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Rheo-optical FT-IR Spectroscopy of LLDPE: Effect of Comonomer and Composite Materials

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Summary: In order to further evaluate the potential of FT-IR spectroscopic investigations on molecular processes during tensile testing experiments, the behavior of monolayer LLDPE films, made with ethylene-butene and ethylene-octene copolymers, was studied. Additionally, multilayer LLDPE films based on the same C4 and C8 copolymers were investigated. The stress-strain data obtained from the monolayer films indicate differences in the strain hardening region. It seems that the film samples PE 469-30-2 (C4-gas phase process) and PE 469-30-5 (C8 solution process) behave similarly whereas the strain hardening for the PE 469-30-3 (C4 solution process) requires lower stress values. The orientation function changes during the stretching of the films indicating that unfolding of the polymer chains occurs at lower strain for PE 469-30-5 (C8) than in the C4 materials. In the multilayer systems the Primplast 44 material (C8) shows a lower tendency for reorientation in the strain hardening region than the Coex 82 (C4) material. In this region of the stress-strain curve the lamellar structure is already transformed into the fibrillar arrangement. Regarding the orientation behavior of the material above 200% strain, a small increase in f_b was observed, which led to a decrease of f_c. In the octene product possibly the bulky side chains influence the unfolding significantly, producing a higher resistance to unfolding and alignment along the stretching direction. In part, this is potentially caused by the more perfect lamellae in the octene copolymer, which do not include the side chains, while the butene copolymer may have weaker lamellae because they contain a fraction of the side chains which create defects. Consequently, the octene copolymer requires higher stress values to be stretched and finally results in a lower stretchability of this material, as observed on an industrial scale during pallet wrapping tests. Based on the ratio of the structural absorbance parameters of the signals at 729 and 719 cm^{-1} changes in the crystallinity were studied. For the continuous stretching experiment, no monoclinic phase was detected even after Fourier self-deconvolution and peak fitting approaches. Literature data, however, describe that this crystalline transformation takes place as a result of mechanical deformation. Therefore, stepwise stretching experiments which allow an improvement of the spectral resolution to 1 cm^{-1} were carried out. In the deconvoluted spectra the monoclinic, orthorhombic and amorphous LLDPE modifications could be assigned. Ultimate stretchability and stretching force of the films, both monolayer and multilayer, was well correlated to the development of crystalline orientation in the films upon stretching. Other mechanical properties like Elmendorf tear and dart impact can also be better understood with these results.

Keywords: comonomers; FTIR; LLDPE; rheo-optical

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Introduction

The end use properties of a polymer are determined by the complex interconnection of molecular structure, morphology and processing parameters. Thus, the mechanical properties of a polymer will be influenced by the processing conditions. By selection of the extrusion conditions morphological parameters such as crystallinity and orientation may be dramatically influenced which can affect the transparency and other properties of the end-product. Recently the effect of type of short chain branching on the mechanical properties of LLDPE has been investigated [1]. Based on their data the authors concluded that the understanding of the branching effect on mechanical properties is still not fully understood and requires further studies to understand the physical process of deformation.

Rheo-optical FT-IR investigations may allow to contribute to the understanding of those effects since the combination of tensile testing experiment and IR spectroscopy enables us to study changes of the crystallinity and orientation of polymer units during tensile testing and lead to a better understanding of the polymer deformation mechanism. The idea of continuous monitoring the structural transitions in polymers during their deformation was realized for the first time in the works of the Zhurov school[2]. In the early 80's an approach of a miniaturized tensile testing equipment which can be placed into the sample compartment of an FT-IR spectrometer was refined[3]. As a result of this experiment stress-strain curves and FT-IR polarization spectra of polymer films can be recorded simultaneously and provide information on the change of the orientation function and the crystallinity of the investigated polymer.

In the present paper we have applied this approach on mono- and multilayer polyethylene films, which were produced from different comonomers. Tensile testing experiments on butene and octene based PE films have shown that the type of comonomer influences the properties in the strain hardening region and the overall stretchability. The purpose of this work was to relate differences in tensile properties to changes in the orientation function or crystallinity.

Our approach to understand the molecular behavior during the stretching process by simultaneous stress-strain and infrared spectroscopic measurements could be described as follows:

- Investigation of the monolayer which was formed from butene and octene copolymers
- Investigation of multilayer films which also contained layers of the different copolymers.

