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Impact of rapid ozone degradation on the structure and properties of polypropylene using a reactive extrusion process

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In this work, rapid ozone degradation of polypropylene (PP) was developed for the aim of rheology control using a reactive extrusion process. Experiments were carried out in a co-rotating intermeshed twin-screw extruder with varied polymer throughput and reaction temperature. Ozone was introduced into the extruder to rapidly oxidize molten PP in just several seconds period. The oxidized PP was characterized through melt flow index (MFI), rheological measurement, differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) spectroscopy tests. The influence of reactive temperature and polymer throughput on the degradation reaction was studied. It was noted that molten PP could be fast and successfully degraded during this reactive extrusion process. The oxidized PP had higher MFI than that of the origin PP resin, indicating the decrease of molecular weight of PP. Carbonyl groups were formed on the PP molecular chains. This rapid oxidization process has higher reaction efficiency than the ozone degradation of PP in solid state and no harmful byproduct would be generated from this ozonizing reaction.

1. Introduction

Polypropylene (PP) is one of the world's most important thermoplastics and its market share is growing fast. PP resins from industrial reactor normally have a broad molecular weight distribution (MWD) and a high molecular weight, as a result of the conventional Ziegler-Natta catalyst systems. To achieve diversity in polymer grades suitable for the differential applications, the molecular weight distribution and molecular weight must be tailor-made.

Post-reactor operations by means of different degradation methods are economical and flexible choices to modify PP commodity resins. Among these methods, controlled-rheology PP (CR-PP) [1,2] is the most important one which has been used in industry for varied applications. CR-PP generally has lower molecular weight and narrower molecular weight distributions than those of the starting commodity resins, exhibiting reduced viscosity and elasticity [3]. There are many studies focused on the production technology and the reaction mechanism [4-7].Reactive extrusion using peroxides as a promoter is the most commonly used approach. The decomposition of the organic peroxide yields a radical species which modifies the molecular weight profile of the resin [8-12]. The decomposition is known to lead to the formation of secondary products such as alcohols and ketones, which can impart a disagreeable odour and taste characteristics to the resin [13]. In these studies of production of CR-PP, the peroxide is either premixed with the polymer or injected in the feed throat or along the extruder [14,15]. The common element is the steady peroxide addition rate. Due to the random nature of the abstraction reaction, peroxide radicals preferentially react with longer chains, resulting in a simultaneous reduction of molecular weight and polydispersity. For the purpose of changing the weight-average molecular weight and polydispersity independently, a pulsed peroxide addition technique was developed [16].

Besides organic peroxides used to produce radicals in CR-PP, other techniques were developed for the initiation of PP degradation, such as electron beams and gamma rays irradiation [17-19]. Compared with electron beams and gamma rays irradiation, ultraviolet (UV) irradiation is a cheaper and safer process and easier to produce. Mechanisms and applications of UV induced polymer reaction were well investigated in previous reports [20-25]. Recently, UV irradiation was used to initiate free radicals in molten PP and modify its molecular structure [26-28].

Mechanical degradation and oxidation degradation are two other ways that could induce the molecular weight decrease of PP. Mechanical degradation easily occurs during extrusion process where shear stress and high temperature can strongly promote the degradation process [29]. If shear deformation of PP occurred below melting temperature, the mechanical degradation would more easily happen due to plastic deformation of the amorphous regions [30]. As we all know, ozone is an advanced form of oxygen and is a powerful oxidizer applied in disinfection, pollution control, water treatment and numerous others. Furthermore, ozone can be used as an aggressive agent causing the aging and degradation of rubbers and plastics. Because of the uniform and rapid reaction with organic compounds, ozone has been used to induce polar

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groups on the polymer surface through oxidation or grafting reactions [31-41]. Most researchers agree that ozone attack is notably a surface reaction. However, for natural rubber, in contrast to synthetic rubber, published data indicate that the ozonization does continue into the bulk of the specimen when prolonging ozonization time [42, 43].

However, all the reported ozone oxidation reactions for polymer modification occurred at solid state and normally needed several hours for detectable oxidation. For our knowledge, there is no report about molten polymers modified by ozone during the extrusion process. The main objective of this paper is to introduce ozone into the extrusion process of PP melts and initiate molecular breakdown and oxidization of PP macromolecules. The rheological properties and crystallization properties were also discussed by examining the effects of varying the reactive temperature and polymer throughput for the reaction extrusion process.

