Gamma-irradiated cross-linked LDPE foams: Characteristics and properties

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ABSTRACT

Foamed polymers are future materials, as they are increasingly considered "green materials" due to their interesting properties at very low consumption of raw materials. They can be used to improve appearance of insulation structures, thermal and acoustic insulation, core materials for sandwich panels, fabrication of furniture and flotation materials or to reduce costs involving materials. Low-density polyethylene is widely used because of its excellent properties, such as softness, elasticity, processibility and insulation. In general, cross-linking is often applied to improve the thermal and mechanical properties of polyethylene products, due to the formation of a three-dimensional network. In particular for the production of PE foams, cross-linking is applied prior the expansion to control bubble formation, cell characteristics and final properties of the foam. However, the usual production process of PE foams is a process in which a gaseous blowing agent is injected into a melted thermoplastic polymer, under pressure, to form a solution between blowing agent and melted polymer. An extrusion system is provided for foaming the polymer, supplied to an extruder and moving through a rotating screw. The pressure must be high enough to keep the gas blowing agent (or foaming agent) in the solution with the melt. The foaming agent is then diffused and dissolved in the molten material to form a single-phase solution. In the present work carbon dioxide was used as the bowing agent, a chemically stable and non-toxic gas, with good diffusion coefficient; gas pressure used varied within a 20–40 bar range. Some requirements for physical foaming are required, as low friction heat generation, homogeneous melt temperature distribution, melt temperature at die exit just above crystallization temperature (die) and high melt strength during expansion. This work studied foams properties gamma-irradiated within 0, 10, 15, 20, 25, and 30 kGy, from a LDPE exhibiting 2.6 g/10 min Melt Index. Accomplished tests: DSC, gel-fraction, swelling ratio in various solvents, rheological measurements, infra-red spectroscopy and melt strength. It was verified that within a given radiation dose range; the material exhibited an optimization in viscoelastic properties, providing the desired melt strength range for obtaining foams.

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1. Introduction

Low-density polyethylene (LDPE) is a commodity polymer used extensively in extrusion operations such as coating, blown film, blow molding, and foaming.

Extrusion of LDPE foams by direct gas injection or the so-called physical foaming can be separated into five distinctive steps, i.e. melting of the solid LDPE pellets, injection and mixing of the liquid gas in the molten LDPE, cooling and shaping of the melt into the expansion condition, foaming of the melt by the expanding gas and finally cooling of the foam.

Although viscosity and melting/crystallization behavior plays an important role in each or most of these process steps, the gas expansion is the crucial step in the foam process.

In order to obtain a good foam quality (regular fine cell size and high closed cell content), the gas laden melt needs to be cooled down to a temperature close to the crystallization temperature of the semi-crystalline polyolefin to increase the melt viscosity and reduce the time needed for the transition from melt to solid phase. In practice, this means for semi-crystalline LDPE that the temperature of the melt at the die exit is always a few degree centigrade above the crystallization temperature.

Successful physical foaming needs a very homogeneous temperature distribution (preferably $\pm 0.5\ ^\circ C$) to prevent an irregular cell size distribution due to viscosity differences. The melt temperature at the die exit is a balance between heat input via the extruder barrel, heat generation in the melt by friction in the extruder as well as in the melt cooler and extrusion die and the cooling of the melt by the cooling section of the extruder and/or melt cooler. When a physical blowing agent is used, such CO_2, an environmental friendly blowing agent (Biesenberger et al., 1998), the neat polymer is initially maintained above the melting temperature. Under these conditions, the polymer/blowing agent

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remains a single phase. As the melt mixture passes through the exit/shaping die the melt rapidly foams and expands, generating foams with small, uniform cell sizes (Haas et al., 2006). The rheology of mixtures of a polymeric matrix and a physical foaming agent (PFA), used for the production of polymeric foams, is largely controlled by the plasticizing effect of the dissolved gas or liquid (Gendron and Champagne, 2004).

