts of PP were treated under the same mixing condition so the same action of shear stress was produced. Apparently, the absence of the antideterionant made PP powder degraded immediately in the initial stage of mixing process to cause its molecule weight fell down to the level matched with that of PP granules. Therefore, the thermooxidative degradation plays greater role for mixing treating PP powder than that for PP granules in the initial stage of mixing process. Figure 4 shows that the torque-time curve of mixing treating PP powder is higher than that of PP granules till the M time of 10 min.

Although from the above discussion it has been found that the thermooxidative degradation plays greater role for mixing treating PP powder than that for PP granules in the initial stage of mixing process, yet it could not come to the conclusion that the mechanism of thermooxidative degradation is the dominant mechanism in this stage from the analysis of the rheological data and the FTIR characteristic functions obtained in this article. Up till now, it can only come to such a conclusion that in the initial stage of mixing process, both the two mechanisms of degradation, the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation, take place simultaneously and compete with each other, while the thermooxidative degradation plays greater role for mixing treating PP powder than that for mixing treating PP granules.

In the middle stage and the later stage, it has been concluded form the discussion of the above paragraphs that the mechanism of mechanochemical degradation is the dominant one in the degradation of mixing treating PP powder. In fact, Figure 4 shows that the torque-time curve of mixing treating PP powder overlaps rather well with the one of mixing treating PP granules after 10 min later to show matching with each other in degradation. Hence in spite of the lack of antiderterionant the action of thermooxidative degradation of mixing treating PP powder was still so small that it is similar to the one of mixing treating PP granules. This means that enough concentration of oxygen near the location of reaction is the necessary condition of the effective action of the mechanism of thermooxidative degradation. Certainly, the action of thermooxidative degradation still take place, merely not so significant, for the reason that the concentration of oxygen is just reduced, not come to zero yet.

It can be summarized from the above discussions to describe the evolution of the degradation of PP powder during the mixing process as follows. During the mixing process, two mechanisms of degradation, the mechanism of thermooxidative degradation

and the mechanism of mechanochemical degradation, take place simultaneously and compete with each other, while the dominant mechanism is generally the one of mechanochemical degradation. The mechanism of mechanochemical degradation acts from the beginning to the end to cause a significant degradation. In the initial stage, that is, before stabilizing time for hydroxyl index t_H, the mechanism of thermooxidative degradation plays greater role than in other stages. In this stage, the two mechanisms, the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation, take place simultaneously and compete with each other. This is caused for the reason that the stack of small gains of PP powder makes high contact area of the surface of the gains before melting entirely with the air to obtain ordinary concentration of oxygen near the location of reaction. The thermooxidative degradation of mixing treating PP powder is greater than that of mixing treating PP granules for the absence of the antideteriorant in PP powder. Unlike the case of mixing treating PP granules, the action of the thermooxidative degradation of mixing treating PP powder not only produces many hydroxyl groups as the side groups on the main chains of the polymer, but also forms carbonyl groups in the stage of rupture reaction to obtain higher carbonyl index than that of mixing treating PP granules. In the middle stage and the later stage of mixing process, that is, after t_H, the behavior of degradation of mixing treating PP powder is very similar to that of mixing treating PP granules even without addition of any antideteriorant. The envelopment of the melt feeding material caused the mechanochemical degradation to become the dominant mechanism. So long as the concentration of oxygen near the location of the reaction decreases, the action of the thermooxidative degradation of the mixing treating PP powder is rather small even without any antideteriorant. The effect of the concentration of oxygen on the formation of the carbonyl groups of mixing treating PP powder is rather small so during the whole mixing process its carbonyl index increases gradually.

CONCLUSIONS

In the mechanism of thermooxidative degradation of PP, not only can the carbonyl index and the hydroxyl index, but also their corresponding FTIR characteristic functions increase with the enhancement of the condition of the thermooxidative treatment. During the mixing treating process of PP, the height of the torque-time curves of both PP powder and PP granules descend gradually with the increase of M time to indicate the gradual degradation of the PP materials. In opposition to the case of thermooxi-

dative treatment, during the mixing treating process the antideteriorant in PP granules could not stop the degradation of PP entirely and in the middle and the later stage of mixing process, even if the degradation of PP increases the hydroxyl index keeps quite stable while the carbonyl index rises.

The necessary condition of the significant occurrence of thermooxidative degradation in either thermooxidative treatment or mixing treatment for PP is $\Delta h_r(i) > 0.05$.

The sufficient condition of the significant occurrence of mechanochemical degradation in mixing treatment for PP is $\Delta h_r(i) \leq 0.05$ ($D_l(i) < 0$, and $i > 1$).

During the degrading process of PP, the concentration of oxygen near the location of the reaction may give significant influence on the formation of the hydroxyl groups on the main chains of PP but little influence on the formation of the carbonyl groups.

The degradation of PP generated by the mechanism of thermooxidative degradation is greatly affected by the concentration of oxygen near the location of the reaction. On the contrary, the action of the mechanism of mechanochemical degradation is hardly affected by the concentration of oxygen, while mainly affected by shear stress. The rupture reaction generated by the mechanism of mechanochemical degradation can take place in the chain initiation stage to lead to chain scission directly by shear stress dispensing with hydroxyl groups as middle-products. The terminals of the main chains of the polymer produced by mechanochemical degradation are not always the carbonyl groups instead of other chemical groups, such as double bond groups, etc.

There exists a stabilizing time for hydroxyl index t_H during the mixing process of PP. Before this time two mechanisms of degradation, that is, the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation, act simultaneously to compete with each other and after that the mechanism of mechanochemical degradation becomes dominant.

It can be described the evolution of degradation of PP granules during mixing process as follows and during the whole mixing process, the mechanism of mechanochemical degradation acts from the beginning to the end giving a very remarkable degradation of PP granules. The antideteriorant in PP granules fails to stop the mechanochemial degradation entirely but restrains the thermooxidative degradation effectively in mixing process. At the initial stage of mixing process, that is, before t_H, the stack of the gains of PP granules before entirely melt gives greater area of contact surface with the air than that of after melt, so the concentration of oxygen near the reaction location is the same as ordinary. As a result, the mechanism of thermooxidative degradation and the mechanism

of mechanochemical degradation act simultaneously to compete with each other. In the middle and the later stage, that is, after t_H, the mechanism of thermooxidative degradation becomes rather insignificant to lead the mechanism of mechanochemical degradation to become dominant. The antideteriorant takes little effect in the two stages in this case of PP granules.

The evolution of the degradation of PP powder during the mixing process is rather similar to the one of PP granules, but it takes some different characters. This is caused by the absence of any antideteriorant in the polymer and by the great area of the surface of the small gains of PP powder compared with that of PP granules. During the mixing process of PP powder, two mechanisms of degradation, the mechanism of thermooxidative degradation and the mechanism of mechanochemical degradation, take place simultaneously and compete with each other. However, the dominant mechanism is generally the one of mechanochemical degradation. The mechanism of mechanochemical degradation acts from the beginning to the end to cause a significant degradation. In the initial stage, that is, before t_H, the mechanism of thermooxidative degradation of PP powder plays greater role than that of PP granules. In the middle and the later stage of mixing process, the mechanism of thermooxidative degradation becomes insignificant in spite of the absence of the antideteriorant. Hence the mechanism of mechanochemical degradation is the dominant mechanism.

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