2. Experimental

2.1 Materials

A commercial polypropylene homopolymer (PP H1030) from TASNEE National Petrochemical Industrialization Company was used in this study, which had a melt flow index of 3.0 g/10min (230 ℃, 2.16 kg). Ozone was generated electrochemically using dry air by an ozone generator (OZ-3G) from Guangzhou Dahuan Ozone Equipment Company. The ozone concentration used throughout this experiment was kept at 10 mg/L and the flow rate was 5 L/min.

2.2 Ozone degradation of PP

A co-rotating twin-screw extruder TSE25/40 with L/D=40/1 (eight heating zones) from the Brabender® GmbH & Co. KG was employed in this experiment. The screw configuration and ozone generator used in the experiments is shown in Fig.1. PP pellets were fed at the first barrel zone and heated to molten state through the extruder. Ozone flowed into the seventh barrel zone where PP was completely melted. Residue ozone was decomposed in an ozone destructor.

Experiments were carried out at three different temperatures (200 ℃, 220 ℃ and 240 ℃) for all the extruder zones with the exception of the feeding zone (120 ℃) and five different polymer throughput (7.3 g/min, 17.3 g/min, 26.8 g/min, 37.3 g/min, 47.0 g/min). Screw rotation speed was fixed at 100 rpm.

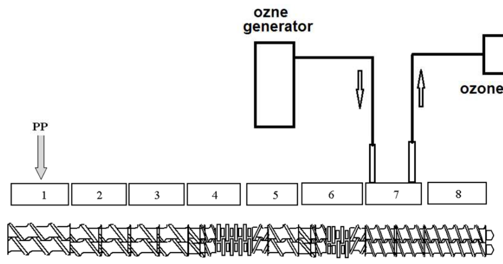


Fig.1 Schematics of screw configuration and ozone generator used in experiment

The strand extrudates were cooled through a water bath and pelletized for further analysis. Samples were identified as PP followed by a number corresponding to the extruding temperature. For example, PP-220-O3 was the ozonized sample extruded at 220 ℃ and PP-220 was the sample extruded at 220 ℃ without ozone.

2.3 Characterization

Melt flow index (MFI) of virgin PP and PP extrudates were measured using a MP993a melt indexer (Tinius Olsen Testing Machine Co.Inc), according to ASTM 1238 at 230℃/2.16 kg. Steady-state shear viscosity was measured at 200℃ using a Ceast capillary rheometer (Smart RHEO 5000) with a die of L/D=40 (D=1 mm).

Physica MCR302 rheometer from Anton Paar equipped with a CTD620 convection oven was used to measure the dynamic rheological behaviour of PP samples. Samples obtained from the extruder were compression-moulded at 210℃ for 5 min and disk-shaped specimens with a thickness of 1 mm and a diameter of 25 mm were prepared. The measurements of the dynamic rheological properties were performed with a parallel-plate fixture (diameter=25 mm), with a gap distance of 1 mm, and the strain was kept at 1% to ensure linear viscoelastic response. The frequency range was 0.1-100 Hz, and the temperature was 200℃. Tests were run under nitrogen purge at a flow rate of 5 ml/min.

FT-IR spectra of the virgin and degraded PP were obtained using a Fourier-transform infrared spectrometer Nexus 670 manufactured by Nicolet Company. Materials for FT-IR measurement were compressed into thin films at 210℃ for 2 min in a hot presser.

Thermal properties were evaluated with a NETZSCH DSC204 differential scanning calorimeter. The temperature and heat flow area were calibrated with indium before the analysis. The samples (ca. 6 mg) were sealed in an aluminium pan and heated or cooled in a nitrogen atmosphere. Initially, the samples were heated from room temperature to 210℃ at a rate of 20℃/min to erase the thermal history and cooled at a rate of 10℃/min to obtain the non-isothermal crystallization. The second heating run was followed at a heating rate of 10℃/min. The crystallinity Xc was calculated by the relative ratio of the enthalpy of crystallization per gram of samples to the heat of fusion of PP crystal (209J/g) [44].