For the processing and foaming part of the choice it is good to know that most of the viscosity related properties depend on the MFI and the MWD. An important parameter is the friction heat generation in the melt, which depends on LDPE shear viscosity character and the shear rate in each particular part of the extrusion process. To reduce the friction heat generation, extruders for physical foaming always should be run within relatively low screw speeds (10–50 rpm) (Cheng et al., 2004).

Long-chain branched LDPE usually has "extensional hardening" characteristics. There is a great deal of long-chains attached to the bone chain of branched LDPE, thereby inducing strong chain entanglement in melt state and enhancing the melt strength. In recent years, research has been conducted on the melt strength behavior of polymers in many industrial applications. The term melt strength can be simply defined as the ultimate force that the polymer melt can withstand while being stretched. In some processes like melt phase thermoforming, the polymer sheet is required to exhibit high melt strength at low shear rates as the sheet is being heated: sag resistance (DeNicola et al., 1996; Dealy and Wissbrun, 1990).

Modification of a polymer using ionizing radiation can be done before or after the polymer has been processed into formed parts. When formed parts made from polymers are modified by radiation, crosslinking is usually the desired reaction, with the purpose to enhance the physical properties of the parts. For radiation modification of polymer resins prior to processing into formed parts, various radiation-induced reactions, including crosslinking, degradation, branching and grafting, can be taken as the advantages to add value to the polymer material (Charlesby, 1960; Woods and Pikaev, 1994).

In the late 1980s and the early 1990s, Himont (which later became Montell) developed "gel-free" high melt strength polypropylene resins (PPs) for extrusion coating by radiation-induced long-chain branching (Sheve et al., 1990); Bradley and Phillips, 1991 reported that the improvement of the melt strength enabled foaming using these novel high melt strength PPs . The commercial success of these PPs helped inspire continued research and development on radiation modification of PP to improve melt strength through long-chain branching (Yoshii et al., 1996; Lugão et al., 2007). A similar approach was applied to polyethylene (PE) by Montell to make high melt strength PE in the 1990s (DeNicola Jr. et al., 1996).

By irradiating PE resins in air at relatively low doses in combination with additional proprietary processing, resins with significant long-chain branching but with insignificant gel content were made and used in various polymer processing methods and applications. The modified PE resins offer significantly improved processability and end-use properties (Cheng et al., 2005; Du Plessis et al., 2006; Cheng and Phillips, 2006). High levels of cross-linking would drastically decrease the melt flow of the polymers and high gel contents would make it very difficult or impossible to process the polymers and convert them into parts. A family of polyethylene pellets and powders were modified by radiation prior to part formation at lower doses (< 25 kGy) and under ambient conditions. The modified resins have low gel content (< 3%). The processability of the polymers is maintained with the low dose modification while significant improvements of practical properties are achieved (Kerluke et al., 2004; Forczek et al., 2004).

Polymer melts are known to exhibit die swell when extruded. This phenomenon reveals itself as an increase of diameter of an extrudate after exiting a die. The amount of die swell is related to the amount of elastic deformation of the material at the inlet of the die. A further fact to be considered is that the degree of die swell (more correctly extrudate swell) is dependent on the length of the die when material is extruded at constant throughput. In other words polymer melts exhibit time dependency as the material forgets the elastic deformation applied at the entrance of the die, the more time the material spends within the die the less die swell. Accurate prediction of extrudate (die) swell in polymer melt extrusion is important as this helps in appropriate die design for profile extrusion applications (Spencer and Dillon, 1948; Metzner et al., 1960; Arai and Aoyama, 1963).

Small amplitude sinusoidal Oscillatory Testing as function of test frequency is a rapid and often used method to measure the viscous and elastic properties of a polymer simultaneously. Two parameters are most often reported—storage (elastic) modulus (G') and viscous (loss) modulus (G'') which represent the relative degrees of the material to recover (elastic response) or flow (viscous response) respectively as the rate of deformation (test frequency) changes (Schramm, 1998).

