

# Study of linear low density polyethylene/polytetrafluoroethylene-g-1,3-butadiene processability

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## Abstract

The extrusion of linear low density polyethylene (LLDPE) is limited by a process related defect known as ‘melt fracture’ or ‘sharkskin’, which is a surface defect of the extruded polymer. This defect results in a product with a rough surface that lacks luster and in alterations of specific surface properties. The aim of this study was to obtain a recycled polytetrafluoroethylene polymer with an olefin that could improve the extrudability of the LLDPE. The copolymer was obtained by irradiating recycled PTFE in an inert atmosphere followed by the addition of an olefinic monomer to graft the latter in the polymeric matrix (PTFE). The olefinic monomer used was 1,3-butadiene. The specimens were studied using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and differential thermogravimetry (DTG). Therefore, in an effort to enhance the processability and so the drawability, it has been found helpful to add a small amount of copolymer. 0.2-2.0 wt% of the copolymer that was obtained was mixed with LLDPE. The rheological properties of the mixture were determined with, a torque Haake rheometer, a rotational Physica rheometer. The results indicated that the process used rendered a copolymer which when added to LLDPE, improved the extrusion process and eliminated the defect ‘melt fracture’.

Keywords: gamma radiation, PTFE, LLDPE, grafting

## 1 Introduction

The radiation-induced grafting for modification of properties from commercial polymer is a largely studied technique. The radiation-grafting of PTFE consists of promoting the generation of free radicals and followed by contacting with the monomer, in order to create branches. A copolymer is obtained from the addition of the monomer on the polymer. This copolymer starts to have the properties of the grafted monomer with most of the original properties of the polymeric backbone.

The radiation-induced grafting of monomers on polymers is a well-known method since 1957 when Chen and Mesrobian studied this copolymerization mechanism [1, 2].

The mixture of a small amount of a fluoropolymer based polymer processing additive (PPA) to the polymer under processing to generate an immiscible blend is a widely industrial method used to modify the limit of the processing and remove the “sharkskin”. A recent overview of various processing aids, their formulations, applications and performance was given by Amos et al and by Achilleos et al. [3,4].

The copolymer produced by this method presents potential industrial application, including its use as additive to process linear polyethylene low density (LLDPE) by extrusion. Published data about the action of this additive show that PTFE acts as a flow promoter close to the walls of the extrusion machine, while the lateral groups produced by the grafting of the 1,3-butadiene promotes the affinity with LLDPE [5].

The aim of this work is to develop the use of recycled PTFE for the synthesis and characterization of a grafted copolymer. The analysis of its use as polymer processing additives (PPA) for LLDPE is also a goal of this work. Therefore, it was studied the radiation-induced grafting of 1,3-butadiene on micronized recycled PTFE from industrial scrap to obtain the copolymer PTFE-g-1,3-butadiene.

## 2 Materials and Methods

### 2.1 Materials

Scrap PTFE in form of fine straps generated in machining process of PTFE pieces was acquired from the industry of PTFE transformation. This Scrap PTFE were washed to clean up oil impurities and irradiated to further micronization in order to get 80% of the particles smaller than 2 microns.

The 1,3-butadiene monomer and N<sub>2</sub> were acquired from White Martins S.A with purity better than 99,9%. Plastic bags of nylon were the recipients used for irradiation as they are inert to oxygen and monomer.

### 2.1.1 Irradiation process

The samples were irradiated by the industrial cobalt-60 irradiator of EMBRARAD - Brazilian Company of Radiation. The activity was around  $1.03 \times 10^{10}$  MBq and dose rate about 5 kGy/h.

The LLDPE used in this work was produced by Braskem S.A. The LLDPE pellets were spherical with the specifications presented in Tab. 1.

Table 1 - Specifications of LLDPE type LH-820/30AF.

Property of Control	Method	Values
	ASTM	
Fluidity index (190 °C, 2,160kg)	D-1238	0,8 g/10 min.
Density	D-1505	0,920 g/cm <sup>3</sup>

### 2.2 Methods

The copolymer synthesis was done by indirect graft, i.e., the polymer is irradiated in the absence of monomer under inert atmosphere. Only after the generation of the active centers as free-radicals, the polymeric matrix is placed in contact with the monomer.