3. Results and discussion

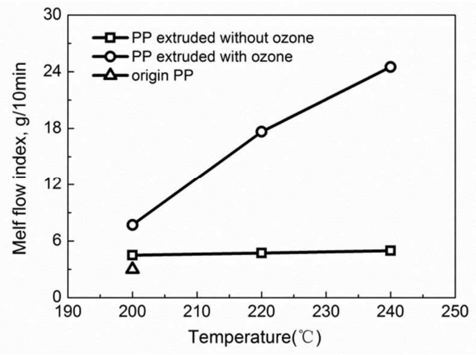


Fig.2 Effect of ozone and extrusion temperature on melt flow index of PP (polymer throughput: 26.8g/min)

As discussed in the previous works [36,37,40], the ozone attack to polymers follows a radical mechanism as evidenced by electron spin resonance studies. Polypropylene is characterized by a number of tertiary carbon atoms, which are more subjected to ozone attack than secondary carbon atoms. During extrusion in extruder, PP is heated to the molten state and most crystalline are melted and we could expect the reaction probability of PP molecules with ozone is higher than that of PP in solid state.

Fig.2 shows the effect of extrusion temperature on the melt flow index (MFI) of PP extruded with or without additional ozone. It can be seen that MFI of PP extruded without the addition of ozone has a slight increase with reaction temperature, from 3.0 g/10min for origin PP to 4.98 g/10min for PP extruded at 240 ℃. This is usually due to the chain scissions of PP at processing temperatures. When ozone is introduced into the extrusion process, the MFI is apparently improved with increasing reaction temperatures. The MFI is 17.7 g/10min and 24.5 g/10min for PP extruded at 220 ℃ and 240 ℃ respectively, with addition of ozone. These results give an indication that ozone could degrade PP very quickly at high temperature, thermal and ozone have a synergic effect for degradation of molten PP. Fig.3 shows the effect of PP throughput during extrusion on MFI of the ozone degraded polypropylene. The MFI of ozone-degraded PP increases with decreasing PP throughput. For a given ozone concentration produced by the ozone generator, lower throughput of PP during extrusion results in relatively higher concentration of ozone reacting with PP molecules, which leads to higher degradation level. In addition, PP melts at lower throughput could have a thinner melt stream so that more PP molecules react with ozone molecules and thereby increase the reaction probability of PP molecules.

Ozone is a stronger oxidizing agent than molecular oxygen or hydrogen peroxide and reacts with most substances at room temperature. At high ozone concentrations, the thermal gas-phase decomposition of ozone is described by a mechanism [46]:

$$\boldsymbol{O_3 + M \rightarrow O + O_2 + M}$$

$$\boldsymbol{O_3 + O \rightarrow 2O_2}$$

Where *O* is an oxygen atom and *M* is a third body. Ozone decomposes only slowly in the absence of UV radiation or catalysts. The half-life $t_{1/2}$ of ozone at atmospheric pressure of 25℃ is 160 h. However, the decomposition rate rises quickly at high temperatures, and the half-life is 210 s and 0.03 s for 100 ℃ and 250 ℃, respectively. Three reactive gaseous species, such as atomic oxygen, molecular oxygen and ozone, may react with the PP molecules.

The mechanism scheme of this oxidative degradation process of PP was showed in Scheme 1. The atomic oxygen from ozone decomposition can abstract hydrogen atoms from tertiary carbon atoms, producing radical carbon sites on the polymer chain. Molecular oxygen may react with the tertiary carbon radical to form a peroxy radical group, which then abstract neighbouring hydrogen to form a hydroperoxide unite. Then, the β-chain scission of PP molecules may occur with formation of an olefin end group at one chain end and a peroxy radical at the other end which rearranges into a ketone group. The ozone degradation proceeds by the degradation of the olefin end group and by further attack of other tertiary carbon atoms in the polymer chains.