Experimental Part

Samples

Monolayer films of three different linear low density polypropylenes (LLDPE's), two 1-butene (C4) copolymers and one 1-octene (C8) copolymer were used. Two of them are 1-butene (C4) copolymers produced by different processes which results in a significantly different molecular structure. Additionally an 1-octene (C8) copolymer made in the solution process was investigated. The molecular weight distribution and the comonomer distribution were analyzed by High-Temperature Gel Permeation Chromatography (HT-GPC) and by CRYSTAF, respectively. The basic descriptive parameters of these resins are given in Table 1 below.

Two sets of conditions were used to evaluate the films: First, mechanical properties of the original films were measured. Second, the films were stretched up to 200% strain using a Highlight stretcher, and selected properties were evaluated on the stretched film.

Additionally, two multi-layer co-extruded films of the A-B-C type were also included in the study. In this case A and B are identical and non-cling material, so mostly higher density LLDPE in the 0.916 to

Table 1.
Description of LLDPE resins used for the monolayer films.

Monolayer films	Process	Melt Flow Index [g/10min]	Density [g/cm^3]	Comonomer
PE 469-30-2	Gas phase	2.6	0.917	C4
PE 469-30-3	Solution	2.0	0.918	C4
PE 469-30-5	Solution	2.3	0.918	C8

0.922 g/cm^3 density range. Layer C (typically 15% of the total thickness) serves as cling layer and is a lower density material in the 0.904–0.912 g/cm^3 density range. The first sample is labeled "Primplast 44" and consists of A and B layers made of a C8 LLDPE made in the solution process with 3.3 g/10 min melt index and 0.917 g/cm^3 density. The second film contains C4 LLDPE, labeled "Coex82".

The stretching performance of these films was measured using a Highlight stretcher, which reproduces conditions of an industrial pallet wrapper. The results of maximum stretchability were 260% for Primplast44 and 356% for Coex82. From DSC data it was determined that the crystallinity of both coextruded films is quite similar and can be estimated at 44 and 46%, for Primplast44 and Coex82, respectively[4].

FT-IR spectroscopy

The samples were analyzed using a self-built stretching device similar to the device which was mounted into the sample compartment of the FT-IR spectrometer. The setup follows the description given in [5]. The initial dimensions of the film are 10 × 15 mm^2. The thickness of the film was appr. 20 μm. Accurate values are given in Table 3. Using a linear velocity of 0.02 mm/min for the clamp movement, the film is stretched up to a stress of ca. 500%. During the continuous elongation of the film FT-IR polarization spectra were recorded with alternating rotation of a KRS5 polarizer using an IFS 66 FT-IR spectrometer (Bruker Optik GmbH, Ettlingen, Germany). 10 scans per spectrum were accumulated in the rapid-scan mode with a spectral resolution of 4 cm^{-1}.

Results and Discussion

Molecular Structure and Film Properties

A summary of the HT-GPC and CRYSTAF results is given in Table 2.

Butene LLDPE samples produced with the gas phase process are generally not as heterogeneous in comonomer distribution (CD) as the gas phase hexene LLDPE's. This is due to the much closer reactivity between butene and ethylene compared to hexene and ethylene. Therefore, the two butene samples have a relatively similar CD shape, in general terms. Still some more heterogeneity is seen for the gas phase sample, as observed by the higher Sigma (more heterogeneous) and the higher soluble fraction, compensated by the higher HDF peak temperature.

Table 2.
HT-GPC and CRYSTAF data on the monolayer films.

Resin	MWD given in g/mol measured by HT-GPC				Comonomer distribution measured by CRYSTAF					
	Mp	Mw	Mn	Mw/Mn	%HDF	HDF Tp in °C	%SF	Sigma	T$_{median}$	Copolym Tp in °C
PE 469-30-2	44076	84176	22580	3.73	17.3	80.2	9.5	14.9	57.8	61
PE 469-30-3	47987	88784	22962	3.87	17.1	78.4	5.2	13.1	62	65
PE 469-30-5	46238	84512	24001	3.52	18.4	81.4	6.6	14.1	62.2	63

HDF: High Density Fraction; SF: Soluble fraction at 30 °C; Sigma: Breadth of the Comonomer Distribution.

Table 3.
Characteristic parameters of the mono-layer films.