The process consists of three steps:

The initiation step consists of the sample irradiation for free-radicals generation. The samples of 25 and 100 g of recycled PTFE were irradiated at dose rate of 5 kGy/h until the specified doses of 20, 50 and 100 kGy at ambient temperature.

The propagation step corresponds to the grafting of the monomer in PTFE. After the irradiation excess monomer is added and kept in contact with PTFE irradiated during 12 days.

The termination step is the stage to promote the annihilation the remaining free radicals by heating the sample to a temperature of higher radical mobility inside the polymeric matrix. This stage consists of a thermal treatment in an oven, initially for 1 hour at 100 °C and later 1 hour more at 140 °C. This treatment is accomplished in the own irradiation device to avoid the contamination with oxygen.

The addition of the monomer always happened 1 day after the irradiation. This procedure is considered appropriate, since one of the PTFE characteristics is to maintain the free radicals for a long time due to its very rigid molecule. The half life of the free radicals at ambient temperature is about 1000 hours [6]. The new polymer material like this was denominated as “PTFE-g-1,3-butadiene”.

### 2.3 The grafting degree

The grafting degrees (%) were determined gravimetrically. The PTFE samples were weighed before and after the irradiation and grafting until constant weight. The calculation of the grafting (%) was made using the following equation A:

$$\text{Grafting (\%)} = \frac{W_f - W_i}{W_i} \otimes 100, \text{ eq. (A)}$$

Where  $w_i$  and  $w_f$  are the initial and final mass after the grafting, respectively.

### 2.4 Spectroscopy of infrared absorption with Fourier transforms (FTIR) [7].

The IR spectra were obtained from recycled PTFE and from PTFE-g-1,3-butadiene copolymer. These materials were mixed with dry KBr and pressed to form a tablet. The IR was acquired in the interval of wave number between 400 to 4000  $\text{cm}^{-1}$ . It was used a spectrometer of Thermo Nicolet, I model Nexus 870 to FT-IR.

### 2.5 Thermogravimetry analysis (TGA) [7].

The radiation-induced grafting of 1,3-butadiene was investigated in PTFE by thermogravimetry analyses of recycled PTFE and of the PTFE-g-1,3-butadiene copolymer. They were performed by dynamics TG using a Mettler Toledo, model TGA/SDTGA 851e. The samples were heated at rate of 10 °C/min starting from room temperature to 700°C, under flow of oxygen, at rate of 50 mL/min.

### 2.6 Torque rheometer.

The analyses of the processing profile LLDPE blended with the PTFE-g-1,3-butadiene was conducted by rheological analyses of the polymer, LLDPE and of the mixtures of LLDPE with PTFE-g-1,3-butadiene with a torque rheometer.

It was prepared the mixtures with mass of 0.2, 0.5, 1.0 and 2.0% of LLDPE/additive. A barrel with a twin-screw was used for extrusion, operating at 60 rpm with to provide of 8.0 g/min of mixture. The heating zones of the cylinder sections 1-4 were controlled at nominal temperature settings of 140, 150, 160 and 170 °C and matrix at 180 °C. The equipment used was a torque rheometer of Haake, Rheometer model PTW16/25D.

## 2.7 Oscillatory Rheometer.

The rheology properties in oscillatory condition are important for almost all the processing types of polymer, as they allow the search of data on viscoelasticity of the melt or the understanding of the molecular structure of the melt.

The polymers, pure LLDPE and the mixture of LLDPE with PTFE-g-1,3-butadiene for the oscillatory rheometry, were heated to 180 °C under flow of nitrogen. The results were obtained using the parameters; width 0.01 to 100 % angular frequency ( $\omega$ ) constant of  $10 \text{ s}^{-1}$  and constant width of 10 % angular frequency 150 to  $0.1 \text{ s}^{-1}$ . By means of that technique it was possible to obtain  $G'$ ,  $G''$  ( $\eta$ ) versus angular frequency and  $G'$  and  $G''$  versus ( $\tau$ ) of the polyethylene's. I was used an oscillatory rheometer model MCR 300, of Physica.

## 3 Results and Discussion

The results showed in figure 1 allowed us to learn that after twelve days there was only a small variation of the grafting degree as it was observed by a continuous decrease in copolymer formation. Thus, it was established for all the experiments that the termination phase were almost completed after twelve days.

It was observed in the Fig. 1 around 8.0, 14.0 and 17.5 % of grafting for dose of 20, 50 and 100 kGy, respectively. The grafting percentage increased with dose, as consequence of scission of the chains, with larger production of radicals, as described in the literature.