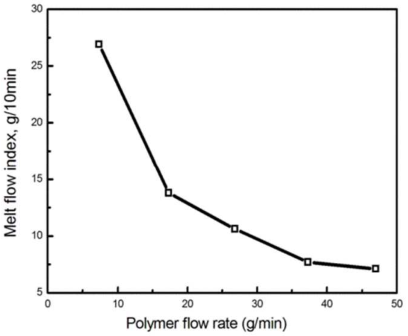


Fig.3 Effect of polymer throughput on MFI of the ozone degraded PP (reaction temperature:200℃)

Fig.4 showed the FT-IR spectrum of the virgin and degraded PP at various polymer throughputs. The main difference between the spectra of virgin and ozone degraded PP was the appearance of new peak bands at approximately 1720cm^{-1}, which corresponds to C=O stretching vibrations. From the FTIR spectra, the carbonyl index (CI) was calculated as follows:

$$\boldsymbol{CI = \frac{A_{1720}}{A_{841}}}$$

where A1720 is the absorbance at 1720 cm^{-1}, characteristic of carbonyl groups and A841 is the absorbance at 841 cm^{-1}, characteristic of the CH_3 groups in the PP backbone. The CI of ozone degraded PP is 0.175 and 0.329 for samples with polymer throughput 17.3 and 7.3 g/min, respectively. This might suggest the presence of carboxylic acid, ester, and aldehyde or ketone functionalities. The intensity of these peaks increased with the decrease of polymer throughput, indicating the oxidation degree increase. Formation of polar groups in PP molecules was reported to increase the miscibility when compounding with other polymers.

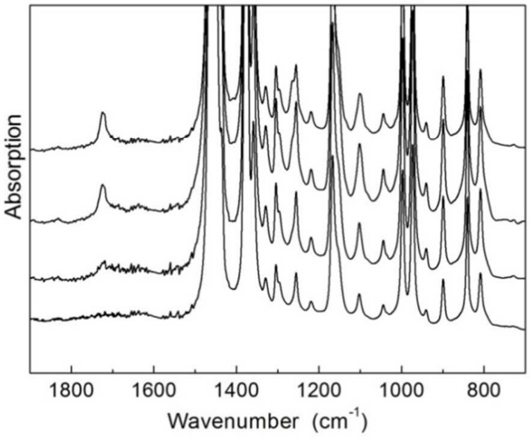
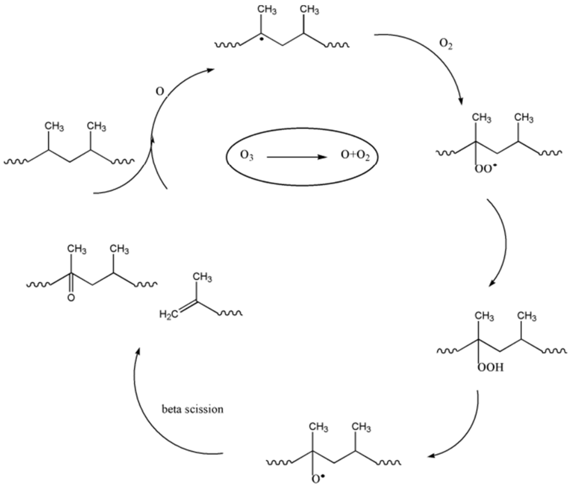


Fig.4 FT-IR spectrum of virgin and ozone-degraded PP with various polymer throughput

From bottom to top: virgin PP; polymer throughput =26.8g/min; polymer throughput =17.3g/min; polymer throughput =7.3g/min



Scheme 1 The mechanism of PP oxidative degradation with ozone during extrusion

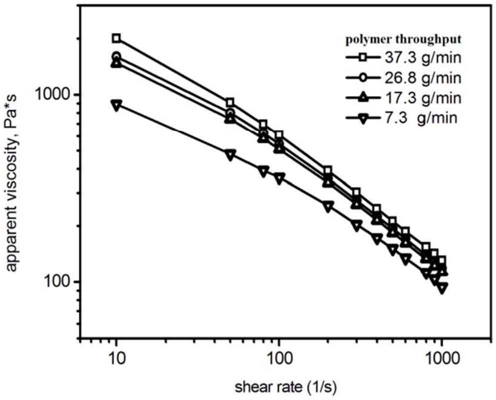


Fig.5 Effect of polymer throughput on the apparent viscosity of PP degraded by ozone (reaction temperature: 200℃)

Fig. 5 shows the steady shear viscosity of degraded polypropylene at various polymer throughputs. It is clear that polymer throughput has dramatic effects on the rheological behaviour of degraded polypropylene. Decreasing polymer throughput leads to lower viscosity and more Newtonian behaviour of ozone-degraded PP. These results were consistent with the MFI results.

