Transmittance analysis for materials suitable as radiative cooling windshield and aging study for polyethylene

Carrobé A, Martorell I, Solé C and Castell A

Sustainable Energy, Machinery and Buildings (SEMB) Research Group, INSPIRES Research Centre, Universitat de Lleida, Lleida (Spain)

Abstract

Nowadays space conditioning with renewable energy is one of the highest challenges of our society. Solar collection is a suitable source of energy for domestic hot water and space heating, but there is no green source to cool the spaces during hot periods or for hot climates. Radiative cooling seems to be a feasible solution for it. Elsewhere the Radiative Cooler Emitter (RCE) is presented, a device with an adaptive cover concept that combines both functionalities: solar collection during daytime and radiative cooling during nighttime. In this study, the solar and IR transmittances are analyzed for five samples: polycarbonate, methacrylate, and three commercial samples of low density polyethylene (LDPE): 17 μm, 50 μm and 200 μm). The aging of 50 μm low density polyethylene film is also studied during two months of environmental exposure in a RCE prototype (summer 2019). Presence of double bonds and C=O groups are detected, which implies a degradation of the polyethylene during the experimental campaign.

Keywords: radiative cooling, polyethylene aging, renewables, experimental analysis, solar transmittance

1. Introduction

In the EU, 40% of the total energy consumption is located in buildings, specifically in space conditioning and domestic hot water (DHW) (European Commission, "Energy performance of buildings directive."). When analyzing the energy consumption in buildings, the Eurostat (European Commission, n.d.) determines that 64.1 % of the total consumption in buildings is dedicated to space heating, 14.8 % to DHW, and 0.3 % to space cooling.

Solar collection is nowadays the most convenient source of renewable energy for domestic hot water, but there is no proper renewable source of energy for space cooling. Elsewhere a new device called Radiative Cooler Emitter (RCE) is presented (Vall, 2020). This equipment combines solar collection during daytime and radiative cooling during nighttime, thanks to an adaptive cover concept.

Radiative cooling uses the sky as a heat sink, benefiting from its effective temperature, which is much lower than ambient temperature (lower than 0 ºC or even −10 ºC (Bell, 1960)). Energy can be dissipated to the sky taking advantage of the infrared atmospheric window (7–14 µm). This window allows infrared radiation to pass directly to outer space without intermediate absorption and re-emission in the atmosphere. Heat dissipation is produced by long wave radiation (thermal radiation) from a surface to the sky.

Before designing and building the RCE, the materials involved in the device should be studied. The glass used in solar collectors blocks infrared radiation and it is not useful for radiative cooling. This is why as said previously an adaptive cover concept is defined. This adaptive cover counts with two different materials: one for solar collection during daytime and another for night radiative cooling. Glass, already widely used in solar collectors, is selected as the material for the solar collection function. The main characteristic that the night radiative cooling material must meet is a high transmission in the long wavelength IR spectrum. Specifically, high values of transmittance in the atmospheric window (7–14 µm)

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during the whole operation lifetime. High solar transmittance is also desirable for maintaining the same solar collection efficiency. Materials found after bibliography review are basically polymeric materials (Tsilingiris, 2003, Xu et al., 2018, Fu et al., 2019, Liu et al., 2019) , non-polymeric materials such as zinc crystals (Bosi et al., 2014, Chen et al., 2016, Laatioui et al., 2018), and cadmium sheets (Benlattar et al., 2006), and chromic materials (Hjortsberg and Granqvist, 1981).

Among these non-plastic candidate materials, crystals have the advantage of having greater resistance to external environmental conditions. However, the high costs of these crystals, and the impossibility of producing them in adequate dimensions for the RCE, make them unfeasible. On the other hand, there is very little bibliography referring to cadmium sheets for radiant cooling applications and the last reference is from 2006. Finally, it should be noticed that chromic materials have very interesting properties as adaptive covers, but further fundamental material research must still be done. Thus, all these materials have been discarded as possible candidates and the material chosen for the adaptive cover will be a plastic. Plastics have less resistance to external environmental conditions, but they can be produced in adequate dimensions and cost, and have been used in previous studies of radiative cooling. According to the literature, polyethylene film is mostly used as cover for radiative cooling. However, polyethylene suffers degradation during exposure time, losing elasticity and deformation capacity, manifested in the appearance of carbonyl groups (Carrasco, 2001).