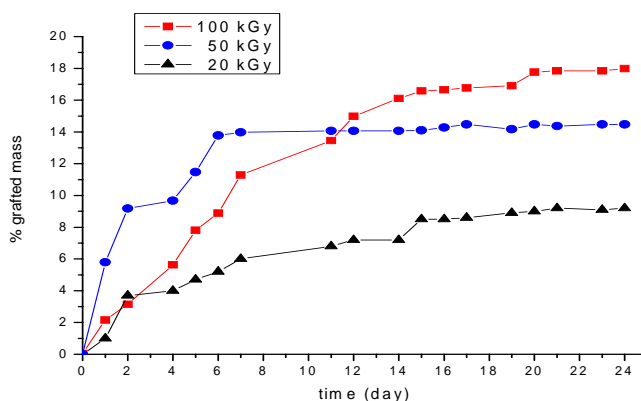


Figure 1 – Percentage of the grafted mass (1,3-butadiene) in function of the time for different doses.

FT-IR was performed to evaluate the grafting of the monomer in the chain of PTFE. In Fig. 2, it was shown the IR of the recycled PTFE samples and PTFE-g-1,3-butadiene copolymer. In the curves of Fig. 2, the section corresponding to the axial, symmetrical and asymmetric deformation of the group  $-\text{CF}_2$  of PTFE, in the wave number region around  $1150$  and  $1240 \text{ cm}^{-1}$ , respectively, as well as the polarization region by  $640$  and  $556 \text{ cm}^{-1}$ . In the spectra of the PTFE-g-1,3-butadiene, besides the region corresponding to PTFE, are still observed the bands of  $-\text{CH}$ ,  $=\text{CH}$  and  $=\text{CH}_2$ , of wave number about of  $2912$ ,  $968$  and  $914 \text{ cm}^{-1}$ , respectively. These values are not exactly the corresponding to the of the 1,3-butadiene pure, because the groups have got the influence of the PTFE structure. These region confirm the occurrence of the 1,3-butadiene grafting in the matrix of PTFE [8,9,10,11].

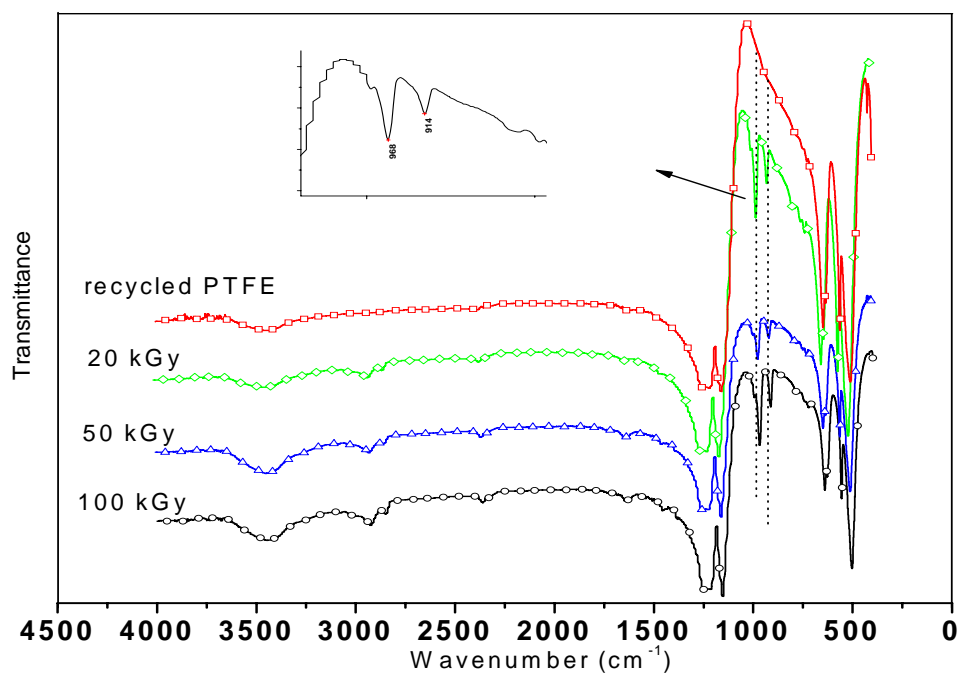


Figure 2 - Spectra of FT-IR for a recycled PTFE and PTFE-g-1,3-butadiene obtained with doses of 20, 50 and 100 kGy.

