Degradation and *In Situ* Reaction of Polyolefin Elastomers in the Melt State Induced by Ultrasonic Irradiation

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ABSTRACT: The degradation and *in situ* reaction with polystyrene (PS) of polyolefin elastomers in the melt state induced through high intensity ultrasonic wave were investigated. The effects of initial molecular weight of polyolefin elastomers, irradiation time, ultrasonic intensity, as well as reaction temperature on the ultrasonic degradation of polyolefin elastomers melt were studied using a "static" ultrasonic vibration system. The results show that the degradation occurs mostly at the tip of the ultrasonic probe, and little or no degradation was observed at the distance of 5 mm or greater from the tip of the probe. The intrinsic viscosity $[\eta]$ of polyolefin elastomers near the tip of ultrasound probe significantly decreases with irradiation time in the first 100 s and tends toward a limiting value for all samples. The degradation rates increased with an increase in ultrasonic intensity and decrease in reaction temperature. The ultrasonic degradation kinetics of polyolefin elastomers in melt state follows the equation: $[\eta]_t = [\eta]_\infty + Ae^{-kt}$. The fitting results by this equation accord well with the experimental data. The feasible ultrasonic degradation mechanism is proposed based on the viscoelastic characteristic of polymer melt. FTIR analysis confirms that the copolymer forms under ultrasonic irradiation for PS/POE mixtures and *in situ* reaction of polymer in melt state can be induced by ultrasonic irradiation. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 138–145, 2007

Key words: ultrasonic degradation; elastomer; kinetics

INTRODUCTION

High-intensity ultrasound is generally applied in the area of cleaning, plastic welding, machining, etc.[1–3] In addition to these conventional applications, many researchers have applied high-intensity ultrasonic wave to assist polymer degradation and polymerization in the solution.[4–8] A widely accepted mechanism of polymer degradation by ultrasonic irradiation is ascribed to the cavitations in the medium. Cavitations occur followed by the growth and rapid collapse of microbubbles when ultrasound propagates in solution. This leads to violent shock waves with a high temperature of ~ 5000 K and a high pressure of ~ 1000 bar, which is highly sufficient to cause the rupture of chemical bonds. In the area of polymer chemistry, a number of researches have suggested a useful way to induce mechanic–chemical degradation and control the molecular weight and molecular weight distribution of polymer through ultrasonic irradiations. When high-intensity ultrasonic irradiation is subjected to polymer solution, the main-chain scission of polymer occurs and consequently the molecular weight is decreased. The macroradicals formed through the chain scission of polymer can be terminated by radical scavengers to produce the polymers with controlled molecular weight and molecular weight distribution.[9–12]

At present, most studies have concentrated on the effect of sonication on the degradation of polymers in the solution. Little work has been concerned with the effect of ultrasonic irradiation on the degradation of polymer melts. Guo et al.[13–15] reported that ultrasonic irradiation can obviously improve the appearance and processability of high-density polyethylene (HDPE), polystyrene (PS), as well as PS/HDPE blends during extrusion. Kim and Lee[16] introduced ultrasound into an internal mixer to examine the degradation of polypropylene and ultrasonic compatibilization of polymer blends. Ultrasound assisted melt mixing can lead to *in situ* copolymer formation between the components and consequently provide an effective route to compatibilize the immiscible

The Composition and Molecular Characteristics of VERSIFY Elastomers (PEE) and ENGAGE Elastomers (POE)

Samples	Melt flow rate at 230°C and 2.16 kg (g/10 min)	Density (g/cm^3)	Comonomer	Comonomer content (wt %)
VERSIFY (PEE)				
DE2300	2	0.866	Ethylene	12
DE2400	2	0.858	Ethylene	15
DE3300	8	0.866	Ethylene	12
ENGAGE (POE)				
POE8150	0.5	0.868	Octane	~ 30
POE8100	1.0	0.870	Octane	~ 20

polymer blends. Our previous work[17] ascertains that *in situ* copolymer formation between PP and ethylene-propylene-diene-terpolymer (EPDM) with ultrasonic irradiation and the copolymer consequently acts as compatibilizers for the blend.

