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# Assessment of Changes Due to Accelerated Weathering of Low-Density Polyethylene/Feather Composites

Iuliana Spiridon,<sup>†</sup> Oana Maria Paduraru,<sup>†</sup> Marek Rudowski,<sup>‡</sup> Marek Kozlowski,<sup>‡</sup> and Raluca Nicoleta Darie\*,†

ABSTRACT: In this study, property changes of controlled aged LDPE/feather composites in comparison to those of nonaged samples were investigated by mechanical tests, dynamic rheological and thermal tests, infrared spectroscopy, and oxygen permeability analysis. The viscoelastic behavior of the aged composites was modified, whereas a pseudoplastic character was observed for the nonaged samples. After weathering, infrared spectroscopy indicated the formation of carbonyl and vinyl groups, and the oxygen permeability became significantly higher than for the reference samples. DSC results showed  $\alpha$ -helix denaturation of keratin after aging and an increase in crystallinity due to reinforcement of composites containing feather fibers upon UV exposure. An aging time of 500 h was found to induce surface degradation of composites, especially for a feather fiber loading of 10 wt %.

#### 1. INTRODUCTION

Environmental concerns have led to a growing interest in replacing traditional materials with "greener" alternatives. 1,2 This is due to both environmental concerns and the foreseen future scarcity of oil and oil-derived products. Currently, efforts are being directed toward developing materials that are environmentally friendly and obtained from renewable resources, particularly polysaccharides, lipids, and proteins. Some experiments have focused on proteins, which might be more robust than carbohydrates.3,4

Keratin is the major structural fibrous protein contained in outer coverings such as feathers, hair, wool, nails, and horns of mammals, reptiles, and birds. 5 Disposal of keratin wastes represents a considerable environmental problem. According to their microstructural characterization, chicken feather fibers have several attractive features such as surface flexibility, toughness, high length-to-diameter ratio, hydrophobicity, and a highly organized morphology characterized by a complex hierarchical structure.<sup>6</sup> Keratin has been found to contain a high percentage of cysteine residues (7-20% of the total amino acid residues). These residues are oxidized to give inter- and intramolecular disulfide bonds, which contribute to the mechanically strong three-dimensionally cross-linked network of proteins comprising keratin fibers. It is possible to develop biodegradable materials based on keratin (e.g., by solution casting to form films). Ideally, the regeneration of disulfide bonds in these materials during the drying of film-forming dispersions could be used as a method to impart water insolubility and good mechanical properties to keratin-based materials. Chemically cross-linked keratin films and keratinchitosan composite films have been characterized.<sup>7-9</sup> At the same time, composites based on polyolefin and keratin fibers have been obtained and characterized. 10-13 The amino acid sequence of feather keratin shows that the protein has 40% hydrophilic and 60% hydrophobic groups. 14 Therefore, keratin feather fibers should be compatible with hydrophobic polymers to a certain degree.

Composite materials are exposed during their lifetime to external effects, such as heat, weathering, and electrical stress, that lead to a deterioration of their mechanical properties. Knowledge of resistance to weathering, not only for aesthetic aspects but also for changes in properties, is thus an important

Our study is focused on material performance analysis. Feather keratin waste from poultry processing was meltblended with low-density polyethylene (LDPE), resulting in clear, flexible polymer blends. The goal was to produce an easily processed, environmentally friendly, value-added product containing a waste stream and to provide more evidence on accelerated weathering-induced cross-linking, which has not previously been reported. The behavior of LDPE/feather composites upon accelerated aging was analyzed, and the changes were investigated by Fourier transform infrared (FT-IR) spectroscopy; differential scanning calorimetry (DSC); and the evaluation of mechanical, rheological, and permeability properties.

#### 2. EXPERIMENTAL SECTION

2.1. Materials. Low-density polyethylene (LDPE), virgin material type A22FMA/002, having a melt temperature of 110 °C and a melt flow index (10 min) of 0.3 g, was supplied by Petrom S.A. (Bucharest, Romania).

A mixture of small and large chicken feathers was washed with ethanol and dried until clean white in color, sanitized, and odor-free. The feathers were then ground in a Retsch PM200

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planetary ball mill and sieved. Fractions of sieved fibers greater than 30  $\mu$ m and smaller than 70  $\mu$ m were used in this analysis. The resulting fibers had average diameter/length ratios of 50  $\mu$ m/0.1–0.2 cm, as determined by laser diffraction (Mastersizer 2000, Malvern Instruments). The resulting feather fibers were semicrystalline, with a density of 0.89 g cm<sup>-3</sup>.

