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Reversible crosslinked low density polyethylenes: structure and thermal properties

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Abstract In the present study, low density polyethylene (LDPE) has been crosslinked at 170 °C with three different systems by a) using peroxide, b) peroxide and accelerator and c), peroxide, accelerator and sulfur. The effect of chemical crosslinking on LDPE structure has been investigated using torque measurements, Fourier transform infrared spectroscopy (FTIR), wide angle X-ray diffraction (WAXS), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Therefore, effects of each crosslinking system on the structural and thermal properties of the material in terms of crystallinity, thermal transitions and stability have been discussed. The reversible crosslinking of LDPE allow the recyclability of polyolefins, increasing the thermal properties.

Keywords LDPE · Reversible crosslinking · Processing technologies · Torque measurements · Structure · Crystallinity · Thermal properties · Stability

Introduction

Polyolefins are today the most widely produced polymers in the plastic industry [1]. Polyethylene, especially low density polyethylene (LDPE) [2] was found to exhibit a very wide range of properties such as low weight, good mechanical properties, excellent electrical isolation, good resistance to chemicals and easy processing [3]. Because of these properties, it is used as insulator material for several applications [4], such as electrical as coating for wires [5], food industry as packaging films [6], trash bags, and recently in greenhouse films [7]. Because of its nonpolar character, polyethylene is well known to exhibit a very low compatibility and adhesion with several substrates such as metals and polar polymers. The incorporation of polar groups into the polymer chain increases its compatibility and enlarges its possibility of interaction, giving rise to the formation of adhesive bonds with the mentioned substrates, thus allowing interesting applications [8]. In some others, it is essential to modify LDPE to enhance certain properties [9].

Crosslinking method is largely used to modify the polymer properties [10, 11]. Several studies have been conducted on polymer crosslinking with different peroxides and other crosslinking agents such as silanes [12]. In addition to external aspects such as crosslinking temperature and time, some structural characteristics of the polymer strongly influence both, the crosslinking ability and the resulting network [13]. Several ways such as chemical methods, lead to crosslinked polymers. The most common method is to add peroxide as crosslinking agent to the resin. When heated above their decomposition temperatures, peroxides provide free aggressive oxy radicals capable of extracting hydrogen from the polyethylene backbone, thus transferring the free radical site to polyethylene [14–16]. When this occurs, polyethylene chains can crosslink together. A second method of crosslinking polyethylene is through the use of irradiation. In this case, the free radical formed on the polyethylene backbone results from an electron beam irradiation [17–20]. The third methodology to provoke crosslinking involves the grafting of a silane upon

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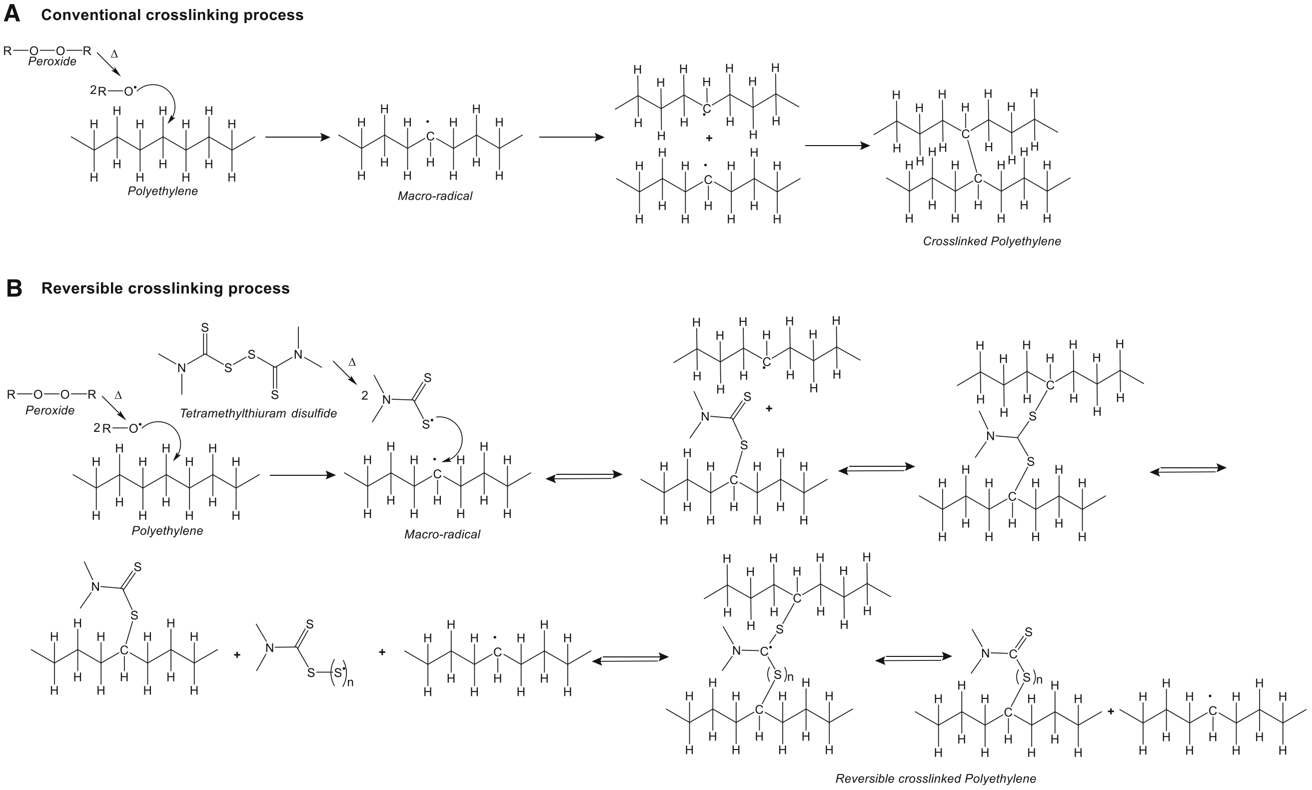
polyethylene and, subsequently, the crosslinking reaction through condensation of the silane grafts by moisture [21–23].