According to the above description, the main impetus for the ultrasonic degradation of polymer solution is ascribed to the cavitational effects initiated in the liquid phase. In the polymer melts, however, such a consequence is hardly expected. Previous work shows that the scission of the polymer chains is possible in the presence of ultrasonic irradiation. However, the exact mechanism of polymer scission is still unclear. There are few reports on the ultrasonic degradation kinetics and degradation mechanism of polymer melts, especially elastomers.

In this work, ultrasound-induced polymer degradation and *in situ* reaction were studied using a ''static'' ultrasonic vibration system. High-intensity ultrasonic irradiation was introduced into novel polyolefin elastomer melts. The degradation kinetics and mechanism of polyolefin elastomer melts were studied. The effects of initial molecular weight, intensity, and distance of ultrasonic irradiation on the degradation were also discussed. The pilot study of *in situ* reaction induced by ultrasonic irradiation for polymer melts was investigated.

EXPERIMENTAL

Materials

The materials studied were commercial products of propylene–ethylene random copolymers (VERSIFY^{TM} Elastomers, denoted as PEE) and ethylene-octane random copolymers (ENGAGE^{TM} elastomers, denoted as POE) supplied by The Dow Chemical Company. The composition and molecular characteristics of the samples are summarized in Table I. PS resins (PG-383M) were purchased from Zhenjiang Chimei Co. (Jiangsu, China) with density = 1.05 g/cm^3 and melt flow rate = 3.0 g/10 min (200°C, 5 kg, D-1238).

Ultrasonic degradation and *in situ* reactions

The ultrasonic degradation of PEE and POE melts was conducted on a specially designed reactor described in Figure 1. The material was filled into the reactor and heated to a given temperature. A probe of ultrasonic oscillation with a maximum power output of 300 W and a frequency of 20 kHz was inserted into the polymer melt in the die. In a certain irradiation time, the degraded samples on the cross section at 1 mm from probe tip were picked out for further characterization.

The mixtures of PS and POE8150 were first extruded by twin-screw extruder (Nanjing, China) with a die temperature of 190°C. The extrudate was filled into the reactor and *in situ* reaction was conducted for PS/POE8150. The samples were heated to a temperature of 200°C and held for 3 min and then irradiated by ultrasonic wave with power output of 200 and 100 W for 5 min, respectively. The reactants on the cross section at 1 mm from probe tip were picked out for further characterization.

To assure the formation of the PS-POE grafting, the reaction products were put into a proper separation procedure by which PS homopolymer (or free
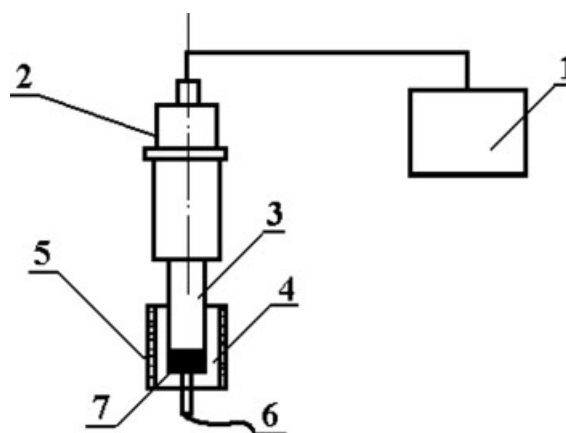

Figure 1 Scheme of static ultrasonic wave system. (1) Ultrasonic generator, (2) piezoelectric transducer, (3) horn, (4) reactor, (5) electric heaters, (6) thermocouple, (7) melt.

PS) was removed completely. The samples were extracted in a Soxhlet extractor with THF for 24 h and dried in a vacuum oven at 70°C for 24 h. The existence of PS units grafted to POE chains was investigated by FTIR.

