

Microscopic Identification of Micro-Fractures and Deterioration In Arid Environments Of Pro-Oxidant Polyethylene (PE) Specimens Utilizing State of The Art Thermal and Morphological Experimental Protocols

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ABSTRACT

Pro-oxidant filled polyethylene (PE) specimens in standard and internationally accepted dimensions and size, were exposed to arid natural and accelerated weathering conditions. The American Society for Testing and Materials (ASTM) protocols for weathering were followed, namely ASTM D 4329 and ASTM D 4329, respectively. The films were deemed to be biodegradable and were secured from commercial outlets in an efforts to reduce waste accumulation in the State of Kuwait, and by conjunction, developing world countries; in standardising their use and formulations. The plastic films were deemed biodegradable of oxo-biodegradable nature containing calcium carbonate (CaCO₃) amongst other prodegradant chemical agents. Scanning Electron Microscopy (SEM) was used to target micro fractures as a means to identify degradation in environment using technology assisted methods. A JSM 6010LA Joel Model microscope was used, equipped with high and low vacuum. The samples were placed on double sided adhesive tape for analysis and imaging. The samples were cut into (50 x 100 mm), coated with gold an placed inside the SEM (JSM 6010LA) for analysis. In addition, energy-dispersive X-ray spectroscopy (EDS) was also used to identify the loss of chemical inducing pro-degradant materials. The combination of both methods can give way to developing a standard technique and protocol in identifying degradation profiles in harsh and arid environments as noted in this research work.

Keywords: technology assisted protocols, sem, oxo-biodegradation, metal additives

1 INTRODUCTION

Biodegradable plastics (encompassing biobased and biodegradable polymers) have been noted as one of the main strategic solutions proposed to solve the accumulation

of plastic solid waste (PSW). Biodegradation of plastics also presents a solution to the dependency on fossil fuels and their price uncertainty on the hydrocarbon market, as they are considered an alternative to conventional synthetic polymeric articles. This is supported by the fact that such articles are being produced in bulk for commercial use nowadays [1]. It is projected that by the year 2020, bioplastics will increase in their global production capacity to reach 4.4 million tons from a mere 0.36 million tons back in 2007 [2]. The main bioplastic polymers being produced are starch based plastic (1.3 million tons), PLA (0.8 million tons), bio-based polyethylene (PE) (0.6 million tons) and polyhydroxyalkanoate (PHA) (0.4 million tons) [3]. One major obstacle still remains for the increase in the popularity of biodegradables among plastic converters and manufacturers, which is the price and breakeven point of their products in local markets. This is especially true for countries and communities where fossil fuel feedstock are cheap and abundant, such as the Gulf Council Countries of the Middle-East. The average price of a biodegradable plastic is 50% higher than conventional polyolefin plastic or synthetic ones [3].

To have a more sustainable practice among plastic producers and reduce associated environmental burdens, governments and communicates must start enforcing very stringent standards and regulations. These will be derived from technical and scientific studies that are applicable to local climates and surrounding environments. Henceforth, the Kuwait Institute for Scientific Research (KISR) was consulted; and as a response to a number of technical problems faced by governing bodies, namely Kuwait Municipality (KM), this project was initiated. This project is executed under the theme of determining the optimal standards required for the supply of plastic bags in Kuwait that are susceptible to degradation, namely biodegradation under the local environment. It should be kept in mind that the plastic bags used as trash plastic bags in Kuwait, are not

determined and supplied via a known standard method of testing. Hence, the design of this project encompasses photo-degradation and biodegradation to cover the possibility of having plastic films that are of a type known to degrade in either route. In addition, a major driving force for the execution of this project is the fact that it was noted as of late that majority of plastic trash and carrier bags in operating landfill sites were non-degradable despite the claims of various producers to supply biodegradable ones. Therefore, this project has also represented a *black-box* dilemma, where in addition to being tasked with verifying the claims of plastic suppliers and cleaning companies, the biodegradation route was also required to be investigated for the climatic conditions of Kuwait.