Moreover, it is well known that crosslinking is capable of influencing the mechanical properties of polymers [24]. During the past 20 years, a growing interest has appeared with the application of Diels–Alder (DA) reaction in macromolecular chemistry [25]. Diels–Alder reaction is well-known as [4 + 2] cycloaddition reaction of dienophile and diene giving covalent bonds, which could be easily broken down [26]. In the recent years, these thermally-reversible crosslinked polymers [27–29] are widely studied to explore their applications as encapsulating systems, structural materials and coatings as well as enrich of recyclability. In the last decade Bouhelal et al. [30–32] have developed for the polyolefines materials an original method of reversibly crosslinking reaction (RXR) in melting state using DA reaction. RXR technique for preparing reversibly crosslinked polymers consists in mixing a polymer with crosslinking agents based on organic peroxide, accelerator and sulfur at high temperatures, to form macro-radicals able to hand up crosslinked materials in solid state. The simultaneous coupling of the macro-radicals with sulfur leads to an optimum reversible crosslinking degree of the final product (see Scheme 1) [30]. The main advantage of this crosslinking process is that it can be straightforward applied to all kind of thermoplastics processing techniques (extrusion, injection or calendering) without addition costs. In the present study, RXR technique was used to modify low density polyethylene crosslinked by three different systems. In the first system, LDPE has been vulcanized with peroxide, in the second with peroxide and accelerator, and the third with peroxide, accelerator and sulfur. The main objective of this study is to compare the effects of each crosslinking system on the structural and thermal properties of the final material. Various techniques has been used including torque measurements, Fourier transform infrared spectroscopy (FTIR) and wide angle X-ray diffraction (WAXS). The thermal properties have been also determined using a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA).

Experimental

Sample preparation

Low density polyethylene (LDPE) was supplied by «Exxon Mobil», Saudi Arabia. Peroxide, di(ter-butyl peroxyisopropyl) benzene (DTBPIB), also called Perkadox 14–40-B-gr, was provided by Akzo Nobel Polymer Chemicals B.V. Amersfoort, Netherlands. The accelerator, tetramethylthiuram disulfide (TMTDS), was provided by Rhodia, France. The sulfur was supplied by Wuxi Huasbeng Chemical Additives Factory, China. All the products were used without further purification.



Scheme 1 **a** Conventional and **b** reversible crosslinking reaction of polyethylene

Formulations were prepared using LDPE and various crosslinking agents. The samples were heated and melted in a Brabender at 170 °C during 30 min, then, compressed into a dreher-type Brabender before undergoing the diverse tests. The films were obtained by compression molding using a POLYLAB manual press between hot plates at 230 °C and at a pressure of 1.5 MPa for 5 min. A quench was applied to the films from the melt to room temperature.

Analysis of polymers

For the Dynamic Rheological Analysis, a plastograph-type Brabender was used. The processability of LDPE blends has been evaluated by torque measurements (torque = moment of force) required to mix the molten components in a heated chamber at 170 °C, at a rotor speed of 30 rpm. To clarify the role of each component in the blends, the torque–time evolution was first measured for the neat peroxide, then for the couple peroxide/accelerator and finally for peroxide/sulfur/accelerator [33].