The objective of this paper is to analyze the solar and IR transmittance of different plastics to determine their suitability for radiative cooling applications. Since the RCE will be exposed to external weather conditions, materials degradation during lifetime is relevant. This is why an aging study for polyethylene is also performed.

2. Methodology

To accomplish with the objectives of the study, the methodology is divided into two parts. First, a transmittance analysis of five possible material samples to be used as adaptive covers of the RCE. These materials should not block the solar collection and must allow the IR radiation from the RCE to cross to the atmosphere. The second part consists of analyzing the aging of the material with the best performance in the transmittance analysis.

The selection of the plastics has considered three different commercial plastics as methacrylate, polycarbonate and polyethylene. Polyethylene is the plastic widely used in radiative cooling applications and this is why three LDPE polyethylene samples with different thickness have been chosen: 17 μm LDPE (transparent film for kitchen use), 50 μm LDPE (transparent film for industrial use), and 200 μm LDPE (greenhouse cover). In order to study the optical behavior of these materials, spectroscopic analysis to cover wavelengths from 200 nm to 15300 nm are performed. For the UV-Vis study, a UV Analytikjena Specord 2010 (190-1100 nm) with a resolution of 1 nm was used; for the near infrared area (NIR) the Foss NDS XDS Rapid Content Analyzer spectrophotometer (400-2500 nm, 62 scans) was used. Each continuous spectrum of the NIR region was recorded in a rectangular cell (15 cm x 3.5 cm) and 62 scans of each sample were performed, covering the wavelength range between 800 and 2500 nm. Although the NIR spectra comprise the visible area (between 400 and 800 nm) only the NIR data between 800 and 2500 nm were used, since the reference capsule absorbs more than the samples. Finally, the analysis by FT-IR spectroscopy (Fourier Transform-Infrared) was carried out with a Jasco FT-IR 6300 series equipment with ATR diamond / ZnSe accessory and TGS detector. Each spectrum is recorded with 64 scans, in the 2500-15384 nm range and with a resolution of 4 cm^{-1}.

The second part of the study is to analyze the behavior of the plastic which performs better in the transmittance test in experimental real conditions. In other words, in contact with the environment and mounted on the RCE prototype. During the experimentation in summer 2019, the plastic was exposed to atmospheric conditions, during a period of 2 months. The plastic was covered by the glass of the solar collector during the day and uncovered at night. A visual inspection of the plastic detected changes in the material due to the variation of temperature and solar radiation. The changes observed are irregular since there are areas that do not present changes, other areas of the film with dark color and regions where the plastic loses firmness. To study the degradation of the plastic, an aging experiment was designed using three samples of the selected plastic: (1) brand new plastic (NEW). This is a plastic that has not been installed in the RCE, (2) plastic exposed 2 months and with visual degradation detection –either dark color, firmness lost or both- (OLD 1), and (3) plastic exposed 2 months but without visual degradation detection (OLD 2). After the two months exposure, three samples of each category were analyzed in UV-Vis and FT-IR using the same equipment described previously. Three repetitions of each sample were performed, which means that a total of 18 spectra were analyzed.

3. Results

3.1. Transmittance analysis of plastics

Figure 1 shows the UV-Vis, NIR and FT-IR (with ATR mode) spectra for the five plastics studied:

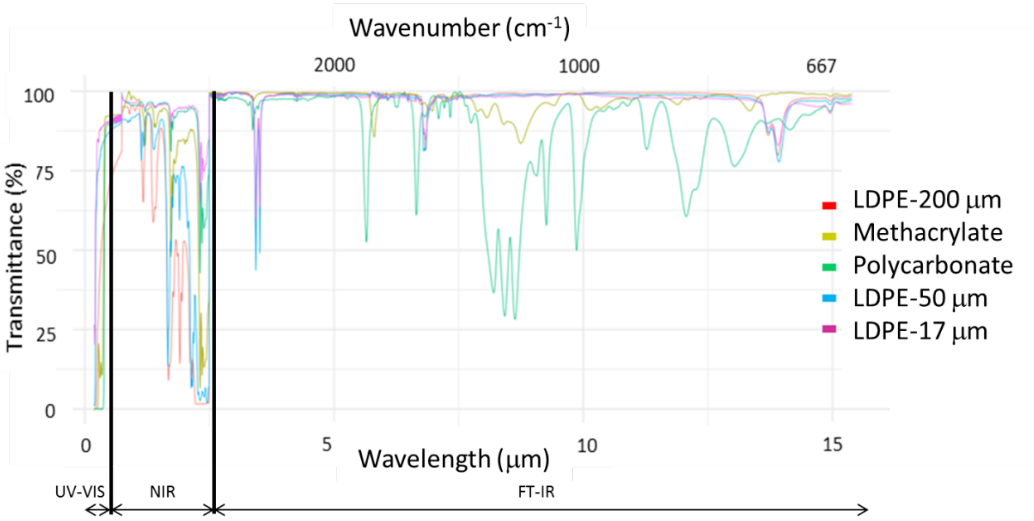


Figure 1. UV-Vis, NIR and FT-IR in ATR mode spectra for the five candidates.

Although the complete spectra for the five plastic materials are presented in Figure 1, it is important to highlight here that for the RCE application, the transmittance regions of interest are the UV-Vis, during the solar collection, and the large IR (FT-IR), during the radiant cooling process. In particular, for the RCE application high transmittance values in the UV-Vis and FT-IR regions are desired in order to allow both solar collection and radiative cooling.

First, looking at the UV-Vis spectrum region it is observed that the transmittance behavior is similar for all plastics. However, when analyzing the transmittance behavior in detail it is detected that transmittance values for greenhouse plastic are 10 % lower. The NIR spectra show that in the near infrared area each material has a different behavior and no common pattern is observed. Finally, when observing the FT-IR spectra, it is seen that absorbance bands (peaks) for the five materials are basically in the same regions, which confirms that all of them belong to the plastics family. However, the intensity of the absorbance bands is different and this will determine the average transmittance values of each material in the FT-IR spectrum. From Figure 1 it is seen that polycarbonate and methacrylate have a very different behavior from the polyethylene samples. It is also important to note that the three polyethylene samples show the absorption bands at the same wavelengths, confirming that the three materials are polyethylene. No significant differences are observed between these three materials in Figure 1.

Next, and in order to determine which of these plastics, from the optical properties point of view, is the best for the radiative cooling application a comparison in the atmospheric window is done. Figure 2 shows transmittance values for the five samples between 7 and 14 µm.

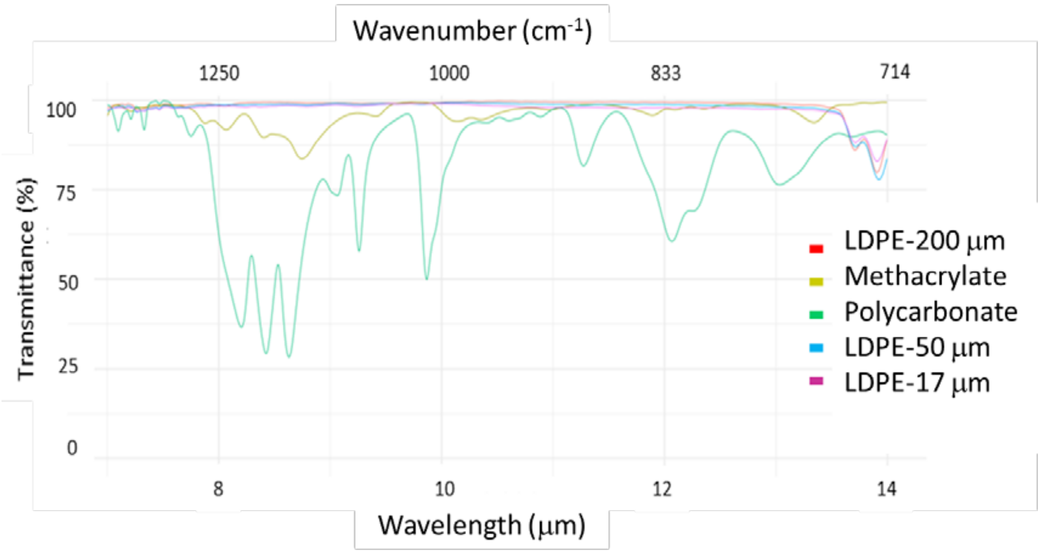


Figure 2. FT-IR in ATR mode spectra for the five candidates in the atmospheric window.