Measurements and characterization

Intrinsic viscosity [η] of polymer was measured at 135°C by Ubbelodhe viscometer according to ISO-1628/1-1984 (E). The length, diameter, and constant of Ubbelodhe viscometer are 110, 0.54 mm, and 0.01190 mm^2/s^2, respectively. The solvent used is decalin.
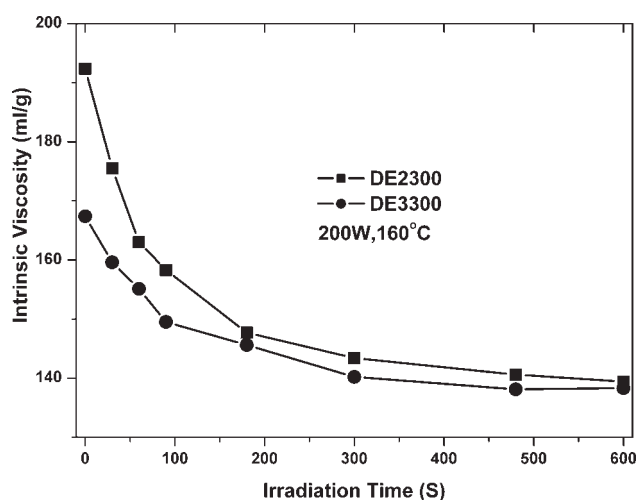
FTIR analysis of degraded and undegraded polymer films was conducted with a Nicolet 170X FTIR spectrometer (Nicolet Co) at a resolution of 2 cm^{-2} and 16 scans.
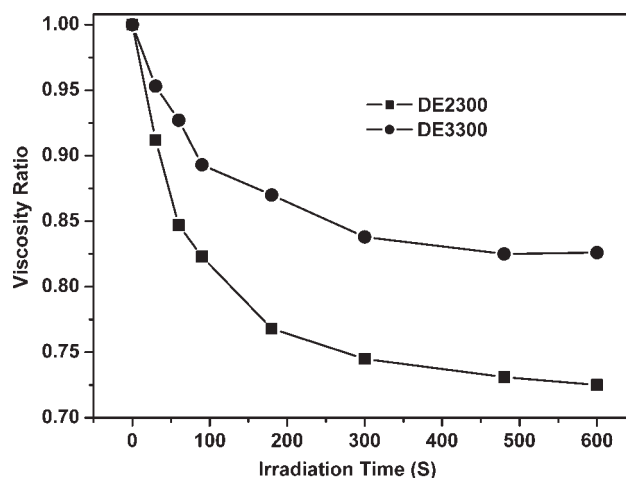
RESULTS AND DISCUSSION

The ultrasonic degradation of polymer in melt state

To eliminate the effect of thermal degradation of elastomer melts under high temperature, the thermal degradation experiments for elastomers were carried out at 160°C for 30 min. Intrinsic viscosity of samples remains almost unchanged before and after holding at 160°C for 30 min. Thus the thermal effects can be neglected in this work.

Figure 2 shows the effect of ultrasonic irradiation time on the degradation of DE2300 and DE3300. It can be clearly seen that intrinsic viscosity [η] of DE2300 and DE3300 decreases significantly with irradiation time in the first 100 s and then reduces slowly with increasing further irradiation time. At last, the intrinsic viscosity [η] of DE2300 and DE3300 tends to a same limiting value. These results show

Figure 3 Viscosity ratios versus irradiation time for DE2300 and DE3300.

there is a critical molecular weight for the scission of chains of DE2300 and DE3300 with ultrasonic irradiation. Figure 3 describes the viscosity ratio versus irradiation time for DE2300 and DE3300. In the case of DE2300, it appears that the ratios are lower than those of DE3300 for the given irradiation times. From the trend shown in Figure 3, it is worthy to note that the degradation rate was affected by the molecular weight of the sample, since increased mobility of the macromolecules favors harmless energy dissipation. In other words, the influence of the characteristic movements in ultrasonic wave is relatively weak and the efficiency of degradation is limited in case of the low viscosity matrix.