An understanding of the degree of crystallinity for a polymer is important as crystallinity affects physical properties such as storage modulus, permeability, density and melting temperature. While most of these manifestations of crystallinity can be determined, a direct measure of degree of crystallinity provides a fundamental property from which these other physical properties can be predicted. DSC is a technique that measures heat flow into or out of a material as a function of time or temperature. Polymer crystallinity can be determined with DSC by quantifying the heat associated with melting (fusion) of the polymer (Wunderlich, 1990).

The swelling ratio decreases with radiation dose. This is the reflection of the gel content curve. It is observed that the results are nearly in accordance with those of gel content, supporting the formation of network structure on irradiation. However upon irradiation the polymers undergo cross-linking, and results in the formation of network structure (Ahmad et al., 2003, Wolf et al., 1991).

Infrared spectroscopy was used to compare characteristics and branching intensity in modified samples, as well their homogeneity. Absorption areas are proportional to carbonyl (C=O) group concentration in the polymer. The more defined the absorbance peak, the more dependency on absorbed dose (Geraldes et al., 2007).

The main objective of this study is the development of foams, using CO_2 as Physical Blowing Agent, from LDPE air gamma irradiated, and to provide their general characterization, selecting the best radiation range dose from all accomplished experiments.

2. Experimental

2.1. Materials

Commercially available polyethylene grade exhibiting 2.6 g/10 min melt index and supplied by Quattor was selected as base resin for radiation modification. The base resin was gamma irradiated at 10, 15, 20 and 30 kGy doses, ^{60}Co, in air, at a 5 kGy/h rate.

2.2. Foams—physical foaming method

LDPE pellets were extruded in a Rheomex 332p, single special screw for foaming, 3:1L/D and 19/33 compression ratio, at 20 rpm, under a processing profile according to

E1   E2   E3   E4   D2
175   200   210   220   200 (°C).

CO_2 was inserted to the melted polymer, under 20 bar pressure, and 6 mm round die shape.

2.3. DSC

The thermal behavior of pure and irradiated polyethylene samples was examined in a DSC Mettler Toledo apparatus, according to ASTM D3418-08—standard test method for decomposition kinetics by thermogravimetry, by using 5–9 mg of sample, within a 25–300 °C program, at a 10 °C/min, in a nitrogen flow of 50 ml/min.

Crystallinity was calculated according to the following equation.

$$X_{DSC}(\%) = \left(\frac{\Delta H_c}{\Delta H_T}\right) \times 100 \qquad (1)$$

where ΔH_T is ΔH_c of 100% crystalline PE (68.4 Cal/g or 290 J/g), heat of fusion (ΔH_c) is the energy involved in the formation and melting of crystalline regions and equal to area under the melting peak (Brandup and Immergut, 2003).

2.4. Swelling measurements

Foams samples from 0, 10, 15, 20 and 30 kGy, were weighed and immersed into xylene, in a fume hood, at room temperature. Within a 15, 30, 45, 60, 90, 120, 150, 240, 420 min period, samples were removed from the solvent and inserted in a Quimis centrifuge, for 1 min, to remove excess of water adhering to the surface, using the same procedure for all samples. Afterwards, samples were weighed to an accuracy of 0.1 mg (using a digital balance) and inserted again in test tubes, up to reach the last period. The degree of swelling was calculated according to Eq. (2).

The swelling test in cyclohexane, hexane, toluene and xylene was performed only for 30 kGy sample:

$$Q\ (\%) = \left(\frac{m-m_o}{m_o}\right) \times 100 \qquad (2)$$

where m_o is the mass of the unswelled sample, and m is its mass after swelling in solvent.

2.5. Melt flow index

According to the ASTM D1238-04C (2004)—Standard Test method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer, samples were evaluated in a Ceast Modular Melt Flow plastometer, at 190° C, 2.16 kg load.

