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Research Article

Thermal and Rheological Response to Ultraviolet Stabilizers Additive in Linear Low Density Polyethylene under Severe Environmental Conditions

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Abstract

Background and Objective: There are different plastic materials for outdoor usage and depending on several factors related to their weatherability selection is made. Polyethylene (PE) is the simplest polymer chemically used for such purposes, it is one of the most common plastics due to their low cost and simplicity of manufacture. Thermal stability and ultraviolet (UV) resistivity are main properties to be considered when any of PE grades are used for outdoor applications. In this paper Ultraviolet stabilizer has been added in different concentrations to linear low density polyethylene (LLDPE) to measure the deterioration of the thermal and rheological properties when subjected to severe conditions such as the gulf desert conditions. **Materials and Methods:** The LLDPE resins mixed with different weight percentages of ultraviolet absorbing additives were compounded in a twin-screw extruder. The prepared films were exposed to severe outdoor weathering conditions, involving high temperature, dust, humidity and intense solar energy, for various periods over 9 months period (Kuwait is one the hottest spots on earth during summer). **Results:** Results were obtained after exposure to outdoor weathering, the films were tested for thermal stability using thermo gravimetric analysis (TGA). It was found that the overall thermal stability has improved with the incorporation of Ultraviolet (UV) additives, however, increasing exposure time beyond 4 months showed lower thermal stability of the samples those contains 0.6% additives as reflected by the temperature at which decomposition is initiated. Moreover, scanning electron microscopy (SEM) results showed a clear surface and morphological change which consequently can affect product rheology. Processability of the samples was also investigated using a discovery hybrid rheometer, the results indicated a predominance of the viscous behavior over the elastic one for samples with 0.3% UV concentration. **Conclusion:** Generally, the study results concluded that the LLDPE containing UV absorbers at a 0.3% concentration have shown better improvement in comparison with other concentrations in terms of thermal degradability and processability.

Key words: Thermal stability, ultraviolet stabilizer additive, LLDPE, morphology, rheology

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Polymers are used in a growing number of applications, in which they are exposed to a variety of environmental loading conditions. Therefore, end users and engineers need information regarding the influence of environmental conditions on alternative polymers and formulations, in order to make an optimum selection of the materials and to improve the design of products for any particular applications. In many outdoor environment applications, polymers might be subjected to aggressive environmental pollutants and extreme weather conditions. Such conditions will influence the mechanical and thermal properties of the polymers and, accordingly, could have a significant impact on the product performance. Environmental outdoor factors may include aggressive chemicals, water, abrasive agents, such as sand and dust as well as sunlight which can have deleterious effects on polymer behavior¹⁻³.

Polyolefin, particularly linear low density polyethylene (LLDPE) are relatively inexpensive and exhibit interesting properties that make them favorable for many applications⁴. However, LLDPE films are susceptible to photo-degradation, which mainly involves the abstraction of unreactive hydrogen atoms from the polymer backbone. This occurs upon exposure to UV radiation in the range of 290-400 nm⁵⁻⁷.

Some studies have been reported the influence of natural weathering on LLDPE and LDPE⁸. Other reports evaluated the performance of light stabilizers under accelerated and natural weathering conditions⁹. Only a few studies have dealt with the response of polymers to harsh desert weather such as in the Gulf countries, which combines high ultraviolet radiation with high ambient temperatures for prolonged durations^{10,11}. It has been found that polyethylene sheets exhibit drastic deterioration after only 6 months of outdoor exposure.

Polymer degradation properties have been the focus of many researchers as it provides important information about the polymer properties and performance¹². Most polymers used as industrial plastics melt at 300°C or more and degrade in a short time at high temperatures. Therefore, the studies of thermal degradation at higher temperature have been conducted for understanding the polymer stability during processing and in high temperature applications¹³. Various studies have been reported thermal degradation of polymeric materials¹⁴⁻¹⁷. Some reports have discussed thermal degradation under accelerated and natural exposure conditions over a long period of time¹⁸. The thermal degradation behavior of polyethylene has been investigated by using thermo gravimetric analysis in order to obtain the degradation temperature¹⁹.