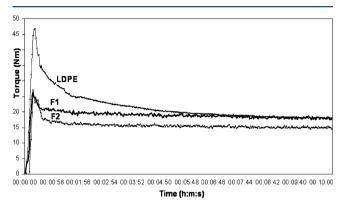
- **2.2. Composite Preparation.** Composites were prepared in a Brabender mixing head with mixer blades rotating at 75 rpm for 10 min, at a temperature of 140 °C. Composites with feather fiber loadings of 5 wt % (F1) and 10 wt % (F2) were obtained. Before mixing, the components were dried in a vacuum oven for 24 h at a temperature of 80 °C. After mixing, the samples were sandwiched between Teflon-coated foils and pressed into thin sheets in a Carver 4394 press at 140 °C for 8 min, of which 4 min were for premelting. After the material had been pressed, it was prepared for mechanical tests.
- **2.3. Weathering Procedure.** LDPE and composite samples were placed in a laboratory chamber, where they were exposed to artificial light from a mercury lamp ( $200 < \lambda < 700$  nm, incident light intensity = 39 mW cm<sup>-2</sup>) to accelerate weathering. The climatic conditions used were a temperature of 40 °C and a relative humidity of 60%. All samples were kept under these conditions and then removed after every 100 h, analyzed, and compared with nonirradiated (reference) samples.
- **2.4.** Investigation Methods. 2.4.1. Mechanical Properties. Tensile tests were conducted according to standard test method SR EN ISO 527-2/1996, using an Instron tensile tester 3345 with a 5-kN load cell at a rate of 30 mm min<sup>-1</sup>. At least seven samples were tested for each composition, and the results are presented as an average for the tested samples.

Charpy impact tests were performed according to standard test method SR EN ISO 179/2001 on a Resil Impactor test machine manufactured by CEAST (Pianezza, Italy). A 50-J Charpy-type hammer was used to impact the un-notched samples. At least seven samples were tested for each composition.

- 2.4.2. FT-IR Spectroscopy. FT-IR spectra of composite materials were recorded on solid sample in KBr pellets by using a DIGILAB Scimitar Series FT-IR spectrometer (Holliston, MA) with a resolution of 4 cm<sup>-1</sup> and a scanning range from 400 to 4000 cm<sup>-1</sup>.
- 2.4.3. Dynamic Rheology. Frequency sweep tests were performed on the melt state using an Anton Paar rheometer equipped with a CTD450 convection heating device, in parallel-plate geometry and oscillatory mode, at a testing temperature of 140 °C. Disk-shaped samples of 1-mm thickness and 25-mm diameter were used.
- 2.4.4. Differential Scanning Calorimetry (DSC). DSC measurements were performed on a model STA 449 F1 Jupiter system (Netzsch, Selb, Germany), consisting of a thermogravimetric analyzer coupled with a differential scanning calorimeter. Samples of about 6 mg were heated from 25 to 600 °C at a rate of 10 °C min $^{-1}$  in a nitrogen atmosphere. Crucibles made of  $Al_2O_3$  were used for both samples and reference materials.
- 2.4.5. Permeability Tests. Oxygen permeability measurements were performed using a MultiPerm oxygen and water vapor permeability analyzer (ExtraSolution, Pisa, Italy) at 25  $^{\circ}$ C and 50% humidity. All samples were pressed into foils with an average thickness of 0.3  $\pm$  0.02 mm. The mean values for sets of three samples are reported.

#### 3. RESULTS AND DISCUSSION

**3.1. Compounding Characteristics.** Figure 1 shows the relationship between mixing torque and processing time. The



**Figure 1.** Torque variation versus mixing time during composite processing.

changes in mixing torque during the compounding of polyethylene with feather fibers can be related to the melt viscosity. During processing in the melt state, the molten polymer should spread over and adhere to the fibers, creating a strong adhesive bond. LDPE demonstrates a high viscosity because of chain entanglement. Addition of feathers lowers the torque compared to that of LDPE alone. This could be due to LDPE orienting along the feathers during mixing and/or the feathers partially disrupting the entanglement of LDPE chains.