From Figure 2 it is seen that polycarbonate is the material that shows the largest absorption bands in the atmospheric window. In addition, these bands are wide, which translates into significantly lower average transmittance values. Thus, polycarbonate can be quickly discarded as a candidate material for the RCE cover. Methacrylate also shows more absorption bands in the atmospheric window than the polyethylene samples and it is also excluded as a candidate material for the RCE application. The other three samples present, on the one hand, a fairly constant behavior, without the presence of significant peaks, and on the other hand, higher transmittance values than methacrylate and polycarbonate. Thus, no significant differences between the three polyethylene candidates are observed in Figure 2.

At this point, the 17 μm LDPE is discarded due to its fragility, considering that the prototype will be located outside. 50 μm LDPE (transparent film) and 200 μm LDPE (greenhouse cover) have a very similar behavior in the atmospheric window. 50 μm LDPE transparent film is finally chosen for two reasons. First, because similar thickness have been used in the radiative cooling application bibliography and offers high values of transmittance in the atmospheric window, and second, because in the UV-Vis region the transmittance average value of the polyethylene is 10 % higher than the one shown by 200 μm LDPE (greenhouse cover). Thus, the cover material selected for the RCE is a polyethylene (PE) in the form of a flexible film 0.5 mm thick.

In order to characterize the material, the main spectral signals present in the 50 μm LDPE in the long infrared zone are determined. For this, three new polyethylene samples are selected and repetitions of three spectra are performed for each sample. The equipment used is the Jasco FT-IR 6300 series with ATR diamond / ZnSe accessory and TGS detector. Each spectrum is recorded with 64 scans and with a resolution of 4 cm^{-1}. Figure 3 shows that all the most intense bands of the FT-IR spectrum correspond to polyethylene, with no other chemical compound. No differences are observed between the nine spectra of the polyethylene either. It is confirmed that the polyethylene selected is a low density polyethylene since an absorption band at 1377 cm^{-1} is detected. The typical absorption bands of polyethylene are: 2915 cm^{-1} asymmetric CH_2 stretching, 2848 cm^{-1} symmetric CH_2 stretching, 1471 cm^{-1} CH_2 bending, 1377 cm^{-1} symmetric CH_3 bending, 1302 cm^{-1} twisting vibration and 719 cm^{-1} CH_2 rocking.

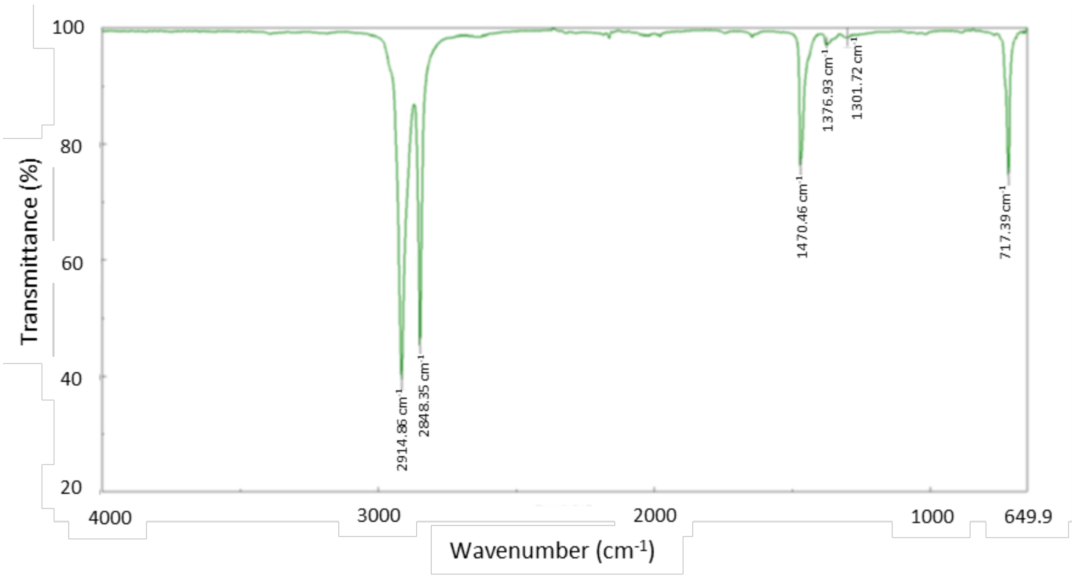


Figure 3. FT-IR using ATR mode for the 50 μm LDPE selected for radiative cooling application.