Moreover, melt rheology data is required by the design engineer to tweak the material structure to ensure better processing performance without affecting the final product's performance²⁰. Studying of how the stress in a material or force applied is related to deformation and flow of the polymer is very important information which is required when evaluating a polymer or a blend for certain application or mass production. Similarly, for used polymer, rheology aids the development of the recycling process to help ensure that the polymer properties are retained during the reprocessing cycle. Thus, analyzing melt rheology of a polymer is essential when product structure might be affected as the transformation process reacts to small changes in the polymer such as blending with another polymer or using additives²¹.

In this study, LLDPE formulations incorporating various percentages of ultraviolet (UV) absorbers were used to evaluate their behavior after exposure to natural weathering conditions in Kuwait. Thermo gravimetric analysis (TGA), scanning electron microscopy (SEM) for morphological structure and rheometer were used to evaluate the effects of outdoor exposure on the LLDPE samples. In particular, the temperature at which decomposition is initiated in TGA was used as an indicator of thermal stability. Currently in the literature there are very few studies directed to the evaluation the enhanced LLDPE with stabilizers for sever thermal applications. Thus, the result of this work is considered of a high value for both manufacturers and users in the gulf region, to understand the level of LLDPE performance exposed to harsh weather such as Kuwaiti desert and how to select the right additives in terms of concentration and blend.

MATERIAL AND METHODS

Experimental site: The experiment was carried out as a field trial at the Petroleum Research Center (PRC), Kuwait Institute for Scientific Research (KISR), Kuwait, The total exposure period was 9 months starting from June until April. Collected samples were later tested in the PRC facilities.

Materials and research: The following materials were used: Linear low density polyethylene (LLDPE) produced locally in Kuwait commercial grade resin (density: 0.918 gm/cc), UV additives were provided by local supplier (Tinuvin 494FB, Tinuvin NOR 371 (Supplier) and Chimasorb 81 (Supplier)).

The masterbatch was prepared by mixing UV additives in different ratios with the LLDPE resin commercial grade (Kuwait). The additives and resins were physically dry mixed for a period of 30 min in a drum blender for each 10 kg of

blend. Different concentrations (weight %) of additives were used, for instance the ratio of UV additives (UV (0.6) were divided as Tinuvin 494 FB (0.15%), Tinuvin 371 NOR (0.15%) and Chimasorb 81 (0.30%) and for 0.3% ratios were divided in half. Similarly different films without additives were also prepared.

Procedure: In order to study the influence of natural weathering conditions on different samples, the durations of weathering exposure were changed and different times of 1, 4 and 8 months were used.

Blend formulations were compounded by using Killion Compounding Extruder diameter (D) = 38 mm, 30:1 L/D). The compounded samples were then extruded in the Mac-Plas

Table 1: Killion compounding parameters used to produce formulation of LLDPE films

Parameters	Settings
Temperature at barrel zone 1 (°C)	165
Temperature at barrel zone 2 (°C)	175
Temperature at barrel zone 3 (°C)	185
Temperature at barrel zone 4 (°C)	195
Clamp ring temperature (°C)	200
Adaptor (°C)	200
Die temperature (°C)	200
Screw speed (rpm)	75
Melt temperature (°C)	220
Head pressure (bars)	164

Table 2: Mac-Plas film extrusion conditions

Parameters	Settings
Temperature at barrel zone 1 (°C)	145
Temperature at barrel zone 2 (°C)	160
Temperature at barrel zone 3 (°C)	160
Temperature at barrel zone 4 (°C)	160
Temperature at barrel zone 5 (°C)	160
Die-1 temperature (°C)	165
Die-2 temperature (°C)	165
Screw speed (rpm)	40
Head pressure (psi)	2890-3630
Melt temperature (°C)	175

film line (size = 55 mm 30:1 L/D) at 175°C to produce film samples. Killion compounding and Mac-Plas extrusion conditions are shown in Table 1 and 2, respectively.

Films were drawn through a metallic die to produce rolls, which were eventually cut with a die cutter (Ray-Ran model, ram stroke: 14 mm) to produce the desired film thickness of 100 µm in accordance with ASTM-D882 (1991).