Fig. 6 shows the flow curves of degraded polypropylenes at different reaction temperatures with additional ozone. Under these conditions, the shear viscosity decreased with an increase of reaction temperature. Compared with numerous hours reaction time for ozone oxidizing solid polymers [37,39,40], this ozone degradation reaction of molten polypropylene has high efficiency. It takes only several seconds to obtain degraded polypropylene with high melt flow index. However, because thermal-degradation cannot be totally avoided for such process, thermal-degradation gives some promotion for this reaction, especially at high temperature.

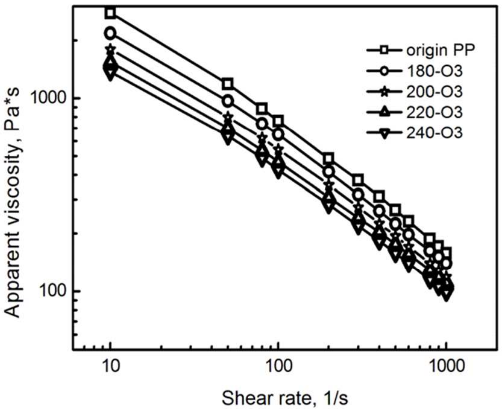


Fig.6 Effect of reaction temperature on the apparent viscosity of PP degraded by ozone （polymer throughput: 26.8 g/min）

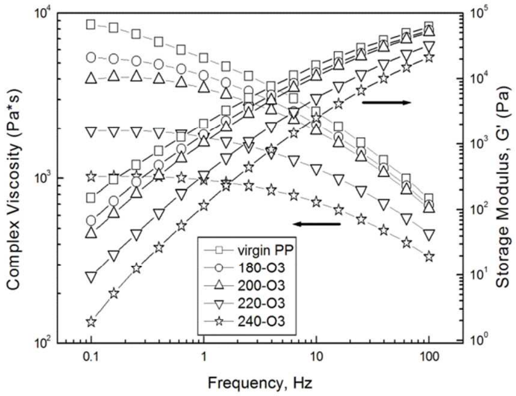


Fig.7 Effect of reaction temperature on the complex viscosity and storage modulus of PP degraded by ozone
（polymer throughput: 26.8 g/min）

The variation of complex viscosity with reaction temperature at different frequencies was demonstrated in Fig.7. Complex viscosity of virgin PP was higher than those of ozone-degraded PP, especially near the zero-shear frequency. The sensitivity of complex viscosity to ozone-degraded PP is greater at low frequencies (terminal zone). With increasing reaction temperature, the complex viscosities of ozone-degraded PP samples were reduced and less shear sensitive in comparison to virgin PP.

The changes of storage modulus with frequency at different reaction temperature were also shown in Fig.7. It can be observed that ozone-degraded PP had lower storage modulus in comparison to the virgin PP. Storage modulus of all samples decreased with increasing reaction temperature, which meant that the ozone-degraded PPs were less elastic than virgin PP. Loss modulus and tanδ of virgin and ozone-degraded PP were illustrated in Fig.8. It could be observed that tanδ value increased with increasing reaction temperature of PP degraded by ozone. Since tanδ is the ratio of loss modulus to storage modulus, increasing of tanδ means loss modulus has been more affected by reaction temperature than storage modulus. Rheological techniques could be used to relate molecular structure to linear viscoelastic properties.

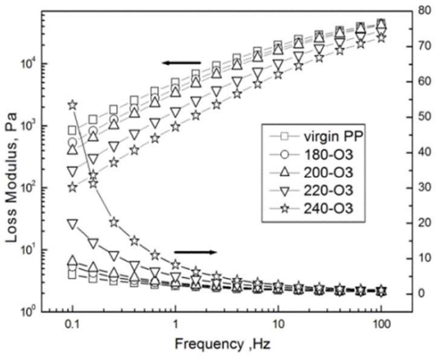


Fig.8 Effect of reaction temperature on the loss modulus and loss angle of PP degraded by ozone （polymer throughput=26.8 g/min）