The spectroscopic analyses were conducted in a Perkin-Elmer FTIR device. The morphological structure of the different systems was measured by wide-angle X-ray scattering (WAXS) using a Bruker D8 Advance diffractometer working in parallel beam geometry. By using a Göbel mirror, the originally divergent incident X-ray beam from a line focus X-ray tube (Cu, operating at 40 kV and 40 mA) is transformed into an intense and parallel beam that is free of K_β radiation. The parallel beam optic required in the secondary beam path is achieved by an equatorial axial Soller slit of 0.2°. The linear detector Lynxeye DE used presents an active area of 14.4 mm × 16 mm. Measurements were performed in reflection (θ-2θ configuration) varying the scattering angle 2θ from 4 to 30° with a step of 0.05°. The measuring time employed was 10 s/point.

Table 1 Sample designation and composition

Sample	LDPE (Parts)	Peroxide (Phr)	Accelerator (Phr)	Sulfur (Phr)
F_0	100	0.0	-	-
F_1	100	0.8	-	-
F_2	100	1.6	-	-
F_3	100	2.4	-	-
F_4	100	3.2	-	-
F_5	100	0.8	0.2	-
F_6	100	1.6	0.4	-
F_7	100	2.4	0.6	-
F_8	100	3.2	0.8	-
F_9	100	0.8	0.2	0.4
F_{10}	100	1.6	0.4	0.8
F_{11}	100	2.4	0.6	1.2
F_{12}	100	3.2	0.8	1.6

Phr: part per hundreds

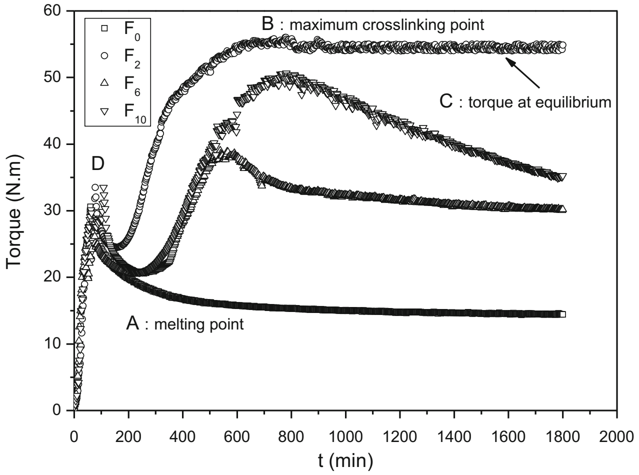


Fig. 1 Rheological curves of various unmodified LDPE and modified samples

The differential scanning calorimetry measurements were performed Thermal analysis was performed in a Q2000 TA instruments. Samples (±10 mg) weighed to 0.002 mg with an electronic autobalance (Perkin-Elmer AD4). The first heating scan was performed at 10 °C/min under dry nitrogen (50 cm^3/min) after decreasing the temperature from room temperature to −70 °C, then samples were heated up to 200 °C and maintained at this temperature during 5 min. Consecutive to the heating process, samples were cooled down to 25 °C at 5 °C/min, and after that a new successive heating and cooling runs were performed as previously.

The thermal stability of these samples was analyzed by using a TA Q500 from TA Instruments, calibrate in weight and temperature. Samples were heated from 25 °C to 800 °C and heating rate of 10 °C/min. All the samples were previously dried at 60 °C.

Table 2 Values of T_B and T_C for the different systems

Sample	T_B (Nm)	T_C (Nm)	Gel content (%)
F_1	42.8	38.1	38.8
F_2	55.8	54.9	54.2
F_3	61.6	60.5	63.4
F_4	72.9	71.0	75.2
F_5	28.9	21.3	16.7
F_6	38.8	30.2	20.9
F_7	42.0	35.6	26.6
F_8	49.5	43.9	66.9
F_9	29.9	24.7	27.1
F_{10}	50.7	35.3	49.3
F_{11}	65.4	47.8	61.6
F_{12}	70.6	57.9	72.8

Fig. 2 Pictures of the films prepared by compression molding between hot plates at 230 °C and at a pressure of 1.5 MPa for 5 min of the samples obtained using 3.2 % of peroxide in the three series; i.e. F_4, F_8 and F_{12}

F_4 F_8 F_{12}

Results and discussion

The formulations were prepared to analyze the effect of the each component on their properties. In Table 1 are collected the amount values of each component used.

