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Thin polyethylene (LDPE) films with controlled crystalline morphology for studying plastic weathering and microplastic generation

Fanon Julienne, Fabienne Lagarde, Jean-François Bardeau, Nicolas Delorme *

Le Mans Université, Institut des Molécules et Matériaux du Mans (IMMM) – UMR-CNRS 6283, Avenue Olivier Messiaen 72085 Le Mans Cedex 9, France

A B S T R A C T

Plastic pollution has become one of the most visible environmental issue. Studying the aging and the fragmentation mechanism of polymers therefore raises environmental and health issues. Since it is particularly difficult to monitor all these processes in the real environment, laboratory studies are still necessary to obtain more accurate data and to identify the pathways leading to the outcome of plastic debris in the environment. In this paper we present a new method to prepare micrometer thick LDPE films with different thicknesses and controlled crystalline morphologies (i.e. spherulite size) using dip-coating process. LDPE films presenting different spherulite dimensions were submitted to an accelerated weathering test which indicates that spherulite size has only a weak influence on the rate of photo-oxidation. However, films presenting large spherulites morphologies seem to be more sensitive to surface erosion and crack initiation. We believe that the method developed in this paper can be used to study with more control and more rapidly (i.e. thin film and accelerated weathering) the influence of crystalline morphology on a wide range of semi-crystalline polymers in different aging conditions and thus help to better understand the fragment production of plastics in the environment.

1. Introduction

Plastic is present in our daily lives and its production is increasing significantly. In 1950, 1 million tons of plastic were produced, in 2019 this figure rose to 368 million tons. This plastic is most often for single use and according to the latest WWF report, in 2016 310 million tons of plastic waste were generated. In many countries, the end of life of plastic waste is still poorly managed leading to massive entries in the environment [1]. Once in the natural environment, it is known that plastics gradually degrade into smaller pieces (meso-, micro- or even nanoplastics) through a combination of photo-degradation, thermal-degradation, mechanical erosion [2]. Fragment sizes can range from micrometric to nanometric scale making possible the ingestion of plastics for species at the base of the food chain (microalgae, daphnia...) as for larger mammals. In addition, fragmentation releases products known to be toxic such as additives and fillers [3].

Studying the aging and the fragmentation mechanism of polymers therefore raises environmental and health issues. It is particularly difficult to monitor all these processes in real environment and laboratory studies are still necessary to obtain more accurate data and to identify the pathways leading to an even-

tual bio-assimilation of plastic debris in the aquatic environment [4]. For the natural weathering of polyolefins, the most important factor is photo-oxidation, a process that requires oxygen and UV-radiation. By exposing the materials to artificial weathering conditions, the degradation processes of polymeric materials can be accelerated and laboratory studies can be performed [5]. In a previous paper we have shown that when blown-extruded films of low density polyethylene (LDPE) or Polypropylene (PP) were submitted to an accelerated weathering the presence of spherulite structures (only in PP) induced the initiation of cracks between the lamellae and led to the formation of an increased number of smaller fragments compared to non-spherulitic crystalline structure (in LDPE) [6]. These results pointed out the importance of taking into account the crystalline morphology to study the fragmentation pathway of plastic waste in the environment.

In order to better understand the effect of the crystalline morphology on the weathering degradation, it would be interesting to have LDPE films with different spherulite sizes. However, it is difficult to control the crystalline morphologies of LDPE films with the usual preparation method (i.e. blown-extrusion process) [7] and post-thermal annealing based method should be banned to prevent any undesired thermal degradation. In addition, the use of thin films (μm thick) will make it possible to save time on the accelerated aging experiments which can last several months if we want to be able to observe the fragmentation of films prepared by blown-extrusion [6].

* Corresponding author.

E-mail address: nicolas.delorme@univ-lemans.fr (N. Delorme).

By controlling the polymer solution solvent evaporation rate, Vayer et al. have demonstrated the ability to control the crystalline morphologies of PLA by using the dip coating method [8]. To our knowledge the method has never been applied to control the morphology of polyolefins. This originates probably by the poor solubility of these polymers in common solvents. In this paper, we present a new method to prepare LDPE films with controlled thicknesses and crystalline morphologies using dip coating process. Films with different crystalline morphologies are weathered artificially in air to study the influence of the crystalline morphologies on the polymer aging and the beginning of the fragmentation.

2. Materials and methods

Low density polyethylene (LDPE) manufactured pellets (Alcudia PE-003) were used. No additive was detected either by Infrared or Raman spectroscopy as well as thermogravimetric analysis. LDPE pellets were dissolved in toluene by refluxing the mixture at 95 °C overnight (~15 h) [9]. Three concentration were used 2,5%, 5% and 10% in mass.

