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Rheological study of polypropylene irradiated with polyfunctional monomers

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Abstract

The aim of this paper is to investigate the rheological properties of polypropylene (PP) modified by ionization radiation (gamma rays) in the presence of two different monomers. The samples were mixed in a twin-screw extruder with ethylene glycol dimethacrylate (EGDMA) or trimethylolpropane trimethacrylate (TMPTMA) with concentration in the range of 0.5–5.0 mmol. After that, they were irradiated with 20 kGy dose of gamma radiation. The structural modification of polypropylene was analyzed in the melt state by measuring melt flow rate (MFR), η^* (complex viscosity) and G' (storage modulus) in the angular frequency range of 10^{-1} to 3×10^2 rad s^{-1}. From the oscillatory rheology data, one could obtain the values of η_0 (zero shear viscosity) that would be related to the molar mass. All results were discussed with respect to the crosslinking and degradation process that occur in the post-reactor treatment to produce controlled rheology polypropylene.

The resulting polymeric materials were submitted the cytotoxicity in vitro test by neutral red uptake methodology with NCTC L 929 cell line from American Type Culture Collection bank. All modified PP samples presented no cytotoxicity.

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Keywords: Gamma radiation; Isotactic polypropylene; Biocompatibility; Monomers

1. Introduction

It is well-known that the production of different grades of polypropylene (PP) matching the market requirements has been attained by polymerizing monomer with advanced catalyzers resulting in linear chains and in a relatively broad molecular weight distribution. Nowadays, however, new catalyzers and processes are able to produce PP with large and narrow molecular weight distribution, as well as PP with short branches and even a minor level of long chain branches. For instance, the so-called visbreaking process is obtained by peroxide degradation of PP, resulting in a narrow molecular weight distribution. The reduction of molecular weight together with the reduction of molecular weight distribution yields a number of specific advantages regarding the processability and final properties of the PP product. Nevertheless, this process increases the costs due to the extra infra-structure, energy and peroxides used [1–6].

On the other hand, there is still a need of PP with specific structural features in order to cope with the increasing requirements from the market. Radiation processing of PP has been utilized to produce PP with a combination of special properties. For instance, the so-called HMSPP (high melt strength polypropylene) produced by radiation-induced grafting presents a structure composed of long

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chain branches of propylene polymer. These radiation-induced grafts can be obtained by at least three known processes: (i) PP irradiated with high energy electrons in N_2 atmosphere followed by a step of free-radical recombination and annihilation as it is stated in Basell patent [4]; (ii) PP irradiated with gamma rays in acetylene followed by free-radical annihilation as it was proposed by our group [5,6]; and (iii) PP mixed with polyfunctional monomers irradiated with high energy electron in N_2 atmosphere followed by a step of free-radical recombination and annihilation as proposed by Makuuchi's group from JAERI – Takasaki [3].

It is well-known that the radiation processing of PP yields crosslinking and chain scission reactions. It follows that the use of polyfunctional monomers can be applied not only to promote grafting but also to enhance crosslinking and reduce chain scission reactions. The balance between these reactions depends on the control of oxygen content. In addition, the control of crystalline morphology is proved to be essential in controlling the kinetics of these reactions [1–11]. When PP is modified by gamma radiation and/or peroxide in the presence of polyfunctional monomers, the reaction is very complex. Degradation reaction makes the molecular weight to decrease; grafting reaction introduces short chain branches and long chain branches as well as crosslinking. If crosslinking reaction prevails, it will result in gelatinization, even though gel formation would completely jeopardize the PP processability. Therefore, a careful control of reaction conditions should be made.

The first goal of this work is to present the radiation-induced synthesis of modified polypropylene with polyfunctional monomers to improve melt elasticity and melt strength, allowing the production of processable materials for fibers and blow molding applications.