Fig. 3 shows the profiles of TG and DTG of the recycled PTFE and PTFE-g-1,3-butadiene sample. With this technique was possible to indicate alteration in the data that demonstrates the presence of the grafting monomer to obtain the copolymer. In the profile of recycled PTFE was observe only one step until the begin of the degradation around 463 °C. On the other hand for PTFE-g-1,3-butadiene copolymer there were three effects: i) - a mass increase around the temperature of 100 to 150 °C due to the polymer oxidation; ii) – the weight loss due to the degradation of the bonds  $-\text{CH}_2=\text{CH}-\text{e}-\text{CH}_2-$  at about 250 °C, and iii) - the degradation of the main polymer chain of the PTFE copolymer [2, 12, 13].

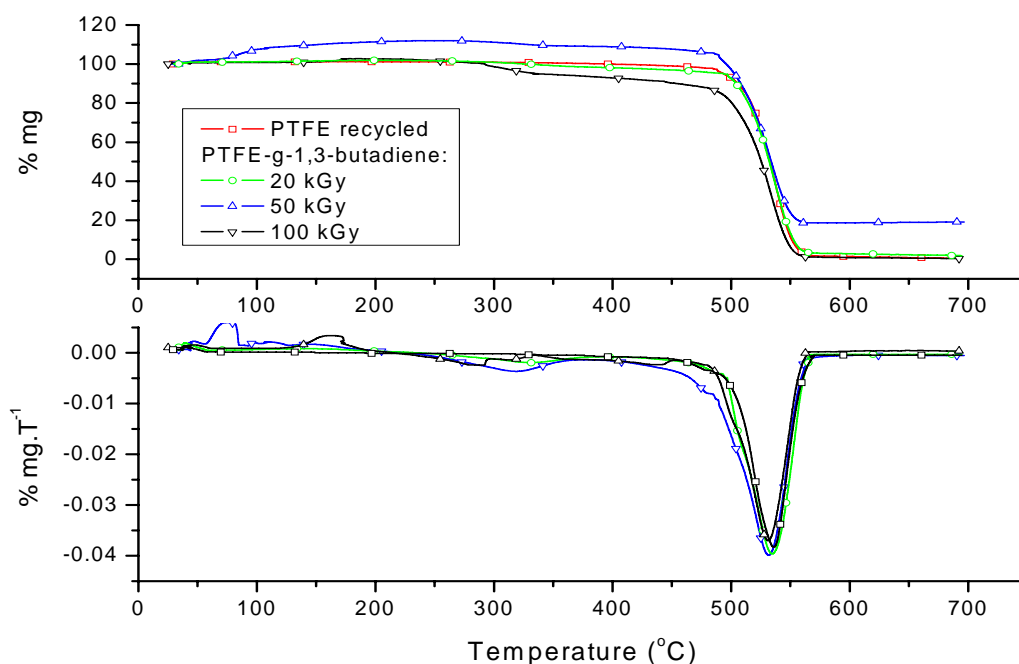


Figure 3 - Curves of TG and DTG as a function of temperature for recycled PTFE and PTFE-g-1,3-butadiene obtained with doses of 20, 50 or 100 kGy

The additive was mixed to the LLDPE with the following mass proportions: 0.2; 0.5; 1.0 or 2.0%. The time of homogenization of the mixture using a roll mixer type was one hour.

The die coating of a extrusion machine that initially contains pure linear low density polyethylene (LLDPE) was achieved by drops of immiscible fluoropolymer migrating somehow to the wall of the matrix during the extrusion. LLDPE slide in the additive/LLDPE coated at the die surface. For a fixed rate of volumetric flow there was a decrease of the pressure of extrusion and the shear rate in the wall.

After the induction time, pressure start to decrease continuously and the “sharkskin” is eliminated gradually. The elimination is not homogeneous, but in fact show a continuous smoothing of the extruded (Fig. 5), until the whole surface of the extruded becomes free from the “sharkskin” [Fig. 5 (f)]. It is known that in order to be effective, the fluoropolymer should be close with the outlet of the matrix, where the LLDPE reduce dramatically the stress and the rate of polymer deformation.