2 EXPERIMENTAL

2.1 Samples Acquisition and Assessment

Three types of plastic bags imported and used on the Kuwaiti market were secured from local dealers with their main characteristics depicted in Table 1. The samples were cut into standard testing dimension specimens accepted by international protocols for thin plastic film characterization as described previously [4-7]. Readers are referred to Al-Salem et al. [8] for more details. The samples were also identified as PE filled films and results were previously published in Al-Salem et al. [9].

Bag/Film	Intended Use/Application	Thickness (per Specimen)
Type I	Trash (General Purpose)	70 μm
Type II	Trash (General Purpose)	40 μm
Type III	Carrier	30 μm

Table 1: Types and Description of Plastic Bags Considered For Testing. Adapted from Al-Salem et al. [8]

2.2 Natural Weathering of Film Samples

In this work, the films intended for characterization post natural weathering were arrayed over non-expanded metal trays of non-corroding aluminium mesh with openings covering $\approx 70\%$ of its surface area in accordance with ASTM D5272-08 [10] using design for exposure rack 'A' with an approximate individual diameter of openings equal to 0.5 cm. Each rack had seven trays, each divided into two segments allowing 60 specimens to be mounted on. All racks were placed at a 45° angle as per ASTM 1435-05 [11] and ASTM D5272-08 [10]. Two sites were chosen to simulate the impact of weather in Kuwait. The first was located in an arid area close to the bay (Shwiakh area, *latitude* N $29^\circ 13' 49''$; *longitude* $47^\circ 58' 31''$ E) with a mean annual ambient temperature of 32°C and relative humidity of 30%. The second, Salmiya area (*latitude* N $29^\circ 33' 33''$; *longitude* $48^\circ 08' 33''$ E), is a seafront area with a

mean annual ambient temperature of 30°C and relative humidity of 60%. The start of the natural weathering loading was on the 26th December 2017 and were kept with the intention of exposing the samples for a continuous period of one year. The film samples were mounted on the trays with a minimum spacing of 11 mm between each individual specimen [6-7,10-11]. The racks were facing southward direction in accordance with ASTM 1435-05 [11]. A minimum of ten specimens of each type were unloaded of each tray at each site after 1, 3, 6, 9 and 12 months for further testing and characterization. The unloaded film samples were carefully placed in plastic bags and rinsed for 3-5 s before drying and conducting the various experiments. Readers are referred to Al-Salem et al. [9] for more details.

2.3 Accelerated Ageing of Test Specimens

The specimens were exposed to accelerated weathering in accordance with ASTM D 4329 [12]. Samples were mounted on the racks facing the ultra violet lamps with no empty spaces in the panels. This is in order to maintain a uniform repeatable test conditions. Cycle A procedure was used for general applications durability testing, i.e., 8 h of UV exposure at 60°C followed by 4 h of condensation at 50°C . Samples were laid to rest for a minimum of 72 hours before characterization following internationally recognised methodologies and laboratory testing protocols of weathering [12]. A minimum of four replicates were exposed to the different exposure durations in the QUV machine chamber. Ultra Violet (UV) lamps irradiance was also selected according to ASTM D 4329 [6,12], and the lamp type was set to be 0.68 W m^{-2} (irradiance) for normal lamp operation, which was maintained for almost 5000 h of operation. The irradiance sensor was calibrated every 400 h of lamp operation during the UV cycle under normal test temperature. The equipment used was cleaned every 800 hours to remove scale deposits resulting from water evaporation during the condensation cycles.

