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NONLINEAR OSCILLATORY SHEAR FLOW AS A TOOL TO CHARACTERIZE IRRADIATED POLYPROPYLENE/MWCNT NANOCOMPOSITES

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ABSTRACT:
The relative intensity and phase of the third harmonic, $I_{3/1}$ and $\Phi_3-\Phi_1$, deduced from Fourier Transform analysis of Large Amplitude Oscillatory Shear (LAOS) experiments were used to differentiate the effect of irradiation and the effect of multiwalled carbon nanotubes (MWCNT) concentration in PP/MWCNT nanocomposites. Alternatively, studies of elastic and viscous non linearities that give shear thinning and thickening or strain softening and hardening were carried out for the same purpose. Using both methods to analyse LAOS data, the conclusion was the same: The influence of MWCNTs is noticed at low/intermediate γ_o strains (10 – 100 %), whereas the effect of irradiation is rather observed at strains above 100 %. This marks a difference with respect to small amplitude oscillatory flow measurements, which are not valid to distinguish between the respective rheological effects of irradiation and MWCNT in polymer nanocomposites. SEC-MALLS-IR-VI analysis was used to determine the long chain branching degree λ of irradiated polypropylene, but this technique is very difficult to be applied for nanocomposites. Face to this shortcoming, an empirical correlation between λ and the value of the $I_{3/1}$ plateau when γ_o tends to infinite, found for irradiated neat PP, was used to evaluate the long chain branching degree of nanocomposites.

KEY WORDS:
Nanocomposites, polypropylene, MWCNT, long chain branching, LAOS

1 INTRODUCTION

The use of polypropylene (PP) in industrial processes such as extrusion-blowing, blow moulding, foaming extrusion and thermoforming is favored by long chain branching (LCB) that brings about stiffer and stronger polymers avoiding or delaying break and thinning when stretching. The behavior is related to the strain hardening phenomenon in elongational flow, which refers to a rapid increase of the uniaxial extensional viscosity beyond a critical strain [1 – 5]. Electron beam irradiation process, among others can be used to form long chain branched polymers [6 – 7]. On the other hand, nanocomposites based on dispersions of multiwalled carbon nanotubes (MWCNT) in a PP matrix give a chance to obtain electrically conductive polypropylene. In a recent paper [8], we have combined both dispersion of MWCNT to obtain electrically conductive MWCNT/PP nanocomposites and irradiation of these nanocomposites to allow processing behavior which is favored by LCB.

One fundamental question which arises within the framework of these nanocomposites is the evaluation of the LCB degree that corresponds to each dose of applied electron beam irradiation. Size Exclusion Cromatography (SEC) combined with Multi Angle Laser Light Scattering (MALLS), Infrared Detector (IR), and Viscosity Detector (VI) is a very suitable tool to evaluate sparse long chain branching level in polyolefins. But this technique is very difficult to use in the case of polymer nanocomposites because proper solutions to be injected in SEC equipment cannot be properly prepared. Therefore, rheological methods are required to face this issue. In recent years, Large Amplitude Oscillatory Shear (LAOS) has revealed as an interesting technique to detect LCB in polymers [9 – 24]. Neidhöfer et al. [9 – 11] and Schlatter et al. [13] observed that Fourier Transform Rheology is sensitive regarding polymer topology. They were able to distinguish branched and linear topologies under non-linear oscillatory shear using the third harmonic $I_{3/1}$ and the phase angle of the third harmonic Φ_3. Vittorias et al. [15 – 16] studied optimal conditions to differentiate branched polyethylene in comparison to linear polyethylene with similar molecular weight. Hyun et al. [17 – 18] considered monodisperse linear and comb

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clude that either in neat PP or in a MWCNT/PP nanocomposite the effect of long chain branching was to increase the shear thinning response ($T < 0$) at large amplitudes.

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