Figure 1 represents the variation of torque as a function of time for different formulations. The curve F_0 represents unmodified LDPE behavior. An abrupt increase in torque was recorded up to point D, probably due to the high resistance provided by the solid pellets. Beyond this point, the torque begins to decrease, because of the LDPE melting from a minimal value to the point A, which is assigned to the complete melting of LDPE. After the point A, the torque remains constant before the appearance of an equilibrium stage C, which indicates the final viscosity of the polymer [33]. The other curves show the different behavior of crosslinking agents used to modify LDPE. The torque was observed to decrease to achieve the minimum value T_A (point A) at which the phase change from solid to melt state occurs, followed by an increase of torque up to a maximum value T_B (point B), which means that the maximum crosslinking reaction is taking place. Then, a partial reduction of torque is observed related to a partial destruction of network formed, until a stage appears for torque with a constant plateau value T_C (value at the point C), which is higher than T_A. The T_B and T_C values depend on working conditions and crosslinking agents. The principle of the reaction consists in creating macro-radicals through peroxide and accelerator decomposition process, then stabilizing them by active sulfur groups. In the first system (in presence of peroxide), the torque is observed to be higher compared to the other systems. Besides, T_B is constant until T_C according to their curves. The second system (with peroxide and accelerator) is lower than the third system (with peroxide, accelerator and sulfur), which presents an intermediate stage between the previous systems. The same behavior is observed in each series at all crosslinking agent contents (see Table 2). In addition, in all the cases the torque increases as amount of crosslinking agent does.

To evidence the reversibility, films were performed by compression molding between hot plates at 230 °C and at a pressure of 1.5 MPa during 5 min. In the first system series, in all the contents used, the samples did not melt when heated to prepare films but they decomposed. In Fig. 2, it is clearly observed in the picture that the sample F_4 film degrades. Consequently, this circumstance indicates that the crosslinking is traditional. On the contrary, second and third sample series are able to form films, as can be also seen in Fig. 2 for samples F_8 and F_{12}. Therefore, they can be reprocessed, which demonstrates their reversibility. From these results, the following characterizations were carried out only in the samples of second and third systems, which are able to be molten again and form films.

To confirm the torque measurements and then, the crosslinking process, the gel content of these samples was determined according to standard ASTM D2765–01 [34] in

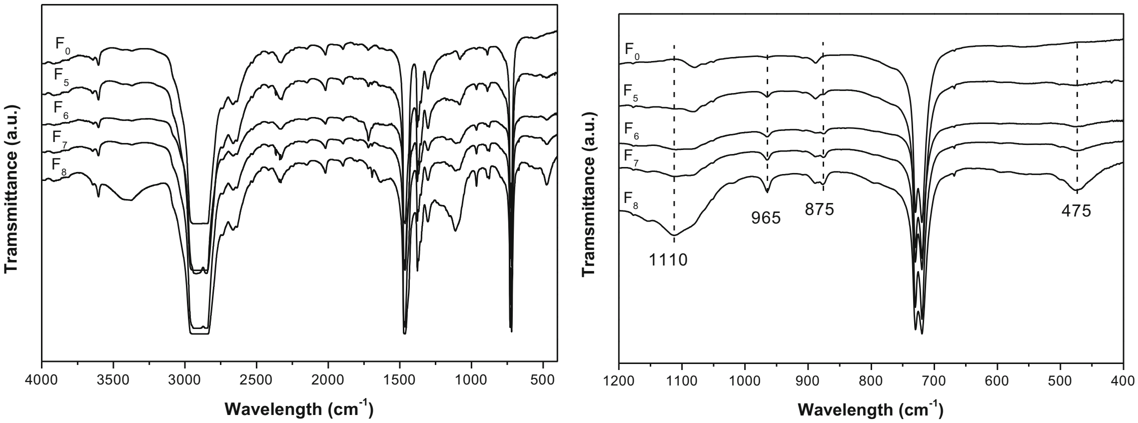


Fig. 3 FTIR spectra of the different crosslinking LDPE samples with peroxide and accelerator

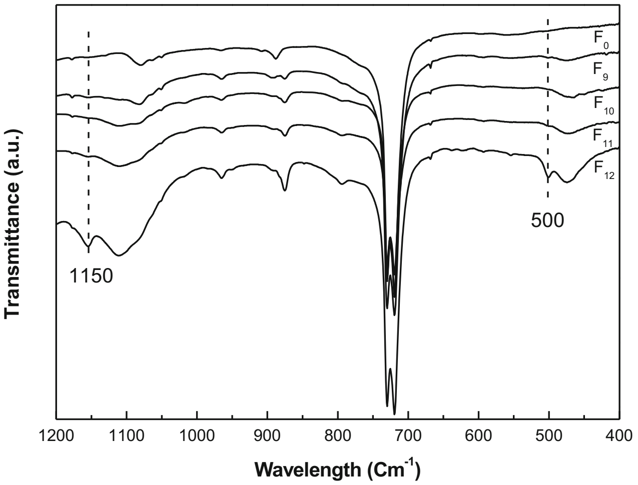


Fig. 4 FTIR spectra of modified LDPE samples with peroxide, accelerator and sulfur

