Effects of processing variables on polypropylene degradation and long chain branching with UV irradiation

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A B S T R A C T

A technique has been developed to modify the melt properties of polypropylene (PP). Photoinitiators along with UV irradiation were employed to introduce long chain branching (LCB) and/or crosslinking (CL). Statistically designed experiments were carried out to study the effect of processing conditions, such as photoinitiator concentration, duration of irradiation, UV lamp intensity, cooling air pressure, and photoinitiator type, on rheological properties, molecular weight characteristics and branching level. Samples were evaluated through linear viscoelastic (LVE) measurements, extensional rheometry, gel content, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). Results clearly indicated that PP can be successfully modified in order to enhance strain hardening behaviour without significant gel formation.

1. Introduction

Polypropylene (PP) is one of the most common thermoplastics in the plastics industry with numerous applications ranging from household appliances to automotive interiors. Each application requires a specific PP grade with a specific average molecular weight (MW) and polydispersity index (PDI). PP molecular weight and PDI affect the melt flow behaviour, processing characteristics and eventually the final applications of PP.

However, its use is limited in applications requiring significant melt strength. Thus, modifying the molecular structure and enhancing strain hardening of PP melt, can lead to uses in areas such as foaming, thermoforming, extrusion coating and blow moulding [1]. The high melt strength of a polymer is either due to long chain branching (LCB) or high MW [2].

Hence, attempts have been made over the years to introduce LCB to PP chains. Methods such as electron beam radiation, gamma radiation or utilizing peroxides in the presence of coagents (like styrene or allylic and acrylic multi-functional monomers) have been utilized to impart LCB and increase the number of long chain branches in the PP chains.

Electron beam radiation of PP has been used extensively to modify its melt strength. Linear PP pellets are irradiated in a vessel with electrons generated by an electron beam accelerator [3–6]. Irradiation of PP is carried out under N_2 atmosphere to discourage chain scission as much as possible. Then, irradiated PP samples are heated at an elevated temperature to bring the entrapped radicals in the crystalline domains into the interface between crystalline and amorphous regions. This is done to encourage bimolecular termination of the trapped radicals, which leads to formation of long chain branches [3,5].

Another technique for rheology modification and increasing of the melt strength of PP is using gamma radiation. In this method, energetic ions and excited states are produced using Cobalt 60 as a gamma ray source. However, good control is lost due to the intensity of gamma radiation. As a result, gamma irradiation can also abstract hydrogens from the PP backbones and cause β-scission [3,7].

Peroxide initiators have been used along with co-agents such as triallyl trimesate (TAM), trimethylopropane triacrylate (TMPTA) and triallyl phosphate (TAP) to modify the rheology of PP by introducing LCB. This technique is popular since it is less expensive (and less energy intensive) than the previous radiation techniques. The effects of allylic and acrylic co-agents on molecular weight and branching distribution were studied by comparing shear and

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elongation viscosities. It was found that a mix of degraded chains, slightly branched polymer chains and hyper-branched chains, which can only be formed after the gel point, were present in the polymer melt when co-agents were used [8,9].

The following mechanism has been suggested for the reaction between PP, peroxide and co-agent. After PP macro-radicals are formed because of the presence of the peroxide initiator, they will attack the carbon double bond on the co-agent, and then a stable radical adduct will be formed. This stable intermediate radical adduct is protected from β-scission. In addition, the hydrogen on this intermediate adduct can react with other degraded polymer chains. These degraded polymer chains are produced from the initial β-scission reaction and contain a terminal double bond. These terminal double bonds react with the intermediate radical adducts, leading to the formation of long chain branches and/or crosslinks. Eventually, the final PP structure will be a function of the yield and the selectivity of the peroxide in the degradation reaction and the co-agent that assists in the crosslinking (CL) step [8].

Yet another technique that can be employed is UV radiation. UV radiation is a cheaper and safer process for generating free radicals in PP and modifying its molecular structure. In this method, PP is mixed with photoinitiators and UV energy is utilized to activate the photoinitiator. After activation with UV radiation, these initiators can abstract hydrogens from the PP backbone. Hydrogen abstraction will be followed by scission and degradation of PP chains. Degradation of PP using UV energy along with photoinitiators was successful in a twin screw extruder to decrease the polydispersity index (PDI) of PP and produce controlled rheology PP [10]. In addition, in order to control the degradation level of PP in the melt state and form long chain branched PP (LCBPP) for foaming applications, multi-functional acrylic coagents were used along with photoinitiators. The radiation was carried out in the last two zones of a twin screw extruder by using a transparent barrel [11].