Sample	Stretch level	Thickness	Elmendorf Tear –CD		Dart Impact	Puncture	Yield Tensile	Ultim. Ten. Strength	Ultim. Elong.	Toughness
	%	micron	g	g/micron	g	J/cm^3	MPa	MPa	%	MJ/m^3
PE 469-30-2	0	18.2	314	17.3	55	7.17	5.5	39.6	401	66.2
	200		277		<50	5.41				
PE 469-30-3	0	21.1	281	13.3	55	7.51	5.9	38.4	330	56.1
	200		260		<50	5.9				
PE 469-30-5	0	17.8	526	29.6	140	17.06	5.8	36.3	335	52.1
	200		351		81	11.33				

The octene LLDPE is narrower in MWD, particularly on the low MW side. The CD is typical for the solution process.

Monolayer film properties, both for the unstretched and the stretched films, are reported in Table 3. Additionally, the stress-strain characteristics of the test in the highlight stretcher are listed in Table 4. The butene gas phase film is slightly more stretchable than the solution process grades. However, the octene grade stands out in terms of mechanical properties.

Stress-Strain Curves

Monolayer

For the mechanism of molecular reorganization different theoretical models are discussed in the literature [6,7]. Whereas one model assumes that the polymer actually melts under stress and then reorganizes, the second idea is based on the assumption that the crystallites themselves rotate as a response to the applied strain. Highly crystalline polyolefins like HDPE show a sharp peak in the yield region. This is due to the break-up of large lamellar crystals into smaller segments linked by newly formed tie-chains [8,9]. In contrast to HDPE, a less defined yield peak is expected in the stress-strain diagram for LLDPE films because the latter contain smaller crystals and lower crystallinity. For all monolayer films only diffuse yield points can be found at about 15 and 70% strain as can be seen in Figure 1. In the initial (elastic) region the monolayer samples behave similarly as expected from the very similar crystallinities. This is the case also for the yield and draw plateau regions. The differences in the stretchability become significant above strain values of ca. 150%. Surprisingly the samples PE 469-30-2 and PE 469-30-5, which are based on C4 (gas phase) and C8 (solution) comonomers, respectively, behave differently than the sample PE 469-30-3, which is also based on butene as comonomer in the solution process. In the strain hardening region the slope of the octene copolymer is higher, as expected, because octene is known to be more effective in building tie chains. More tie chains lead to an increase in the resistance of the sample to be stretched, therefore building up stress faster. Comparing the two butene copolymers, there is no clear reason why they should have the observed difference.

Table 4.
Tensile data of the raw material.

Sample	Highlight Performance Data		
	Max. Stretch %	Max. Str. Force N	Av. Str. Force N
PE 469-30-2	244	321	274
PE 469-30-3	227	340	312
PE 469-30-5	210	346	327

Multilayer

The differences caused by the use of butene and octene comonomers in LLDPE become more obvious in the multilayer films. Only a diffuse yield point can be observed for these films which are at similar strain amplitudes for both materials. In the strain hardening region Coex82 (C4) shows a lower slope than the Primplast 44 (C8) material. Again, this is expected from the higher tie-chain

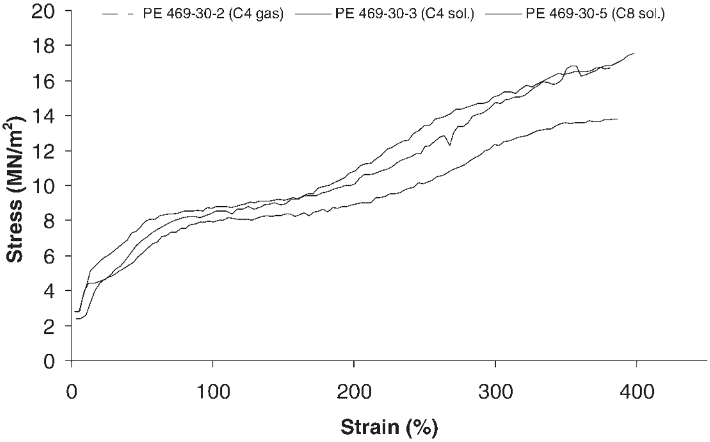

Figure 1.
Stress-strain curves of the monolayers

capability of the hexyl branches from 1-octene, compared to the ethyl branches from 1-butene.

Infrared Spectra

The infrared spectra of the multilayer samples (thickness: 18 μm) are given below (Figure 3). The infrared spectrum of semicrystalline polyethylene has been studied extensively by numerous authors and the detailed band assignment is described in [10–13]. In the spectrum below the $\nu(CH_2)$ bands are, even at this thickness, too intense and thus not appropriate for further analysis. However, the crystallinity sensitive bands in the out-of -plane deformation range between 750 and 680 cm^{-1} are accessible at appropriate absorbance intensity.

