PREDICTION OF AN EFFECTIVE PHYSICAL FOAMABILITY OF LLDPE/LDPE BLENDS FROM RHEOLOGICAL ASSESSMENTS

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Abstract

LLDPE has a much lower melt strength, due to no long chain side branched molecules, only short chain branching, generally; consequently, foams cannot typically be produced from 100% LLDPE. Foams are very hard to be produced with LLDPE because of wall rupture from lack of melt strength; foams with uniform, closed cell structure were made susceptible using the irradiated LLDPE, but showed strain hardening elongation rheology. So, foaming experiments were carried out with blends of gamma-induced irradiation long-chain branching LLDPE and LDPE; LDPE is often used for foaming, because of their good melt strength, but offer inferior properties when compared to LLDPE. Another advantage of foams made from radiation branched polymers is that it is not crosslinked, so, recyclability is not affected. The market size of non-crosslinked polyolefins foams was estimated to be around 150 million kg. With excellent cushioning properties, good chemical and oil resistance and high moisture barrier, low-density polyolefins foams have wide applications in insulation, packaging, flotation, sports, hygiene products, medical and pharmaceutical applications. LLDPE with radiation-induced Long Chain Branching (LCB) and improved foaming processability may have very great potential in large-scale commercialization. This work aims to investigation of rheological properties as per: Melt Index at 190^o C, Melt Strength and Extrudate Index at 150, 160, 170 and 190^o C, in LLDPE/LDPE blends (10, 20, 30 / 90, 80, 70), LLDPE irradiated at 10, 20 and 30 kGy doses. Complementary studies will comprise physical foaming using CO_2 as blowing agent in a Haake extruder with mono-screw specific for foaming, in order to indicate ideal LLDPE/LDPE formulation at a lower gamma-irradiation dosis, in order to provide an effective foaming.

Introduction

The use of ionizing radiation to modify polymers and to improve material properties is well known (Charlesby, 1960 It is well known that the melt strength of polyolefins is related to the molecular structure of the polymers, including the molecular weight distribution and the degree of branching. Long chain branching in polyolefins is known to decrease the melt flow rate and enhance the melt strength of the polymers [1]. LLDPE does not have the melt strength some processors need for foams, blown film, extrusion coating, and thermoforming. Gamma irradiation of LLDPE pellets reportedly can induce long-chain branching that provides processability similar to that of LDPE while retaining the superior mechanical properties of LLDPE. Irradiation increases the molecular weight, adding melt strength. The long-chain branching makes the resin more shear sensitive; and at very low melt indexes, excessive extrusion pressures and shear heating can be avoided.[2] [3]. It is known that the melt strength of PE increases with the decrease of the melt flow [4] [5]. The most striking change for the radiation-modified PEs is the drastic decrease of the melt flow index; so the increase of melt strength is expected. Rheology is the study of material flow. Thermoplastics flow behavior during melt processing is governed mainly by the polymers molecular weight, molecular weight distribution and degree of branching [6]. Rheotens, a strain controlled extensional device for polyethylene melts, has found widespread use in determining the extensional flow properties, as melt strength and melt extensibility. This is mainly due to the simplicity of the test, excellent reproducibility and close modeling of many polymer processes such as film blowing, fiber spinning and foaming. In standard Rheotens test, the drawdown force needed for the extension of an extruded melt strand is measured as a function of drawdown velocity, the melt strength being defined as the drawdown force required to break the melt strand [7][8]. Direct foaming of thermoplastics having a low melt flow rate (MFR) is prejudiced by heat interference from the friction; so, an ideal composition of LDPE and LLDPE must have a good balance between melt strength and processability. Radiation modification of LLDPE, prior to blends with LDPE has brought about significant improvement of various properties of the resins and products made from them using extrusion based processes. Rheological characterizations via Rheotens measurements were carried out on irradiated LLDPE and non-irradiated LDPE resins. Resins gamma irradiation usually significantly enhances the melt strength due to long chain branching, consequently very beneficial to the processability of radiation-modified resins for applications that demand higher melt strength, as in foaming process. This work aims to a brief investigation on melt strength, at four temperatures, in LDPE and LLDPE non-irradiated and irradiated, at 10, 20 and 30 kGy. From 10, 20 and 30% irradiated LLDPE in LDPE blends, it will be selected the effective blend, according to Extrudate Swell and Expansion Index, in order to provide an effective foam.

Experimental

Two commercial polyethylenes (PEs), LLDPE (Flexus 7200) and LDPE (PB 681/59) both supplied by Braskem were used in the work.

LLDPE was gamma-irradiated at 10, 20 and 30 30 kGy. In LLDPE, non-irradiated and irradiated and LDPE was investigated Melt Strength, at 150, 160, 170 and 190 C. Irradiated LLDPE was homogeneized in a single screw, 3:1 L/D and 19/33 compression ratio Haake Rheometer, according to: LLDPE/LDPE blends (10, 20, 30 / 90, 80, 70); admixtures obtained were analyzed as per: Melt Flow Index (190 C), via Ceast Plastometer and Extrudate Swell and Expansion Index, both at 160 and 170 C, from 40 to 70 rpm, in rheometer above described. According to results obtained from these assessments, there will be performed the physical foaming, by using CO_2 as PBA.