In order to determine the average transmittance of the candidate material in the atmospheric window, a FT-IR spectrum is carried out in Transmission mode using a FT-IR Thermo Nicolet is50 equipment with a DTGS detector and KBr beam splitter with a resolution of 4 cm^{-1}. The transmission spectrum obtained with 64 scans of the 50 μm thick polyethylene is shown in Figure 4. The average transmittance of this polyethylene in the atmospheric window (7-14 μm) is 80,69 %, a value very similar to literature (Hu et. al. 2015).

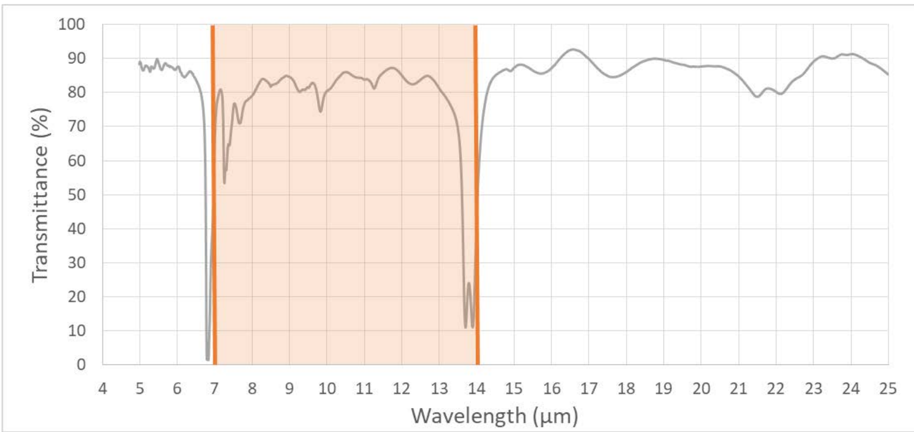
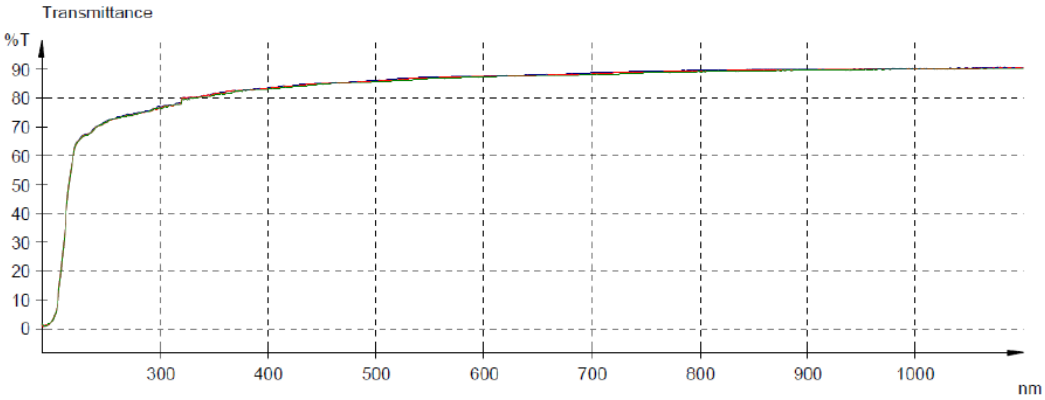


Figure 4. FT-IR spectrum in Transmission mode of the 50 μm polyethylene. The atmospheric window is shadowed.