Glass slides substrates (Knittel®) were rinsed with ethanol. Once dried, they were soaked during 20 min in a crystallizer containing MeOH / HCl (1:1) solution for 10 min. After rinsing several times in ultrapure milli-Q water and N₂ drying, each the glass slide was irradiated 5 min in a UV-Ozone cleaner (Jelight Company Inc., California, USA) system. After this cleaning steps a total wetting of the glass surface with a drop of ultrapure water was observed demonstrating the presence of silanol groups onto the surface [10]. Samples were then used immediately to avoid further contamination.

For glass surface functionalization, 10⁻³ M solution of octadecyltrichlorosilane (OTS) in bicyclohexyl both purchased from Aldrich was used.

Thin films were deposited onto functionalized glass substrates using a homemade dip coater allowing the control of the dipping/withdrawal speeds and temperature of the solution. Dip coating dipping speed was fixed at 6 mm/s and withdrawal speed was varied between 1 and 15 mm/s. Before characterization, films were placed under vacuum in a dark chamber for a minimum time of 15 h to allow the removal of solvent traces and to avoid photo/thermal aging. Two replicates per sample were prepared and used for the investigation.

Optical confocal profilometry S-Neox (Sensofar) was used to determine both the surface morphology and the thickness (step height measurement after film scratching) of the deposited LDPE films. Spherulite mean diameter were measured by calculating 2D-radial Power Spectral Density (2D-rPSDF) and by extracting the position of the maximum of this function (λ_{\max}). The mean spherulite diameter is given by $D = 2\pi/\lambda_{\max}$ [11]. Images processing, roughness and 2D-rPSDF functions were calculated using Gwyddion software.

Atomic Force Microscopy images were obtained in intermittent contact mode in air ($k = 40$ N/m) with a CSI Nano-observer. Images were processed using Gwyddion software.

Accelerated weathering was performed by placing the LDPE films in a Sunset XLS+ (Atlas) chamber equipped with a xenon lamp. The UV irradiance was around 60 W/m², corresponding to a daily radiant exposure of 5 MJ. The weathering exposure was continued in varying steps up to a maximum of 73 days equivalent to an UV radiant exposure of 380 MJ/m². During the test, the chamber temperature was controlled using Black Panel Temperature (BPT) fixed at 65 °C. For the duration of the experiment the resulting averaged temperature was $T = 39$ °C. The measured standard deviation (2 °C) was in accordance to the cycle 1 of ISO 4892-2:2013 standard.

FTIR spectra were acquired using a Vertex 70 V, Bruker®, in ATR mode with a diamond crystal. The spectrum were accumulated from 30 scans, and averaged over 3 different locations on each sample. After baseline and ATR correction of the spectrum (i.e. in such a way that the position and intensity of the absorption bands are similar to those of a spectrum acquired in transmission mode) the carbonyl index (CI) was calculated as the ratio of integrated intensities between 1850 and 1660 cm⁻¹ (i.e. carbonyl bands) and the reference bands between 1495 and 1430 cm⁻¹ [12]. Such method of determination of the CI of LDPE was recently validated by the work of Almond et al. [13].

Amorphous fraction (x_A) of LDPE film was determined by Raman spectroscopy. The Raman measurements were performed at room temperature using a WITec Alpha 300R confocal Raman spectrometer (WITec GmbH, Ulm Germany). Raman spectra were collected under a microscope equipped with a Zeiss EC Epiplan-Neofluar® 100× objective (numerical aperture of 0.9) focusing the 532 nm line of a Solid State Sapphire laser (Coherent INC., Santa Clara, USA) on the samples. Raman spectra were systematically recorded 10 times with an integration time of 6 s and averaged over two different areas. The spectral analysis was performed using the WITec Project FIVE plus software (version 5.248, WITec GmbH, Germany) and two-Lorentzian peak fitting method. Amorphous phase fraction (x_A) of LDPE film was calculated using the formula: $x_A = 0.54 \times (I_{1306}/I_{1294})$ where the integrated Raman intensities ratio I_{1306}/I_{1294} is attributed to the amorphous fraction (Figure S2) [14]. The multiplicative coefficient 0.54 was determined by comparing the crystallinity fraction determined by DSC and Raman on a reference LDPE sample.

3. Results and discussion

3.1. Thin film elaboration

3.1.1. Control of dip-coating temperature and substrate surface energy

It is important to note that in order to prepare homogeneous LDPE films, dip coating has to be performed with a LDPE solution at a temperature above 100 °C. Indeed, below this temperature, LDPE in toluene solution precipitates leading to the formation of a heterogeneous film (Supporting info S1). In addition, even if the solution and substrate temperature are kept above 100 °C, when cleaned glass substrate was used, dip-coated films were very rough ($S_q > 2$ μm for a 100×100 μm area) and partly dewetted. This result can be explained by the high difference of measured surface energy between cleaned glass substrates ($\gamma_S = 290$ mJ.m⁻² with 99,9% polarity) and LDPE ($\gamma_S = 28$ mJ.m⁻² with 14% polarity). Such difference led to a low spreading coefficient and a high work of adhesion [15]. So in order to prepare homogeneous LDPE films, we have chosen to decrease the polar contribution to the surface energy of the substrate by performing surface functionalization with octadecyltrichlorosilane (OTS) [10]. Fig. 1 shows the evolution of the static water contact angle as function of the dipping duration of clean glass substrates in OTS solution in Bicyclohexyl (10⁻³ M).

