

## Structure and properties of ultrafast photo-degraded molten polypropylene in a transparent barrel extruder

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### ABSTRACT

A novel single screw extruder, with high transparent quartz glass as barrel, was employed to carry out reactive extrusion for ultrafast photo degrading molten polypropylene (PP). Ultraviolet (UV) was adopted to irradiate the molten PP to induce radical reaction and hereby to degrade PP macromolecules during extrusion. Compared with photo degradation of PP in solid state, reaction efficiency and uniformity in this process were greatly improved. Reactive degree was controlled by varying screw speed and photosensitizer (benzophenone, BP) concentrations. The structure and properties of degraded polypropylene was characterized by melt flow rate (MFR), Fourier Transform Infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC) and tensile properties test. After extrusion with UV irradiation, the melt flow rate increased and crystallization temperature decreased of the degraded samples. FT-IR showed no obvious C=O groups were formed in molecular structure, indicating the oxidation reaction was very minimal.

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### 1. Introduction

Polypropylene (PP) is one of the world's most important thermoplastics and being used in numerous applications in the plastics industry. Because of its desirable properties such as low cost, high melting point, low density, high strength and stiffness, and excellent chemical resistance, its market share is growing fast. To achieve the diversity in polymer grades suitable for the different applications of polypropylene, the molecular weight and molecular weight distribution (MWD) must be tailor-made to fit the performance requirements of each application.

The peroxide-promoted degradation of polypropylene is now a well recognized manufacturing process. The product is termed as controlled-rheology polypropylene (CR-PP). This process converts the low melt flow index commodity resins to polymers with higher melt flow index that have superior processing properties because of the reduced viscosity and elasticity [1,2]. There are a large number of publications that describe the process of peroxide degradation of PP. The effects of processing conditions on their molecular structures, processing parameters and kinetics of controlled degradation process have been studied extensively [3–8].

The prominent drawbacks of peroxide-promoted degradation technique typically involve the generation of noxious fumes and byproducts of peroxide degradation. Thereby employing physical techniques to incite PP degradation are good choices to avoid these drawbacks. Some irradiation methods, such like electric beam and  $\gamma$ -ray, has been chosen to modify structure and performance of PP in some reports [9–11]. UV irradiation is one kind of high-energy irradiation and has been used as a modification method in polymer research for a long time. A considerable amount of work has been devoted to UV-irradiated polymerization, degradation, surface grafting and crosslinking reactions [12–22].

Allen et al. [14] presented an in-depth account of the complex mechanisms involved in both thermal and photochemical oxidation of polyolefin, with particular emphasis on polypropylene. Tang and Qu et al. [15] investigated the effects of chemical structure and synthesis method on photo degradation of polypropylene and found that copolymerization with amount of ethylene monomer is an effective approach to obtain high stability of PP to UV-irradiation. Rabello and White [16,17] investigated the role of physical structure and morphology in the photo degradation behavior of PP and found that the initial physical structures of PP, which include the degree of crystallinity, crystal, and molecular orientation, as well as crystal size, influence the photo oxidation by affecting the oxygen permeability and UV absorption characteristics. Qu et al. [18] provided a new mechanism of benzophenone

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photoreduction in photo-initiated crosslinking of polyethylene and its model compounds. Pan et al. [19] explained the efficient photografting sensitized by BP by two possible mechanism processes: the sensitization of the formation of the excited triplet state of maleic anhydride (MAH) by BP and electron transfer followed by proton transfer between MAH and the benzopinacol radical, which may operate together.

Mechanisms of UV induced PP reaction and applications in polymer modification, like surface grafting functional monomers onto polymer and functionalized polymers by UV irradiation in solid state, were well investigated [15,16,23–29]. However, UV technique has seldom application in polymer matrix modification especially for thick samples, because of its low penetration ability for solid polymers.

The objective of the paper is to develop a novel technique to carry out UV induced degradation of PP in reaction extrusion processing using a transparent barrel extruder. The “photo-induced” reactive extrusion process, instead of a peroxide-induced one, has advantages like: 1) no residual and byproducts of peroxides in PP resin; 2) low temperature dependence since it is not a thermal incite reaction, and 3) precisely starting and terminating induce reaction. In this paper we reported the molecular structure and crystallization properties of degraded PP were characterized for understanding this photo-degradation process.