Experimental design and data collection: The prepared film samples were mounted on metallic plates which are allocated in the north of Kuwait, the middle portion of the film was allowed to be exposed to sunshine for better natural weathering procedure. For each selected concentration of additives 5 specimens per test (TGA, rheology and SEM) in addition to 5 blanked samples were lined mounted on the metallic plates. The plates were then placed on a board facing southwards at a 45 degree angle with the plane of the earth as per ASTM D1 435-94 (1994). Exposed samples were periodically removed from the plates and washed gently with distilled water. Data of samples for each condition after exposure were collected after being tested for targeted parameters. Table 3 shows the seasonal variations of temperature and humidity for the state of Kuwait during the corresponding period.

Parameters, thermal, morphology and rheology: To study the thermal degradation of the exposed films, Shimadzu TGA-50H (from Japan) was used under air at a flow rate of 40 mL min⁻¹. The experimental temperatures were varied from ambient temperature to 600°C with a heating rate of 10°C min⁻¹ for rheology a rheometer manufactured by TA Instruments Model HR 3 Discovery (Germany). Selected samples were subjected to A scanning electron microscope (TESCAN TS-5135) with an INCA energy dispersive X-ray spectroscopy system (Oxford Instruments) was used to

Table 3: Average total hours of sunshine and wind direction for the years 2015-2017

Month	Temperature (°C)	Humidity (%)	Average total h of sunshine/year			Wind direction (degrees)		
	Average	Average	(Years)			(Years)		
			2015	2016	2017	2015	2016	2017
January	17	67	192	225	180	WNW (292)	ESE (112)	WNW (292)
February	20	65	161	205	187	WNW (292)	W (270)	W (270)
March	24	60	261	204	217	SE (135)	NW (315)	ESE (112)
April	31	60	225	198	154	E (90)	S (180)	WSW (247)
May	39	57	226	215	143	NW (315)	SSE (157)	NW (315)
Jun	41	55	325	272	123	WNW (292)	NW (315)	NW (315)
July	45	42	317	340	308	W (270)	WNW (292)	NW (315)
August	44	50	314	336	312	NW (315)	WNW (292)	NW (315)
September	42	58	312	296	245	NW (315)	NW (315)	N (360)
October	34	62	291	273	E (90)	ESE (112)	NW (315)
November	22	62	210	229	225	WSW (247)	S (180)	ESE (112)
December	18	68	199	179	261	SE (135)	SSE (157)	SE (135)

Source: Kuwait Meteorological Center

examine the morphology to investigate the damages to the polymer matrix structure after exposure. All test results were repeated 3 times to for quality check.

Statistical analysis: The experiment was conducted based on 5 samples per condition and the results were analyzed statistically with the use of average of 3 technique with less than 1% error in results for each condition.

RESULTS AND DISCUSSION

Kuwait climatological data: The climatological data for the years 2016 and 2017 were obtained from Kuwait Meteorological Department²², Table 3 shows the average temperature and humidity for years 2016 and 2017. These data show that the highest peak temperatures were in the months of June, July and August, where the average temperature exceeded 40°C. This indicates that the highest average daily sunshine was obtained during the summer, i.e., the months of June, July and August. These results support the argument that the most detrimental effects on the samples should take place during this period.

In terms of wind direction, the samples were initially placed in the direction of incoming wind, this was done in order to achieve maximum exposure of the samples. During this period of time, it is expected that the maximum potentially damaging exposure of the samples took place due to the higher temperature and long daytime exposure.

Thermal degradation and stability: Thermal stability is a very important property when a polymer is mixed with additives or is subjected to different processing conditions. Thus, the prepared samples were tested for thermal degradation using TGA to evaluate their ability to handle temperatures for specific application. This technique is used to analyze samples that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture).

The thermo gravimetric (TGA) curves of the blanks and the samples exposed to weathering outdoors (WO) for periods of 1, 2, 4 and 8 months will be discussed below. Test results are reported for blank samples and samples with and without additives.