As expected, the water contact angle increases with the functionalization duration until it reaches a plateau value (i.e. 105°) indicating that the glass surface is saturated with OTS molecules [10]. For a functionalization duration of 120 s the resulting surface energy of the substrate was $\gamma_S = 23$ mJ.m⁻² with $\text{pol}=3$ leading to an improvement of both the spreading coefficient and work of adhesion and the formation of an homogeneous film with a lower roughness ($S_q < 300$ nm for a 100×100 μm area).

3.1.2. Control of the film thickness

The dip-coating process consists in immersing a substrate into a reservoir of solution and withdrawing the substrate from the solu-

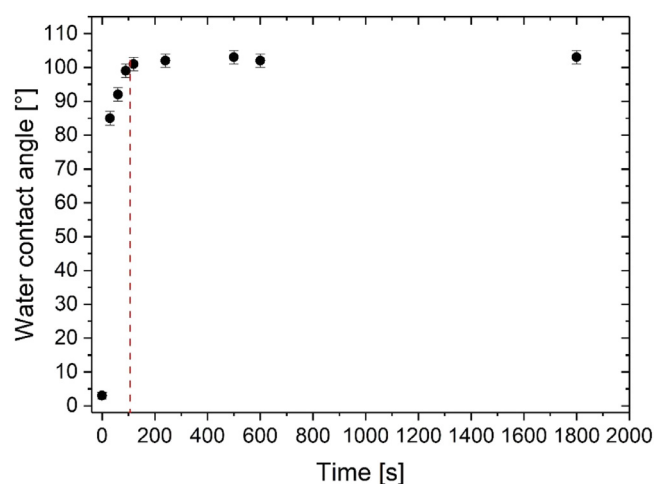


Fig. 1. Evolution of the static water contact angle of the glass substrate as function of the functionalization duration in OTS solution.

tion at a controlled speed. After evaporation of the solvent, a uniform polymer film can be deposited. Depending on the withdrawal speed film deposition can follow two different mechanisms. For low withdrawal speed (typically below 1 mm/s) a capillary regime is observed where surface tensions govern the film formation and film thickness decreases with the decrease of the withdrawal speed [16]. For higher speed, a regime called draining regime is observed. In this case the Landau-Levich model predicts that the film thickness (h), resulting from the competition between the viscous drag and the adhesion of the fluid on the substrate, is proportional to the withdrawal speed (Eq. (1)) following a power-law [17]

$$h = K \times l_c \times \left(\frac{\eta V}{\gamma} \right)^\beta \quad (1)$$

where l_c = capillary length, K = constant, η = solution viscosity, V = withdrawal speed, γ = solution surface tension and β = power law factor with $\beta = 2/3$ in Landau-Levich model

As shown in Fig. 2, for the three considered concentrations ($C = 2.5\%$, 5% and 10%), film thickness increases with the withdrawal speed following a power law, indicating that the draining regime has to be considered. However, the observed power factors β differ from the expected value of $2/3$ given by the Landau-

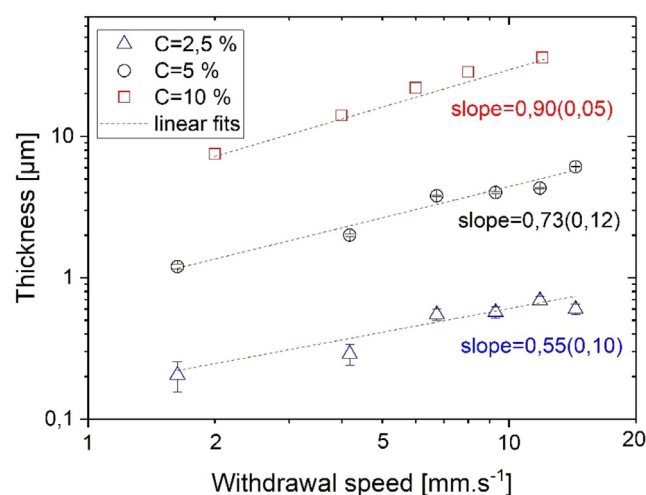


Fig. 2. Evolution of LDPE film thickness with the withdrawal speed for two different LDPE concentrations. For each concentration, the power law factor and the corresponding uncertainty is indicated.

Levich model. Such result has already been observed for a multitude of systems due to the non-Newtonian nature of polymeric solutions because viscosity and surface tension change with solvent evaporation [18]. Smaller values of β indicate a weaker dependency of thickness with withdrawal speed for the lowest concentrations. Fig. 2 also indicates that for the same withdrawal speed higher concentration leads to higher thickness. Since higher LDPE concentration leads to higher viscosity for the same withdrawal speed, the amount of liquid moving upwards with the substrate is larger since the drag force is proportional to the solution viscosity (Eq. (1)).