Experiments have been carried out with increased multifunctional monomers' concentration from 0.5 to 5.0 mmol, keeping the gamma ray dose constant at 20 kGy. Two monomers were used: ethylene glycol dimethacrylate (EGDMA) and trimethylolpropane trimethacrylate (TMTPMA). The samples were studied in the molten state by measuring melt flow rate (MRF), values of η^* (complex viscosity) and G' (storage modulus) in the range of angular frequencies from 10^{-1} to 3×10^2 rad s^{-1}. Another set of measurements was performed on the same materials, calculating for each samples the values of η_0 (zero shear viscosity) by frequency sweep experiments. From the value of molecular weight of the pure PP obtained by gel permeation chromatography (GPC) the molecular weight for each η_0 was estimated. These results are discussed with reference to the selection of proper conditions of the crosslinking and degradation process, both aiming at achieving a desired MFR, rheological behavior and melt elasticity for selected applications.

This new family of resins, i.e. PP with modified rheology, allows the expansion of its industrial applications. One of them is the application in the manufacturing of packing materials for food industry, and the other, as a biomaterial in the field of medicine. However, polyfunctional monomers used to modify the PP are often carcinogenic and mutagenic. Moreover, these PP used as biomaterial in clinical application should not be the source for any adverse reaction in the organism and endanger consumers' life. Any material meant to be used as part of a device must be safe for human use, proved by biological evaluation. They have to be not only non-toxic and hypo-allergic, but also tested to carcinogenicity and to mutagenicity [12,10]. The main question is whether the residual monomer presence into PP samples can be harmful to human health. The International Organization for Standardization (ISO) provides a biological evaluation of medical devices programme [11], which should be considered in combination with the nature and mobility of the ingredients in the materials used to manufacture the device [11].

The second goal of the present work is to perform a preliminary evaluation of biocompatibility through in vitro test of cytotoxicity by the neutral red uptake methodology of two kinds of modified polypropylene.

2. Experimental

2.1. Material and sample preparation

The isotactic polypropylene (iPP) homopolymer used in this study was a reactor grade from Braskem in the spheres, with a melt flow index (MFI) of 1.5 g 10 min^{-1} at 230 °C.

EGDMA and TMPTMA at a concentration of 0.5–5.0 mmol/100 g of iPP were mixed at room temperature, and extruded in a twin-screw extruder Haake with a die diameter of 2 mm. The extruded polymer strand was cooled at room temperature and cut. After that, all samples were irradiated with gamma radiation (^{60}Co) at a dose of 20 kGy under nitrogen gas atmosphere, using the source from Embrarad with a dose rate of 10 kGy/h and the dosimetry was performed with Harwell Red Perspex 4034.

The M_w for pure iPP was measured in a Waters GPC 150 CV chromatography, with a refractive index detector and three waters styragel HT columns with a 10 μm particle size, able to separate samples with M_w in the range of 10^2–10^6 g/mol. The iPP were solubilized during 1 h in 1,2,4-trichlorobenzene at 160 °C and pumped at a flow rate of 1 mL/min. Calibration curves were obtained with 14 monodisperse polystyrene standards. M_w was determined by Millennium 2010 software with manual adjustment of the baseline.

2.2. Melt flow index

The melt flow rate (MFR) of the modified polypropylene was measured in a Melt Flow Junior equipment Mod. 09237 in which the samples were flowed through an orifice of 2.0 mm diameter under a loading of 2.16 kg at 230 °C (ASTM D 1238).

2.3. Oscillatory test

The rheological measurements were conducted using a Physica MCR 300 rheometer equipped with an electrically heated temperature chamber. All experiments were carried out at 200 °C, with parallel-plate geometry (diameter of 25.0 mm) and a 1.0 mm of gap. The frequency sweeps were carried out between 0.1 and 250.0 s^{-1}, and a strain (γ) of 5% was used. The oscillation test was used to measure the zero shear viscosity (η_0) at very low frequencies. In the range of zero viscosity a substance behaves like a Newtonian fluid; i.e. viscosity does not depend on the angular frequency.

