FTIR and DSC Study of HDPE Structural Changes and Mechanical Properties Variation When Exposed to Weathering Aging During Canadian Winter

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SYNOPSIS

The aging of high-density polyethylene (HDPE) when exposed to drastic climatic conditions (Canadian winter, characterized by low temperature and abrupt temperature variations between the night and the day) was studied. The importance of degradation was determined by evaluating the microstructural changes in HDPE (i.e., oxidations, ramifications, and polymeric chain breaking) by means of FTIR spectrophotometry. The crystallinity variation in HDPE by FTIR and DSC was also studied. Both techniques led to coherent results: there was a loss of crystallinity due to weathering degradation. This crystallinity reduction produced a drastic decrease in impact energy. However, the other properties evaluated were not significantly affected. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Weather exposed polymeric materials undergo degradation phenomena of aging that has aroused great interest in the specialized scientific world because the aging influences the working life of the polymer. Consequently, several research works were carried out whose main objective was predicting the durability of these materials. Tabb and Koening[1] were the first authors to use the FTIR technique to evaluate the degradation of polyethylene (PE) under given environmental conditions. These authors and D'Esposito and Koening[2] used some film samples and applied the spectral subtraction between the samples aged by UV radiation and the nonirradiated PE. More recently, other works on the accelerated aging of polymers in the laboratory (photo- and thermooxidation reactions) were carried out and their effect was quantified by FTIR spectrophotometry[3] and photoacoustic FTIR.[4] Other studies on the variation of the me-

chanical properties of composites (with PE as a matrix) exposed to low temperature climatic conditions were also analyzed.[5,6]

This work studies the influence of the climatic conditions during the Canadian winter using high-density PE (HDPE) samples exposed to weather conditions during different periods of time. Under these conditions, it is reasonable to think that the chemical changes caused by the climatic degradation will at first sight be due to photochemical reactions (sunlight) and, to a lesser extent, to hydrolytic reactions (environmental moisture). FTIR was used to study the microstructural changes. Similarly, many of these microstructural modifications are thought to originate some changes in the crystalline content. As is well known, crystallinity is closely related to the macroscopic properties of the polymer and this knowledge is fundamental in engineering applications. Therefore, another objective of this work is the study of the crystallinity variation of the polymer subjected to drastic environmental conditions by using two techniques: FTIR and DSC. The variation of the mechanical properties of HDPE exposed to the indicated climated conditions was also analyzed.

EXPERIMENTAL

Materials

HDPE (HDPE 2909, Du Pont, Canada) is a thermoplastic polymer with the following properties: density 960 kg/m^3 and melting flow index 1.35 g/min.

Preparation of HDPE Samples

Samples were prepared in a mold according to ASTM D-638 (type V). The HDPE, previously milled and screened, was compacted in a mold at 3 MPa pressure for 20 min at room temperature. Then it was heated to 150°C and pressure increased to 3.2 MPa for 20 min. Demolding was accomplished by slowly quenching the mold until room temperature to prevent bubble formation.

Environmental Conditions

Samples were weather exposed during different periods of time: 0, 15, 30, 60, and 90 days. Figure 1 shows the daily data about minimum and maximum temperatures during the time studied. In addition to the low temperatures there is a very accentuated difference of temperature between day and night (i.e., thermal fatigue). As a result, treatments can be considered as doubly drastic.

Analytical Techniques

Microstructural changes in the HDPE were determined by FTIR spectrophotometry. In relation to the variation of crystallinity, two instrumental analytical techniques were used: FTIR and DSC.

FTIR Spectrophotometry

A Nicolet 510 M with CsI optics was used to obtain the FTIR spectra. The method to prepare the samples consisted of dispersing the surface of the finely divided sample (9 mg) in a matrix of KBr (300 mg), followed by compression at 167 MPa to compact the pellet.