3.1.3. Control of the crystalline morphology

For semi-crystalline polymer such as LDPE, if crystallization is carried out in dilute solution then during crystalline lamellae growth, additional layers may be formed and well-ordered multilayered crystals are formed. If, however, the growth rate is fast then complex lamellae aggregates that are either sheaf-like or spherical in outline are formed. Such aggregates are commonly called spherulites [19]. Crystalline morphology is known to depend on various experimental parameters such as the cooling temperature, the solvent nature, the solution concentration and the polymer chain length [20]. Solvent evaporation rate is another parameter that can govern the crystalline morphology. For instance Pramod et al. have shown that by controlling the evaporation rate of the 2-butanone, crystallinity of poly(vinylidene fluoride) film can be modified [21]. Fig. 3 shows the evolution of surface morphology for LDPE films prepared at different conditions (withdrawal speed and concentrations).

In Fig. 3, it can be seen that the surface morphology of LDPE films is constituted by spherulites which protudes at their centers. Such structures are usually observed for LDPE thick films and the protusion indicates that nucleation has taken part near the surface of the spherulite [22]. In addition, although the dip coating process may induce preferential orientation due to the withdrawal direction, no short range orientation is observed. The lack of any directional alignment is a consequence of random nucleation both at the contact lines as well as in solution [23]. Fig. 3 also shows that the size and number of spherulites vary with the preparation conditions.

In order to identify the factor governing the size distribution, we have performed a statistical analysis to determine the spherulite diameter as function of the preparation conditions. Fig. 4 indicates that for the same withdrawal speed, spherulite diameter increases with concentration and for the same concentration, spherulite diameter increases with the withdrawal speed.

It is known that spherulitic crystallization in polymers occurs by creation of the spherulite core by nucleation, followed by radial growth of fibrillar crystals at a constant rate due to the deposition of parts of chains onto the growing surface [24]. The spherulite size is thus governed by the balance between the number of nucleating site and the availability of polymer chains of the solution to participate in the spherulites growth [25].

In the case of the dip coating process, at higher concentration the quantity of polymer chains in solution will favor the formation of large spherulites. However, an increase of concentration implies also an increase of the solution viscosity which should limit the chain mobility and thus limit the growing rate of the spherulites. In the small range of concentration used in this work the variation of viscosity is not significant to modify the mechanism of spherulite formation. Vayer et al. observed an opposite behavior with PLA but their films were thinner (<300 nm) and in that case, interactions with the substrate may influence the spherulite growth [26].

Concerning the effect of the withdrawal speed, we have seen that for a constant concentration, under the draining regime

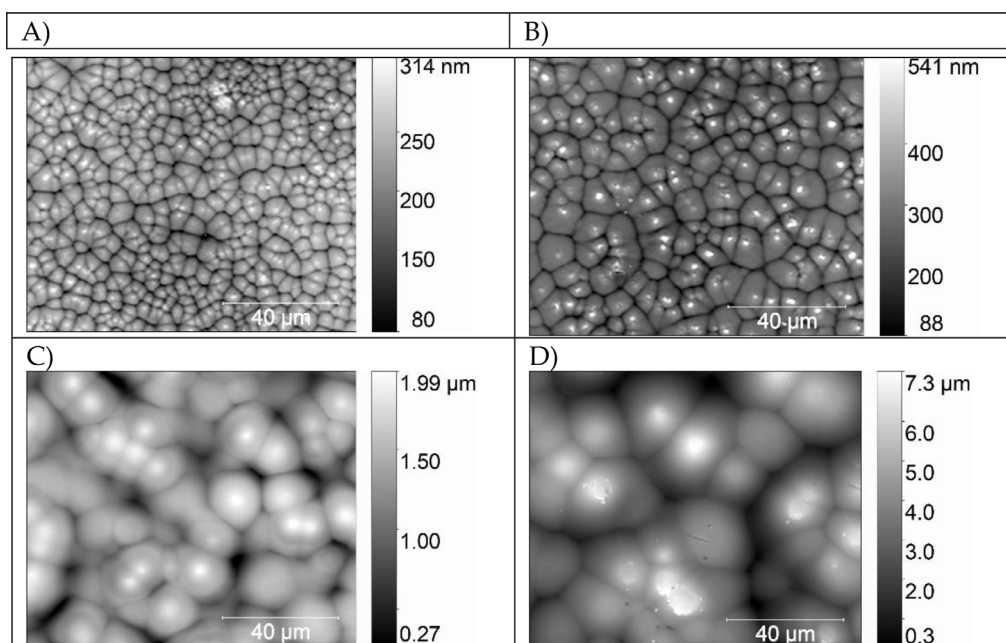


Fig. 3. (Left) Optical profilometry images showing the evolution of the surface morphology with the preparation conditions (concentration-withdrawal speed in mm/s) (A) 2,5%–1,6, (B) 2,5%–14,4, (C) 5%–1,6 and (D) 10%–4. For editorial reason, height scale are presented in color scale with tails cut off.