The industrial extrusion of the LLDPE was simulated using a rheometer with twin-screw, model PTW16/25 from Haake. The temperatures in those zones were 140/150/160/170 °C and of 180 °C in the matrix, whose circular hole has a diameter of 4 mm. The feeding rate of the extruder was 8.0 g/min and the rotation was 60 rpm.

The Fig. 4 shows the torque curve in relation to the time of LLDPE mixed with PTFE-g-1,3-butadiene. In these experiments the mass of the additive was varied of 0.2; 0.5; 1.0 and 2.0 %. It was observed in all of percentage with additive a larger torque in relationship with pure LLDPE presented in the Fig. 5 (a), due to presence of the additive. The observations in relation to swell, fractures melting and “sharkskin” is visual (Fig. 5 (e) and (f)) and in the mixtures with percentage of 0.2 and 0.5 %, LLDPE/additive doesn't present the imperfections and there was a decrease of the swell of 10 % in relation to the extrusion of pure LLDPE (Fig. 5)[14].

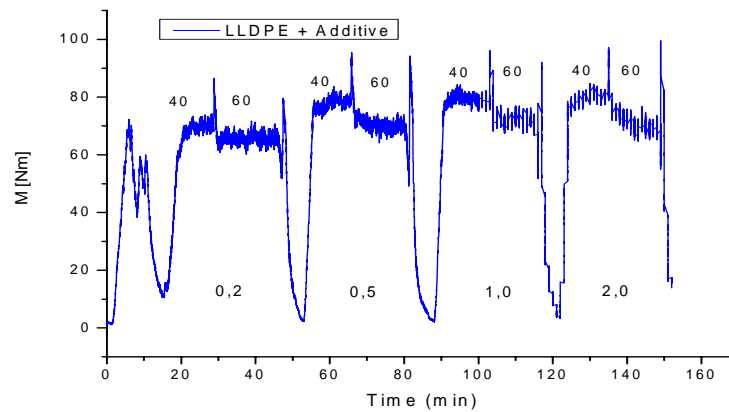


Figure 4 – Torque vs. mixture time of LLDPE and additive.

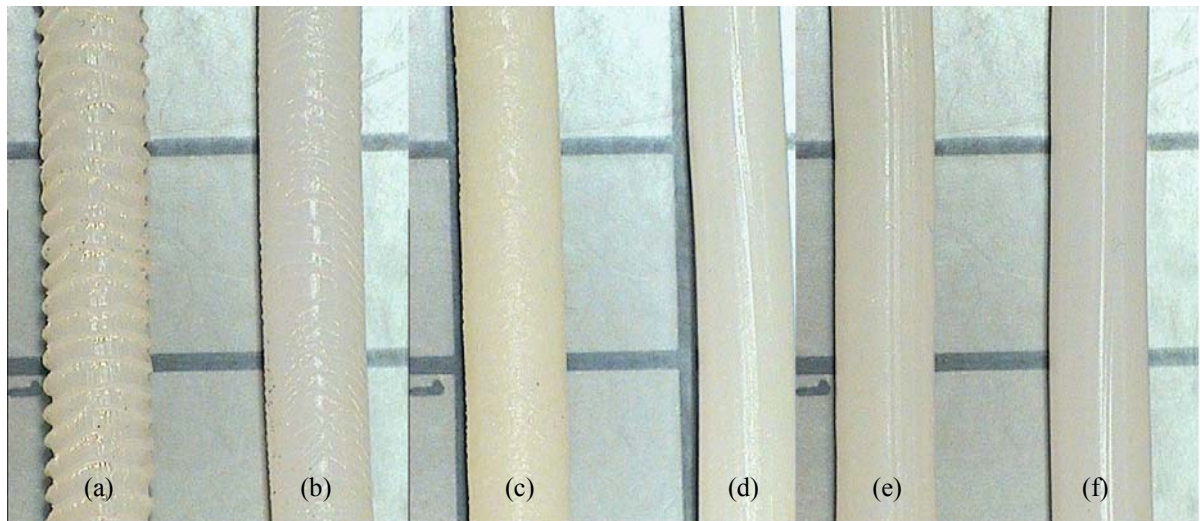


Figure 5 - Extruded material LLDPE pure (a) and (b); mixture of LLDPE sample with additive in the ratio of 2.0 (c); 1.0 (d); 0.5 (e) and 0.2 % (f) in weight.

