Comparative study of gamma-irradiated PP and PE polyolefins part 2: Properties of PP/PE blends obtained by reactive processing with radicals obtained by high shear or gamma-irradiation

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ABSTRACT

Compared with neat polypropylene (PP), the addition of low contents (typically <20wt %) of polyethylene (PE) can improve the impact strength of PP based blends. In order to improve tensile properties as well, reactive extrusion has been carried out with radicals obtained by high shear or γ-irradiation. The addition of a γ-irradiation step in the processing sequence, between extrusion and injection, can be considered as an efficient way for improving the properties of our PP/PE blends. The improvement of mechanical properties has been discussed in terms of creation of secondary interactions or covalent bonds at the interface of the γ-irradiated polymers, γ-PP and γ-PE. On one hand, the rheological measurements have highlighted an increase of the complex viscosity of the γ-irradiated blends at low frequencies. On the other hand, the EPR spectrum simulation shows that the radicals are not the same in the blend and in the genuine γ-PP and γ-PE. Besides, the increase of temperature in the sample affects the shape of the EPR spectra, revealing that some macroradicals react one to another, which creates new macroradical structures of rather alkoxyl type.

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1. Introduction

Polypropylene and polyethylene are among the most common polyolefins in the plastic worldwide production. Individually, they are used in a lot of diversified fields with applications owing to their particular mechanical properties and chemical inertness [48,66], etc. Mixing them together offers many intermediate desirable properties even if they are not miscible that can be a limitation to the development of their blends [1,39,58,69]. Nevertheless, a lot of studies have been developed over the past two decades to improve their properties by several routes based mainly on i) controlling the cooling rate [9,58,61,65], the amount and composition of the dispersed phase [1,7,29,63], ii) adding copolymers or fillers in the formulations [[8,14–16,25–27,30,31,34–36,39,38,51,70]]. Most of these studies point out the presence of some miscible domains between polypropylene PP and polyethylene PE under specific conditions. Furthermore, the addition of little amounts of copolymers or fillers has an impact on the morphology of the blends as well as on their final mechanical properties. Authors put an emphasis on the direct impact of copolymers or fillers on the interfacial tension between PP and PE, by creating a "core–shell" structure between the polymer matrix and the dispersed phase. This structure can significantly enhance the mechanical properties.

Other studies investigate the reactive blending of polyolefins. In this context, γ-irradiation is gaining interest. Initially applied to sterilize implants in the medical industry [[17,37,50]], this technology is now used to modify both molecular structure and chemistry of materials in the solid state (Part I [5,19,20]; 2006 [12,23,42,49,53,56,57]; Valenza 1993). It is based on the creation of macroradicals through covalent bond cleavage without necessity of dissolving and/or purifying the materials [11]. The main chemical transformations in the polymer are due to oxidations, cross-linking

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and further chain scission reactions.

The main purpose of γ-irradiation process is often to increase the compatibility between polymers or between polymers and fillers. For instance [3]; tried to improve the compatibility of polyamide 6 PA6 and PP by addition of a maleic anhydride grafted polypropylene obtained under γ-irradiation of polypropylene and maleic anhydride. They observed the formation of peroxides in a pre γ-irradiated PP for doses up to 100 kGy that favour direct chemical interactions with the amino groups of PA6, thus increasing the miscibility of both phases as revealed by smooth surface fractures [67]. have investigated the effect of γ-irradiation over the mechanical properties of PA/linear low density polyethylene LLDPE blends. Adding 10 wt % of γ-LLDPE increase the elongation at break from 8 to 21% and the impact strength from 39 to 65 J m^{-1} (with Izod method) compared to the neat blend, without any other treatment or addition of compatibilizer. Another application of γ-irradiation consists in enhancing the coating properties of polyolefins [6]. have studied the impact of γ-irradiation on the mechanical properties of PP filled with sisal or wood flours. Improvement of elongation at break was marked out for the composites obtained with γ-irradiated PP matrices at 25 kGy (i.e. 25 kJ kg^{-1}). Moreover, doses higher than 25 kGy do not affect the impact strength of the composite while this latter decreases for neat γ-irradiated PP.

