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Degradation of Polyolefins Prepared with Fischer-Tropsch Derived Olefins

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Summary: Degradation of some copolymers of ethylene with Fischer-Tropsch derived olefins was investigated. Hydroperoxide and carbonyl formation in samples of ethylene copolymers with heptene-1, and ethylene multiple polymers with the Fischer-Tropsch derived 3,4 methyl-pentene and linear olefins were monitored by IR spectroscopy. The results correlated with results obtained from thermogravimetry, multiple extrusion and rheology in previous studies. It was shown that degradation of ethylene with Fischer-Tropsch derived olefins is related to the type of branch introduced into the chain by the copolymerization with the particular olefin.

Keywords: degradation; ethylene copolymers; Fischer-Tropsch derived olefins

Introduction

The unprecedented growth of polyolefins since the late fifties was triggered by the development of ethylene and propylene copolymerization with alpha olefins by making use of a host of transitional metal catalysts. The most complex pool of comonomers is available from the Fischer-Tropsch process which is gaining momentum as a major comonomer market source. This process offers, in addition to yielding the known even-numbered alpha olefins, some less explored possibilities: odd-number alpha olefins and branched alpha olefins. These comonomers, used individually or in combination, will make it possible to extend the application limits of polyolefins beyond the currently known margins.

In the past decade numerous new co- and terpolymers of ethylene and propylene with Fisher Tropsch derived olefins have been synthesized. Many of these polymers have particular microstructure and morphology according to the type of branch introduced into the polymer chain by making use of a particular Fischer-Tropsch derived olefin as comonomer. Propylene/pentene-1 random co-polymers, the first family that reached industrial application, have excellent application properties [1-3]. Other propylene

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copolymers with higher alpha olefins also have potential for particular applications where high impact strength and high melt strength are required [4,5]. Ethylene copolymers with Fischer-Tropsch olefins are extremely diverse and it is possible to extend copolymerization to terpolymerization and multiple polymerization, ultimately preparing materials which have applications beyond today's commercial polyethylene [6-9].

Unfortunately, like all polyolefins, these new polymers also degrade. At present no literature on the degradation and stabilization of polyolefins prepared with Fischer-Tropsch derived olefins is available. A preliminary investigation showed that ethylene copolymers with Fischer-Tropsch olefins behave in a similar manner to current commercial polyolefins. Further investigation showed features related to the size and type of the branches. These were comfirmed by systematic studies of both degradation and stabilization of particular polyolefins prepared with Fischer-Tropsch derived olefins [10,11]. In the present paper some of these findings are reviewed and additional data on degradation of some particular Fischer-Tropsch derived polyolefins are presented. An attempt is made to relate degradation properties to polymer stucture. Here degradation is illustrated by hydroperoxide and carbonyl formation for some of the most interesting ethylene copolymers with prepared Fischer-Tropsch olefins:

Ethylene/heptene-1 copolymers were selected to illustrate copolymers with odd-carbon-number Fischer-Tropsch derived olefins and ethylene/branched/linear alpha olefin polymers were seleced to illustrate ethylene polymers with more than one comonomers.

Experimental

Ethylene/heptene-1 copolymer samples were prepared according to methods previously described [8,12]. Ethylene polymers with branched and linear alpha olefins were prepared also according to methods previously described [13].

For the determination of the copolymer composition ^{13}C NMR analyses were done at 120°C on samples dissolved in *o*-dichloro benzene on a Varian 400 MHz machine using a 90° pulse angle, a pulse width of 10, 25 000 scans with a 30 sec. delay.

Melt flow index was done according to ASTM D 1238 and density according to ASTM D 6002.

Thermal properties were done on a Perkin Elmer DSC-7. The samples were heated from 50 to 200°C at 20°C/min, held at 200°C for 1 minute, cooled to 50°C at a rate of 20°C/min. and held for 1 min after which the analysis was recorded between 50 and 200°C at a heating rate of 10°C/min.