2.6. Gel fraction

Gel fraction was accomplished in 0.3 g of pellets sample, previously wrapped in a stainless steel 120 mesh, immersed in 150 mL of xylene. According to (ASTM D2765-01, 2001)—Standard Test Methods for Determination of Gel Content and Swell ratio of Crosslinked Ethylene Plastics, this system remained for 24 h in reflux (round bottom flask, in a heating mantle, 135 °C). Non-reticulated fraction remains in the solvent and reticulated fraction is kept in the stainless steel mesh, being this assembling dried in a circulating air oven, at 60° C, for 15 h, and afterwards maintained in a dissicator, at room temperature, for 1 h, up to the final weighing. The calculation, in percent, of the extract (gel) follows the following equation :

$$Gel\,fraction\,(\%) = \frac{m_f}{m_i} \times 100 \qquad (3)$$

where m_i is the mass before extraction and m_f is the mass of the dried sample after extraction.

2.7. Melt strength, extrudate swell and expansion index

In the Rheotens test performed, the tensile force needed for elongation of an extruded filament was measured as a function of the draw ratio, while the polymer melt has been stretched underwent uniaxial extension. The Rheotens test consists of a pair of rollers rotating in opposite directions. The polymer melt strand downwards from a capillary die is drawn by the rotating rollers, whose velocity increases at a constant acceleration rate.

For extrusion of the polymer strand, Haake Rheomex 332p was used in combination with a Rheotens 71.97 apparatus manufactured by Göttfert, and samples were previously extruded at 200° C. The Rheotens test was performed in the following way: at the beginning of the experiment, the take-up speed of the Rheotens wheels was adjusted to 14.7 mm/s, the velocity of the extruded polymer strand for a tensile force zero. Then the experiment was 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.

Extrudate swell and Expansion Index were evaluated just after the resin filament outlet, in Haake rheometer, at 5 rpm.

2.8. Linear viscoelastic shear experiments

Results for dynamic-mechanical experiments are typically presented as G' (storage modulus) and G'' (loss modulus) as a function of the angular frequency ω, with ς^* the complex viscosity closely related to viscous contribution or energy dissipation for each cycle. 1 mm thick and 25 mm disk samples were produced by compression molding at 190° C and fast cooled by a water bath and the experiments were performed using a Physica rheometer (MCR 300), 25 mm parallel plate geometry, 1.0 mm gap. The linear viscoelastic strain employed for the frequency sweep measurements was 5% strain, within a 0.1–100 (s^{-1}) frequency range.

The measurements were performed from melt temperatures 200 °C in air atmosphere.

2.9. Infrared spectroscopy

IR spectra were obtained from a Thermo-Scientific spectrophotometer, the Nicolet 6700-FT-IR model, by using Attenuated Total Reflectance (ATR).

Setup collection sample was adjusted for 64 scans, within a 4000–500 cm^{-1} range. Sample films were prepared by molding them on a press using heated plates at 200° C, for 15 min, with a 5 MPa pressure. Molten samples were rapidly quenched in water.

3. Results and discussion

Foams samples obtained from physical foaming using CO_2 as physical blowing agent, were characterized according to the various tests above mentioned and showed following results.

3.1. DSC

A summary of thermal behavior for 0, 10, 15, 20 and 30 kGy foams samples is shown in Fig. 1.

Table 1 presents thermal behavior results obtained by each individual foam sample.

Using the DSC enthalpy of fusion and taking 290 J/g (Wunderlich, B.—Thermal Analysis; Academic Press, New York (1990)) as the value for the 100% crystalline LDPE, results within a 29.4–32.0% range of crystallinity was found.
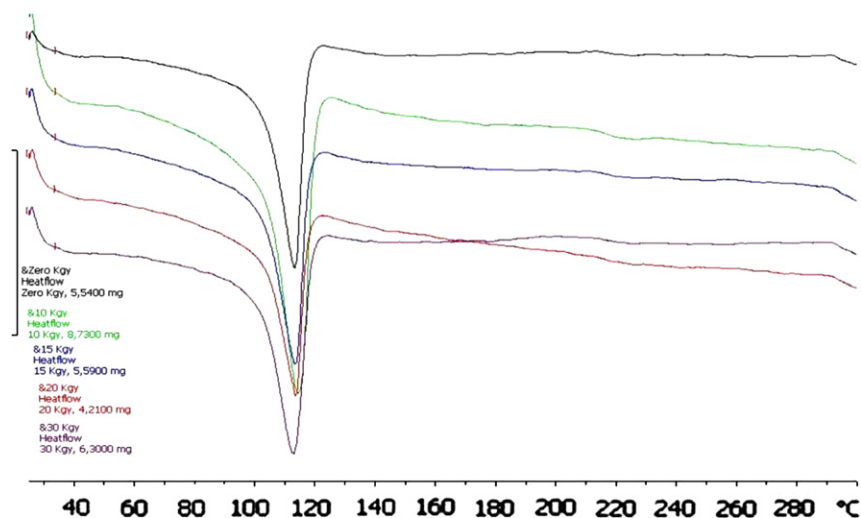
Fig. 1. Thermal behavior presented by 0, 10, 15, 20 and 30 kGy foams samples.