The objective of this work is to reinforce PP/PE blends with radical reactions induced by physical routes: i) high shear or ii) γ−irradiation. Whereas no residual macroradicals have been detected on our samples processed under high shear, their presence after γ−irradiation was confirmed using Electron Paramagnetic Resonance EPR spectroscopy according to part 1 [71] of this study. Then, parameters influencing the radical reactions − shear or γ−irradiation − were studied with particular attention on thermal, rheological, morphological as well as mechanical properties. The reinforcement expected during the blending process should enable to manufacture lighter parts from our materials. In addition, the present study proposes an alternative for polymer recycling without need of perfect sorting [10,39] as it is a mere adjustment of the classical processing steps and formulation that adds value to polyolefin blends.

2. Materials and methods

2.1. Materials

2.1.1. Polymers

The two polyolefins used in this study are i) a polypropylene PPH 7060 (Total Petrochemicals, France), called PP; and ii) a high density polyethylene Lupolen 4261 AIM (LyondellBasell, France), called PE. The melt flow index (MFI) of these two polyolefins are 12 g/10min (503 K and 2.16 kg) and 15 g/10 min (463 K and 21.6 kg), respectively.

For the blends, 80 wt% of PP and 20 wt% of PE have been used. The corresponding notation is PP/PE.

2.1.2. Twin screw extruder

Polyolefin blends have been prepared using a ZSE 18 HPE Leistritz high-shear extruder. The L/D ratio of the screw is 60 and the screw profile is displayed in Fig. 1. The different screw elements are called: (GFA) and (GFF), conveying screw elements; (KB), mixing screw elements; (GFA L), left-handed screw elements and (GFM) conveying and mixing screw elements. The associated numbers represent the geometry of the different elements. The pellets were introduced in the twin screw extruder (TSE) without any physical or chemical treatment. The barrel temperature was set at 473 K. The screw rotation speed was fixed at 300, 800 or 1200 rpm. If not specified, the screw rotation speed used is 300 rpm. Moreover, during the different extrusions, the atmosphere was controlled at the feed throat by an injection system of air.

2.1.3. Injection

The injection of polymer blends was performed using a Battenfeld Unilog B2 device. The temperature of injection was set at about 493 K and 523 K, the cycle time was lower than 1 min, and the temperature of the mould was set to about 323 K.

2.1.4. γ-irradiation

Irradiation was performed by Ionisos SA (France), on the pellets of the neat polymers and of the extruded polyolefin blends. The gamma device used was a 2.10^6 ^{60}Co source, under air atmosphere, at ambient temperature and at solid state. Irradiation dose was controlled with a precision of around 15%. Dose rate was 2 kGy h^{-1}(i.e 2 kJ kg^{-1} h^{-1}). Final dose was set at 25 kGy (i.e 25 kJ kg^{-1}). Then, irradiated pellets were stored at 253 K.

2.2. Methods

2.2.1. γ-Irradiation sequence

The classical way to process polyolefin blends in industrial field is ruled by two steps. The first one consists in realizing the blend by using an extruder. Then, the polymer strand is cooled at room temperature in air or water, and pelletized in small pellets. In a second step, these latter can be injected to form different test samples: dumbbell, Charpy impact or disc shapes. This process is called process A and used as a reference (Fig. 2). Process A carried out at 1200 rpm aims at creating radicals by chain scissions under high shear. Then, in a process B, radicals were obtained by irradiation. In process B, the blends were γ-irradiated between extrusion at 300 rpm and injection step as shown in Fig. 2.

Besides, for process B, some samples have been tested before the injection step, and will be called 1-B, whereas those tested after the injection step will be called 2-B.

The specific mechanical energy (SME) is calculated thanks to Eq. (1) [39,68]:

$$SME = \frac{\tau \times N}{Q} \tag{1}$$

with:

τ = drive torque (kJ) N = Screw rotation speed (.min^{-1}) Q = throughput (kg.h^{-1}).

For the different blends, with a throughput of 4 kg h^{-1} and a screw rotation speed of 300 rpm, the SME is around 300 kJ kg^{-1}, and once screw rotation speed is 1200 rpm, the SME is around 910 kJ kg^{-1}. This means that a rise in the screw rotation speed for a given throughput increases the SME.

Thus, the SME is 12 or 36 times the gamma-irradiation dose.

2.2.2. Mechanical tests

■ Tensile tests:

Tensile tests were performed on a MTS 2/M device at a speed of 30 mm min^{-1}. Then, at least ten dumbbell shaped samples were tested at room temperature to check the reproducibility of the measurements. Young's modulus was calculated for a deformation less than 1%, elongation at break and tensile strength were determined once the samples broke.