The thermal stability was measured by means of a Perkin Elmer TGS-2 instrument controlled by a System 4 Microprocessor. Data was supplied to a PE TADS data station. Four heating rates were used (20,15,10 and 5 °C/min) with Nitrogen as purge gas at a flow of 40ml/sec.

Oven exposure was performed in a convection oven at different temperature in air on compression moulded film.

For carbonyl and hydroperoxide formation IR determination was performed on a Nicolet Magna 560 FTIR instrument on compression moulded film.

Multiple extrusion was performed on a Brabender Plasticorder 2200 C single screw extruder, at 90 rpm and temperature: zone 1 (190°C); zone 2 (200°C); zone 3 (210°C); zone 4 (220°C)

Results and Discussion

The relationship between the size and content of the branch and crystallinity for ethylene copolymers with linear Fischer-Tropsch olefins was previously presented [6,7]. It was shown that the inability of comonomer units to fit into the polyethylene crystal results in a decrease of crystallinity and the longer the branch, the easier the crystallinity is decreased. It was expected that both crystallinity and branch content will effect the degradation of particular copolymers. In a recent study [10] it was showed that the degradation temperature is increasing slightly with the length of the branch.

Different samples of 0.2 mm thick film prepared from an ethylene / heptene-1 copolymer having a heptene-1 content of 3 mol % (sample Nr 1)were aged in a forced draft air for 24 hours at different temperatures. As can be seen from Fig. 1 the carbonyl and hydroperoxide content of the polymer is increasing with the temperature.

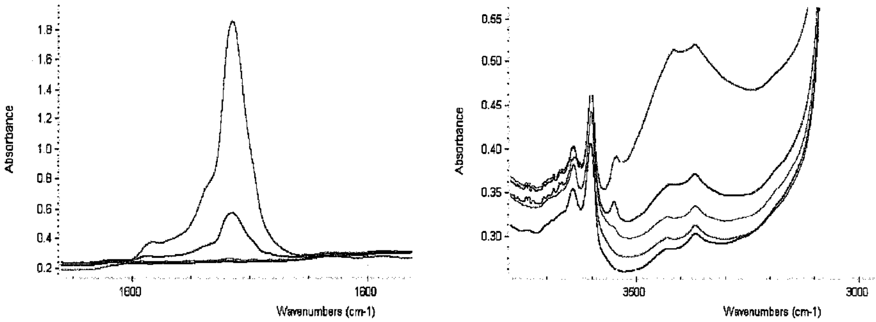

Figure 1. The increase of carbonyl and hydroperoxide IR absorbance peak before exposure and after exposure at 60°C, 80°C, 110° C, 120°C. (Absorbance increases according to temperature increase).

Historically, investigation of thermal oxidation of polyolefins followed the discovery and application of every single family of polyolefins. Thermal oxydation of polyolefins in solid state has also been the object of previous investigation [14]. To monitor functional group formation in the thermal oxidation process, IR spectrophotometry is one of the most useful tools. The carbonyl and hydroxyl groups concentration are usually used to asses degradation of polyethylene. The data are mostly expressed as the absorbance at the wavelength corresponding to the maximum of the absorbance band of about 1715 $cm^{-1}$for the carbonyl group and 3559 cm^{-1} and 3410 cm^{-1} respectively for free and associated hydroperoxides. Finally, the deterioration of mechanical properties correlates well with carbonyl group concentration in the polymer.

Another recommended method to assess degradation of polyolefins is multiple extrusion [15].

Multiple extrusion was performed on ethylene / heptene-1 copolymers with the same content and different melt flow index. The decrease of melt flow index with the number of passes through the extruder is presented in Table 1 for the copolymer with a melt flow index of 2.50 g/10 min (sample 1a) and for the copolymer with a melt flow index of 9.80 g/10 min (sample 1b).

Table 1. Degradation stability of ethylene/heptene-1 copolymer; multiple extrusion at 220°C.