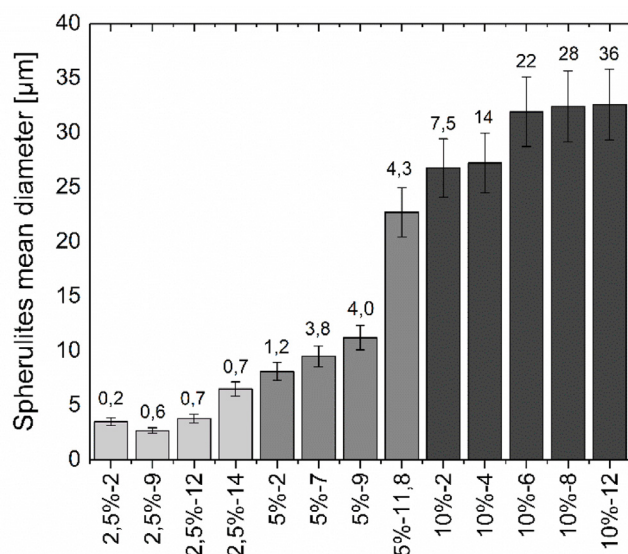


Fig. 4. Spherulites mean diameter as function of the sample preparation conditions (concentration in% and withdrawal speed). Values above the bars are respective film thicknesses in μm.

the higher the withdrawal speed the higher the thickness of the deposited film and the before the solvent evaporation. Since for higher withdrawal speed the quantity of polymer chains will be higher, the growth of large spherulite will be promoted [18].

We have demonstrated that LDPE thin films with controlled thickness and crystalline morphology (spherulites sizes) can be prepared by controlling both the polymer concentration and the withdrawal speed. In the following, films with different crystalline morphologies will be submitted to an accelerated weathering in order to study the influence of the polymer morphology on the aging of LDPE.

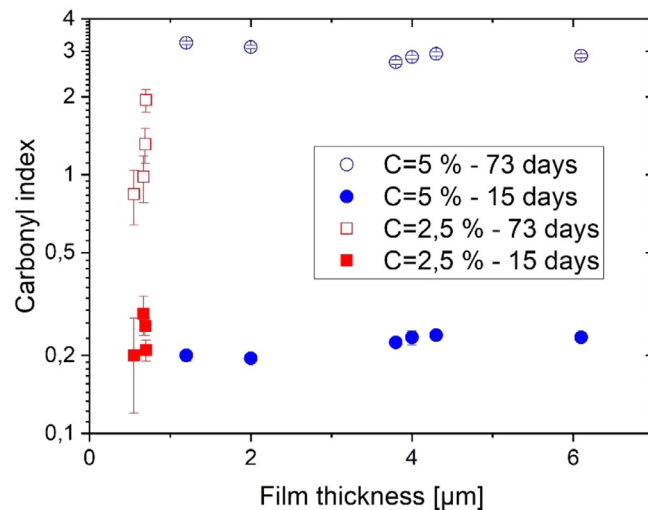


Fig. 5. Evolution of the Carbonyl Index (CI) as function of the film thickness, for two different concentrations in% and for two different weathering durations (15 and 73 days).

3.2. Accelerated weathering

3.2.1. Chemical modification of the film during the weathering

It is known for years that under natural and accelerated weathering, combination of the action UV radiation and oxygen leads to the appearance of carbonyl species, i.e. ketones, esters, acids, lactones and ketoacids in LDPE [27]. Chemical modification of LDPE films exposed to an accelerated weathering were monitored by studying the evolution of the Carbonyl Index (i.e. proportional to the evolution of the carbonyl characteristic bands) as function of the weathering time.

As shown by Fig. 5 if the film thickness is lower than 1 μm, the CI increases with the film thickness and a high dispersity of CI values are observed. For films thicker than 1 μm, CI values seem to be independent of the film thickness. This result can be explained