TGA thermograms of LLDPE samples with and without UV additives are shown in Fig. 1-4. The pristine LLDPE (no additives) had single-stage degradation with 80% weight loss at around 455°C as expected shown in Fig. 1 for different exposure periods. However, samples with additives after exposure to natural weather for different periods 4 and

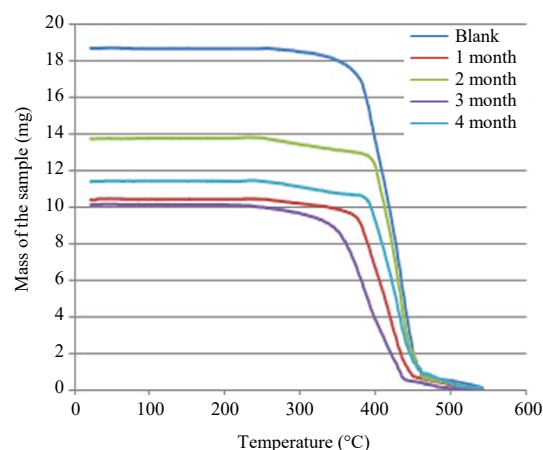


Fig. 1: Direct comparisons of samples without additives (non additives) for different WO duration

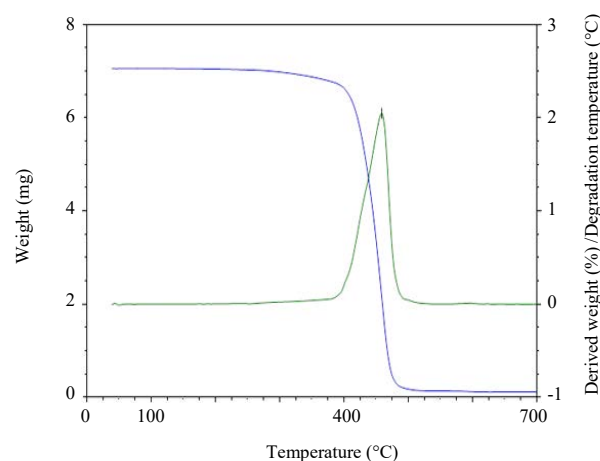


Fig. 2: Thermal degradation of samples with 0.3% UV exposed to natural weathered for period of 4 months

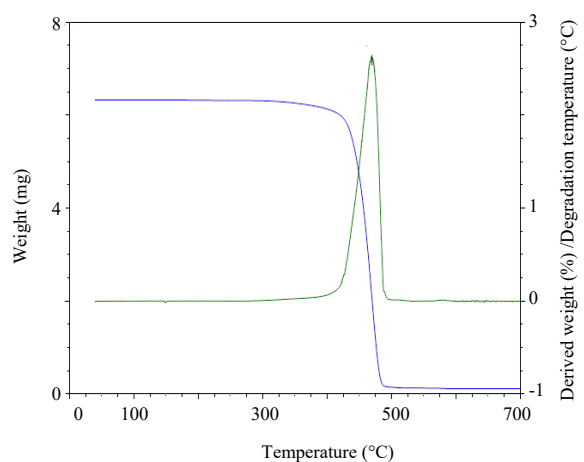


Fig. 3: Thermal degradation of samples with 0.3% UV exposed to natural weathered for period of 8 months

8 months have shown similar single stage behavior, which is to be ascribed to the stability of the polymer matrix and good UV stabilization even after exposure to harsh natural weather. Moreover, non-minor peak near to degradation temperature can be attributed to the suitable percentage presence of additives.

TGA results for samples with 0.3% UV additive: In Fig. 2 it can be observed that the thermal degradation of samples with additives after 4 months was detected at 401°C, with the maximum weight loss rate at 490°C and complete decomposition was observed at around 630°C for both samples (non-additives and with additives) the degradation curve shows a single step degradation process, which is consistent with general behavior of all samples as described earlier. However, a genuine thermal stability is observed as the non-additives sample started to degrade at 330°C with maximum weight loss (1 mg) at 430°C. Samples exposed to WO for longer period (8 months, in Fig. 3) have shown similar stability with single stage degradation but have started earlier maximum weight loss at 480°C and that can be attributed to UV high intensity UV during summer days (sever desert conditions, Table 3).