2.4 Scanning Electron Microscopy/Energy Dispersive Elemental Spectroscopy

Scanning Electron Microscopy (SEM) was used to determine the extent of degradation and investigate the micro-cracks on the surface of the films studied. The morphological analysis was conducted on the samples before the exposure to any degradation media and post exposure to the various degradation media. A JSM 6010LA Joel Model microscope was used equipped with high and low vacuum. The samples were placed on double sided adhesive tape for analysis and imaging. The samples were cut into (50 x 100 mm), coated with gold and placed inside the SEM (JSM 6010LA) for analysis. 15 KeV was used for the imaging and elemental analysis. Images were taken with various magnifications between (50 to 500 X). The coated samples were also submitted to Energy Dispersive

Elemental Spectroscopy (EDS) analysis. For this particular analysis, gold peaks were subtracted from the results to eliminate the interference of the coating action on the surface of the plastic films [13-14].

3 RESULTS AND DISCUSSION

All samples exposed to the action of weathering in this work appeared consistent and comparable by touch at start of testing protocols. Physical observations were noted as a first stage and a means of initial assessment for impact of accelerated and natural weathering on the exposed samples. Signs observed visually can lead to the early detection of deterioration and can indicate the severity of the weathering tests conducted. The natural weathering samples were monitored continuously and observational notes were taken with regard to the weather and any signs of deterioration that prevents the samples from being further analysed. The samples had a stable and gradual degradation with respect to exposure time judging by the visual appearance of the plastic films of all three types. The winter season faced in Kuwait this year was noted with a somewhat cloudy weather at the start of the experimentation stage with an average direct sunlight exposure of five hours. Statistical analysis is shown elsewhere with respect to weather parameters [15]. It should also be noted that signs of crazing and haziness were visible from the first unloading session (i.e. 30 days) on the 25th January 2018.

Samples appeared more crazed with respect to their thickness as noted for the first two unloaded batches in this work for both sites. It was also apparent that the photodegradation of the polymers serving as substrates to the biodegradable blends, was clearly related to the metrological conditions which accelerated the degradation process with the changes in seasons of exposure. Increase in blistering and crazing was noted with both site loadings as well, as a function of weathering time. Understanding the mechanism of photodegradation is essential to study the phenomena itself and analyse the status of the samples after various exposure durations. There were no samples that deteriorated and fragmented (totally) with time, only cracks appeared as a results of exposure. Over 40% of the samples had cracked for the intended period of exposure (1 year) however it was noted that 40% and more were broken by the ninth month, which led to the termination of the test by that time.

The samples studied after accelerated weathering have shown a gradual decrease in weight after each exposure duration extending to the threshold limit. However, polyolefin polymers are known to be hydrophobic materials by their nature that will not trap any residual moisture from washing or the surrounding atmosphere. Hence, the weight gain behaviour witnessed in some of the formulations in this work against weathering durations varying between accelerated and natural tests can be attributed to the photo-

degradation mechanism triggered by UV exposure and cross-linking behaviour of the oxo-biodegradation process. Similar observation were noted previously in published technical communications [16-18].

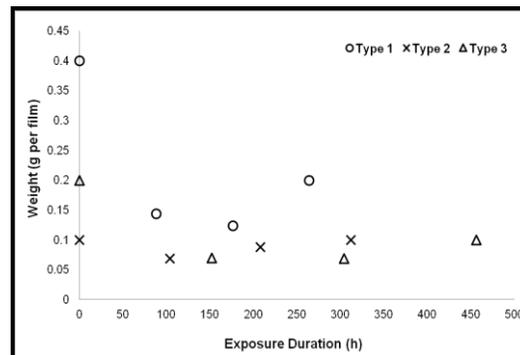


Figure 1: Weight Loss Analysis As A Function of Exposure Duration (hours) Under Accelerated Weathering. Source: Al-Salem et al. [15].

Various images were taken for the three types of samples at 50X, 100X, and 500X magnifications. In addition, an elemental spectroscopy (EDS) analysis was conducted for the three control samples. For this particular analysis, only carbon peaks were detected and a very small unnamed peaks were noticed which were associated with metals of pro-degradant additives. These peaks were identified as calcium (Ca) which corresponds clearly to the amount of CaCO_3 present in the film samples, which identifies them as an oxo-biodegradable polymer filled with pro-degradants. The images show clear evidence of crystals bulging out within the polymeric matrix which is consistent of PO polymers micrographs. It is typically noted to have such behavior for PO polymers due to their semi-crystalline state. There were also notable starches and puncture holes that are consistent with manufacturing and compounding of plastic articles. The material was also rendered as a carbon based one with no evidence of any other contamination except by trace which can be a result of touch the samples by hand (as a commercial product).