2.4. Cytotoxicity test

The selection and evaluation of any material or device intended to be used in humans requires a structured program of assessment such as a biological evaluation. The International Standard ISO 10993 gives guidance for biological evaluation of medical devices. The first assay for initial evaluation tests is the in vitro cytotoxicity, which is used as a screening test for materials to be employed in the production of biomedical devices. The cytotoxicity assay was carried out with the exposure of NCTC L929 cell cultured in a 96 wells microplate to the extract obtained by the immersion of samples in cell culture medium, MEM (minimum Eagle's medium, Sigma Co., São Paulo, Brazil), for 24 h at 37 °C. The cell line was acquired from American Type Culture Collection (ATCC) bank. The cytotoxic effect was evaluated by neural red uptake (NRU) methodology, according to Ciapetti et al. [9], preview work [10] and International Standards [11]. Negative control used was non-toxic PVC pellets and positive control used was 0.02% phenol solution. Positive and negative controls are necessary to confirm the performance of the assay.

3. Results and discussion

It was observed that the values of MFR for all samples of modified iPP were higher than those of virgin iPP, showing that the chain scission process is more severe as compared with branching and crosslinking, even in the presence of polyfunctional monomers. Moreover, for low monomers' concentration (0.5 and 1.0 mmol) of EGDMA and TMPTMA the results exhibited even higher values of MFR in comparison with the high monomers' concentration (1.5–5.0 mmol) and virgin polypropylene (Fig. 1). This fact leads to the conclusion that the amount of monomers was not enough to allow the grafting reaction with PP molecules. So degradation was not prevented and grafting was not enough to link PP molecules. The EGDMA monomer shows lower efficiency as a crosslinking promoter than TMPTMA of low concentration, which allows the formation of a crosslinking promoter only after the recombination of the radicals. Also, their molecular structure can affect the efficiency of the monomer by interaction and solubility during the reaction.

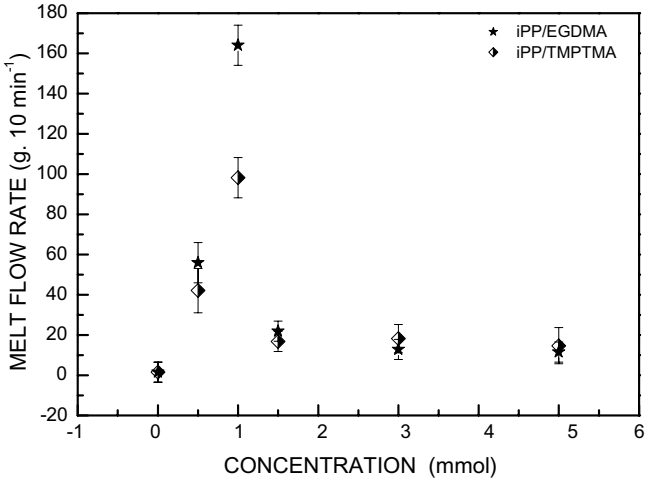

Fig. 1. Influence of different monomers' concentration in the melt flow rate of distinct modified polypropylenes in comparison to pure resin. A dose of 20 kGy.

The complex dynamic shear viscosity $\eta^*(w)$ was measured at a temperature of 200 °C and the results obtained can be visualized in Fig. 2. The values for modified polypropylene show a decrease of complex viscosity over the entire frequency range, which means that the viscosity is dominated by the molar mass reduction. Nevertheless, the Newtonian behavior in the molten state was not observed at low frequencies. In the same way the behavior of G' for all samples showed a viscoelasticity behavior increasing at high frequency and on the other hand a complex behavior at low frequency. With the addition of EGDMA and TMPTMA, G' increases at low frequency. In the case of EGDMA (Fig. 3(a)), it is more evident at 3.0 and 5.0 mmol. This behavior suggests a low crosslinked network formed from radical reactions. Concerning 1.5, 1.0 and 0.5 mmol, the slope at low frequency can be ascribed to the branched chain.

The simplest correlation between the rheology and the molar mass distribution can be formulated between M_w and the zero shear viscosity (η_0). The η_0 was determined from frequency sweep in oscillatory test at a very low frequency, making an extrapolation using an exponential fit for all curves, see the inset of Fig. 2(a) and (b) for each monomer. With the value of M_w obtained by GPC for pure isotactic PP corresponding to η_0, it was possible to estimate the molecular weight for each η_0 of modified polypropylene, as can be seen in Table 1. From these data the sample iPP/EGDMA with 5.0 mmol showed a value of M_w near to the pure resin.

