



Rheological behavior of polyolefins during UV irradiation at high temperature as a coupled degradative process



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ABSTRACT

The photo-rheology method was applied to determinate the differences in the rheological behavior of selected polyolefins (PP, HDPE and LDPE) over a range of temperatures, higher than melting temperatures (160–200 °C) and during UV irradiation as a coupled degradative conditions in air atmosphere. Both, UV mercury lamp and UV LED were used as irradiation source. Multiwave experiments were performed and viscoelastic data were plotted in the complex plane to obtain Cole–Cole plots at different conditions. It helped to assess the molecular evolution of the examined materials.

The competition between chain scissions and chain recombination (crosslinking) was observed. Chain scission reactions occurred in PP and for HDPE and LDPE crosslinking reactions predominated, especially over 180 °C. UV irradiation intensified these effects. In the case of HDPE chain scission reactions were also observed especially below 180 °C in processes performed without UV. At higher temperature and under UV irradiation crosslinking reactions and increase of viscosity began to dominate. Despite different energy and emission spectra of irradiation sources, the similar effects were observed.

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1. Introduction

Polyolefins (PP, LDPE, HDPE) are the most important group of plastics with many advantages like no odor, non-toxicity, relatively good chemical resistance, easy processing. In combination with low price they result in the highest worldwide production together with PVC, around 230 million tons in 2009 [1]. The high demand for plastics finally results in the formation of a large amount of post-consumer waste – plastic solid waste (PSW). The natural mechanism occurring in the environment for degradation of polymers is very slow and the collection in landfills is not sufficient. That's why we need looking for new more efficient alternative methods of polymer waste processing or utilization like mechanical and chemical recycling methods as well as energy recovery [2,3].

The mechanical recycling, involves a number of treatments and preparation steps like: shredding, contaminant separation, washing, drying and extrusion and should be limited only to single-polymer plastic waste (like PP, PE, PS, PET etc.) [3–5]. Mechanical recycling has been commercialized all over the world since the 1970s and it is still a subject of many R&D projects [6–8].

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During chemical recycling processes the plastic materials are converted to monomers (monomer recycling) or gaseous and liquid petrochemicals useful as fuel components (feedstock recycling). The different processes can be employed e.g. pyrolysis, gasification, liquid–gas hydrogenation, viscosity breaking, steam or catalytic cracking and the use of PSW as a reducing agent in blast furnaces [2]. In comparison to the material recycling the heterogeneous and contaminated polymers can be used also as feedstock, however some pre-treatment is desirable. The most important and elaborated are pyrolysis (BASF [9], PyroMelt [10] and BP [11] technologies) and gasification (Energos [12] or Westinghouse Plasma [13]) processes. They occur at high temperature, from 500 to 800 °C for pyrolysis up to 1600 °C in the case of gasification (3000 °C – plasma technology) and very often in corrosive environment (e.g. PVC). Therefore, large amounts of energy and correspondingly expensive devices are required.

The PSW have a high caloric value, so the combustion of them allows to recovery of energy and reduces consumption of fossil fuels. However a big attention should be given to control air pollutants emission [3]. PSW use as a feedstock in cement kilns is also very popular [14].

As it has been shown above all the degradation processes that claim chemical recycling are developed with high intensive single parameters (Ex Pyrolysis or Thermolysis = High temperature without Oxygen). Our idea is use of the coupling degradative conditions (UV + T) that may allow getting milder and more easily controllable conditions for polymer waste utilization or polymer processing.

UV-irradiated modification of polyolefins is well known and popular research topic in recent years. Especially in the case of PP the UV-irradiated polymerization, degradation, surface grafting and PE crosslinking reactions were described [15–19]. Nevertheless peroxide-promoted degradation of polypropylene process is still dominated on an industrial scale despite of some disadvantages like the generation of peroxide decomposition by-products or risk of peroxides explosion [20]. This process has been very well known and examined and allowed to control processing parameters e.g. melt flow index [21,22].

The crosslinking of polyethylene with peroxides is also more favored than crosslinking by UV radiation because it is slower process, needed to use photo-initiators like benzophenone, and a depth of UV polymer penetration is only a few millimeters [23]. Moreover the peroxide method gives up to 90% degree of crosslinking while radiation crosslinking yields are between 34% and 75% [24].

However in recent years some studies concerning UV irradiated extrusion process of molten PP have been published. He and Tzoganakis [25] and Cao et al. [26] investigated the effect of ultraviolet irradiation on the structure and properties of molten PP during extrusion process using a single screw extruder with quartz glass barrel. Due to the high reactive temperature and photo-sensitizer (benzophenone) added into PP melt, this UV-promoted degradation process has very high efficiency to break PP molecular chain.

In our investigation we wanted to exemplify the application of a relatively new photo-rheology method [27] which allows the simultaneous control physical changes (viscoelastic) during UV exposition and over a wide range of temperatures. By this way we can determine the molecular evolutions through the rheological behavior of examined materials like PP, LDPE and HDPE. Moreover we used both UV mercury lamp (polychromatic) and UV LED (monochromatic) as source of irradiation to show the application possibility of the last one on an industrial scale. We believe that our results can be helpful in polymer waste utilization and polymer processing as well.

2. Experimental section

2.1. Materials

Polyolefins used were PP (Borealis PP HG 455FB) with anti-gasfading stabilisation as well as non-stabilized HDPE and LDPE (from Versalis). All polymers were without UV stabilizers. The weight-average (M_w) and number-average (M_n) molecular masses as well as molecular mass distributions (M_w/M_n) and melting temperatures (T_m) are shown in Table 1.

2.2. Rheological device

A dynamic rheometer (ARES Rheometric Scientific) was used. The experimental setup (Fig. 1), has been described previously [27,28]. The two parallel plate-holders (the top fixture corresponding to the transducer and the bottom to the motor) of the rheometer were adapted. The top plate holder was scooped out to permit the insertion of a 45° mirror, which was used to reflect the UV irradiation onto the sample placed between the disks. The upper consisted of a quartz window with 8 mm

Table 1
The SEC properties and melting points of polyolefins used.

Polymer	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	M_w/M_n	T_m (°C)
PP	150,000	360,000	2.4	166.1
HDPE	120,000	224,000	1.8	133.1
LDPE	31,000	207,000	6.7	111.1

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