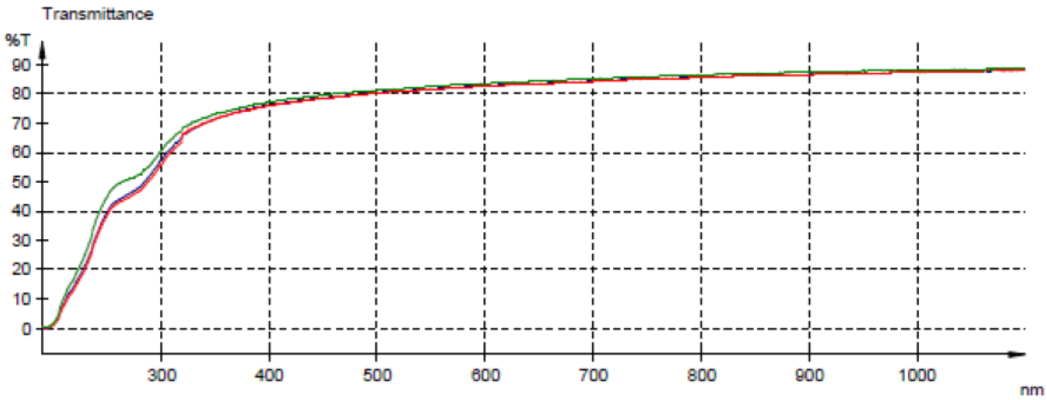
3.2. Aging study for polyethylene

The next step is to study the 50 μm polyethylene behavior under experimental conditions in the RCE. To do so, a RCE prototype was designed and constructed using a solar collector. The glass screen of the solar collector was removed to install the 50 μm polyethylene film. Once the polyethylene was located, the glass was placed at the original place. The prototype works collecting the sun during daytime and once the day is over, the cover glass is removed and the plastic enables the radiative cooling mode. Experiments were performed during two months in summer 2019.

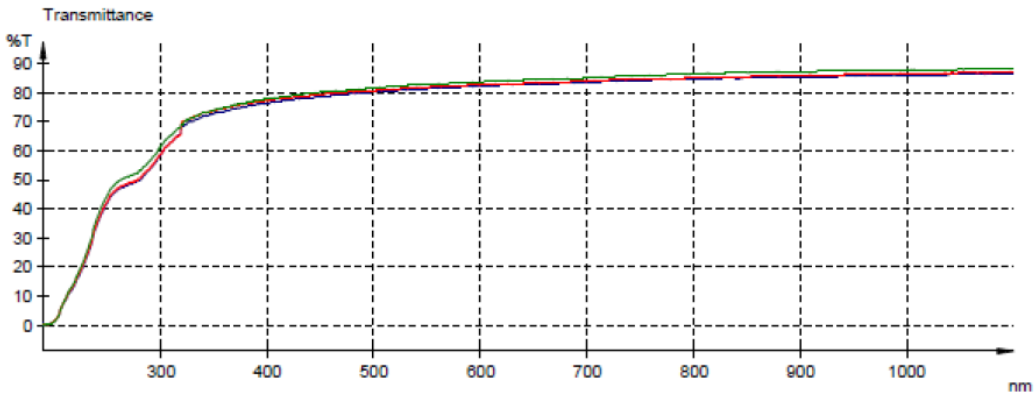
As explained in the introduction section of this paper, a total of nine 50 μm polyethylene samples were studied. Three samples correspond to the NEW polyethylene, the one that has not been exposed to external conditions, three more samples were selected for the part of the plastic that showed visual degradation (OLD 1) and three more for the part that did not show visual degradation (OLD 2). In order to determine the polyethylene degradation process spectrophotometric analysis in UV-Vis and FT-IR are conducted in the same equipment mentioned above (Figures 5 and 6, respectively).



(a) NEW



(b) OLD 1



(c) OLD 2

Figure 5. UV-Vis spectra of the 50 µm polyethylene.

Looking at Figure 5 it is seen that no significant differences for the three samples of each category (NEW, OLD 1, and OLD 2) exist. However, when looking at the transmittance values between 200 and 550 nm, samples OLD 1 and OLD 2 show lower transmittance values that the NEW samples. These results indicate the appearance of double bonds in the plastic due to environmental exposition and C-H bonds degradation.

Figure 6 presents the FT-IR spectra for the NEW, OLD 1 and OLD 2 samples. In this case, a comparison of the average spectra for the NEW, OLD 1 and OLD 2 samples is presented in order to compare the absorbance bands positions and intensity. From Figure 6 it can be concluded that the descriptive absorbance bands of low density polyethylene do not disappear after the environmental exposition. However, new absorbance bands are present in the OLD 1 and OLD 2 samples.