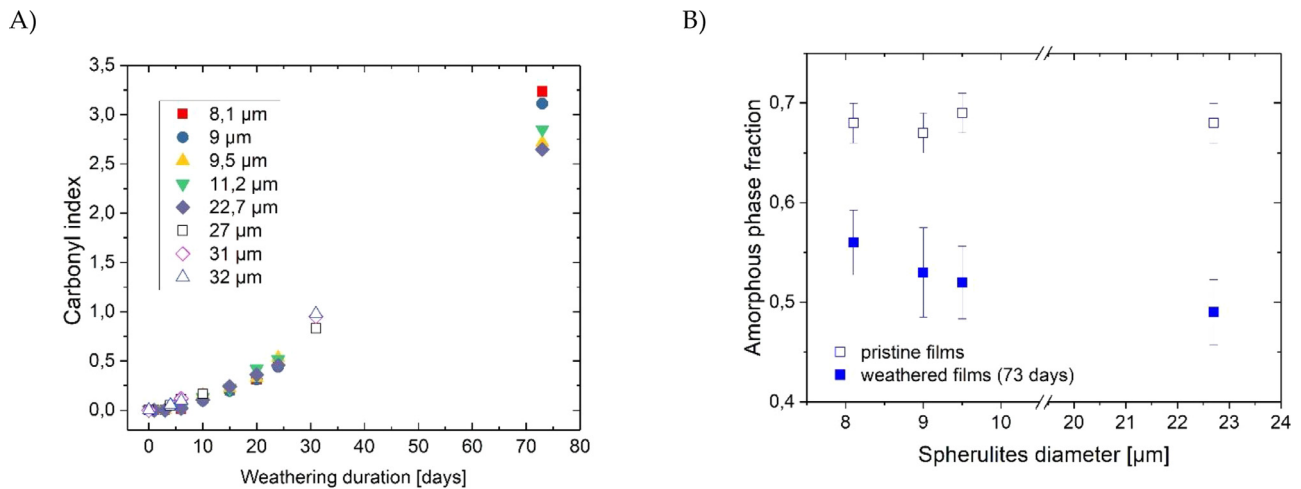


Fig. 6. (A) Evolution of the Carbonyl Index as function of the weathering duration for films with different spherulite diameter ($C = 5$ and 10%) and (B) Amorphous phase fraction as function of the mean spherulite diameter for 73 days weathered films ($C = 5\%$).

by the fact that when the film thickness is lower than the penetration depth of the IR light, reflexion on the substrate will influence the IR spectrum making quantitative measurements difficult to perform [28]. Indeed the penetration depth (d_p) of the evanescent wave in ATR can be expressed as:

$$d_p = 2\pi \times n_c \sqrt{\sin^2 \theta - (n_s/n_c)^2} \quad (2)$$

where n_c and n_s denote the refractive indices of the ATR crystal and sample, θ is the angle of incidence and λ is the wavelength of the IR beam. With $n_c = 2.4$ (diamond) and $n_s = 1.5$ for LDPE, for IR wavenumbers between 2000 and 1000 cm^{-1} the penetration depth in our experiment can be estimated from Eq. (2) to be $1 < d_p < 2 \text{ μm}$. As a consequence in accordance with Fig. 4, only the results concerning films thicker than 1 μm will be discussed in term of weathering.

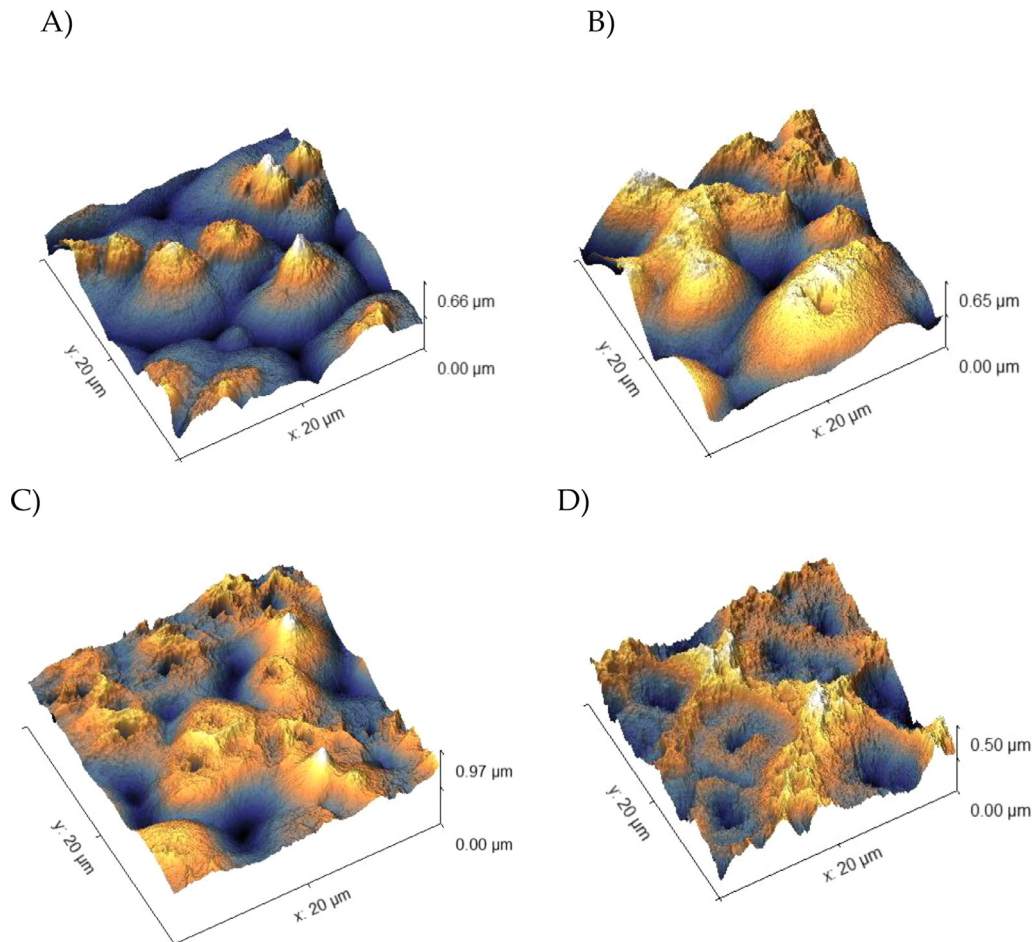


Fig. 7. AFM topography images of the 73 days weathered films for $C = 5\%$ with different spherulite diameters A) 8.1 μm , B) 9 μm , C) 11.2 μm and D) 22.7 μm .