The melt strength and extensibility behavior of all modified PP are observed in Table 2. For modified PP, the smaller value of melt strength showed a high value of extensibility. This implies that extensibility is governed by the width of the average molecular weight distribution. In this process to synthesize the modified polypro-

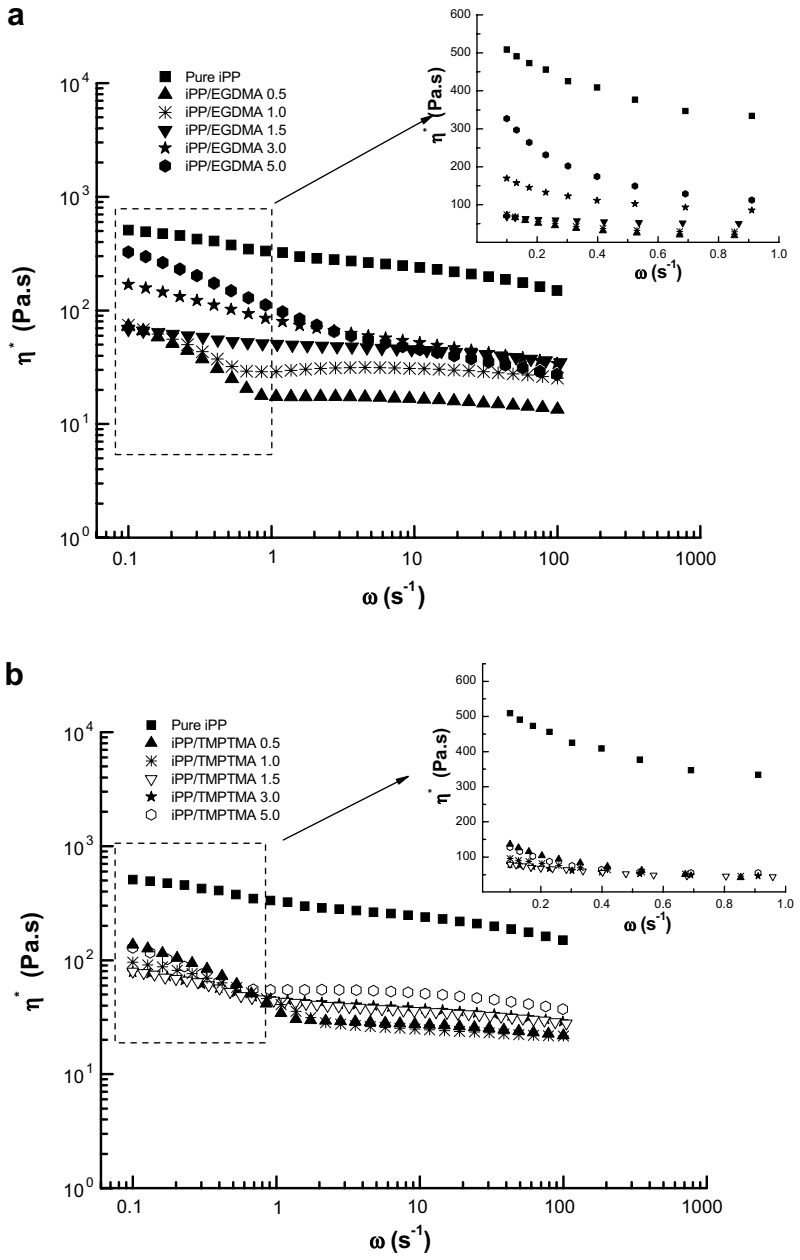

Fig. 2. Complex viscosity curves for all monomers' concentration: (a) EGDMA and (b) TMPTMA.

pylene with polyfunctional monomers, the degradation by chain scission was favored to grafting and crosslinking process.

The evaluation of cytotoxicity test can be by qualitative or quantitative method. Qualitative evaluation examines microscopically any changes in morphology, vacuolization, detachment, cell and membranes lyses. Quantitative evaluation measures cell death, inhibition of cell growth, cell proliferation or colony formation as well the number of cells, amount of protein, enzymes, release of vital dye, etc.