The DE2300 and DE2400 are the propylene–ethylene random copolymers with the similar molecular structure and molecular weight, and have different comonomer content. Figure 4 compares the variation
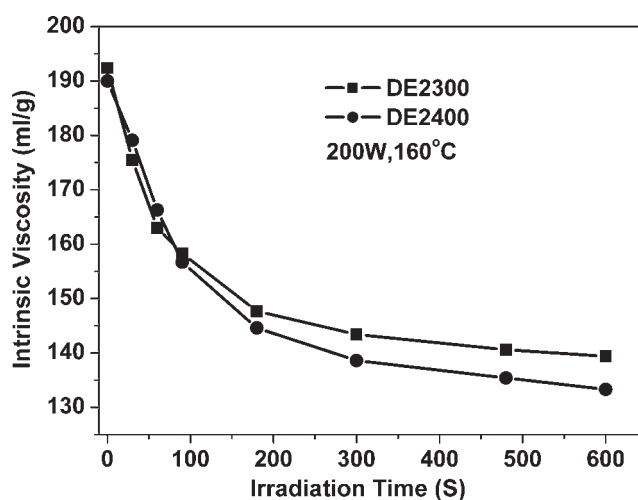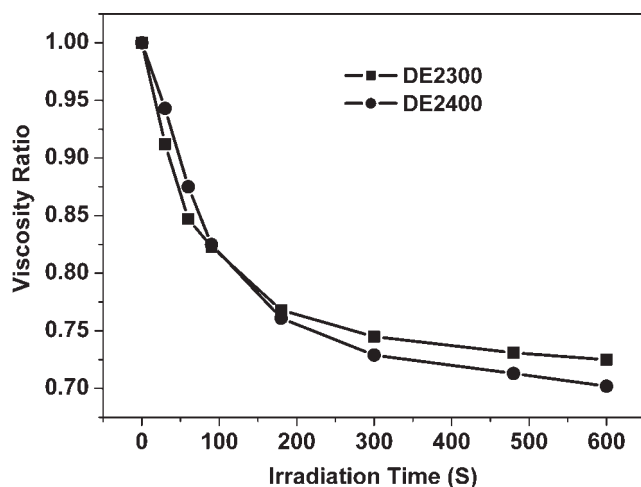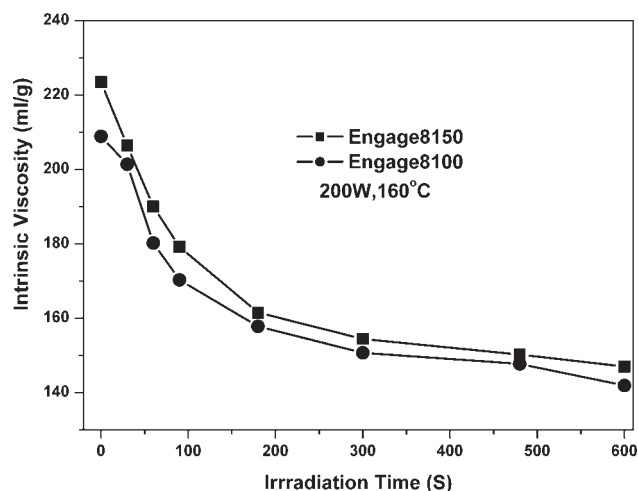

Figure 2 Dependence of [η] of DE2300 and DE3300 on ultrasonic irradiation time (reaction temperature: 160°C; irradiation intensity: 200 W).

Figure 4 Dependence of [η] of DE2300 and DE2400 on ultrasonic irradiation time (reaction temperature: 160°C; irradiation intensity: 200 W).

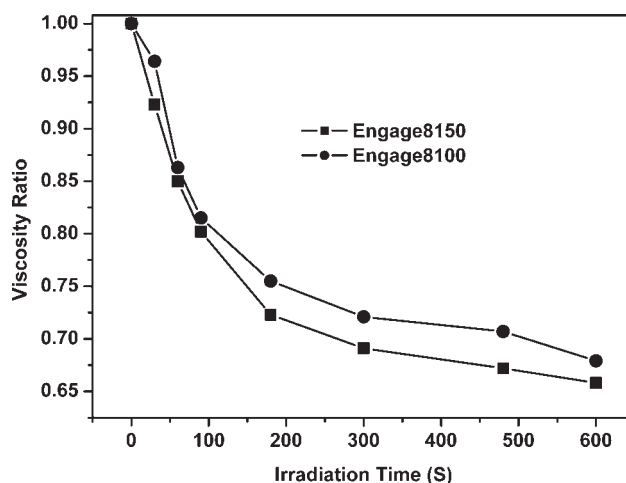**Figure 5** Viscosity ratios versus irradiation time for DE2300 and DE2400.