To evaluate microstructural changes undergone by the HDPE samples, the pertinent spectra were obtained for each of the treatment periods (from 0 to 90 days). Based on the spectral recordings, called "basic," the variations that occurred were analyzed: formation/disappearance, increase/decrease, and displacement of the various bands. To evaluate these differences, subtraction between the various spectra was used by enlarging the spectrum zones that give better information, 775–1540 and 1600–1800 cm^{-1}.
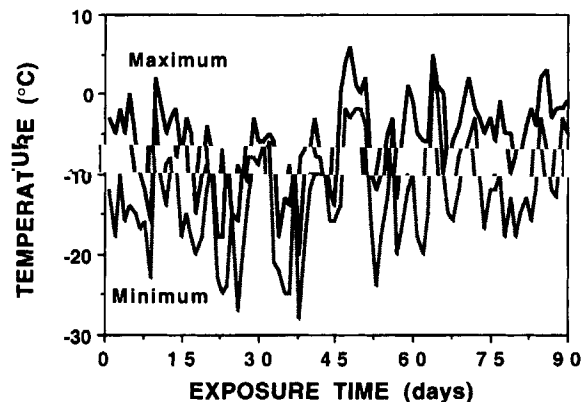

Figure 1 Maximum and minimum values of HDPE temperature during the exposure period to environmental conditions.

These zones include and surpass the spectral zones used in previous works to study the PE aging.[2]

Concerning the crystallinity, the literature indicates that it was first determined by the ratio of the absorption intensities at 1303 cm^{-1} corresponding to the amorphous phase of the solid and melted states.[7] This method implies incertitude as the absorption coefficients in both states are not the same. A procedure based on a universal calibration constant and on the measure of the absorption intensity at 1303 cm^{-1} of the amorphous phase was later developed. Unfortunately, this method can only be applied if the film density and thickness are known.[8]

Zerbi et al.[9] recently suggested the use of spectral bands corresponding to the bending vibrations: 1474 and 730 cm^{-1} (crystalline phase) and 1464 and 720 cm^{-1} (amorphous phase). This procedure was selected for this work as the preparation technique in pellets provides intense absorptions in such spectral bands while the absorption at 1303 cm^{-1} gives low intensity due to the high crystallinity of the HDPE. Therefore, mainly two spectral zones were analyzed: 600–800 cm^{-1} (containing the bands 720 and 730 cm^{-1}) and 1400–1550 cm^{-1} (containing the bands 1464 and 1474 cm^{-1}).

DSC

This technique was used to support the results of crystallinity obtained by FTIR. A DSC 30 Mettler analyzer, with liquid nitrogen, capable of reaching a maximum sensitiveness of 0.4 mJ/s per each 100 divisions of the recording paper was used to obtain the thermograms. The sample weight varied between 2.0 and 3.0 mg. Weights sufficiently small were selected to prevent heat transfer problems, such as was already proved in previous thermogravimetric

studies.[10] The heating rate was 20 K/min, which means a balanced compromise between the measuring speed and the peak resolution. The temperature range analyzed was 50–200°C. The temperature and energy calibration was achieved by means of In, Pb, and Zn standards, under identical analytical conditions of the HDPE samples.

Mechanical Properties

The tensile strength, elasticity modulus, and impact energy were determined by standardized procedures to study the influence of aging on the mechanical properties.

RESULTS AND DISCUSSION

Analysis of Chemical Changes

With the spectral subtractions of the different samples exposed during various periods of time, taking as reference the nondegradated HDPE sample, tables were prepared in which the most relevant results are shown. Table I shows the most significant bands studied and their distinctive functional group. Table II defines the behavior of all the bands specified that are listed according to generated, transformed, or invariable functional groups as the result of the exposure undergone during a period of 15 days. The progress of the microstructural phenomena of configuration as the exposure time increased is shown in Table III.

A comparative study with the results found by D'Esposito and Koening[2] shows a significant coin-

Table II   Functional Groups Resulting from HDPE Aging for 15-Day Exposure Time (by FTIR)

Spectral Bands (cm^{-1})	Generated Groups
(7) 1177	$-CH(CH_3)_2$
(8) 1368	$-C(CH_3)_3$
(10) 1374	$-CH_3$
(9) 1360	$-CO-CH_3$
(11) 1410	$R-CH_2-CO-CH_2-R'$
(13) 1692	$R-CO-OR'$
(14) 1738	$R-CO-OR'$
	Transformed Groups
(2) 909	$R-CH=CH_2$
(12) 1653	$RHC=CHR'$ (cis), terminal insaturations related to (2)
	Unchanged Groups
(1) 900	$R'RC=CH_2$
(3) 971	(trans) $RCH=CHR'$
(4) 990	$RCH=CH_2$
(5) 1068	$RCH_2-CHOH-CH_2R'$
(6) 1131	$-CH_2-C(CH_2R)OH-CH_2$

cidence in most of the bands studied, although some discrepant bands also occur. These discrepant values are corroborated by characteristic and original bands pertaining to the region of 1700–1800 cm^{-1} that were not included in the above-mentioned work, even though these bands are confirmatory of groups obtained within the range 750–1425 cm^{-1}. On comparing