Melt Flow Index 190/2.16; g/10min				
Sample	Before extrusion	First extrusion	Third extrusion	Fifth extrusion
1a	2.50	2.25	1.75	1.05
1b	9.80	8.70	6.90	3.90

The relationship between the size and content of the branch and crystallinity for ethylene copolymers with branched Fischer-Tropsch olefins and for polymers with more than one comonomer (linear or branched Fischer-Tropsch olefins) was also previously presented [7]. The branched olefins decrease density more than linear olefins with the same carbon number and the terpolymer data point is situated between those of the corresponding copolymer data points. As the branched / linear ratio increases, the densities decrease towards those of the copolymers containing branched olefins.

It was previously shown [10] that the degradation temperature is increasing more with the length of the branch when ethylene is polymerized with the 3,4 methyl-pentene-1 mixture and linear alpha olefins than for the case of copolymers. The degradation temperature values are situated between 450°C and. 465°C.

Different samples of 0.2 mm thick film prepared from the ethylene multipolymer with 3-methyl-pentene-1, 4-methyl-pentene-1 and hexene-1 having a content of 0.2/ 2.31/ 6.07/ mol% (sample 2) and from ethylene terpolymer with 3,4methyl-1-pentene having a content of 0,5/5.5 mol% (sample 3) were aged in a forced draft air oven at 110 °C. The carbonyl and hydroperoxides absorbance of the film is presented in Fig 2 respectively Fig 3 for a different aging time.

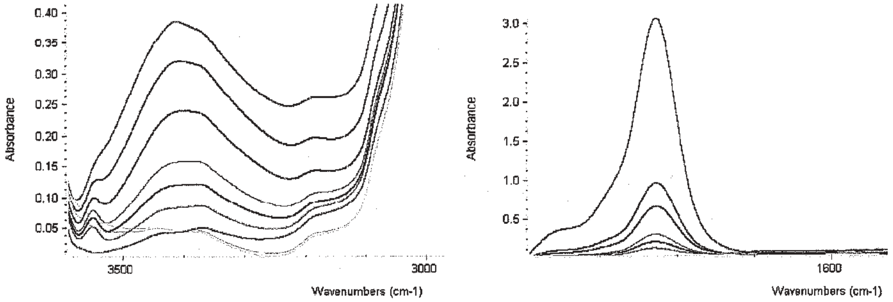

Figure 2. Changes in IR absorption spectra of sample 2 on thermal oxidation at 110 °C. Film thickness 160 μm. Aging times (days): 0, 2, 5, 9, 12, 14, 16, 19, 22, 26 (Absorbance increase according to exposure time).

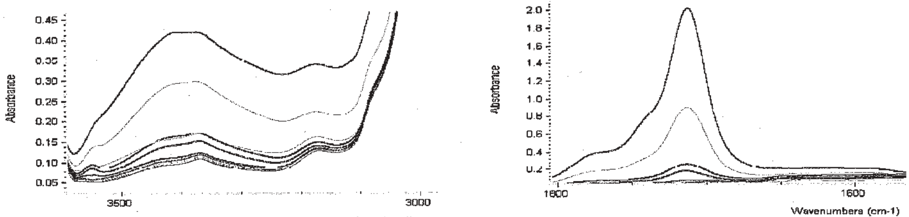

Figure 3. Changes in IR absorption spectra of Sample 3 on thermal oxidation at 110 °C. Film thickness 160 μm. Aging times (days): 0, 4, 7, 10, 11, 12, 14, 17, 19, 24, 31 (Absorbance increase according to exposure time).

Different samples of 0.2 mm thick film prepared from the ethylene multipolymer with 3-methyl-pentene-1 and 4-methyl-pentene-1 and pentene-1 having a content of 0.05/ 0.53/ 7.72 mol% (sample 4) were aged in a forced draft air oven at 110 °C. The carbonyl and hydroperoxides absorbance of the film is presented in Fig 4 for a different aging time.