The torque approached a stable value after about 8 min in the processing of LDPE alone, whereas for LDPE/feather systems, a constant blending torque was reached after only 1–2 min, probably because of shear thinning from the orientation of the fibers in the flow (Figure 1). The torque recorded during melt processing for composites containing feathers decreased as the feather fiber content was increased from 5 to 10 wt %. In these cases, the rotor's movement was not constrained as it was in the processing of neat LDPE.

**3.2.** Mechanical Properties of the Composites. *3.2.1. Impact Results.* The impact energy is a combination of crack initiation and crack propagation phenomena, which depend on various factors such as fiber-to-matrix adhesion, toughness of the matrix and fiber alone, defects in the packing of fiber/matrix, and crystalline morphology. <sup>15</sup>

The impact strength of the LDPE/feather composites was higher than that of the neat polyethylene matrix. A high degree of the impact strength of the composites derives from the matrix (LDPE) itself, given that it represents 95 wt % of sample F1 and 90 wt % of sample F2, but keratin also plays a role. The feather fibers appear to act as stress concentrators in the polymer matrix, thus reducing the crack initiation energy and consequently enhancing the impact strength of the composites.

The structure of keratin, the primary constituent of chicken feathers, affects the chemical durability. Because of extensive cross-linking and strong covalent bonding within its structure, keratin provides high resistance to degradation.<sup>16</sup>

The decrease of impact strength of the composites after 100 h of exposure to accelerated weathering can be explained by a reorganization of the fiber's structure at the surface. From the impact results obtained in our study and plotted in Figure 2, there seems to be a critical exposure time between 300 and 400 h under the studied weathering conditions, after which the

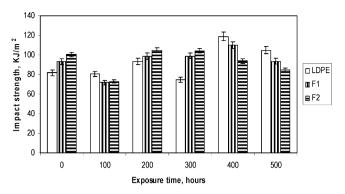


Figure 2. Impact strength variation with exposure time for LDPE, F1, and F2.

composites with 10 wt % feather fibers lose their impact strength; the same trend was recorded between 400 and 500 h for composite F1 (5 wt % feather loading). The chemistry of keratin is still under research, and few studies have investigated its modification under accelerated weathering conditions, especially when used in composites. von Endt et al. reported that the disulfide bonds of cysteine are susceptible to reduction, whereas both the S-methyl group of methionine and the thiol group of cysteine are susceptible to oxidation. The At longer exposure times, keratin degradation leads to the formation of chromophoric groups that accelerate the material's photo-oxidation and deteriorate its impact strength. It seems that, because of its higher keratin content, composite F2 was affected by the weathering conditions used in this study more than composite F1.

3.2.2. Tensile Results. Tensile strength is one of the most important properties of plastic composites, as heterogeneous substances incorporated into a homogeneous matrix affect the composite properties.

Linear polyolefins and their copolymers are preferred for applications involving exposure to different weather conditions. Keratin's well-ordered structure gives it a high tensile strength even before being added to a composite. Keratin essentially "heals" itself when subjected to a mechanical load through structural rearrangements in the molecular chain. It was found that, under normal conditions, the incorporation of feather fibers increased the Young's modulus of the studied composites. The effect became stronger as the feather fiber content increased. Specifically, an improvement of 28% in the Young's modulus value was obtained for the composites with a 10 wt % loading of feather fibers, as compared to that of LDPE, so reinforcement of the LDPE polymer matrix can be achieved by addition of keratin-containing feather fibers. The exact mechanism of the aging process is not known. However, when the systems were exposed to accelerated weathering, they predominantly underwent cross-linking and started losing their rubbery characteristics, which resulted in progressively increasing brittleness. Figure 3 provides evidence for some structural change occurring upon weathering, such as crosslinking between the fibers and matrix. The modulus data do not show any conclusive evidence of chain scissioning of the LDPE, so there had to be changes in the keratin and/or keratin/LDPE

It was observed that the elastic modulus changes for LDPE were limited to the first 400 h of irradiation, during which a slight increase of the Young's modulus values was recorded for composite F2, thanks to the stiffening effect of the feathers. At a

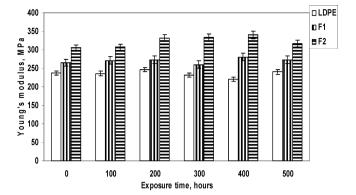


Figure 3. Young's modulus values for LDPE, F1, and F2 plotted as a function of the exposure time.

longer exposure time (500 h), just a 10% reduction of the Young's modulus value was observed for composite F2 compared with the value obtained at 400 h, but the overall elastic modulus values were not affected for LDPE and composite F1 as compared to the values recorded under normal conditions. The modulus drop after 500 h for composite F2 was probably caused by some breakdown in the keratin because the LDPE was not much affected.