Table I   Spectral FTIR Bands Studied

Wave Number (cm^{-1})	Functional Groups	Type of Vibration
(1) 900	$RR'C=CH_2$	$C-H$ rocking
(2) 909	$RCH=CH_2$	$C-CH_2$ out of plane bending
(3) 971	(trans) $R'CH=CHR$	$=C-CH$ bending, R and R' are alkyl groups
(4) 990	$RCH=CH_2$	$=C-H$ out of plane bending, related to (2)
(5) 1068	$RCH_2-CHOH-CH_2R'$	$C-O$ stretching, corresponding to a secondary alcohol, R and R' are groups with insaturations
(6) 1131	$RCH_2-COH(CH_3)-CH_2-$	$C-O$ stretching, corresponding to a tertiary alcohol
(7) 1177	$-CH(CH_3)_2$	$C-C$ stretching and $C-C-H$ bending
(8) 1368	$-C(CH_3)_3$	Doblet in $C-H$ bending
(9) 1360	$-CO-CH_3$	$-CH_3$ symmetric vibration in a ether
(10) 1375	$-CH_3$	$C-H$ symmetric bending
(11) 1410	$RCH_2-CO-CH_2R$	$-CH_2-$ scissoring
(12) 1653	(cis) $R'CH=CHR$	Terminal bond vibration where R and R' are alkyl chains
(13) 1692	$R-CO-OR'$	$C=C$ stretching where R and R' are vinyl groups
(14) 1738	$R-CO-OR'$	$C=O$ stretching where R and R' are alkyl groups

Table III   Types of Spectral Bands Resulting from HDPE Aging for 15, 60, and 90-Day Exposure Time to Environmental Conditions (by FTIR)

Intensity Increase, Generated groups (cm⁻¹)	Intensity Decrease, Transformed Groups (cm⁻¹)	Unchanged Intensity (cm⁻¹)
15 Days		
900, 1177, 1368, 1375, 1360, 1410, 1692, 1738	909, 990, 1653	971, 1068, 1131
60 Days		
900, 971, 1368, 1375, 1360, 1131, 1692, 1738	909, 990, 1068, 1653	1177, 1410
90 Days		
900, 971, 1368, 1375, 1360, 1131, 1692, 1738	909, 990, 1068, 1653	1177, 1410

the results of the first 15 and 30 days of exposure, the trend followed by the increase bands (generation of groups) and the decrease bands (transformation of groups) remain unchanged. Bands at 900 and 990 cm⁻¹ initially belonging to the invariant group are incorporated, respectively, to the increase and decrease blocks. Results at 60-days degradation confirm the previously mentioned values. The characteristic block of transformed groups was increased by the incorporation of an invariant band while the characteristic block of generated groups did not change. In view of these results, it was confirmed that the microstructural changes undergo alterations during the first 60 days of exposure, thus becoming stable.

The results confirm the microstructural configuration modifications occurring in the polymeric chains. Such modifications are defined by a series of mechanisms involved in the HDPE degradation:

1. *chain breaking* with the formation of characteristic groups (methyl, terbutyl, isopropyl, and end insaturations) due to homolytic and heterolytic dissociations reflected in the positive evolution bands (900, 1177, 1368, 1375, and 1678 cm⁻¹);
2. *chain branching* with generated groups defined by bands 1177, 1368, and 1375 cm⁻¹ and with transformed groups (909, 990, and 1653 cm⁻¹) that confirm these modifications;
3. *crosslinks* between polymeric chains caused by additive reactions on double linkages. The characteristic groups defining this type of modification appear in the negative evolution bands (909 and 1653 cm⁻¹);

4. *oxidation phenomena* defined by the positive evolution bands (1760, 1410, 1692, and 1675 cm⁻¹) and involving the formation of peroxides, alcohol groups, and carboxylic groups.