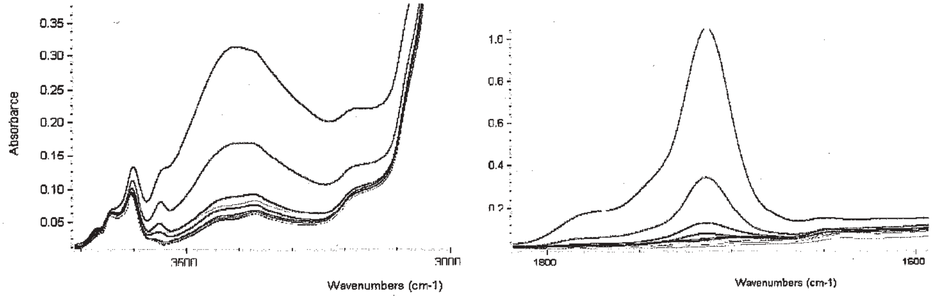

Figure 4. Changes in IR absorption spectra of sample 4 on thermal oxidation at 110 °C. Film thickness 200 μm. Aging times (days): 0, 4, 7, 10, 11, 12, 14, 17, 19, 24, 31 (Absorbance increase according to exposure time).

Different samples of 0.2 mm thick film prepared from the ethylene multipolymer with 3-methyl-pentene-1 and 4-methyl-pentene-1 and butene-1 having a content of 0.076/ 0.76/ 9.06 mol% (sample 5) were aged in a forced draft air oven at 110 °C. The carbonyl and hydroperoxides absorbance of the film is presented in Fig 5 for a different aging time.

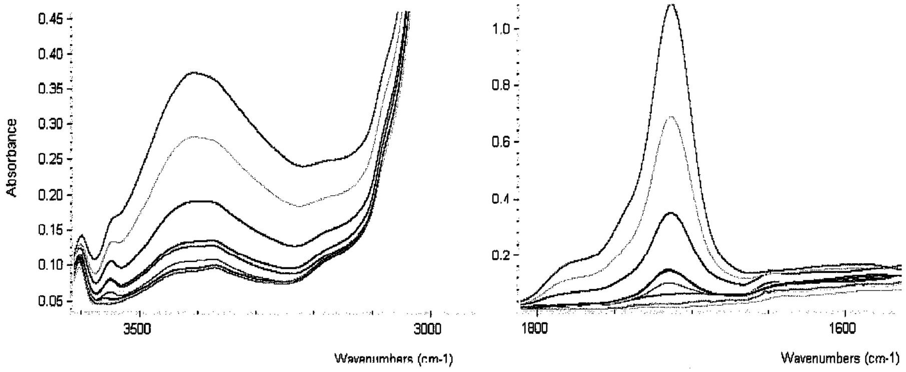

Figure 5. Changes in IR absorption spectra of Sample 5 on thermal oxidation at 110 °C. Film thickness 150 μm. Aging times (days): 0, 4, 7, 10, 11, 12, 14, 17, 19, 24, 31 (Absorbance increase according to exposure time).

Different samples of 0.2 mm thick film prepared from the ethylene multipolymer with 3-methyl-pentene-1 and 4 methyl-pentene-1 and heptene-1 having a content of 0.2/ 2.33/ 5.17 mol% (sample 6) were aged in a forced draft air oven at 110 °C. The carbonyl and hydroperoxides absorbance of the film is presented in Fig 6 for a different aging time.