The decline observed at 500 h for composite F2 can be attributed to the embrittlement caused by the extent of crosslinking, which restricts the degree of orientation of the polymer chains. Slow displacement of LDPE from between the surface coating of keratin molecules could also occur, resulting in keratin molecules being closer together, which would allow an increase in cross-linking. Enhancement of the mechanical properties of polymers can be explained by the orientation of polymer molecules under stress factors, although the Young's modulus will decrease if cross-linking hinders the degree of orientation of the molecular chains. 18 Therefore, the Young's modulus decline for composite F2 after 400 h reflects the extent of cross-linking achieved upon UV exposure. D'Arcy and Watt reported that the minimum-energy configuration of a hydrogen-bonded network substrate is required for stabilization of an aged fiber, but also for prevention of rearrangements to higher energy levels in environments with different levels of humidity. 19 In the case of the studied composites, because the feather fibers were covered by the LDPE matrix, for the weathering time employed, the fibers were not significantly affected. These results show that, when subjected to accelerated weathering up to 500 h, feather fibers generally have good mechanical properties, as compared to the polymer matrix, probably because the photo-oxidation mainly affects the polymer itself under the applied experimental conditions or when exposed to climatic conditions. The carbonyl and vinyl frequencies in the FT-IR spectra were thus investigated for evidence of chemical changes from aging.

**3.3. FT-IR Spectroscopy.** Keratin proteins give rise to several characteristic absorption bands known as amide A (3286 cm $^{-1}$ ), amide B (3056-3075 cm $^{-1}$ ), amide I (1600-1700 cm $^{-1}$ ), amide II (1480-1580 cm $^{-1}$ ), and amide III (1220-1300 cm $^{-1}$ ). The C-S stretching vibration corresponds to a 718 cm $^{-1}$  peak in the IR spectrum, whereas the C-S bending vibration can be found at 500-400 cm $^{-1}$ 20

The spectra plotted in Figure 4 for neat LDPE and the studied composites under normal conditions showed that, for F1 and F2, two peaks belonging to keratin appeared at 1260

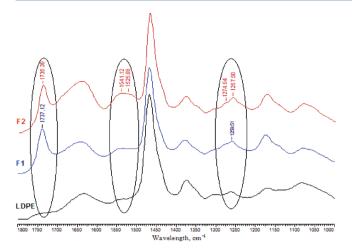


Figure 4. FT-IR spectra related to the amide region of LDPE, F1, and F2.

and 1540 cm<sup>-1</sup>, meaning that the amide II and III absorption bands were recorded for the composites containing feather fibers. The peak at ~1550 cm<sup>-1</sup> corresponds to N–H bending coupled with C–N stretching. The 1680–1620 cm<sup>-1</sup> range is related to alkene C=C stretching, possible formed due to melt (thermal) processing. FT-IR spectroscopy was used to obtain evidence of composite modifications occurring under accelerated weathering conditions through the investigation of changes in the carbonyl group. Carbonyl groups are postulated to be the main light-absorbing species responsible for the photochemical-induced degradation reactions of UV-exposed polymers, partly responsible for the formation of nano-/microcracks at the surface of the polymer. The structural changes in the matrix upon weathering were investigated by following vinyl group formation in both neat LDPE and LDPE/feather composites.

The carbonyl index and vinyl index were calculated using the equations

carbonyl index = 
$$I_{1715}/I_{2912}$$
 (1)

and

vinyl index = 
$$I_{908}/I_{2912}$$
 (2)

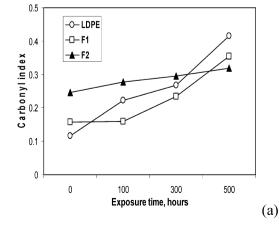
where *I* represents the peak intensity at a given wavenumber.<sup>21</sup> The peak intensity at 2912 cm<sup>-1</sup>, which corresponds to the

alkane CH stretching vibration, was chosen as the reference because it changed the least during weathering.