Table 3 Structural parameters of different samples obtained by WAXS measurements: the interplanar crystal spacing (d^{110}), full width at half maximum degree of crystallinity (β^{110}), (χ_c^{WAXS}) and crystal size (L_c^{110})

Sample	$2\theta^{110}$ (°)	d^{110} (Å)	β^{110} (°)	χ_c^{WAXS} (%)	L_c^{110} (Å)
F_0	21.54	4.12	0.48	34.0	177
F_5	21.48	4.13	0.46	36.7	184
F_6	21.57	4.11	0.55	31.3	153
F_7	21.22	4.18	0.47	27.3	179
F_8	22.01	4.03	0.66	26.0	128
F_9	21.47	4.13	0.43	31.1	196
F_{10}	21.51	4.13	0.49	30.9	172
F_{11}	21.56	4.12	0.48	35.5	176
F_{12}	21.58	4.11	0.48	38.4	175

refluxing xylene for 12 h. The obtained values are also collected in Table 2 and show that the use of sulfur induces higher crosslinking and it increases with the content of crosslinking agent.

Figure 3 displays the FTIR spectra of different samples performed with the second crosslinking system. The observed characteristics are similar in all the systems used. Absorbance bands appear near 2900 and 1470 cm^{-1} due to C-H stretching and CH_2 deformation vibration, respectively. A specific strong sharp doublet in the 730–700 cm^{-1} region indicates CH_2 rocking motion. This doublet band appears only when crystalline ethylene units are present in the blend, while single band is observed for amorphous polyethylene systems [35]. A clear difference is observed in intensity and in shape between the LDPE spectrum and the spectra of modified LDPE materials. The band observed at ca. 3400 cm^{-1}, assigned to the -OH stretching frequency, increases as a function of the crosslinking agent content, being more noticeable in the case of modification with peroxide and accelerator than with peroxide, accelerator and sulfur.

In this third system, new characteristic weak bands of S-S bonding of disulphide around 500 cm^{-1} and C-S at 1150 cm^{-1} appear (see Fig. 4), which do not appear in the second system. New weak bands are also observed in both systems at 875 cm^{-1} due to the swinging of N-H, emerged from the reaction with the accelerator. A trans-vinylene absorption band is observed at 965 cm^{-1}, and 1110 cm^{-1} assigned to C = S stretch. The bands at 475 cm^{-1} corresponds to the S-S stretch vibration in aryl-S-S-aryl, respectively, which varies proportionally with the content of crosslinking agent.

Figure 5 shows the WAXS patterns of LDPE blend and representative crosslinked LDPE samples for both systems. Three main peaks can be observed: two sharp peaks at ca. 21.5° and 23.8°, and a broad halo. The two sharp peaks, assigned to (110) and (200) crystalline reflection peaks of the polyethylene orthorhombic crystal, slightly decrease as crosslinking agent content increases. Then, the broad halo, attributed to the amorphous part of the polymer [36], increases

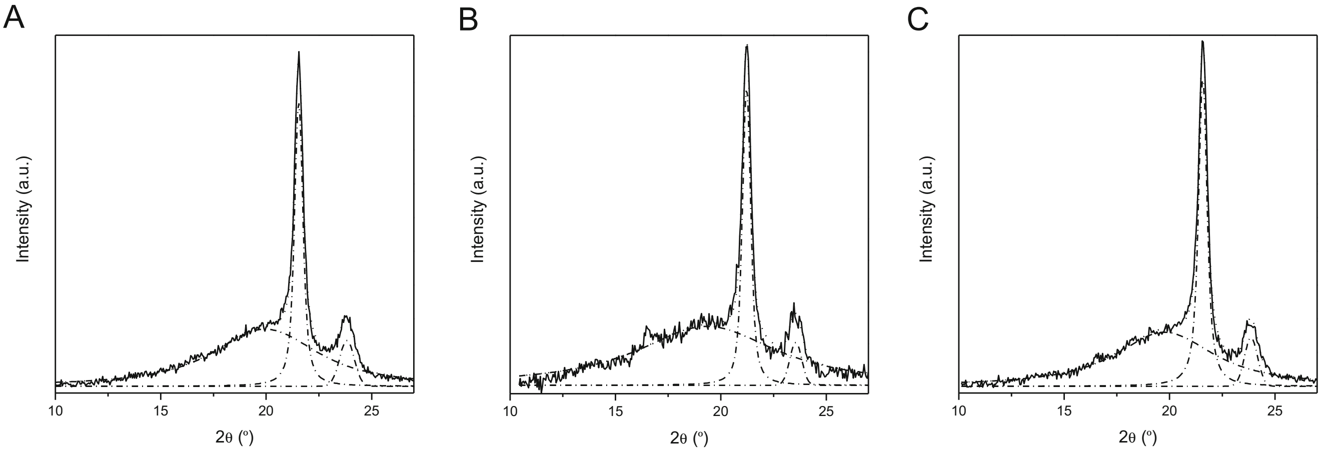


Fig. 5 WAXS diagrams of (**a**) neat LDPE (**b**) F7 sample (LDPE with peroxide and accelerator), (**c**) F12 sample (LDPE crosslinked with peroxide, accelerator and sulfur)