Table 1
Thermal behavior shown by 0, 10, 15, 20 and 30 kGy foams samples.

Foam sample (kGy)	ΔH (mJ/mg)	T_m (°C)	Crystallinity (%)
0	91.0	110.5	31.4
10	92.0	111.3	31.7
15	92.7	110.6	32.0
20	87.6	110.6	30.2
30	85.3	109.9	29.4

Low values obtained for crystallinity recommended lower temperatures settings on the extruder die, and it meant a relevant parameter for the physical foamability of polyolefins (Henk, 2005).

3.2. Swelling experiments

A comparison among foams samples, non-irradiated and irradiated (10, 15, 20 and 30 kGy), in the swollen state, was accomplished, using, at first, xylene solvent. Results gathered and presented in Fig. 2 were practically identical for 0, 10, 15 and 20 kGy, printing a different behavior for 30 kGy foam sample.

A new experiment, using 30 kGy foam sample, was performed, using besides xylene, cyclohexane, toluene and hexane. Results for immersion in xylene confirmed previous behavior for 30 kGy foam sample and a better swollen xylene capacity when compared to other solvents, as shown in Fig. 3 (Clarence et al., 1991).

This unexpected better performance for swelling experiment, verified for 30 kGy foam sample was probably due to degradation caused by gamma radiation imparted to LDPE resin and corroborated by the poor melt strength result.

3.3. Gel fraction and Melt Flow Index

In spite of low gel content levels— ≤ 2%, it was not feasible to run Melt Flow Index in LDPE gamma modified within the 10–30 kGy dose range, due to their high viscosities.

3.4. Melt strength

Melt strength increases as the molecular weight distribution (MWD) becomes broader and it is well known that not only the increase in the average molecular weight (MW) of a polymer results in higher melt strength (Clough, 2001), but also in lower MFI.
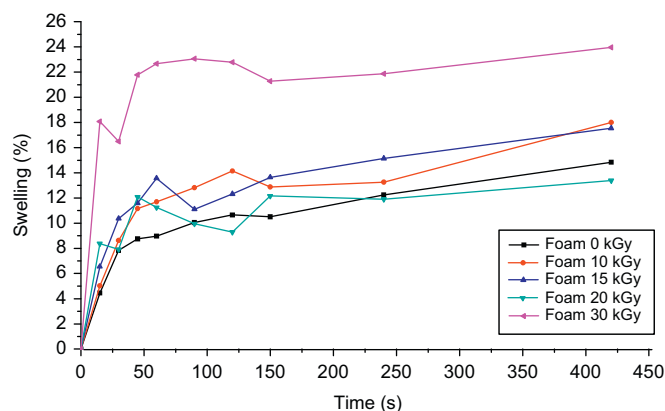

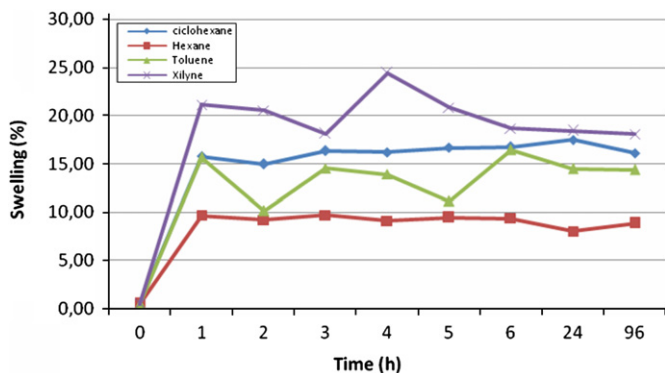Fig. 2. Swelling kinetics for 0, 10, 15, 20 and 30 kGy foams samples immersed in xylene.