In other applications, Zamotaev et al. [12] investigated the effect of different photoinitiators and coagents on the amount of gel formed in PP films radiated with UV energy. Moreover, different photoinitiators along with coagents were used to introduce LCB to linear PP and increase its melts strength [13]. In our work [14], PP was modified by UV radiation without applying any coagents. Modification was done in the solid state and degradation was controlled by manipulating several variables: conditions such as photoinitiator concentration, duration of radiation, UV lamp intensity, cooling air pressure and type of photoinitiator all affected the formation of the long chain branches on the PP backbone.

In the current paper, we present results on the effects of the process operating conditions (photoinitiator concentration, duration of radiation, UV lamp intensity, cooling air pressure, type of photoinitiator, and combinations thereof), in order to identify regions that maximize the LCB level in the PP structure. Since linear viscoelastic (LVE) properties are known to be affected significantly by changes in polymer molecular structure characteristics such as LCB, MW and molecular weight distribution (MWD), these properties are tracked in order to achieve the desired LCB balance. After an optimizing experimental design, extensional viscosity, gel content, MWD and crystallinity of these runs are discussed selectively in order to confirm the presence of LCB (and/or CL) in different samples.

2. Experimental

2.1. Design of experiments

The processing condition/variables chosen to be studied are given in Table 1, along with their selected levels. These factors will be referred to as A to E.

Table 1
Selected factor and ranges.

Factor	Process variable (units)	Ranges
A	Photoinitiator concentration (wt%)	0.1−0.5 (with respect to polymer mixture)
B	Duration of radiation (s)	120−600
C	UV lamp intensity (%)	47−100 (with respect to total lamp intensity)
D	Cooling air pressure (%)	0−100 (with respect to total air flow pressure)
E	Type of photoinitiator (N/A)	BPH and DEBPH

In Table 1, factor A levels are with respect to total weight in the polymer mixture. These ranges for photoinitiator concentration are typically found in the literature [10] and chosen based on preliminary screening experiments. Factor C, the UV lamp intensity, was adjusted as a percentage of the total UV lamp intensity, which was 1.42 W/m^2 at a distance of 1.3 cm from the lamp. Factor D, the cooling air pressure, was expressed as a percentage of the total available air flow (line) pressure (which was 8247 kPa), and adjusted via a pressure regulator. Cooling air pressure was used as a surrogate variable in order to control temperature during the radiation. Of course, an increase in lamp intensity (factor C) and decrease in cooling air pressure (factor D) result in a higher temperature level. For all experimental trials, and within the putative range of factors C and D, the temperature level (of the environment) beneath the lamp varied between 35 and 135 °C. Finally, factor E, the photoinitiator type, included the choices of benzophenone (BPH) and 4,4′ bis-diethylamino-benzophenone (DEBPH).

Based on the process variables and levels of Table 1, Design-Expert 8 software (DesExp) was used to obtain the experimental runs (trials) of Table 2. The 32 runs of Table 2 are based on the D-optimal design option, which results eventually in models with

Table 2
Design of experiments for D-optimal design.

Run ID	A	B	C	D	E
1	0.5	120	47	0	BPH
2	0.25	300	47	0	BPH
3	0.1	600	47	0	BPH
4	0.1	120	100	0	BPH
5	0.1	120	100	0	BPH
6*	0.5	600	100	0	BPH
7	0.5	600	100	0	BPH
8	0.3	600	47	50	BPH
9	0.3	360	74	50	BPH
10	0.1	600	100	50	BPH
11*	0.1	120	47	100	BPH
12	0.1	120	47	100	BPH
13	0.5	600	47	100	BPH
14	0.26	600	79.2	100	BPH
15	0.5	120	100	100	BPH
16	0.1	378	100	100	BPH
17	0.5	120	47	100	DEBPH
18*	0.1	600	47	100	DEBPH
19	0.1	600	47	100	DEBPH
20	0.1	120	76	100	DEBPH
21	0.28	120	100	100	DEBPH
22*	0.5	600	100	100	DEBPH
23	0.5	600	100	100	DEBPH
24	0.1	120	47	0	DEBPH
25	0.5	600	47	0	DEBPH
26	0.1	402	69	0	DEBPH
27	0.5	302	67	0	DEBPH
28	0.35	422	100	0	DEBPH
29	0.1	600	100	0	DEBPH
30	0.5	120	100	0	DEBPH
31	0.3	360	74	50	DEBPH
32	0.1	120	100	50	DEBPH