Figure 6 Dependence of [η] of POE8150 and POE8100 on ultrasonic irradiation time (reaction temperature: 160°C; irradiation intensity: 200 W).

of [η] with irradiation time for the ultrasonic degradation of DE2300 and DE2400 in the melt state to investigate the effect of the comonomer content on the ultrasonic degradation of PEE. It can be seen that the trend of the ultrasonic degradation of DE2400 is similar to that of DE2300 in despite of the comonomer content in the initial stage. At last the intrinsic viscosity [η] of DE2400 also tends to a limiting value less than that of DE2300. This indicates that the degradation degree of DE2400 is slightly larger than that of DE2300. Figure 5 shows that viscosity ratio versus irradiation time for DE2300 and DE2400. The DE2300 and DE2400 also exhibit the identical degradation rate. The results indicate that the comonomer content has no obvious effect on the degradation rate of PEE under ultrasonic vibration. The effect of molecular weight on the ultrasonic degradation of PEE is more obvious than that of the comonomer content.

In addition, the ultrasonic degradation of POE8150 and POE8100 in melt state was also examined, as shown in Figures 6 and 7. POE8150 and POE8100 are ethylene–octane random copolymers, which is different from PEE, which is the propylene-based copolymer. It can be seen that the variation of intrinsic viscosity [η] with irradiation time for POE8150 and POE8100 is similar to that of PEE, except that the ultrasonic degradation ratio of POE is larger than that of PEE postulated as the result of higher viscosity. It is well known that the degradation degree of POE should be less than that of PEE in the thermal condition. It is interesting to note that the experimental results from ultrasound degradation are different from the conventional predictions based on thermal-initiated degradation. The cause of this result is probably because of two following factors. One is

the fact that the degradation mechanism induced through ultrasonic wave is different from that of the thermal-initiated degradation where the position and numbers of chain scission could be very different. On the other hand, POE has higher molecular weight and higher branch content. Consequently, chain scission is easier and the degradation is more severe compared to PEE under ultrasonic wave irradiation.

The effect of ultrasonic intensity and reaction temperature on the degradation of DE2300 was shown in Figures 8 and 9. With the increase of ultrasonic intensity, the intrinsic viscosity of DE2300 is further reduced in the whole experimental time (Fig. 8). The limiting value of intrinsic viscosity [η] decreases and the degradation rate increases with increasing the ultrasonic intensity. This indicates that the degradation


Figure 7 Viscosity ratios versus irradiation time for POE8150 and POE8100.
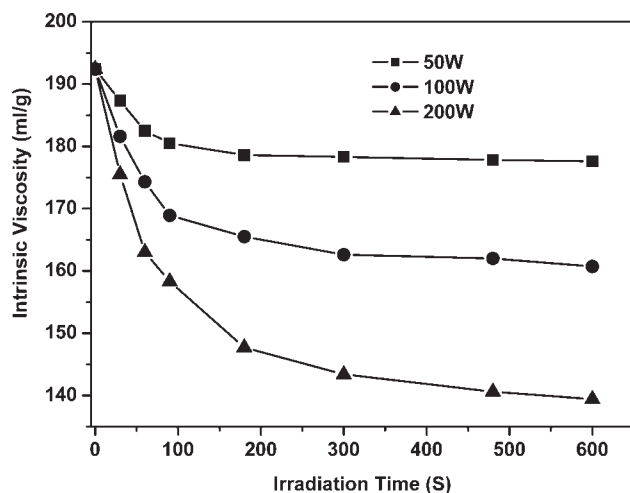
Figure 8 Dependence of [η] of DE2300 on ultrasonic irradiation time at various irradiation intensities (reaction temperature: 160°C).

extent of DE2300 increases with the rise of ultrasonic intensity.