Melt Flow Index, Melt Strength, Extrudate Swell and Expansion Index Evaluations

Melt Flow Index analyses were accomplished in a CEAST apparatus, *modular line.* Samples were analyzed at 190^o C, 2.16 kg load, 240 seconds pre-heating time, according to ASTM D1238-04C. Haake Rheomex 332p, single-screw, 3:1 L/D and 19/33 compression rate, was connected to a Rheotens 71.97, Göttfert, that consists of a pair of rollers rotating in opposite directions; the polymer melt strand from a capillary die is drawn by the rotating rollers, whose velocity increases at a constant acceleration rate, registering the tensile force needed for elongation of the extruded filament as a function of the draw ratio, while the polymer melt has being stretched underwent uniaxial extension [7]. Test conditions: take-up speed of the Rheotens wheels initially equal to 14.7 mm/s, 2 mm die and velocity of extruded polymer strand adjusted for a tensile force zero. The experiment is started by slowly increasing the take-up speed of the Rheotens wheels until the polymer filament breaks; each Melt Strength experiment was repeated five times.

Essays temperature readings were accomplished at: 150, 160, 170 and 190^o C, adjusting melt strand output at 6 rpm.

Expansion Index - EI (*Ø sample/ Ø sample*) is a common phenomenon observed in the polymer extrusion; accurate prediction of the dimensions of an extrudate is important for indicating ideal material for foaming applications . Similarly, accurate predictions of extrudate swell can help in optimizing the rheology and hence the molecular structure of polymers so as to suit a given profile extrusion application. [10].

Foaming

Accomplished in Haake rheometer, Rheomex 332p, L/D 3:1, 19/33 compression ratio, foaming mono screw special, 4mm die and CO_2 as PBA(Physical Blowing Agent). Extruder profile temperature was adjusted according to Table 1:

Table 1: Extruder temperature zones (^{o}C)

Polymer	Feed	Compression	Shear	Die
LLDPE/LDPE **Blends**	110	135	185	190

Foaming extrusion conditions kept at 15 rpm and 2 bar.

Results and Discussion

In Table 2 are shown Melt Strength results, at 150, 160, 170 and 190 ^{o} C:

	MS (cN) 150 C	MS (cN) 160 C	MS (cN) 170 C	MS (cN) 190 C
LDPE 0 kGy	0.74	0.43	0.06	0.01
LLDPE 0 kGy	0.17	0.12	0.04	0.03
10	0.35	0.18	0.08	0.06
20	1.00	0.88	0.79	0.70
30	3.58	2.25	2.64	1.83

Table 2: Melt Strength (MS) evaluations for LDPE and LLDPE, non-irradiated and irradiated:

Values obtained in Table 2 indicate that LLDPE 20 kGy sample, at 190^{o} C, has almost the same Melt Strength presented by LDPE at 150^{o} C.

Considering that extruder profile for obtaining LDPE foams is about 160 and 170 ^{o}C, there were performed Melt Flow Index, Extrudate Swell and Expansion Index, according to Table 3:

Table 3: Melt Flow Index and Expansion Index (EI) of LDPE and LLDPE, non-irradiated and irradiated:

	Dose (kGy)	MFI, 190 C (dg/min)	EI 160 C	EI 170 C
LDPE	0	3.80	1.58	1.62
LLDPE	20	0.98	1.39	1.42
LLDPE 10 kGy, 10% in LDPE	---	2.88	1.60	1.65
LLDPE 10 kGy, 20% in LDPE	---	2.43	1.64	1.76
LLDPE 10 kGy, 30% in LDPE	---	2.40	1.71	1.66
LLDPE 20 kGy, 10% in LDPE	---	2.49	1.60	1.62
LLDPE 20 kGy, 20% in LDPE	---	1.71	1.69	1.72
LLDPE 20 kGy, 30% in LDPE	---	None flow	1.74	1.70
LLDPE 30 kGy (*)	---	---	---	---

(*) Sample non assessed, because previous sample presented no flow in the plastometer.

Summary and Conclusions

It is known that LCB LDPE usually has "extensional hardening" characteristics; so, the great deal of long-chains attached to the bone chain of branched LDPE will induce strong chain entanglement in melt state and will enhance the melt strength.[8]. LLDPE 20 kGy showed at 190^{o} C a Melt Strength similar to that one presented by LDPE, at 150^{o} C, a more favorable condition, as shown in Table 2.

Results obtained for LLDPE 20 kGy 10% in LDPE sample presented a total compatibility with LDPE sample, in terms of Melt Flow Index and Extrudate Index, at 160 and 170^{o}C; so, it was the indicated blend for providing an effective foam, according Figure 1:


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Figure 1: LLDPE 20 kGy 10% in LDPE foam.

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