In the spectra the band doublet at 729 cm^{-1} and 719 cm^{-1} which can be assigned to the in- and out-of-plane CH_2 rocking vibrations of LLDPE, are the most important absorptions for the characterization of orientation. This band pattern is rather complex due to of orthorhombic and monocline crystalline and amorphous components [14]. For the analysis of the orientation behavior during tensile testing of LLDPE

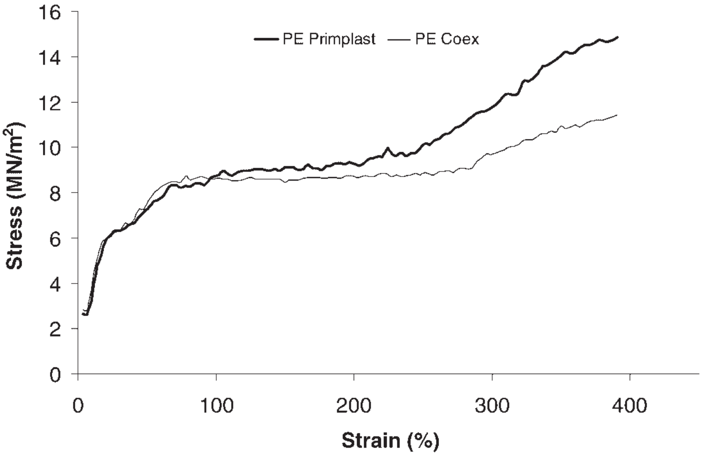

Figure 2.
Comparison of the stress-strain curves of the multilayer films

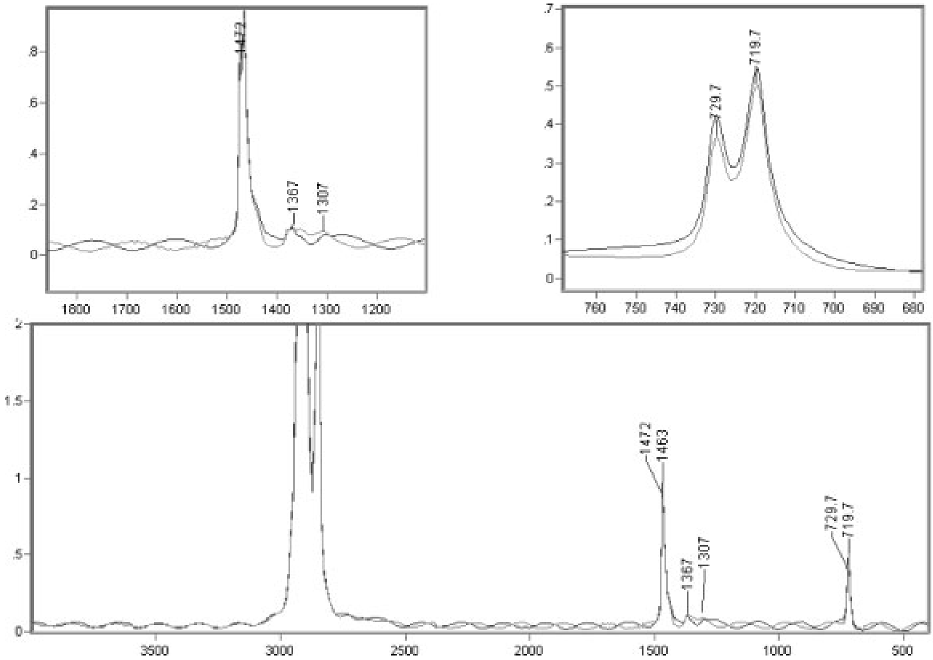

Figure 3.
Infrared spectra of Coex82 (red) and Primplast 44 (blue)

the assumption was made that the contribution of the amorphous component to the 719 cm^{-1} band is relatively small. The validity of this assumption will be discussed based on the deconvoluted spectra in the later paragraph.