Table 1 Polydispersity of virgin and degraded PP from dynamic rheological test (Extruded at 200℃, throughput=26.8g/min)

samples	G_c, kPa	ω, rad/s	PI	Modsep@1000Pa
Virgin PP	27.85	23.28	3.59	3.65
180-50-03	30.71	36.43	3.26	3.75
200-50-O3	31.12	42.45	3.21	3.80
220-50-03	36.02	103.1	2.78	4.60

According to the "crossover modulus", the rheological polydispersity index, PI, is defined as follows [45]:

$$PI = 10^5/G_c$$

Where G_c is defined as the modulus value at the "crossover frequency ω_c", where the storage and loss moduli are equal. The "modulus separation" ($Modsep$) technique can also be used to compare the MWD for linear polypropylene. From the same frequency sweep data, the distance between the G' and G'' curves is measured at a constant modulus value, namely, 1000 Pa. Then, the modulus separation ($Modsep$) is defined as:

$$Modsep = \omega'/\omega''$$

where $\omega' = \omega$ (G'=1000 Pa) and $\omega'' = \omega$ (G''=1000 Pa). Table 1 summarized experimental results and calculated values for the virgin and ozone-degraded PP. It could be seen that the crossover modulus, crossover frequency and $Modsep$ increased with the reaction temperature, but PI decreased with the reaction temperature. All these results indicated that ozone-degraded PP had narrower MWD than the virgin PP.

The crystallization behaviours of virgin and ozone-degraded PPs were shown in Fig.9 and the thermal properties could be seen in table 2. The crystallization temperature, the onset temperature and crystallinity of PP decreases after ozone and thermal degradation. The crystallization behaviour of polypropylene could reflect the chain length of molecules. Due to chain break of PP molecules, shorter molecules of PP are produced and can only be "frozen" at a lower temperature than longer molecules of PP, thus decreases the crystallization temperature when cooling. The decrease in crystallinity of degraded PP is probably due to some of the degraded molecular chain cannot crystallize when the temperature is cooled down.

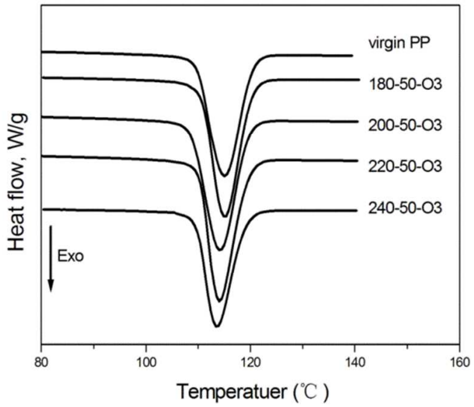


Fig.9 The crystallization behaviors of virgin and ozone-degraded PP (Extrusion conditions at 200℃, throughput=26.8g/min)

Table 2. Crystallization behaviors of ozone-degraded PP at 200℃ with polymer throughput 26.8 g/min

Samples	T_c , ℃	H_c, J/g	Crystallinity, %	T_m , ℃
Virgin PP	115.4	93.0	44.5	165.0
180-50-O3	115.1	91.4	43.7	163.9
200-50-O3	114.2	90.4	43.3	164.2
220-50-O3	114.1	88.8	42.5	161.6
240-50-O3	113.6	75.6	36.2	161.7

T_c, crystallization peak temperature; H_c, enthalpy of crystallization; T_m, melt peak temperature

Conclusions

Ozone-thermal degradation reaction of molten PP was carried out during reactive extrusion by a twin-screw extruder, to control molecule weight and rheological properties of PP. The results proved that ozone and thermal had synergic effect for the degradation reaction of PP. This process has higher reaction efficiency than the ozone degradation reactions of PP in solid state, considering that ozone came to contact with melt for just several seconds period. After extrusion with the addition of ozone, the melt flow index of the degraded PP increased and carbonyl group was introduced onto polypropylene molecules. The degraded PP had a lower viscosity and narrower molecular weight distributions than those of virgin PP. The crystallization temperature and crystallinity of degraded PP decreased. This ozone-induced PP degradation approach might provide a method in production of controlled-rheology PP for industrial applications.

Acknowledgements

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