In this work the evaluation of toxicity was performed by the release of vital dye, neutral red and measuring optical density (DO) in an ELISA reading Spectrophotometer Sunrise from Tecan at 540 nm. The DO results were used to calculate cell viability percentage in relation to cell control, considering 100% viability. Cell viability curves were obtained in a graphic traced with these cell viabilities percentages against extract concentration. The cytotoxicity index $IC_{50\%}$ is obtained in the graphic and means the extract concentration which injures 50% of the cell population in the assay. The sample with cell viability curve above $IC_{50\%}$ line is considered non-cytotoxic and if under $IC_{50\%}$ line is considered toxic. The samples can be considered cytotoxic if their sequence of results cross the level of $IC_{50\%}$ line and the cytotoxicity index is obtained by projecting a line from the intersection to extract concentration axis.

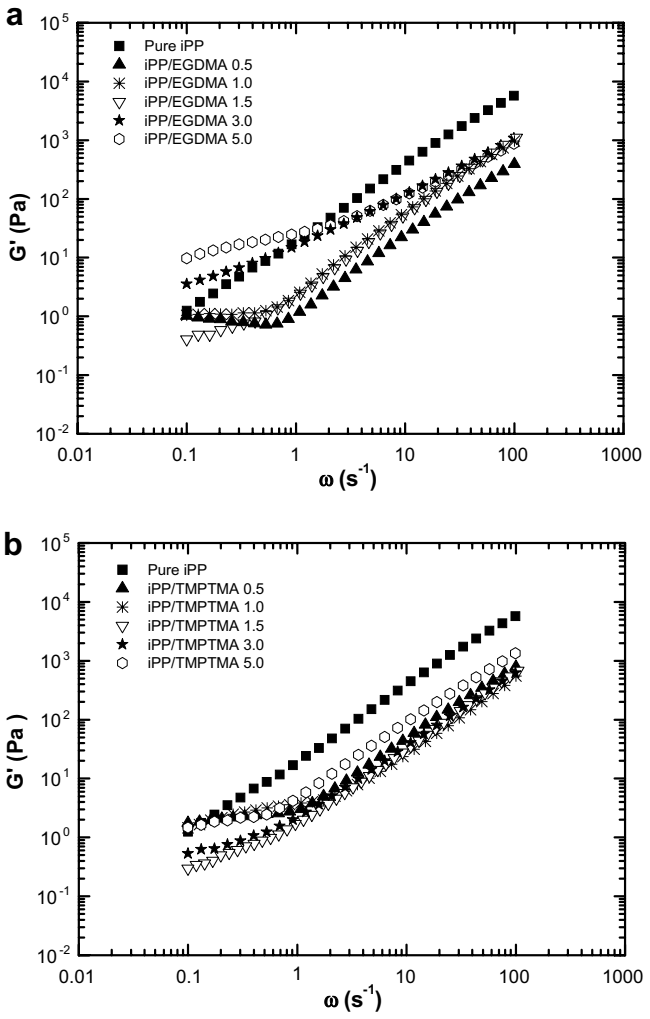

Fig. 3. Dynamic module curves for all monomers' concentration: (a) EGDMA and (b) TMPTMA.

Table 1
Estimated molecular weights for iPP modified using η_0 from the low frequency limit of the complex viscosity

Samples	Zero shear viscosity, η_0 (Pa S)	M_w (g/mol)
Pure iPP	565.7	478.000
iPP/EGDMA 0.5	102.0	294.000
iPP/EGDMA 1.0	103.0	295.000
iPP/EGDMA 1.5	75.8	270.000
iPP/EGDMA 3.0	202.8	357.000
iPP/EGDMA 5.0	414.2	437.500
iPP/TMPTMA 0.5	166.9	338.000
iPP/TMPTMA 1.0	109.9	300.000
iPP/TMPTMA 1.5	93.3	286.500
iPP/TMPTMA 3.0	93.0	286.000
iPP/TMPTMA 5.0	193.8	352.500

Fig. 4 shows the viability curves of the tested samples and all of them presented a similar behavior in comparison to the negative control, which means that all samples presented non-cytotoxic effect. Only positive control presented toxicity, as expected, with $IC_{50\%}$ of about 43.