TGA results for samples with 0.6% UV additive: In Fig. 4 it can be observed that the thermal degradation of samples with additives after 4 months exhibit 2 stages degradation starting at 260°C, the thermal stability of the samples reveal early thermal degradation compared to the other samples. This is probably due to loss of the additives in this temperature range. However, the main degradation (second stage) of these samples starts at delayed temperature (410°C) when compared with other samples exposed to WO and reached maximum degradation at 510°C. This may be due to the possibility that higher percentage of additive could cause insignificant cross linking of the polyethylene molecules resulting initial minor degradation followed by main stage degradation. Samples exposed to WO for eight months in Fig. 5 have shown more stability and smooth one stage degradation, however, it matches the late degradation temperature (around 410°C).

In general, for the samples with additives after exposure the major weight losses were noted in the range of 400-410°C, which corresponds to better thermal stability when compared to non-additives samples (weight loss range 320-360°C). Moreover, samples with 0.3% UV additives have shown more polymer matrix stability resulting in consistent thermal stability (one stage degradation).

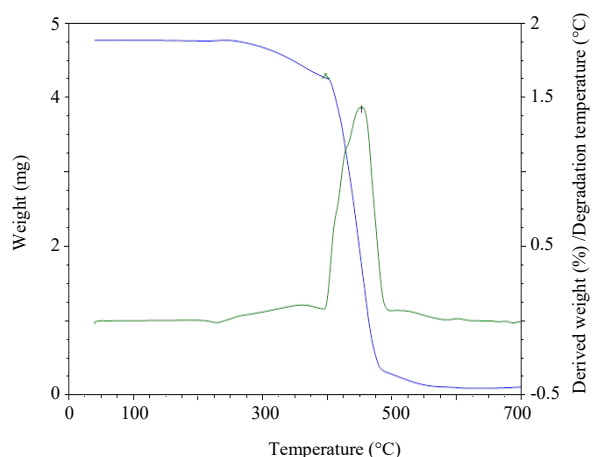


Fig. 4: Thermal degradation of samples with 0.6% UV exposed to natural weathered for period of 4 months

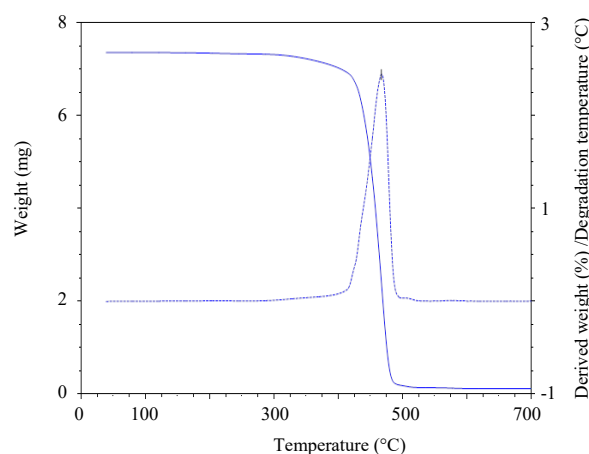


Fig. 5: Thermal degradation of samples with 0.6% UV exposed to natural weather for period of 8 months

Morphological Analysis, Scanning Electron Microscopy (SEM):

Figure 6 a and b show SEM micrographs of the surface of unexposed and exposed samples, respectively. It is obvious that significant surface and morphological changes occur as a result of outdoor exposure. These images show a difference between the morphology of the samples during the weathering exposure and observed the presence of some surface cracks. From the images it can be noticed that the surface of the unstabilized LLDPE samples is attacked more than the stabilized LLDPE samples. This is attributed to the increase in the amount of absorbed ultraviolet radiation and there by failure in the samples. Change in temperature and humidity are also key parameters that are capable of changing the surface morphology of the samples specially when subjected to desert environment. The resultant morphologies