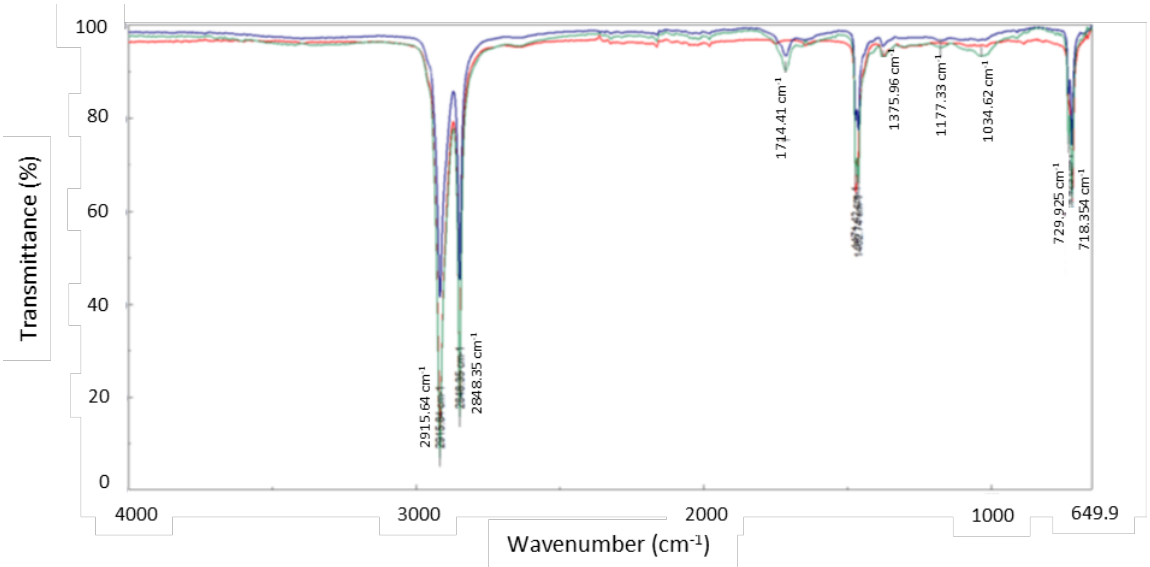


Figure 6. FT-IR spectra of the 50 μm polyethylene: NEW (red), OLD 1 (green) and OLD 2 (blue).

In order to study the new bands, the FT-IR spectra for the NEW, OLD 1 and OLD 2 polyethylene samples in the atmospheric window is presented in Figure 7.

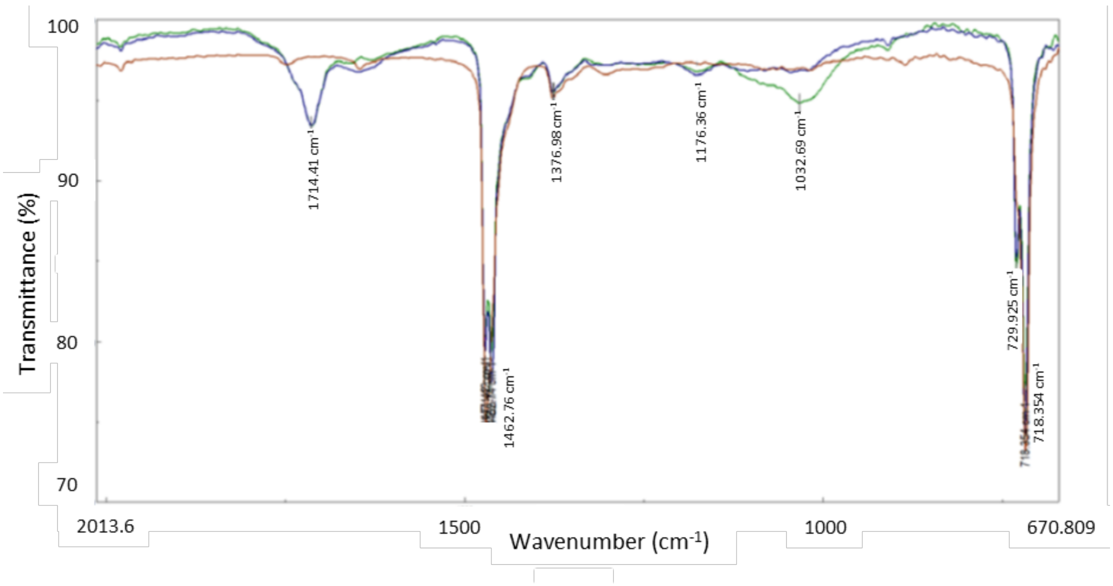


Figure 7. FT-IR spectra of the 50 μm polyethylene in the atmospheric window: NEW (brown, OLD 1 (green) and OLD 2 (blue).