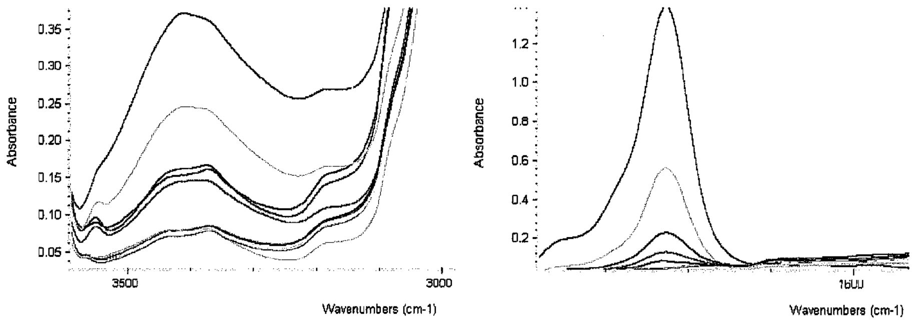

Figure 6. Changes in IR absorption spectra of Sample 6 on thermal oxidation at 110 °C. Film thickness 190 μm. Aging times (days): 0, 4, 7, 10, 11, 12, 14, 17, 19, 24, 31 (Absorbance increase according to exposure time).

Different samples of 0.2 mm thick film prepared from the ethylene copolymer with 4 methyl-pentene-1 having a content of 6.6 mol% (sample 7) were aged in a forced draft air oven at 110 °C. The carbonyl and hydroperoxides absorbance of the film is presented in Fig 7 for a different aging time.

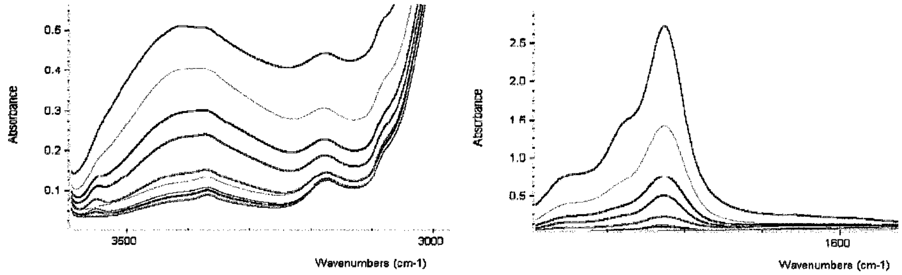

Figure 7. Changes in IR absorption spectra of Sample 7 on thermal oxidation at 110 °C. Film thickness 160 μm. Aging times (days): 0, 4, 7, 10, 11, 12, 14, 17, 19, 24, 31 (Absorbance increase according to exposure time).

In the series of ethylene polymers with branched olefin investigated, the ethylene multipolymer with 3-methyl-pentene-1 and 4-methyl-pentene-1 and hexene-1 (sample 2) has similar density to the ethylene terpolymer with 3,4-methyl-pentene-1 (sample 3), namely 0.890 g/cm^3 . The ratio between the surface area corresponding to maximum of carbonyl absorbance and thickness of the sample 2 was 525.8 after 26 days of oven exposure at 110 ° C while for sample 3 it was 534.2 after 31 days of exposure in similar conditions. Sample 3 with a total comonomer content of 6 mol% is more stable to thermo-oxidative degradation than sample 2 having a total comonomer content of 8.6 mol%.

The ethylene multipolymer with 3-methyl-pentene-1 and 4-methyl-pentene-1 and pentene-1 (sample 4) and ethylene multipolymer with 3-methyl-pentene-1 and 4 methyl-pentene-1 and butene-1 (sample 5) have similar densities of 0.896. The ratio between the surface area corresponding to maximum of carbonyl absorbance and thickness of the sample 4 was 222.2 after 31 days of oven exposure at 110 ° C while for sample 5 was 227.7 after 31 days of exposure in similar conditions for sample 3. The molar content for the total 3-methyl-pentene-1 and 4-methyl-pentene-1 is in the same order of magnitude, respectively 0.58 for sample 4 and 0.83 for sample 5. The content of butene-1 in sample 5 is 9.6 mol% while the content of pentene-1 in sample 4 is 7.7 mol%. Apparently this difference confers a higher thermo-oxidative stability to sample 4 and both sample 4 and 5 have better thermo-oxidative stability than samples 2 and 3 having lower density than samples 4 and 5.