The calculation of the orientation functions for the crystallographic axes of the orthorhombic unit cell can be done using the dichroic ratio, R, of the signal at 729 cm^{-1}, which is polarized along the crystallographic a-axis and the signal at 719 cm^{-1} is polarized along the crystallographic b-axis. Thus, the orientation functions for the three crystallographic axes a, b and c can be calculated according to the following equations:

$$f_a = \frac{R_{729} - 1}{R_{729} + 2}$$

and

$$f_b = \frac{R_{719} - 1}{R_{719} + 2}$$

The orientation function of the crystallographic c-axis is then obtained from the orientation functions f_a and f_b[15]:

$$f_a + f_b + f_c = 0$$

Orientation Function

According to Peterlin the application of stress results in tilting, orientation and ultimately fragmentation of the material which corresponds to the transformation of a chain folded lamellar structure to a fibrillar arrangement[8,9]. As a result of the molecular processes of the lamellar orientation and partial chain-unfolding, the orientation function of the crystallographic axes will change[9]. Onogi and Asada[16] have predicted for transformation of the lamellar unit that the f_b will increase whereas f_a will show up. The unfolding mechanism should result in a decrease of both orientation functions f_a and f_b.

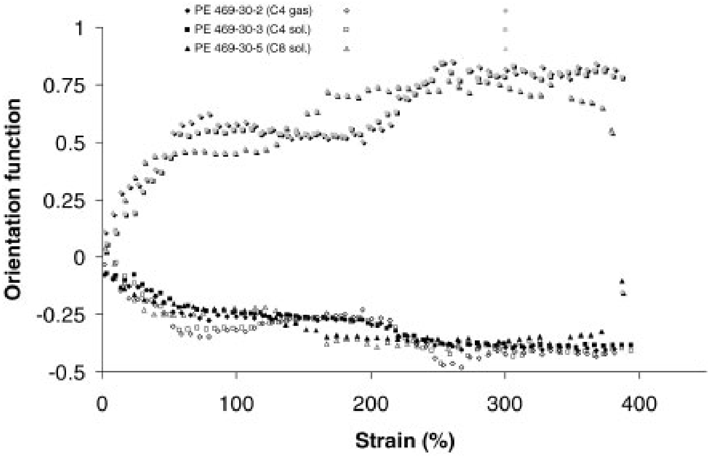

Figure 4.
Orientation function vs. strain of the monolayer LLDPE films (symbols indicate different LLDPE films, orientation functions: grey: f_c, black: f_b open: f_a)

The orientation function f_a, f_b and f_c for the crystallographic axes a, b and c of the orthorhombic structure are shown in Figure 4 and 5.

Monolayer

In terms of the orientation vs. strain behavior the curves in Figure 4 can generally be divided into four regions. At low strain amplitudes the elastic elongation below the yield point is observed which will not lead to substantial changes in the lamellar arrangement (<70% strain). In the following region the lamellar structures will be aligned towards the drawing direction. This will affect the orientation functions in such a way that orientation function f_a decreases significantly while there is no or only a small increase monitored in f_b and f_c.(strain: 70 to 140% for the C8 copolymer, 70 to 200% for the C4). Even f_c of the gas phase butene seems to decrease slightly.

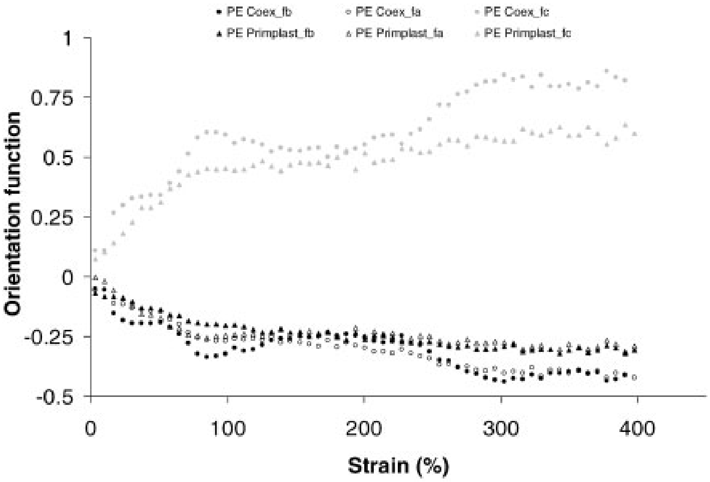

Figure 5.
Orientation function vs. strain curves of the crystallographic axis (symbols indicate different LLDPE films, orientation functions: grey: f_c, black: f_b open: f_a)

According to Siesler [3] this behavior can be interpreted as an effect of rotational motion of the c and b axis towards the direction of the applied stretch.