Fig. 6A shows the evolution of the CI as function of the weathering duration for different films with different spherulite mean diameter. It can be observed that for all the samples the CI increases with the weathering duration indicating that the photo-oxidation of the LDPE films is occurring [12]. In addition, for accelerated weathering duration below 24 days spherulite diameter has no influence on the value of the CI indicating that the oxydation of the material is similar for all morphologies. For longer weathering duration (i.e. 73 days) the CI seems to increase when the spherulite diameter are smaller.

Fig. 6B shows that for pristine films the amorphous phase fraction is independent of the spherulite dimensions. After 73 days of accelerated weathering, a clear decrease of the amorphous phase fraction is observed which can be explained either by a chemocrystallization of the material exposed during the weathering or by a preferential degradation of the amorphous phase [29]. After weathering, the decrease of the amorphous phase fraction is stronger when the spherulite size is bigger indicating that the degradation path of LDPE is dependent of the crystalline morphology.

3.2.2. Erosion of the films during the weathering

These results could at first sight be analyzed as the proof of an influence of the size of the spherulites on the photo-oxidation mechanism of LDPE films. Fig. 7 shows the surface morphology of films with different spherulite diameter after 73 days of accelerated weathering. We can clearly observe an erosion (loss of mass)

for the different samples and this erosion is more important for the film with larger spherulites. As observed for Fig. 7A and 7B, the erosion seems to take place at first in the center of the spherulites and then to progress inside and between the spherulites (Fig. 7C and D). On Fig. 7D, one can see that the height of the spherulites has decreased strongly and is now lower than the interspherulite region which indicate a consequent loss of matter.

As a consequence, the observed decrease of the amorphous phase fraction after weathering is mainly due to the preferential erosion of the amorphous region. Our results tend to show that the larger the spherulites, the stronger the erosion of the film will be and thus that the fragmentation pathway will also be dependent of the spherulite size. The lower CI value observed for weathered sample with larger spherulites can be attributed to a higher erosion of the film and not to a decrease of the photo-oxidation process.

3.2.3. Crack initiation and propagation

During the aging process of polymer films, fragmentation of the film can be described as the result of micro-crack initiations followed by their propagation in the surface and volume of the film. Once several micro-cracks are merging a fragment is formed.

A) ($845 \times 705 \mu\text{m}^2$) 5%–11,8 ($D = 22,7 \mu\text{m}$) weathered 73 days; B) ($112 \times 94 \mu\text{m}^2$) 10%–6 ($D = 32 \mu\text{m}$) and C) ($112 \times 94 \mu\text{m}^2$) 10%–8 ($D = 32,3 \mu\text{m}$) both weathered 31 days.

As shown on Fig. 8, the presence of micro-cracks was only observed on the surfaces of films presenting the largest spherulite