Fig. 3. Swelling kinetics for 30 kGy irradiated foam immersed in xylene, toluene, hexane and cyclohexane.

The increase in MW is associated with a decrease in MFI (Table 2) and an increase in melt strength (Table 3).

3.5. Rheological measurements

In a review concerning the effect of LCB on the linear viscoelasticity of polyolefins recently published by Vega et al. (2002), it was shown that the introduction of LCB induces higher elastic modulus than a broad molecular weight distribution in polymers

Table 2
Gel fraction and Melt Flow Index results in 0–30 kGy foams samples.

(kGy)	Gel fraction (%)	Melt Index ($g \times 10^{-1}$ min^{-1})
0	0.47	2.62
10	0.42	Material did not flow in the plastometer
15	1.08	
20	0.88	
30	2.00	

Table 3
Melt strength, extrudate swell and expansion index for 0–30 kGy foams samples.

Foams samples (kGy)	Melt strength at 200° C (cN)	Extrudate swell at 200° C[a] (%)	Expansion Index[a]
0	0.0017	29.58	1.42
10	0.0543	35.48	1.55
15	0.0595	33.99	1.52
20	0.0776	33.77	1.51
30	–	34.21	1.52

[a] Extrudate used to measure Extrudate Swell and Expansion Índex was taken from melting filament, at 200° C, when performing the melt strength test, at 200° C.Obs: Extrudate swell $(\%) = \frac{\Phi_{sample} - \Phi_{die}}{\Phi_{sample}}$ and Expansion index $= \frac{\Phi_{sample}}{\Phi_{die}}$

Fig. 4. Complex viscosity as a function of angular frequency for 0–30 kGy foams samples.

Fig. 5. Dynamic modulus as a function of angular frequency for 0–30 kGy foams samples.

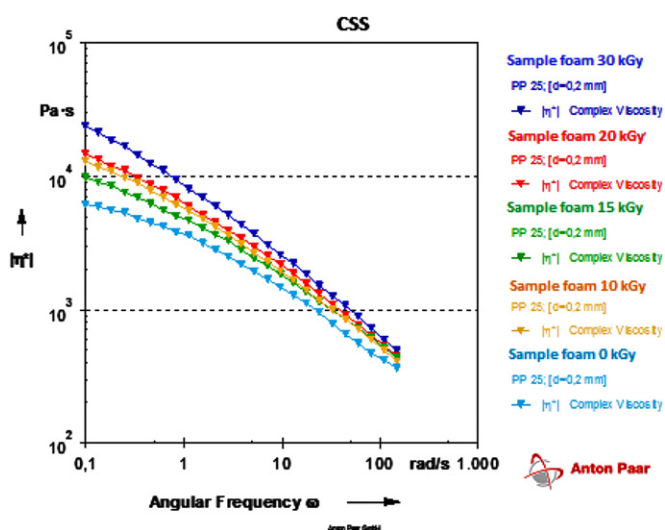**Fig. 6.** Loss modulus as a function of angular frequency for 0–30 kGy foams samples.

with similar mass weight. The complex viscosity plotted as a function of angular frequency is presented in Fig. 4.

Foam samples showed expected results for complex viscosity, gradually increasing from 0 to 30 kGy, according to gamma radiation dose.

G' (storage modulus) and G'' (loss modulus) as a function of the angular frequency ω, were plotted according to Figs. 5 and 6, respectively. By comparing both graphs, the loss or viscous modulus is higher than the elastic modulus, on the whole range of angular velocities tested: 0.1–100 rad/s.

3.6. Infrared spectroscopy

Infrared spectroscopy was accomplished in order to compare branching characteristics and intensity on pure and modified samples as well their homogeneity.