Table 2
Melt strength and drawability for all samples of modified PP

Samples	Melt strength, cN (190 °C)	Drawability, mm/s (190 °C)
Pure iPP	21.5	6.0
iPP/EGDMA 0.5	1.7	12.7
iPP/EGDMA 1.0	2.9	25.3
iPP/EGDMA 1.5	5.8	9.7
iPP/EGDMA 3.0	5.9	7.9
iPP/EGDMA 5.0	5.9	8.1
iPP/TMPTMA 0.5	–	–
iPP/TMPTMA 1.0	2.6	15.3
iPP/TMPTMA 1.5	3.9	16.2
iPP/TMPTMA 3.0	4.5	14.1
iPP/TMPTMA 5.0	5.3	14.0

The cytotoxicity assay results demonstrated that the use of both monomers and the processing conditions employed did not affect the toxicity of the studied polymer.

4. Conclusions

EGDMA was more effective in reacting with PP to modify elongational flow than TMPTM in the studied

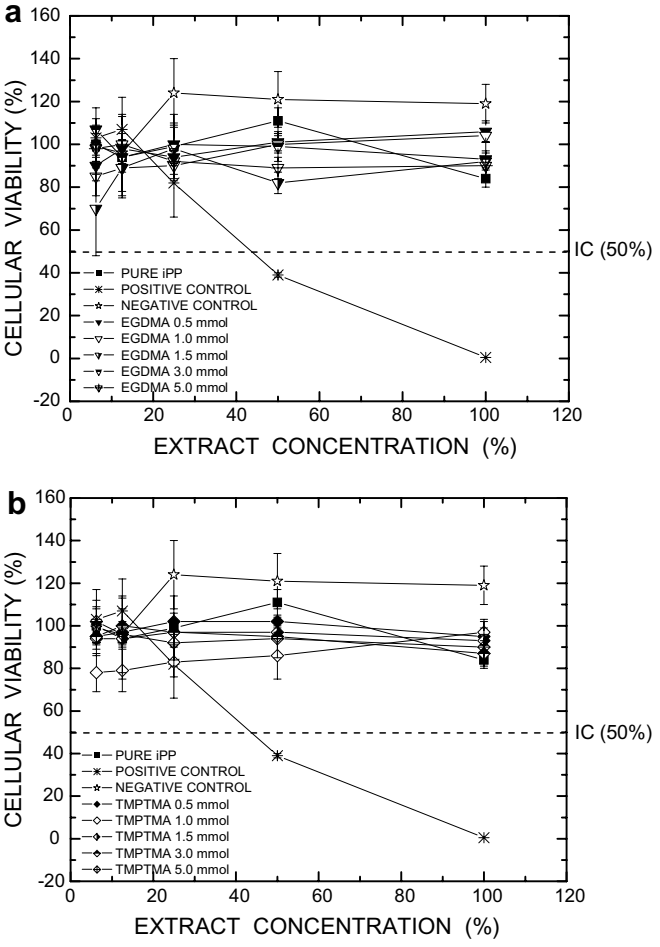

Fig. 4. Cell viability curves of cytotoxicity test by neutral red uptake methodology. (a) Samples with different concentrations of monomer EGDMA and (b) samples with different concentrations of monomer TMPTMA.

conditions. This was more apparent at higher concentrations as demonstrated by the results of MFR, η^* (complex viscosity), G' (storage modulus) and consequently by the values of η_0 (zero shear viscosity). The elevated values of extensibility mainly for lower concentrations of monomers are an indication that the samples can be useful where the elongational flow is dominant, for example, for fibers and blow molding applications. Melt rheology experiments revealed themselves as powerful tools to investigate the molecular characteristics modification. Finally, the modified polypropylene with two different monomers, EGDMA and TMPTMA, studied in this work showed no evidence of toxic effect. Therefore, after in vitro evaluation of cytotoxicity, one could come to a conclusion that these materials may be used as biomaterials. Nonetheless, studies of biocompatibility should be still carried out in an attempt to apply these materials in the manufacturing of food packings.

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