In the third region unfolding of the folded chains determine the orientation functions and will result in an increase of f_c while f_a and f_b decreases until all orientation functions reach a plateau, which is the fourth region. Further stretching of the films will cause a slight improvement in the alignment of the crystallographic axes and will finally end in the fracture of the material.

Discussing the differences of the behavior of the monolayer samples in the region above a strain of ca. 150% becomes important. As seen in Figure 4 at this stage the crystallographic axes are already aligned and the orientation function for the c axis approaches values of 0.5 whereas f_a and f_b approach values close to -0.25. Further stretching of the films results in an increase in the orientation function, f_c, for PE 469-30-5 (C8) at ca. 150% strain. In contrast, the C4 based PE films show the effect of strain hardening at slightly higher strain values (ca. 200%). Furthermore, the changes in the orientation along the c-axis are smaller for PE 469-30-5 (C8) than for the C4 copolymers. Obviously the unfolding of the chains can be better accomplished by the C8 comonomer. It seems that the larger side chains in the C8 copolymer force the unfolding of the chains (strain hardening) to start at a lower strain for the C8 copolymer. They also prevent the lamellae from aligning with the stretch direction as much as the lamellae in the C4 copolymers do.

Multilayer

The differences of the behavior of both samples in the region above a strain amplitude of 200% becomes important. As seen in Figure 5 at this stage the crystallographic axes are already perfectly aligned and any increase in the elongation needs to be assigned to further unfolding of the chains which can obviously be better accomplished in Coex 82 (butene based) than in Primplast 44 (octene based). The orientation functions f_c and f_b are affected by the unfolding of the chains. Obviously the hexyl side chains hinder the formation of all-trans conformers more significantly than the ethyl groups.

For the multilayer films the results discussed in the previous section on monolayer films can be confirmed. Clearly the Coex 82 (C4) can be oriented to a higher degree than the Primplast 44 (C8) film, and this is translated into the higher ultimate elongation or stretchability that can be achieved under industrial conditions (260% for the C8, 356% for the C4). Regarding the degree of orientation, the monolayer results and the results on the Primplast film show similar trends. However, it could not be observed that there are differences in the strain values which initiate the second phase of the orientation.

Crystallinity

Apart from the characterization of the changes in the orientation behavior during elongation, the structural absorbance of the band at 729 cm^{-1} should provide a tool for monitoring the distortion and destruction of the orthorhombic crystalline modification during deformation. However, in the absence of another thickness-relevant band in the spectrum, the intensity of the 719 cm^{-1} band was used as a fairly reliable reference signal. Hence the intensity ratio $A_{0(729)}/A_{0(719)}$ directly reflects any consequences of the mechanical treatment on the orthorhombic crystal lattice.

Keeping in mind that Figure 6 shows only trend changes due to the aforementioned approximation, some basic conclusions can be drawn.

From Figure 6 it can be concluded that the monolayer films behave similarly with reference to the changes in the crystallinity. The intensity ratio changes only at low strain amplitudes ($<70\%$) until the diffuse yield point is formed. In all following phases described above the fraction of

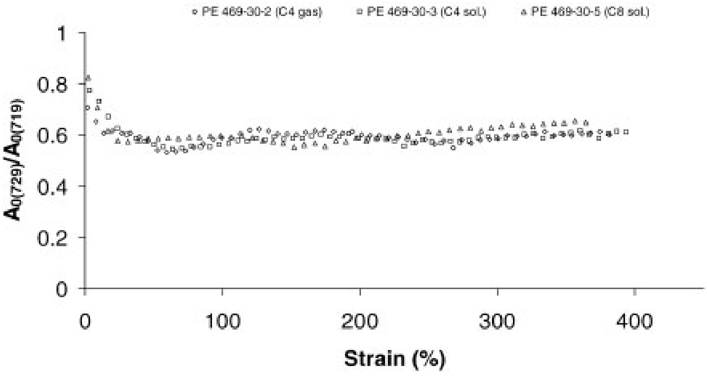

Figure 6.

Plot of the $A_{0(729)}/A_{0(719)}$ structural absorbance ratio vs. strain for the elongation of the PE monolayer films up to ca. 400% strain

orthorhombic crystalline material is constant. This observation is confirmed by Siesler for butene and octene LLDPE. As a significant difference to his study, the concentration of the crystalline polymer is higher in our films, and also the plateau region is already reached at low strain values [15].