The Figs. 6 and 7 shows that the rheology properties of LLDPE pure extruded is practically the same to the one of LLDPE mixed additive extruded in the percentage of 0.2 and 0.5%. This shows that the additive did not influence in the rheology properties, storage module in shear ( $G'$ ), loss module in shear ( $G''$ ) and complex viscosity ( $\eta^*$ ).

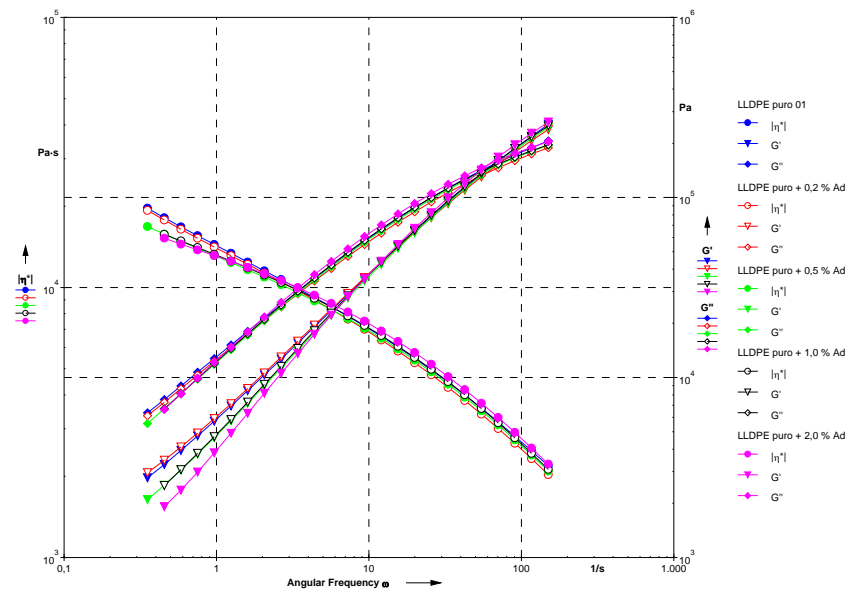


Figure 6 – Complex viscosity and shear modules as a function of frequency.

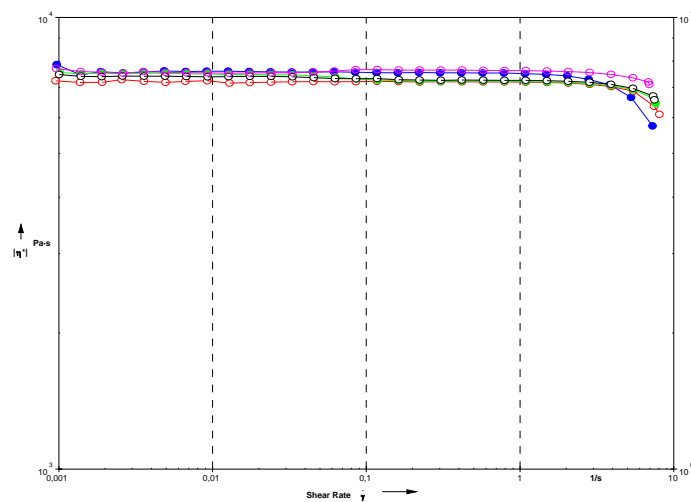


Figure 7 - Complex viscosity as a function of shear tension.

#### 4 Conclusions

PTFE-g-1,3-butadiene copolymer was synthesized by radiation-induced grafting of recycled PTFE with the 1,3-butadiene monomer, The spectroscopy measures in the infrared range evidenced this fact for the characteristic absorption frequency of  $-CH$ ,  $=CH$  and  $=CH_2$ , wave number about of 2930, 1060 and 861  $cm^{-1}$ , respectively.

The PTFE-g-1,3-butadiene samples presented 7 to 15% of mass loss, before the starting the PTFE degradation, showing that a more volatile structure was added to the main chain polymer (PTFE).

The rheometry showed that the mixture of the PTFE-g-1,3-butadiene copolymer to LLDPE were effective as a PPA for LLDPE extrusion. Therefore, this material can be used in the modern plastic transformation industry to coat the matrix of the extrusion machine, decreasing the shear tension and eliminating the “sharkskin”.

It was also showed another use of recycled PTFE.

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