The effect of reaction temperature on the intrinsic viscosity [η] of DE2300 at ultrasonic intensity of 200 W can be clearly seen from Figure 9. The degradation rate decreases with the rise of polymer melt temperature. The melt temperature was measured through the thermocouple inserting into the polymer melts accessing to ultrasonic probe. The samples on the cross section at 1 mm from probe tip were cut out for the measurement of intrinsic viscosity. The critical value of [η] also is further reduced when the reaction temperature is lowered to 120°C, which indicates that the critical molecular weight falls off with the decline
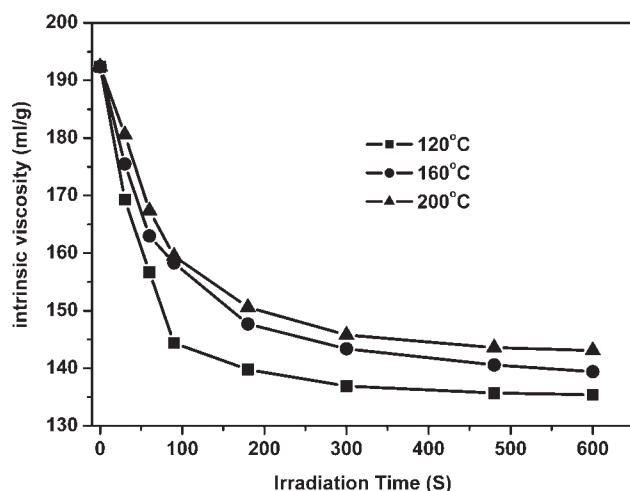
Figure 9 Effect of reaction temperature on intrinsic viscosity [η] of DE2300 (irradiation intensity: 200 W).

TABLE II
The Relative Strength of the Characteristic Absorbance Bands of PP and PE in DE2300

Irradiation time (s)	PP (A1159)	PE (A732)	A1159/A732
0	51.28	14.48	3.54
60	47.29	16.82	2.81
300	62.96	24.60	2.56

of reaction temperature. The mobility of the molecule chains increases with the increase of reaction temperature. Retarded degradation at the higher melting temperature is explained by reduced the relaxation time of polymer molecules because the relaxation time is temperature dependent. This key factor should be considered for the underlying mechanism of the ultrasonic degradation in the polymer melt.

FTIR spectroscopy is sensitive to the constitution of molecular chains and can be used to judge the position of chain scission for DE2300 under ultrasonic irradiations by calculating the absorbance ratios of PP and PE bands in FTIR spectra. The absorbance bands around 1159 cm^{-1} are associated with $[CH_2CH(CH_3)]_n$ of PP, and the bands around 732 cm^{-1} are associated with $[CH_2]_n$ of PE. Therefore, the change of relative content of PP and PE chain during ultrasonic irradiation can be obtained by calculating the absorbance ratios of PP (A_{1159}) to that of PE (A_{732}) in the FTIR spectra, which are employed to denote the relative strength of the characteristic absorbance bands of PP and PE, as shown in Table II. The ratio falls off with the increasing of irradiation time, which indicates that PP content in DE2300 decreased with the increase of irradiation time. This result maybe indirectly show the degradation of DE2300 melt is caused by the scission of PP chain. The more convictive evidences are needed to be provided further.

Ultrasonic degradation kinetics

Barambiom proposed that the degradation kinetics of polymer melt under stress should be expressed as eq. (1), which is applied to describe the kinetics of ultrasonic degradation in this work.

$$-\frac{d\left(\frac{M_t - M_\infty}{M_\infty}\right)}{dt} = k\left(\frac{M_t - M_\infty}{M_\infty}\right) \tag{1}$$

where M_∞ and M_t are the limiting and average molecule weight at irradiation time t, respectively; k is the rate constant of degradation reaction.
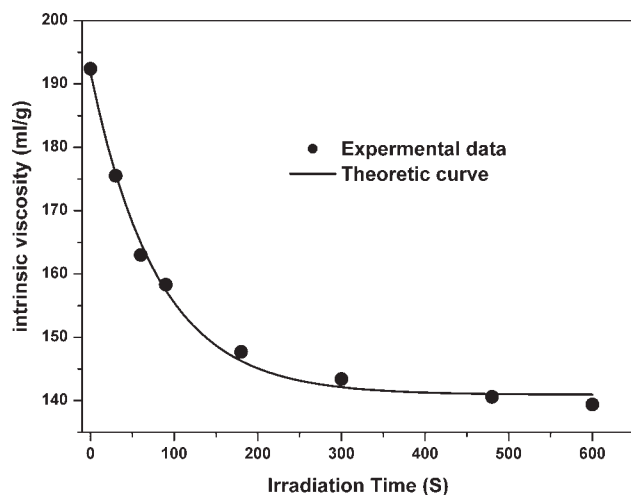
Figure 10 Dependence of [η] for DE2300 on ultrasonic irradiation time. The fits are given by the solid lines (reaction temperature: 160°C; irradiation intensity: 200 W).