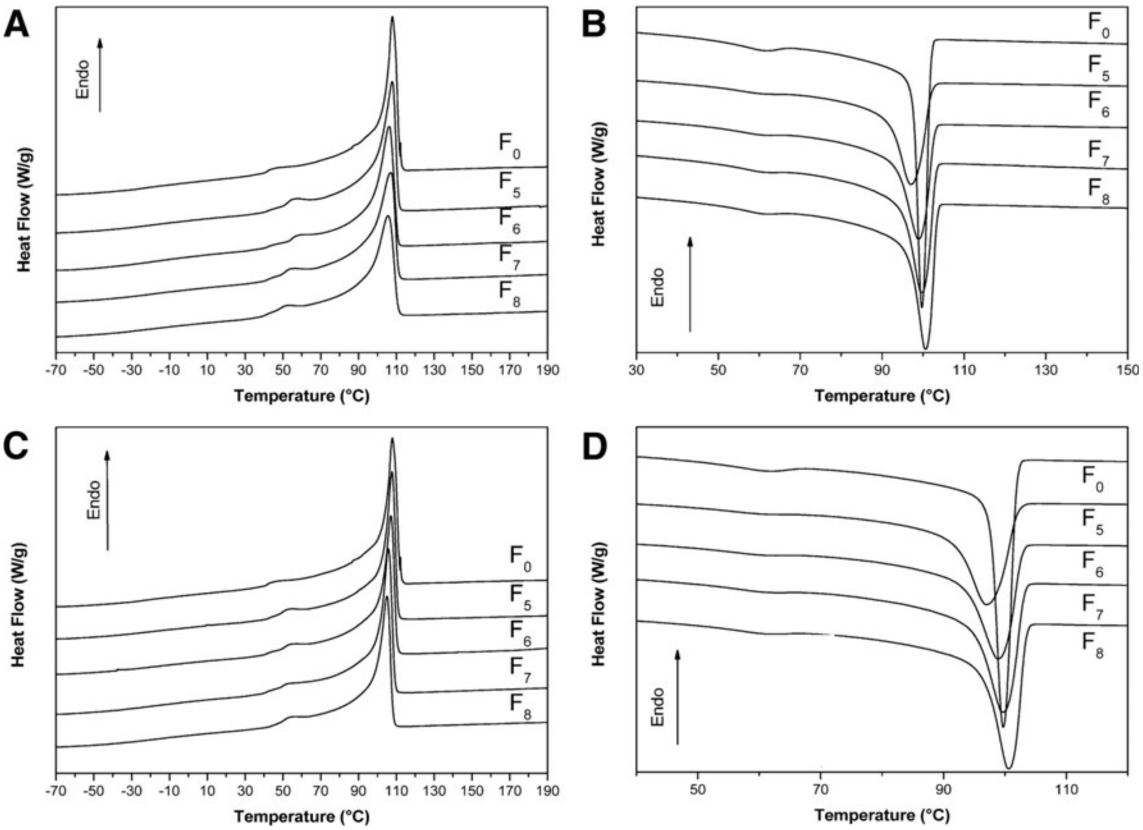


Fig. 6 DSC thermographs of first heating and cooling runs of (**a**, **b**) LDPE crosslinked with peroxide and accelerator, (**c**, **d**) LDPE crosslinked with peroxide, accelerator and sulfur

with the increment of crosslinking agent used. From the WAXS profiles, the degree of crystallinity (χ_c) can be measured using the following equation (Eq. 1) [37, 38]:

$$\chi_c^{WAXS} = I_c/(I_a + I_c) \tag{1}$$

where I_c and I_a are the integrated intensities corresponding to the crystalline and amorphous phases, respectively. Deconvolutions of profiles were performed to integrate the different peaks.