Initially, the carbonyl index was higher for feather/LDPE composites than for neat LDPE (Figure 5a), being proportional to the amount of feather fibers incorporated in the matrix. As result of UV exposure, the carbonyl index increased with exposure time, as a result of chain scission.<sup>22</sup> The increase in carbonyl group formation for polyethylene upon weathering is known to be proportional to the number of chain scissions occurring in the polymer. These results indicate that chain scission might have occurred upon exposure and that the number of chain scissions and, thus, surface oxidation for LDPE/feather composites increased at an exposure time of 500 h. Higher values of the carbonyl index were recorded for composite F2 up to a 400-h exposure time, following an almost constant trend. The formation of vinyl groups is an indication of polymer chain scission, which can be a result of carbonyl degradation through a Norrish type II reaction.<sup>23</sup> During weathering, evidence was found for the formation of vinyl groups (Figure 5b). It was found that, in the early stage, vinyl group formation was delayed, but a longer UV exposure time resulted in an increase in the vinyl index for the LDPE matrix. The change in vinyl group concentration is thought to be mainly due to degradation of the LDPE matrix of LDPE/ feather composites.

**3.4. Rheological Behavior.** The rheological behavior of low-density polyethylene/feather fiber composites was investigated in the melt state for two feather loadings through oscillatory rheological tests in the linear domain of viscoelasticity. The storage modulus (G') is more sensitive to structural changes in the polymer than the loss modulus (G''). The effects of keratin content and 500-h exposure time on G', G'', and the complex viscosity  $(\eta^*)$  of LDPE and composites F1 and F2 were investigated, and the results are shown in Figure 6a–d. From the crossover frequency  $(\omega_i)$ , the relaxation time  $(\theta)$  can be calculated as  $\theta = 1/\omega_i$ .

Figure 6a shows the viscoelastic response of a well-entangled LDPE melt. At low oscillation frequency ( $\omega$ ), G'' exceeds G', whereas at high  $\omega$  value, elastic behavior is predominant. The crossover frequency,  $\omega_i$  (where G' = G''), is located at 0.36 s<sup>-1</sup>, which corresponds to a relaxation time of 2.77 s. Below this critical frequency, the polymer melt presents a liquidlike relaxation, as was also found by Khan and Prud'homme.<sup>25</sup> Upon the incorporation of feather fibers, the rigidity of the matrix polymer increased, which resulted in an increase in G'.



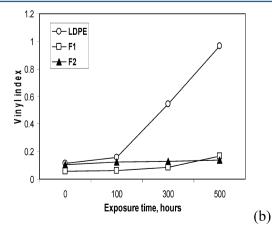


Figure 5. Variations in (a) carbonyl index and (b) vinyl index with exposure time for the studied samples.

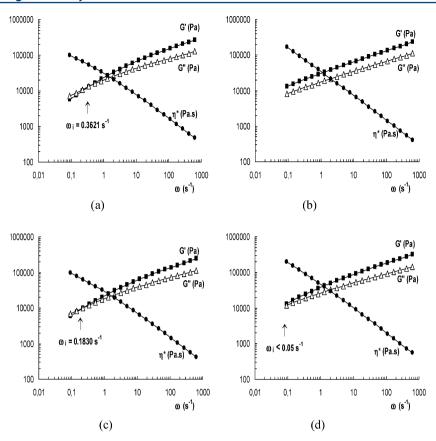


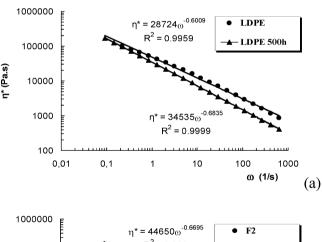
Figure 6. Correlation between viscous and elastic behaviors for nonaged and aged systems: (a) LDPE, (b) LDPE 500 h, (c) F2, and (d) F2 500 h.

These results show that reinforcement of the polymer matrix can be achieved through the addition of keratin-containing feathers.

By analyzing the plots presented in Figure 6, one can observe that, for low  $\omega$  values ( $\omega$  < 0.36 s<sup>-1</sup>), most of the samples had a predominantly viscous behavior (G'' > G'), except for LDPE that underwent accelerated conditioning. In this case, modulus crossover was not realized, as G' was higher than G'' for all testing frequencies. For the aged sample containing 5 wt % feather fibers (F1 500 h), a 22.5-fold increase in relaxation time was observed compared to the same composite before aging, whereas for sample F2 500 h, the same parameter increased by a factor of 5. These results can be attributed to the fact that, at low frequency, there is enough time to unfold the chains, so they relax slowly. This high relaxation tends to reduce the G' and G'' values. However, when polymer chains were deformed at higher frequency, the entangled chains have less time for reorientation, resulting in increased moduli.