The main differences that have been detected between the three 50 μm thick polyethylene samples are the increase in the signal around 1035 and 1177 cm^{-1}, especially in the OLD 1 sample. The 1035 cm^{-1} area corresponds to the absorption frequency of CO bonds. A new signal also appears at 1714 cm^{-1}, corresponding to the absorption of C = O bonds, which seems to indicate a degradation of polyethylene through an oxidative process. It is important to note that no formation of hydroxyl groups is observed (broad bands around 3200-2550 cm^{-1}).

On the other hand and when doing a detailed analysis of the absorbance bands, it is also detected that the 1470 cm^{-1} signal has shifted to 1471 cm^{-1} and a new band has appeared at 1462 cm^{-1}. Also the 718 cm^{-1} signal has shifted to 717 cm^{-1} and a new signal has appeared at 730 cm^{-1}. All this is possibly due to changes in the polymeric structure of polyethylene, but specific tests should be performed in order to identify with precision the nature of these polymeric structure changes.

To know the degree of chemical degradation, the carbonyl and vinyl indices have been calculated, as in Albertsson et al. (1987) and Muthukumar et al. (2014). The vinyl index is a measure of the concentration of double bonds and the carbonyl index is a measure of the concentration of carbonyl groups. To calculate the vinyl index, the area between 1680-1583 cm^{-1} has been integrated and divided by the area 1511-1417 cm^{-1}. For the calculation of the carbonyl index, the area between 1640-1804 cm^{-1} has been integrated and divided by the area 1511-1417 cm^{-1}. The areas have been calculated with the program of the FT-IR team of the Servei Científico-Tècnic of the UdL "Spectra analysis" with the conditions "two-point base" and "add under baseline". Table 1 shows the results.

Tab. 1. Vinyl and carbonyl average indices and standard deviations (SD) of 50 µm polyethylene NEW, OLD 1 and OLD 2.

	Vynil index (average)	SD	Carbonyl index (average)	SD
NEW	0.04	0.01	0.02	0.00
OLD 1	0.02	0.00	0.36	0.07
OLD 2	0.06	0.04	0.44	0.11

The results in Table 1 show a clear increase in the carbonyl index between the NEW sample (0.02) and the OLD 1 (0.36) and OLD 2 samples (0.44). These values corroborate the oxidative process detected with the FT-IR spectra. On the other hand, the values of the vinyl index seem to indicate that there is no clear increase trend of double bonds during the two months of exposure of the 50 µm thick polyethylene in the RCE equipment.

Finally, the average transmittances in the atmospheric window for OLD 1 and OLD 2 are 80.39 % and 79.89 %, respectively. A decrease of only 0.3% respect the NEW sample is observed for OLD 1 and a decrease of 0.8 % respect the NEW one is observed for OLD 2.

4. Conclusions

After performing transmittance analysis (UV-Vis and FT-IR) of five plastics candidates (polycarbonate, methacrylate, 17 µm LDPE, 50 µm LDPE, and 200 µm LDPE) for the RCE prototype, a 50 µm low density polyethylene has been selected for being the plastic with higher transmittance. The average transmittance in the atmospheric window (7-14 µm) of the 50 µm low density polyethylene, calculated using FT-IR in Transmission mode, is 80.7 %.

A 2 months aging study has proved that the chemical structure of the polyethylene changes by the fact that the plastic is placed on the RCE prototype and exposed to outdoor environmental conditions. FT-IR analyses show that new functional groups appear indicating oxidative processes. Although double bonds and carbonyl groups detected in the polyethylene after the two months exposure, indicate a change in the structure, transmittance decreases only by 0.3 % for OLD 1 and by 0.8 % for OLD 2, compared to the NEW polyethylene sample. These results show a stable behavior of the transmittance for polyethylene.

5. Acknowledgments

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