It has been shown in the literature that the structural changes during elongation are superimposed by a partial transformation from the orthorhombic to a monoclinic crystal phase [17]. Due to its packing in the unit cell the monoclinic structure exhibits only one absorption band at 717 cm^{-1} for the CH_2 rocking mode. We have specifically looked for the identification of this signal, which is overlapped by the absorptions of the orthorhombic modification. Using Fourier self-deconvolution techniques, derivative methods and band fitting procedures in order to enhance the spectral resolution we have not been successful in analyzing this signal. Reasons for this result might be due to the low resolution (4 cm^{-1}) which was used in this experiment to using the rapid scan mode.

Therefore, in a second test the multilayer samples were stretched in a discontinuous mode (steps of 40% elongation) using a spectral resolution of 1 cm^{-1}. The spectra were corrected by subtraction of the overlapping sinusoidal fringing pattern and transferred to a band fitting program (Jandel Scientific). This program creates a fitting file based on the number of signals found in the second derivative of the spectra (Figure 7).

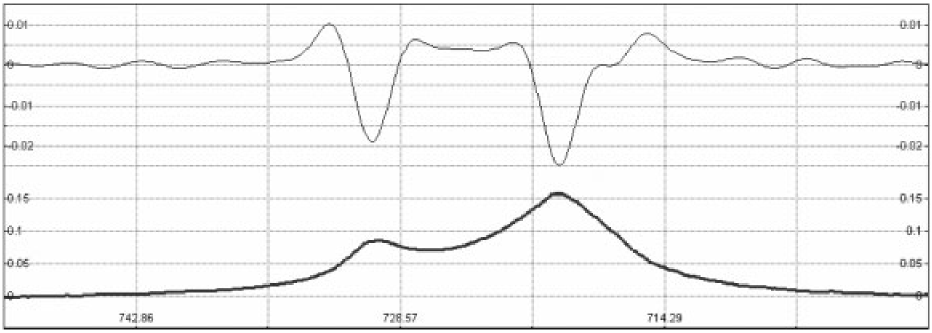

Figure 7.

Absorbance spectrum of Coex 82 at a strain of 440% and its 2nd derivative

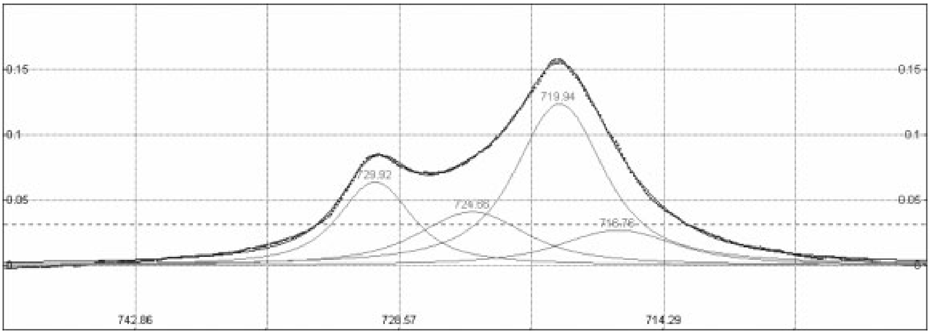

Figure 8.
Absorbance spectrum of Coex 44 at a strain of 440% overlaid by the four separate functions.

From the behavior of the 2nd derivative it becomes obvious that the band profile can be fitted with at least four separate functions. Two of them can be assigned to the two crystal axes of the orthorhombic LLDPE whereas the band at 717 cm^{-1} is due to the monoclinic modification. The broad overlaying band at 724 cm^{-1} can be assigned as amorphous PE. The results of the fitting procedure are shown in Figure 8.

If the relative changes of the intensities of the four bands with respect to its contribution to the total area are studied in dependence of the applied strain, then Figure 9 is obtained. Clearly the changes observed in the plot do not follow a trend. Hence even with this refined methodology we cannot verify the effect of a crystalline phase transition.