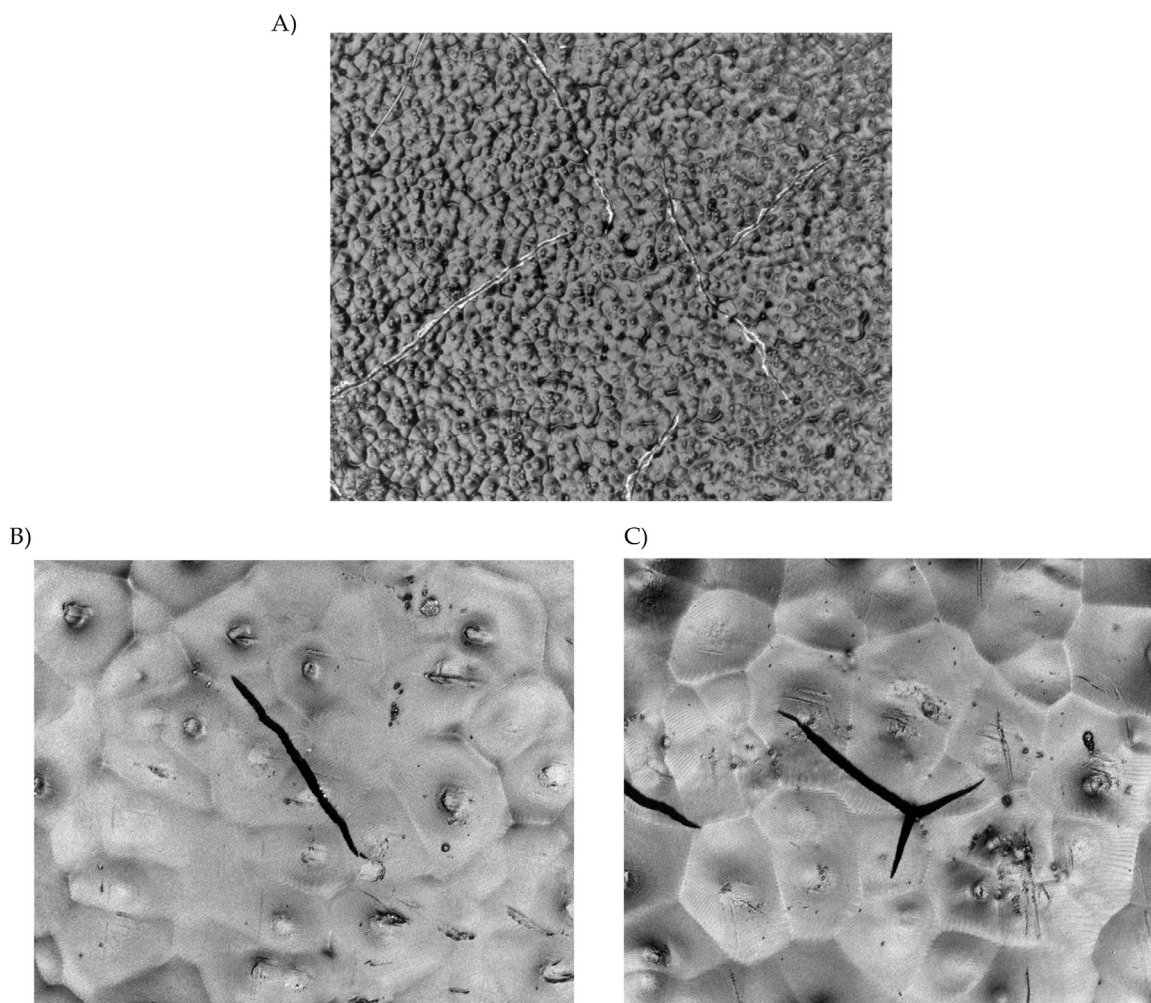


Fig. 8. Optical microscopy image showing the initiation and propagation of micro-cracks for LDPE samples.

dimension. The highest the diameter the sooner the crack apparition was observed (i.e. $t = 73$ days for $D = 22,7 \mu\text{m}$ and $t = 31$ days for $D > 32 \mu\text{m}$). This result is consistent with observations made on PLA films where cracks were less likely to develop for small spherulites ($<1 \mu\text{m}$) [30] and with the deleterious effect of spherulite size on various mechanical properties reported in the literature for years [31].

According to our observations it seems that the majority of the crack initiation occurred in the center of the spherulite and then propagate in a main direction to form linear cracks (Fig. 8A and B). At this point, we don't know if the initiation of cracks in the center of the spherulite can be related to the strongest erosion observed in Fig. 7. Some tri-branches cracks (Fig. 8C) can also be observed. These cracks are known to occur mainly in nuclei centers and are caused by parallel aligned sheaf-like lamellae orienting perpendicularly to substrates [30]. Fatigue crack propagation in polyethylene has been intensively studied in the past. When a crack meets a spherulite there may be two possible paths for the propagating crack depending on the matching on the crack plane of the direction of lamellae in two adjacent spherulities. In case of good matching, the crack will follow the interlamellar region up to the spherulite center and continue down to the other edge. When there is a poor matching, the easier modes of propagation are obstructed and interspherulitic cracking occurs [32]. In our observation, the poor matching scenario was scarcely observed.

4. Conclusions

We have shown that by controlling the solution concentration and the dip coating withdrawal speed we were able for the first time to our knowledge to prepare micrometer thick LDPE films with different thicknesses and crystalline morphologies (i.e. spherulite size). The accelerated weathering indicates that spherulite size has only a weak influence on the rate of photo-oxidation. However, films presenting large spherulites morphologies seem to be more sensitive to surface erosion and crack initiation. Such results suggest that films presenting larger spherulites will be more fragile toward the fragmentation process when submitted to environmental aging. We believe that the method developed in this paper can be used to study with more control and more rapidly (i.e. thin film and accelerated weathering) the influence of crystalline morphology on a wide range of semi-crystalline polymers in different aging conditions and thus help to better understand the fragment production of plastics in the environment.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Fanon Julienne: Conceptualization, Investigation, Writing – review & editing. **Fabienne Lagarde:** Funding acquisition, Resources, Supervision, Writing – review & editing. **Jean-François Bardeau:** Formal analysis, Writing – review & editing. **Nicolas Delorme:** Formal analysis, Investigation, Methodology, Supervision, Writing – original draft.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.polymdegradstab.2021.109791](https://doi.org/10.1016/j.polymdegradstab.2021.109791).

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