The EDS results for Type I showed carbon presence of 98% as a response to electric charge. The EDS analysis has also confirmed similar nature (i.e. carbon based) of the sample to Type I with 99.93%. Type II micrographs can also indicate the smoother surfaces of the material produced with a carbon content of 97.68%. The carbon content determined using the EDS analysis is not as accurate for calculations conducted for biodegradable testing as they are based on the charge of the materials to the coating of SEM which was gold (Au) due to coating of the samples. Cracks were more visually apparent on the surfaces of the materials. The micro-cracks were increasingly visible by the termination of the accelerated weathering and towards the threshold limit. The cracks were measured at larger than 3 mm which is a clear indication that degradation took

place on the surfaces. These cracks can also serve as evidence that oxo-biodegradation took place for type I as the plastic product was sensitive to UV radiation.

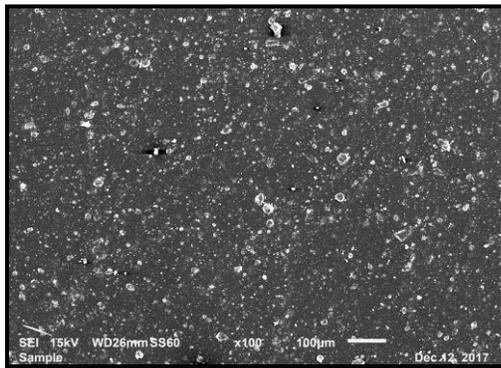


Figure 2: Micrograph For Sample Type I (Control) Determined Using X 100 Magnification. Source: Al-Salem et al. [15]

Type II of the studied samples exhibited similar behaviour to the type I based on the morphological assessment post accelerated weathering. The crystallinity of the samples also are in-line with the analysis shown in this work. The crystalline regions were noted to be less visible when the exposure to the surface was at 2/3 of the threshold limit, and almost all of the crystalline region had diminished with exposure time. Blisters were also noted to be more visible towards threshold limit of UV exposure revealing that the UV degradation has shown clear and visible action triggering degradation on the surfaces. Branching and cross-linking was evident on type III the studied samples, especially by the duration of 2/3 and TL. This was noted clearly with the SEM micrographs and is also consistent with thin oxo-biodegradable bags behaviour.

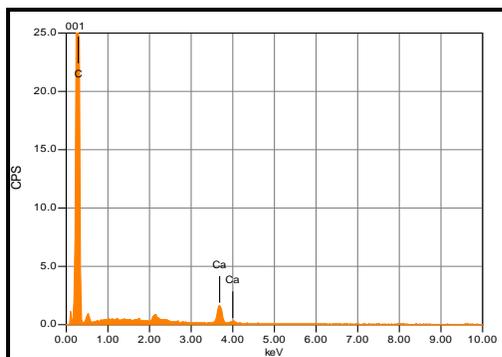


Figure 3: Elemental Analysis Conducted By EDS For Type 1 (Control) – Uncoated Specimens. Source: Al-Salem et al. [15]

4 CONCLUDING REMARKS

Samples deemed (oxo-biodegradable in nature) were exposed to natural and accelerated routes of photo-degradation. The humid environment of site no.2 resulted in clear deterioration on the samples exposed to natural weathering. However, judging by the micrograph images, it can be noted that arid and dry climates had a more adverse effect. Type III showed also similar behaviour between both sites, where it was noted that the increase in crystallinity was apparent with exposure showing the branching of the polymeric chains. Crystalline zones and cracks were evident with time of exposure. However, in comparison to site no.2 the samples were more deteriorated due to the action of pro-degradant oxidation under more humid conditions. The same was noted with the other samples at both sites.

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