Relationships with Final Film Properties

As shown in Table 3 for the monolayer films, the C8 based film results in a lower maximum stretchability under industrial conditions, and it needs slightly higher force to be stretched. This is well in line with the observed stress-strain curve and the relationship between orientation functions and percentage of strain. A lower degree of orientation of the lamellae in the direction of stretch (machine direction MD) may contribute to a higher Elmendorf tear resistance in cross direction (CD). The orientation of the amorphous phase could be another morphological factor. The key role of the octene comonomer on the generation of tie chains is reflected in the

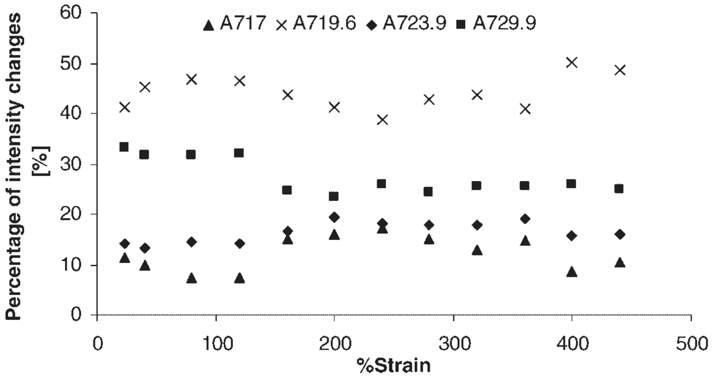

Figure 9.
Relative changes of the intensity of the fitted bands with respect to the applied strain as measure for the cryatlllinity changes during film stretching

excellent balance of tear and dart impact, both for the un-stretched and the stretched films. The hexyl side chains oppose more resistance to stretching, as shown by the lower crystalline orientation, earlier onset of lamellar unfolding and the higher slope of the strain-hardening region. The lamellar unfolding also releases a new number of tie chains that contribute to mechanical properties like tear and dart impact, and this starts to happen at a lower strain for the C8. At the same time, the fragmented lamellae from the C8 may be more effective in anchoring the stretched structure (providing toughness), as they do not contain defects, like the ethyl branches in the case of the C4 copolymers. It is possible that the weaker lamellae in the C4 copolymers are one reason for the different orientation behavior as described above.

The multilayer films, as discussed above, again confirm that a lower crystalline orientation is achieved for the octene film at a given strain, which indicates a stronger resistance of the lamellae to become aligned in the stretching direction. This results in a higher stress and therefore a lower ultimate stretchability: 260% for the Primplast44 film, 365% for the Coex82 (C4) film.

Conclusions

In an effort to further evaluate the potential of FT-IR spectroscopic investigations of the molecular processes during tensile testing experiments, the behavior of monolayer LLDPE films, produced with butene and octene comonomers, was studied. Additionally, multilayer LLDPE films based on the same C4 and C8 copolymers were the subject of our investigation.

With regard to the stress-strain data the monolayer films indicate differences in the strain hardening region of the curves. It seems that the samples PE 469-30-2 (C4) and PE 469-30-5 (C8) behave similarly whereas the strain hardening for the PE 469-30-3 requires lower stress values. The orientation function changes during the stretching of the films; the unfolding of the polymer chains occurs at lower strain for PE 469-30-5 (C8) than in the C4 materials.

In the multilayer systems the Primplast 44 material (C8) shows a lower tendency for reorientation in the strain hardening region than the Coex 82 (C4) material. In this region of the stress-strain curve the lamellar structure is already transferred into the fibrillar arrangement. Regarding the orientation behavior of the material above 200% strain, a small increase in f_b was observed which reflects on f_c where a decrease in the orientation was found. In the octene product the bulky side chains influence the unfolding significantly, producing a higher resistance to unfolding and alignment along the stretching direction. Consequently, the octene copolymer requires higher stress values to be stretched and finally results in a lower stretchability of this material, as observed also on an industrial scale during pallet wrapping tests.

Based on the structural absorbance ratio of the bands at 729 and 719 cm^{-1} changes in the crystallinity were studied. For the continuous stretching experiment the monoclinic phase could not be identified even after the performance of Fourier self-deconvolution and peak fitting approaches. Literature data, however, suggest that this crystalline transformation takes place as a result of mechanical deformation. Therefore, discontinuous stretching experiments which improved the spectral resolution to 1 cm^{-1} were carried out. The deconvoluted spectra now allow the assignment of the monoclinic, orthorhombic and amorphous LLDPE modifications. Analyzing the changes of the intensity of these bands with the elongation does not prove the orthorhombic-monoclinic transformation in the LLDPE films.

Ultimate stretchability and stretching force of the films, both monolayer and multilayer, was well correlated to the development of the crystalline orientation in the films upon stretching. Other mechanical properties like Elmendorf tear and dart impact can also be better understood with these results.

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