Absorption area is proportional to carbonyl group (1699, 1716 and 1743 cm^{-1}) concentration; the more defined the absorbance peak, the higher dependency on absorbed dose (Fig. 7).
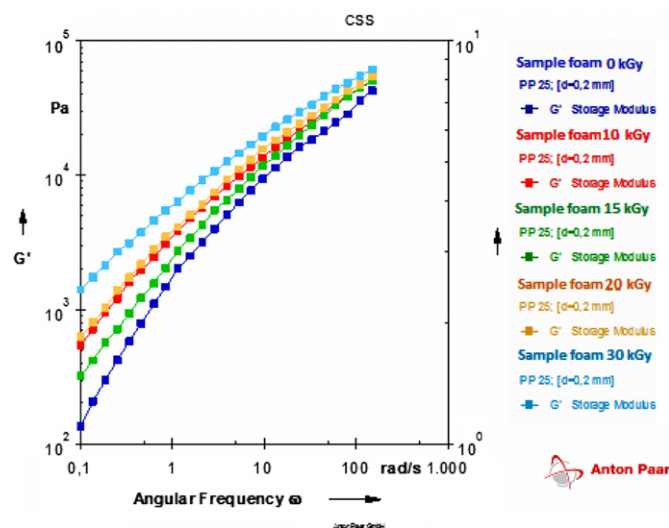
In this case, no peak was observed within the 1699–1743 cm^{-1} range for carbonyl group identification for all foam samples tested.

4. Conclusion

Results obtained for melt strength tests demonstrated that gamma radiation on 0, 10, 15, 20 and 30 kGy foams samples, under ambient conditions induce long chain branching, once it could not detect carbonyl groups via Infrared analyses.

The modified samples showed low values for gel fraction ($\leq 2\%$), and rheological tests confirmed the existence of branching and crosslinking, from 5 kGy sample performance on melt strength evaluations. Low values obtained for crystallinity—29.4–32.0% – showed a strict relation with rheological measurements, according to values present for loss modulus (G'') and Storage Modulus (G'): $G'' > G'$, indicating the predominance of viscous behavior for samples tested. The difficulty experimented by accomplishing Melt Index evaluations in >5 kGy samples confirmed this observation. Even presenting low gel content ($<3\%$),
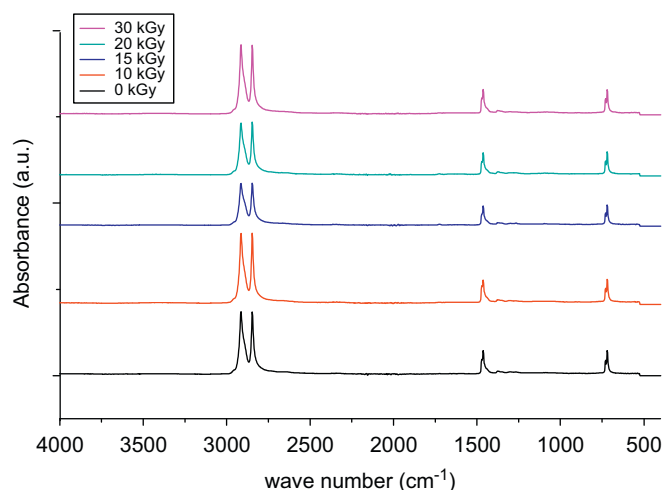
Fig. 7. ATR spectra for 0–30 kGy foams samples (identification of carbonyl range: 1699, 1716 and 1743 cm^{-1}).

foams processability are able to be maintained within a lower dose range modification: ≤ 15 kGy.

Swelling experiments showed very close and low results for 0, 10, 15 and 20 kGy foams samples, when immersed in xylene, except for 30 kGy sample. By repeating the swelling test with xylene, immersions in hexane, toluene and cyclohexane were accomplished too, and the highest result for 30 kGy sample with xylene was confirmed, indicating that the swelling test should not be considered a parameter for an effective evaluation for radiation doses lower than 30 kGy.

In summary, a gamma dose radiation lesser than 15 kGy for providing effective LDPE foams is recommended.

Acknowledgments

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