To summarize this study, Table IV shows the evolution of the different characteristic bands that define every phenomenon occurring in the configurational variations and their relationships to the various exposure times.

Crystallinity Variation

The empirical relation proposed by Zerbi et al.[9] was used to evaluate crystallinity:

$$X = \frac{\dfrac{1 - I_a/I_b}{1.233}}{1 + \dfrac{I_a}{I_b}} \cdot 100$$

where X is the percentage of the amorphous content, I_a and I_b the intensities of absorption in the bands of 730 and 720 cm⁻¹ or, alternatively, at 1474 and 1464 cm⁻¹, respectively. The constant 1.233 corresponds to the relations of intensity bands of fully crystalline HDPE.

Table V illustrates the variation of the HDPE amorphous and crystalline content as a function of the exposure time and the calorimetric features (initial and final melting temperatures and the melting enthalpy). Results show relevant discrepancies according to the spectral bands selected for

Table IV   HDPE Microstructural Variations as a Function of Exposure Time (by FTIR)

			Chain Breaking		
Days	900 cm^{-1}	971 cm^{-1}	1177 cm^{-1}	1368 cm^{-1}	1374 cm^{-1}
15	inv	inv	+	++	inv
30	+	inv	+	++	+
60	++	+	±	++	++
90	++	++	±	++	++

				Chain Branching			
	900	909	971	990	1177	1368	1374	1653
15	inv	−	inv	inv	+	++	inv	− − −
30	+	− −	inv	−	+	++	+	− − −
60	++	− − −	+	−	±	++	++	− −
90	++	− − −	++	−	±	++	++	−

		Oxidation Phenomena		
	1360 cm^{-1}	1410 cm^{-1}	1692 cm^{-1}	1738 cm^{-1}
15	+	+	++	++
30	++	+	+++	++
60	+++	±	+++	++
90	++	±	++	+++

Inv, unchanged; (+) increase; (−) decrease; (±) slight increase.

the evaluation of the content in both the amorphous and crystalline phases. The intensity ratio 730/720 cm^{-1} leads to random results for crystallinity without the possibility of establishing the level of degradation in terms of its duration. In addition, the crystallinity varies in the range 71.5–76.6%, values too low for the HDPE, which is a highly crystalline polymer. The density and also the melt flow index of HDPE confirm that it is a material prepared with a Phillips-type catalyst, whose crystallinity is around 90%.[11] The conclusion from these facts is that the measurement of crystallinity through the bands 730/720 cm^{-1} is not adequate. On the contrary, the bands 1474/1464 cm^{-1} indicates that the crystallinity progressively decreases, while the weathering exposure time increases, from 98 to 95%. Moreover, these

Table V   Variation of HDPE Amorphous and Crystalline Contents (by FTIR), Temperatures, and Melting Enthalpy (by DSC) as a Function of Exposure Time

|	Spectral Bands					
	$I_a = 730 \text{ cm}^{-1}$ $I_b = 720 \text{ cm}^{-1}$		$I_a = 1474 \text{ cm}^{-1}$ $I_b = 1464 \text{ cm}^{-1}$		Initial and	
Exposure Time (Days)	Amorphous Content (%)	Crystalline Content (%)	Amorphous Content (%)	Crystalline Content (%)	Final Melting Temperatures (°C)	Melting Enthalpy (J/g)
0	28.10	71.90	2.02	97.98	126.7–149.8	221.4
15	28.52	71.48	3.76	96.24	127.3–145.9	215.3
30	26.98	73.02	4.16	95.84	127.1–145.2	212.8
60	26.35	73.65	4.80	95.20	126.3–145.7	211.2
90	27.38	72.62	4.88	95.12	123.6–142.1	210.7
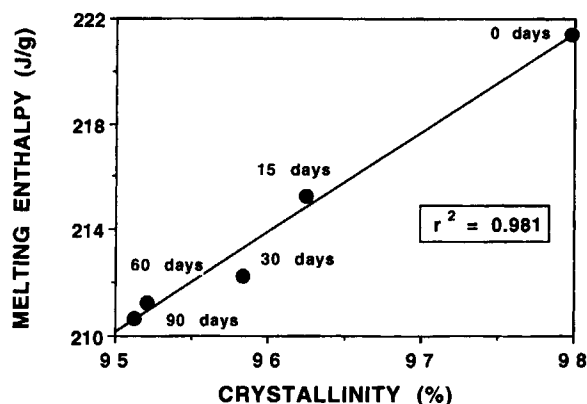
Figure 2 Relation between melting enthalpy and crystallinity of HDPE.