The crystallite dimension, L_c^{WAXS}, of unmodified and LDPE crosslinked samples are calculated by Scherrer equation (Eq. 2) [39]:

$$L_c^{WAXS} = 0.94\,\lambda/\beta\,\cos\theta \tag{2}$$

λ is the wavelength of X-ray ($\lambda = 0.154$ nm), β is the full width at half maximum (FWHM) intensity in diffraction profile, and θ is Bragg's angle. The obtained crystallite size and

Table 4 Melting (T_m), crystallization temperatures (T_c) and enthalpies (ΔH_m, ΔH_c) for different samples and crystallinity degree (χ_c^{DSC}) and crystal size (L_C^{DSC}) obtained by DSC measurements. Initial degradation temperature (T_{Onset}), the temperature at the degradation maximum (T_{max}) and the -dw/dT at this temperature

Sample	T_c (C°)	T_m (C°)	Δ H_c (J/g)	ΔH_m (J/g)	χ_c^{DSC} (%)	L_c^{DSC} (nm)	T_{Onset} (C°)	T_{max} (C°)	-dw/dT (%/°C)
F_0	99.7	107.9	118.3	122.1	41.7	7.09	435.4	463.8	2.20
F_5	100.6	107.8	119.0	134.0	45.7	7.07	437.5	464.9	2.37
F_6	99.6	106.3	122.4	129.6	44.2	6.80	434.6	464.1	2.16
F_7	98.9	107.0	115.1	132.9	45.4	6.92	438.3	466.9	2.31
F_8	97.0	105.6	102.9	127.4	43.5	6.69	440.5	469.4	2.25
F_9	98.9	107.7	115.1	130.8	44.6	7.05	443.7	469.2	2.47
F_{10}	97.8	107.2	105.7	127.8	43.6	6.96	449.1	473.4	2.66
F_{11}	96.8	105.8	106.3	131.1	44.7	6.71	457.9	478.9	2.98
F_{12}	95.5	105.1	100.9	120.8	41.2	6.59	458.9	480.8	2.91

Standard deviation (±): temperature 0.5 °C, enthalpy 0.5 J/g, crystal size 0.09 nm, and crystallinity degree 0.5 %

intensity are collected in Table 3. It is clearly observed that the degree of crystallinity is lower in the case of second system and decreases as the crosslinking agent content increases. Similar trend is found in the case of crystallite size, which is due to the restricted mobility of the polyethylene chains caused by the presence of crosslinked points [36].

Figure 6 displays the DSC thermographs of unmodified and LDPE crosslinked samples, and the results are collected in Table 4. The temperatures of melting or crystallization seem to be relatively maintained with the crosslinking in comparison with the unmodified LDPE. However, the enthalpic energy decreases with the addition of crosslinking agent [24]. This effect is more pronounced in the case of introducing sulfur in the crosslinking reaction.

Additionally, the crystallinity of these samples was calculated using the melting enthalpies according to the following equation (Eq. 3) [24]:

$$\chi_c^{DSC} = \Delta H_m / \Delta H_m^0 \tag{3}$$

where ΔH_m is the melting enthalpy obtained from the DSC melting endotherms and $\Delta H_m^0 = 293$ J/g is the melting enthalpy of 100 % crystalline polyethylene at the equilibrium melting point, $T^0_m = 418.5$ K.

The crystallite sizes can be also calculated using the melting temperature by means of Thomson-Gibbs' equation[40] (Eq. 4) as follows:

$$L_c^{DSC} = 2\sigma T_m^0 / \left(T_m^0 - T_m\right) \Delta H_m^0 \rho_c \tag{4}$$

where $\sigma = 93$ mJ/m is the fold surface free energy and $\rho_c = 1$ g/cm^3 is the crystal phase density [27]. The crosslinking introduces an increment in the crystalline degree in comparison with the neat LDPE. However, this crystalline degree decreases as the crosslinking proportion increases, especially in the modified samples with the incorporation of sulfur into the process. Moreover, the crystal size does not significantly change with the increment of crosslinking agent although a slightly diminishment is noticeable. This variation is more evident in the cooling process where the temperature is shifted to lower temperatures. Network sites in the crosslinked polyethylene disturb the chain motion of the macromolecules, preventing polyethylene chains from forming regular sized spherulites during crystallization [36]. In the case of sulfur series, these variations are larger than that of the second system. It is important to mention that obtained values are in concordance with those previously estimated, although DSC data are slightly higher than those estimated with WAXS analysis.

Having this in mind, TGA analysis was conducted on the samples of LDPE in two crosslinking systems to evaluate the thermal stability of the materials. Figure 7 shows the TGA curves, from which, a slight difference is observed between