The ethylene multipolymer with 3-methyl-pentene-1 and 4-methyl-pentene-1 and heptene-1 (sample 6) has lower density than the ethylene multipolymer with 3-methyl-pentene-1 and 4-methyl-pentene-1 and pentene-1 and ethylene multipolymer with 3-methyl-pentene-1 and 4 methyl-pentene-1 and butene-1, namely 0,887 g/cm^3. It was expected thus to have a lower thrmo-oxidative stability due to lower crystallinity and higher oxygen intake in the amorphous phase. Compared to the ethylene multipolymer with 3-methyl-pentene-1 and 4-methyl-pentene-1 and hexene-1 for the same amount of total 3-methyl-pentene-1 and 4-methyl-pentene-1, namely 2.55 mol% the amount of heptene-1 in sample 6 is 5.17 mol% while in sample 2 the amount of hexene-1 is 6.07 mol%. This may account for a higher thermo-oxidative stability of sample 6. The ratio between the surface area corresponding to maximum of carbonyl absorbance and thickness of the sample 6 was 332.0 after 31 days of oven exposure at 110 ° C. The ethylene copolymer with 4 methyl-pentene-1 (sample 7) has the lowest density of all the series of samples investigated, namely 0,83 and has also the lowest thermo-oxidative stability. The ratio between the surface area corresponding to maximum of carbonyl absorbance and thickness of the sample 7 was 931.9 after 31 days of oven exposure at 110 ° C.

The main advantage of using higher alpha olefin and branched olefins lies in the rather sharp decrease of crystallinity and density with the increase of the comonomer content. As it is known [13], oxidation of polyethylene proceeds in the amorphous domain and degradation will increase as the crystallinity decreases. However the same density is obtained with a lower amount of the longer and bulkier branches. The longer or bulkier the branch, the density depression will be higher. This will account for less tertiary carbon in the polymer chain when using higher carbon number linear or branched olefins. Literature data [16] shows a dissociation energy of 98 Kcal/ mol for tertiary carbon as compared with 92Kcal/ mol for secondary carbon. The radical formation during the initiation step is likely to happen at a tertiary carbon. Furthermore, the fixation of oxygen onto a carbon atom centered free radical is a rather fast reaction, leading to a peroxy radical. The hydrogen extraction from another polymer chain by the peroxy radical determines the rate of the chain propagation and this is related to both the bond strength of the carbon-hydrogen that generates the radical and the radical stability. On the other hand, the electron-donating effect is increasing with the length of branch and bulkiness of the branch and this confers a higher stability of the peroximacroradical. When using branched olefins as comonomer the steric hindrance of the macroradical due to the bulky substituent increases the macroradical stability. All these effects account for the particularities in degradation of ethylene polymers with Fischer-Tropsch derived long chain or branched chain olefins.

Preliminary experimental data on degradation of ethylene polymers with Fischer-Tropsch derived olefins points to increased stability of the polymer with longer or bulkier branches. However a more accurate view will need to monitor change in degradation species and in particular change of functional groups with time and temperature.

Conclusion

The Fischer-Tropsch process offers without doubt the most complex pool of olefin comonomers for the Polyolefin industry. Ethylene / heptene-1 copolymers have a good balance of properties in the polyethylene families. Multipolymerization with branched and linear olefins diversify the application field and provide new operational opportunities. However the new polymers are subject to thermo-oxidative degradation like all polyolefins.

Hydroperoxide and carbonyl development can be used to assess degradation. Less tertiary carbon in the chain introduced by the longer or by the more bulkier branch and a more stable peroxy radical is responsible for better thermo-oxidative stability. Multiple extrusion presents the ethylene / heptene copolymer with a good thermo-oxidative stability and small change in viscosity during processing. For multipolymers having the same density, better stability is obtained for the comonomer with a higher carbon number. These results confirm the results obtained previously by thermogravimetry: higher degradation temperature for the degradation of ethylene branched multipolymers and ethylene / higher alpha olefin copolymers.

Copolymerization with Fischer-Tropsch olefins offer the polymer scientist new challenges and a large field of investigation. This preliminary study needs to be complemented with experimental work to establish particular degradation mechanisms and kinetics.

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