For all samples, the variation of complex viscosity  $\eta^*$  as a function of angular frequency decreased linearly with an increase in the angular frequency, because of the shear thinning behavior of the blend in the molten state, <sup>26</sup> thus showing the pseudoplastic character of the studied materials.  $\eta^*$  was found to vary as  $\omega^{-0.6}$  for LDPE and as  $\omega^{-0.63}$  for composite F2 under normal conditions.

Figure 7a shows that, at low oscillation frequencies, no significant differences could be observed between LDPE's dynamic viscosities under normal conditions and after 500 h of exposure, whereas for  $\omega > 0.5~{\rm s}^{-1}$ , the chains are reoriented, giving different values of the  $\omega$  exponent in the viscosity relation and a decrease of the viscosity after 500 h of irradiation, thus supporting chain scissioning. The rheological tests were



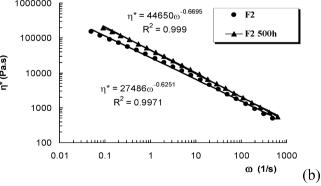
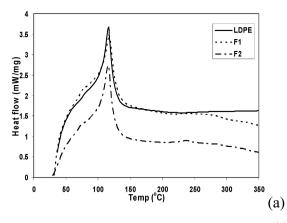


Figure 7. Variation of complex viscosity with angular frequency for nonaged and aged LDPE and composite F2.



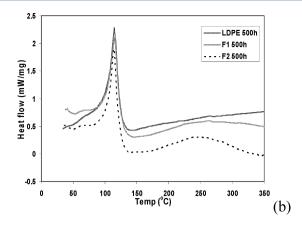


Figure 8. DSC thermograms for studied LDPE/feather composites (a) before and (b) after artificial aging.

performed in the melt state; it is possible that, in the solid state, at the modified surface of LDPE after 500 h of exposure, the scissioned chains interacted, leading to some extent of crosslinking, correlated with increases in the Young's modulus and impact strength.

The increase in viscosity with the time of exposure to accelerated weathering induced cross-linking of the blends. After 500 h of UV exposure time,  $\eta^*$  varied as  $\omega^{-0.68}$  for LDPE and as  $\omega^{-0.67}$  for composite F2 (Figure 7a,b). Thus, it is evident that the processability of the blends was affected by UV exposure.

**3.5. Thermal Analysis of LDPE/Feather Fiber Systems.** The thermal properties of LDPE and the composites were assessed using differential scanning calorimetry (DSC). The first heating cycle yields information about the state of the polymer as a function of processing conditions; therefore, these results are reported herein. The melting temperature during the first heating cycle,  $T_{\rm m}$ , and the melting enthalpy of the first heating cycle,  $\Delta H_{\rm m}$ , were determined. The crystalline fraction of each polymer and composite was determined from the DSC

$$X = \Delta H_{\rm m} / \Delta H_{\rm m}^{\circ} (1 - m_{\rm f}) \tag{3}$$

results using the equation 1

where  $\Delta H_{\rm m}^{\circ}$  is the theoretical melting enthalpy of 100% crystalline PE, namely,  $\Delta H_{\rm m}^{\circ}=290~{\rm J~g^{-1}},^{27}$  and  $m_{\rm f}$  is the mass fraction of feathers incorporated in the blend. Joseph et al. and Barone determined the crystallinities of polyolefin composites in a similar manner.

When semicrystalline polymers are used as the matrix material for short-fiber-reinforced composites, a "trans-crystalline" layer can develop at the fiber/polymer interface. 28 The fiber surface can serve as a nucleation site for polymer crystals, and the crystals that form at the fiber surface are different from the crystals formed in the bulk polymer. Figure 8 shows the DSC curves of the systems containing feather keratin produced by melt blending compared with that of the pure LDPE used as the matrix under normal conditions (Figure 8a) and after controlled weathering (Figure 8b), and the thermal data obtained from DSC curves are presented in Table 1. By following the results recorded under normal conditions, one can observe that the incorporation of feather affected the melting temperatures  $(T_{\rm m})$  and melting enthalpies  $(\Delta H_{\rm m})$  of the composites in different ways compared to the LDPE matrix. A slight increase in  $T_{\mathrm{m}}$  was recorded for composite F1 (incorporation of 5 wt % feather fibers in LDPE), whereas composite F2 (10 wt %) exhibited a 2  $^{\circ}$ C decrease of  $T_{\rm m}$ .