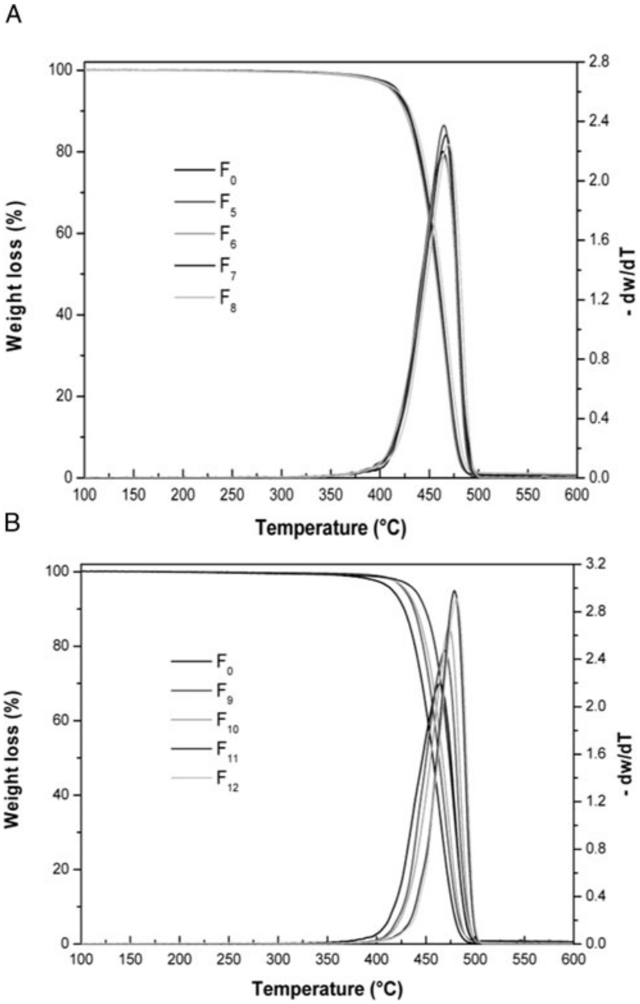


Fig. 7 TGA and DTG curves of (**a**) LDPE crosslinked with peroxide and accelerator, (**b**) LDPE crosslinked with peroxide, accelerator and sulfur samples

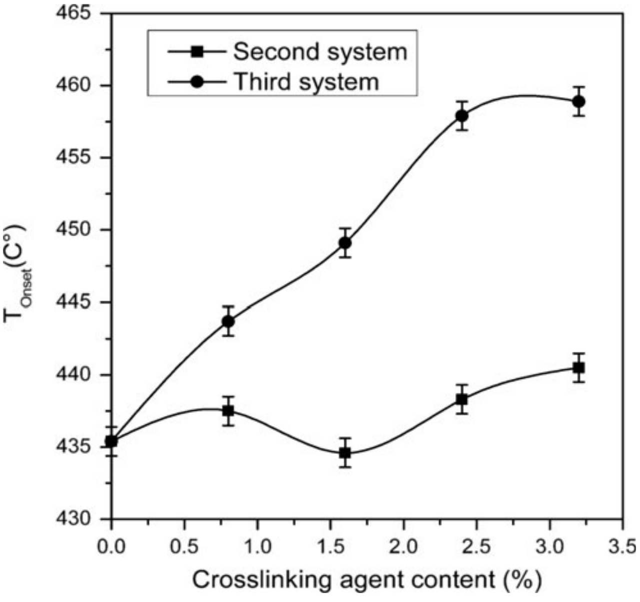


Fig. 8 Variation of temperature of decomposition according to crosslinking agents

the unmodified and crosslinked LDPE in the second system. However, a significant difference is observed between the unmodified and crosslinked LDPE in the third system. The latter exhibiting a high thermal stability. The curves are almost similar for all the samples, though the decomposition of the crosslinked samples occurred at higher temperatures than for neat LDPE, as can be seen in Fig. 7. This increase may be explained by the presence of sulfur in the third system, contrary to the second system.

The differential thermogravimetry (DTG) curves, also presented in Fig. 7, show a single decomposition process and the temperatures involving the maximal decomposition velocity for each material. A slight difference is also observed between the pure LDPE and crosslinked LDPE in the second system. However, a significant difference in decomposition process is clearly appreciated between the pure and the crosslinked LDPE in the third system. Table 4 also gathered the values of T_{Onset}, T_{max}, and -dw/dt. In general, all the samples enhance the thermal stability with the crosslinking process being more pronounced in those with sulfur component. The variation of initial temperature of degradation as a function of crosslinking agent content is displayed for clarity in Fig. 8. Here it is easily noticeable the drastic increase of stability of LDPE treated with sulfur.

Conclusions

Reversible crosslinked LDPE with different degree of crosslinking were prepared by RXR technique using low peroxide contents and accelerator with or without sulfur addition. The structure of LDPE was modified in terms of crystalline degree and crystal size as well as the thermal properties, principally, the thermal stability. These effects are remarkably superior in LDPEs prepared with the incorporation of sulfur in the formulation. From this new preparation method and looking T_C values, it can be clearly stablished that the second and third systems offer the possibility to control the viscosity with higher values, as demonstrated by the torque values, being of great interest from the industrial point of view. Therefore, these crosslinked polymers can be used in the preparation of recyclable materials.

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