values are rather similar to the HDPE ones of this study. On the other hand, the calorimetry study that follows supports the validity of using the bands 1474/1464 cm^{-1}. In effect, from the thermograms obtained it is clear (see Table V) the melting enthalpy decreases (i.e., crystallinity decrease) as the exposure time increases. This article has demonstrated that aging is caused by specific chemical transformations undergone by the polymeric chains. These reactive phenomena decrease the linear character of the polymeric chains caused by the formation of bulky groups, which leads to an increase of the amorphous content. Therefore, the crystallinity results found by DSC are in accordance with those recorded by FTIR in the bands 1474/1464 cm^{-1}. Figure 2 proves the actual linear relation between the melting enthalpy and the HDPE crystallinity degree. This correlation indicates that per each 1% of less crystallinity due to the aging process, the melting enthalpy decreases by 3.8 J/g. By extrapolation of the straight line at 100% crystallinity, a melting enthalpy of 229.0 J/g is obtained, corresponding to the fully crystalline HDPE.

Table VI shows the evolution of the mechanical properties studied. The decrease of the impact energy caused by the formation of bulky groups, im-

parting stiffness to the polymeric chains, is remarkable. The rest of the mechanical properties evaluated (tensile strength and Young's modulus) do not vary significantly with exposure, something to be expected as their characteristics basically depend on crystallinity. To be noted is that the HDPE crystallinity varies not more than 3% (environmental exposure of 90 days).

CONCLUSIONS

HDPE undergoes aging when submitted to drastic climatic conditions such as the Canadian winter: low temperature and sharp temperature changes between day and night (i.e., intense thermal fatigue). This aging becomes apparent by a series of chemical changes in the polymeric chains and a progressive decrease of HDPE crystallinity if the weathering exposure time increases.

The study of the spectral bands of samples degradated during different weathering exposure times demonstrated the existence of a series of microstructural modifications: chain breaking, chain branching, crosslinking, and oxidation. These configuration changes obviously influence the polymer crystallinity that was evaluated by quantifying the absorption intensity FTIR in two spectral bands: one characteristic of the amorphous phase and another of the crystalline phase. Two zones of the spectrum corresponding to vibrations of deformation, 730/720 cm^{-1} and 1474/1464 cm^{-1} were analyzed. The use of the bands 1474/1464 cm^{-1} was appropriate for the evaluation of crystallinity while the bands 730/720 cm^{-1} yielded random and too low results (71–77% with respect to the values that should be obtained for HDPE prepared with a Phillips-type catalyst, usually higher than 90%). Consequently, the use of the latter bands to evaluate the percentage of the polymer crystalline character was rejected. The results of DSC ratify the results accomplished by FTIR at 1474/1464 cm^{-1}, as the

Table VI   Variation of HDPE Mechanical Properties as a Function of Exposure Time

Exposure Time (Days)	Tensile Strength (MPa)	Young's Modulus (GPa)	Impact Energy (mJ)
0	23.1	1.46	80.6
15	24.5	1.49	70.2
30	22.6	1.53	64.9
60	22.6	1.52	41.9
90	23.6	1.40	37.7

melting enthalpy, and therefore crystallinity, decrease with the weathering exposure time. Similarly, a linear relation between the melting enthalpy and crystallinity was made evident in such a way that 1% less crystallinity involves a 38 J/g decrease of the melting enthalpy. By application of this straight line and extrapolation at 100% crystallinity, a value of 229.0 J/g for the melting enthalpy was found, which should correspond to an ideal, fully crystalline HDPE. The property most affected by aging phenomena is the impact energy owing to the stiffness of the polymeric chains. The other mechanical properties evaluated (tensile strength and elasticity modulus) remain almost constant as they basically depend on the crystalline content of the polymer that decreases approximately 3% after 90 days of weathering exposure.

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