Table 1. Melting Temperatures, Melting Enthalpies, and Crystallinity Degrees of the Studied Blends from DSC Data

	T <sub>m</sub> (°C)		$\Delta H_{\rm m} \; ({ m J/g})$		
sample	peak I	peak II	peak I	peak II	$X_{\rm total}$
LDPE	116.4	_	110.60	-	0.38
F1	116.9	250.1	119.43	23.13	0.47
F2	114.5	247.2	117.60	25.63	0.44
LDPE 500 h	114.8	_	104.78	_	0.36
F1 500 h	115.6	252.5	71.81	95.15	0.55
F2 500 h	112.9	230.4	70.58	75.16	0.45

The crystallization behavior of a polymer in a blend is affected by many factors, such as composition, thermal history, interfacial interactions, size of dispersed particles, and size distribution. If the dispersion is fine enough, other equilibrium and nonequilibrium phenomena should be considered. In the presence of very small particles, the character of nucleation changes: Different types of heterogeneous nuclei become activated, or even homogeneous nucleation occurs.<sup>29,30</sup> In the DSC curves recorded for our systems, a smaller melting peak could be identified over 200 °C for the composites containing keratin. The endothermal peak occurring in the 200-250 °C temperature range is related to  $\alpha$ -helix denaturation, and the area under the curve is a measure of the  $\alpha$ -helix content.<sup>31</sup> whereas the endothermal peak falling at ~260 °C is caused by the denaturation of  $\beta$  structures.<sup>32</sup> The fact that the crystallinity of the samples increased upon incorporation of feather fibers within the LDPE matrix might be due to an increase in larger crystals residing closer to the fibers.

For a doubling of the amount of fibers (10 wt % in composite F2), the architecture of the chains affected the interaction of the polymer with the fibers, so a slightly decrease of the crystallinity degree was recorded for sample F2 as compared to sample F1, both under normal conditions and after a 500-h exposure time.

**3.6. Permeability Tests.** According to the oxygen permeability measurements (Table 2), the use of feather fibers influenced the oxygen barrier properties of the studied systems. The linear arrangement of keratin molecules from feather fibers, together with their porosity, explains the increased permeability of the composites.

After artificial weathering, the oxygen permeabilities of LDPE and composites F1 and F2 were significantly higher than those of the reference samples. The higher mobility of the chains resulted in easier  $\rm O_2$  diffusion through the analyzed films.

Table 2. Oxygen Permeability Characteristics of the Studied Systems

	oxygen perme [cm³·mm/m²·(2	eability 4 h)·bar]	oxygen transfer rate $[cm^3/m^2 \cdot (24 \text{ h}) \cdot bar]$		
sample	normal conditions	after 500 h	normal conditions	after 500 h	
LDPE	210	256	742	795	
F1	220	274	749	814	
F2	234	305	799	1114	

#### 4. CONCLUSIONS

From the reported investigations, it can be concluded that keratin-containing feather fibers can be directly incorporated into polyethylene using a standard thermomechanical mixing technique, with the lightweight feather fibers replacing parts of the petroleum-based polymer without compromising product strength or flexibility.

The aging behavior of LDPE/feather composites due to accelerated weathering was analyzed. FT-IR spectroscopy was used to determine carbonyl and vinyl group formation during weathering, and the obtained results indicated an increase in polymer chain scission. When the systems were exposed to accelerated weathering, the mechanical properties exhibited a positive trend up to an exposure time of 400 h, whereas after 500 h of UV exposure, composite F2 predominantly underwent cross-linking and started losing its rubbery characteristics, becoming brittle. Keratin-containing feather fibers act as a reinforcing agent for the LDPE polymer matrix under normal conditions.

Rheological studies showed that the composites with feather fibers behaved as pseudoplastic materials. Increasing the keratin content reduced the amount of plastic in the composite, and the global effect on the durability of the composite materials is positive if one considers the levels of degradation of the composite and of the pure polymer after the same aging time. Thermal and oxygen permeability results confirmed that a UV exposure time of 500 h induced surface degradation, especially for the feather fiber loading of 10 wt %.

The obtained results suggest that feathers fibers present an opportunity for replacing nonrenewable-resource-based raw materials in composites with an environmentally friendly and renewable byproduct.

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#### Notes

The authors declare no competing financial interest.

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