According to the relation between molecule weight and intrinsic viscosity of polymer, the similar kinetics equation can also be described by the dependence of the intrinsic viscosity [η] on irradiation time, as following:

$$-\frac{d\left(\frac{[\eta]_t-[\eta]_\infty}{[\eta]_\infty}\right)}{dt} = k\left(\frac{[\eta]_t - [\eta]_\infty}{[\eta]_\infty}\right) \quad (2)$$

where $[\eta]_\infty$ and $[\eta]_t$ are the limiting and intrinsic viscosity at irradiation time t, respectively.

By integrating and considering that at $t = 0$, $[\eta]_t = [\eta]_0$ (where $[\eta]_0$ is the initial intrinsic viscosity), eq. (2) can be expressed as

$$[\eta]_t = [\eta]_\infty + ([\eta]_0 - [\eta]_\infty)e^{-kt} \quad (3)$$

If it is assumed that the constant $A = [\eta]_0 - [\eta]_\infty$, eq. (3) is converted into

$$[\eta]_t = [\eta]_\infty + Ae^{-kt} \quad (4)$$

The limiting viscosity, $[\eta]_\infty$, and the rate constant of the degradation reaction, k, can be extracted. The fit-

TABLE III
The Fitting Parameters Given by eq. (4)

Polymer	$[\eta_\infty]$	A	k
DE2300	140.93	50.80	0.0125
DE2400	134.20	56.73	0.0094
DE3300	138.28	28.61	0.0091
POE8150	148.63	75.32	0.0097
POE8100	144.71	66.42	0.0094

ting results by eq. (4) shown in Figure 10 agree well with the experimental data and the fitting parameters are presented in Table III. It is interesting to note that the limiting viscosity, $[\eta]_\infty$, seems to be independent of the molecular weight and the comonomer content, suggesting that chain scission caused by ultrasound may only occur at minimum molecular weight. And the constant A, which means the degradation degree, is increased with increasing the molecular weight. The fitting equation for DE2300 can be expressed as:

$$[\eta]_t = 140.93 + 50.80e^{-0.0125t} \quad (5)$$

As expressed in eq. (5), the calculated limiting intrinsic viscosity of DE2300 should be 140.93, which is very close to the experimental data of 139.40. This result indicates that if the intrinsic viscosity of DE2300 is below 139.40, which is a critical value, polymers do not undergo any chain scission that is a characteristic of ultrasonic degradation.

The similar degradation kinetics equation of POE8150 can also describe the dependence of the intrinsic viscosity on irradiation time through eq. (4) The theoretical curve shown in Figure 11 also agrees well with the experimental data of ultrasonic degradation kinetics for POE8150. The equation of the theoretic curve can be expressed as

$$[\eta]_t = 148.63 + 75.32e^{-0.0097t} \quad (6)$$

As expressed in eq. (6), the theoretic limiting intrinsic viscosity of POE8150 should be 148.63, which is very close to the experimental data of 147.00.
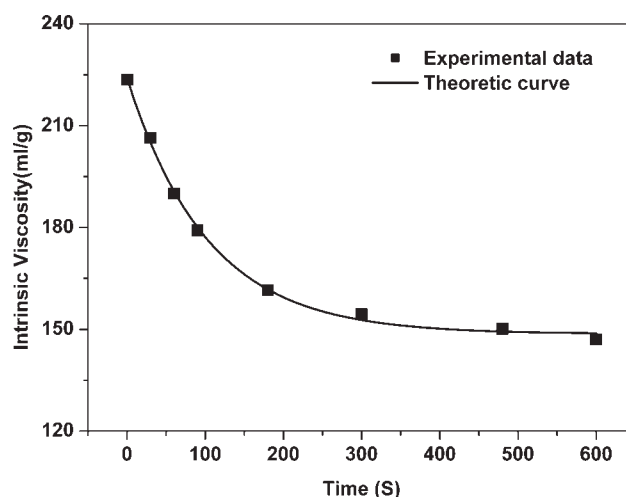
Figure 11 Dependence of intrinsic viscosity [η] for POE8150 on ultrasonic irradiation time. The fits are given by the solid lines (reaction temperature: 160°C; irradiation intensity: 200 W).
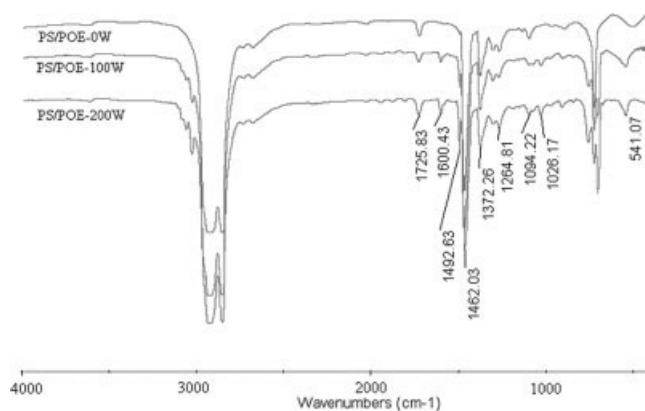
Figure 12 FTIR spectra of PS/POE8150 (50/50) blends with various ultrasonic intensities.