## 2. Experiment

### 2.1. Material

A commercial polypropylene homopolymer (PP-T30S) from Maoming Petrochemical Co., Ltd was used in this study, which has a melt flow index of 3.0 g/10 min (230 °C, 2.16 kg). Benzophenone (BP) was purchased from China Tian Jin Bodi chemical company and was used as received.

### 2.2. Equipment

The reactive experiments were carried out in a self-designed single screw extruder with  $L/D = 15/1$  ( $D = 20$  mm) which has three heating zones (Fig. 1). The barrel of this extruder is made of quartz glass that UV could penetrate and irradiate on the surface of molten PP. Far ultra-red heater was used to melt PP material in the extruder.

UV source was adopted a 1.0 kW mercury lamp from Tongfang UV Supply Inc. The spectrum of this lamp has a spectrum broad band in the UV 250–450 nm, but the intense emission lines occur at 254 nm, 285 nm, 315 nm and 365 nm and 365 nm is the strongest emission line. Some visible light and infrared radiation

are also generated. The lamp was set at the third zone of the extruder where PP was in molten state. The lamp was set above the barrel and has a distance of 10 cm from the barrel surface.

### 2.3. Sample preparation

To facilitate homogeneous distribution of BP in PP resin, the required amount of BP was dissolved in acetone before mixing with PP and then pelletized by a co-rotating twin-screw extruder. Concentration of BP in PP matrix varied between 0 and 0.5 wt%. Experiments were carried out at 200 °C for the third zone of the extruder. The extrudate was cooled through a water bath and granulated.

### 2.4. Characterization

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

Molecular weight distributions (MWD) of the modified polypropylene were determined by size exclusion chromatography (Polymer ChAR) equipped with a triple detector. Samples were dissolved in 1,2,4-trichlorobenzene at 145 °C and injected in the column with a flow rate of 1.0 ml/min. Universal calibration using polyethylene standards (SRM 1475a, NIST) were applied to determine the molecular weights.

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

Thermal properties were measured 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 aluminum pan and heated or cooled in a nitrogen atmosphere. Initially, the samples were heated from room temperature to 210 °C at a rate of 20 °C/min to erase the thermal history and cooled at a rate of 10 °C/min to obtain the non-isothermal crystallization. The crystallinity  $X_c$  was calculated by the relative ratio of the enthalpy of crystallization per gram of samples to the heat of fusion of PP crystal (209 J/g) [30].

The tensile properties were measured using an Instron universal tester (Model 5566) at room temperature with dumb-bell-shape specimens at a crosshead speed of 25 mm/min, with an initial gauge length of 25 mm. Tensile stress at break, modulus of elasticity, and elongation at break were recorded.

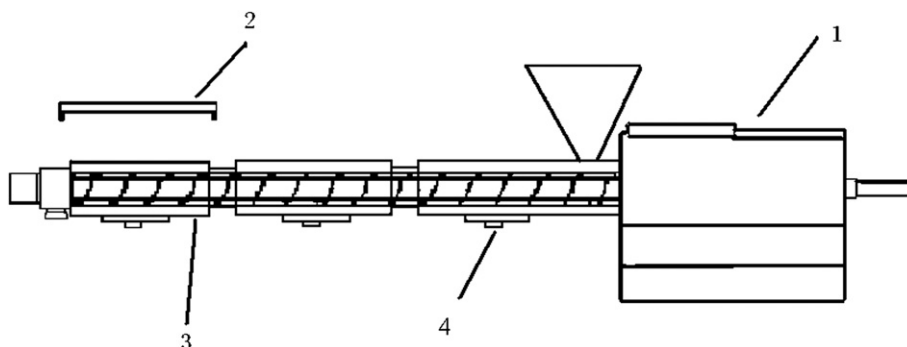


Fig. 1. Schematic diagram of UV induce reactive extrusion for polypropylene 1. Single-screw extruder; 2. UV lamp; 3. Transparent barrel; 4. Thermal couple.

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