Ultrasonic degradation mechanism of polyolefin elastomer melts

As described in the previous section, the primary impetus for the ultrasonic degradation in polymer solution is ascribed to the cavitational effect initiated in the liquid phase. In the polymer melts, however, such a consequence is hardly expected. Therefore, Kim and Lee[16] propose a plausible mechanism in conjunction with the viscoelastic behaviors of polymer melt. Based on this principle, retarded degradation at higher temperature is explained by reduced the relaxation time of polymer melt.

It is well-known that ultrasound is a kind of elastic mechanic wave of frequency 10^4–10^8 Hz. When ultrasonic irradiation was applied to the polymer melt, time between successive expansion and compression of ultrasound is much shorter than the relaxation time of polymer melt (typically order of few seconds at the experimental temperature[19]). Thus, successive high intensity impact of ultrasonic waves can cause the random scission of polymer chain because polymer molecules will not be able to relax in time. The chain scission of higher molecular weight polymer melt is easier than that of lower molecular weight polymer melt because of longer relaxation time of higher molecular weight chains. Therefore, in the initial stage, the ultrasonic degradation is significantly obvious and the degradation rate is very high because of the presence of lots of long chains (Figures 2–7). After some time of ultrasonic irradiation, the degradation rate decreases because of the increase of short chain. Based on this principle, retarded degradation at lower molecular weight and high temperature is also explained.

In situ reaction of polyolefin melt initiated by ultrasonic irradiations

Molecules of polymer melts are exposed to successive expansion and compression under ultrasonic

irradiations. On the molecular lever, this suggested a rapid strike act on the molecules that cannot relax between successive ultrasonic waves, which causes eventually bond rupture in the macromolecules and thus produces the macromolecule radicals. Therefore, it is possible that *in situ* copolymers are formed by the combination of different macroradicals during ultrasonic irradiation.

An evidence for the copolymer formation was found by FTIR analysis of samples prepared by removing free PS from the sonicated mixture of PS and POE8150. As shown in Figure 12, the characteristic absorption band of a benzene ring in PS appeared at 3058, 3024, 1600, 1492, and 700 cm^{-1} in the spectra of the samples with ultrasonic irradiation, whereas there are no such peaks in PS/POE blend without ultrasonic irradiation. These IR spectra confirm the formation of copolymer in the ultrasonically treated PS/POE (50/50) blend.

CONCLUSIONS

In this article, ultrasonic degradation of polyolefin elastomers is explained based on the viscoelastic nature of polymer melt. In the initial stage, the intrinsic viscosity [η] of polyolefin elastomers near the tip of the ultrasonic probe significantly decreases with irradiation time and trends toward a limiting value at last stage of degradation. The limiting intrinsic viscosity for PEE and POE decreases and the degradation rate increases with the rise of ultrasonic intensity and the fall of reaction temperature.

The degradation kinetics of DE2300 melts under ultrasonic irradiation can be described by following equation:

$$[\eta]_t = 140.93 + 50.80e^{-0.0125t}$$

where the limiting intrinsic viscosity is 140.93 and the degradation rate constant is 0.0125.

FTIR analysis indicates that the copolymers of PS and POE are formed by a combination of the corresponding macroradicals and confirms that the copolymerization reaction of polyolefin melt can be initiated through ultrasonic irradiation.

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