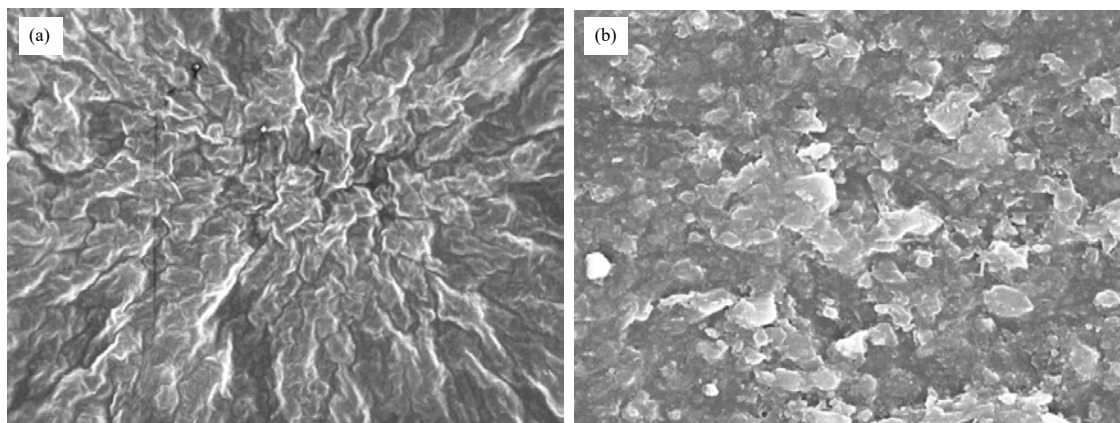


Fig. 6: SEM micrographs of the surface of (a) zero time exposure and (b) 8 months time exposure

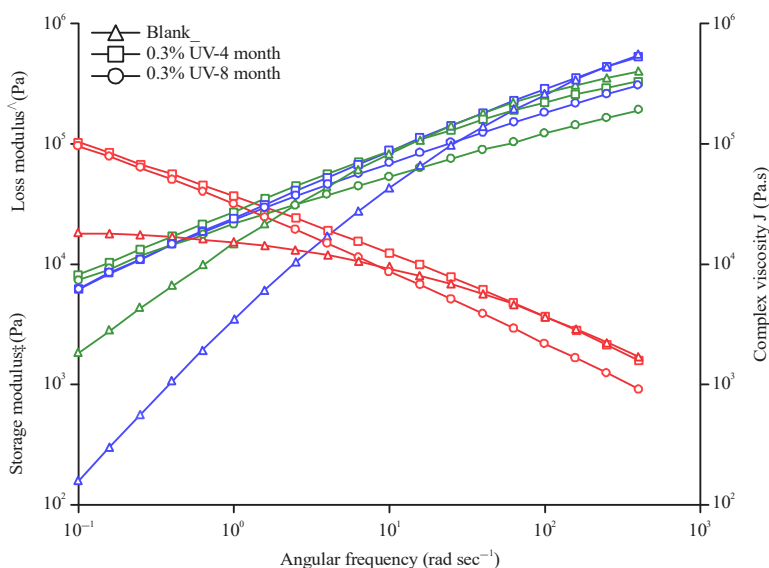


Fig. 7: Rheological analysis of LLDPE/UV 0.3% for exposure period 4 and 8 months

Storage modulus G' (Pa) (blue lines), Loss modulus G'' (Pa) (green lines), Complex viscosity (Pa.s) (red lines)

are a consequence of the photo-oxidation reactions that brings breaking of chemical bonds of the macromolecular backbone of polymers. Moreover, chemical changes such as depolymerization and cross linking might contribute significantly to the observed changes. Furthermore, the presence of dust and other particles can affect the degradation rate of the polymer surface. In general these results show that the unstabilized LLDPE films experience a remarkable degradation under weathering factors (UV, O_2 , humidity), in addition to aggressive chemical pollutants.

Rheology: When using a blend of polymers or additives to enhance properties it is very critical to study the melt behavior

as blending or additives can impact the internal structure of the polymer and hence processing properties. The rheological properties are mainly dependent on chemical changes happening during UV radiation process by chain scission and cross linking. The angular frequency dependence of shear storage modulus (G') and shear loss modulus (G'') with complex viscosity (η^*) at 180°C is plotted in Fig. 7 and 8. The angular frequency range chosen was from $0.1\text{-}400\text{ rad}\cdot\text{sec}^{-1}$, geometry 25 mm parallel plate under a frequency Sweep procedure, for samples with 0.3% UV stabilizer additives, there was a predominance of the viscous behavior over the elastic one as shown in Fig. 7. Where, in Fig. 8 the dominance of the viscous behavior effect lasted to higher frequency. Also it is important to understand that the elastic behavior of the

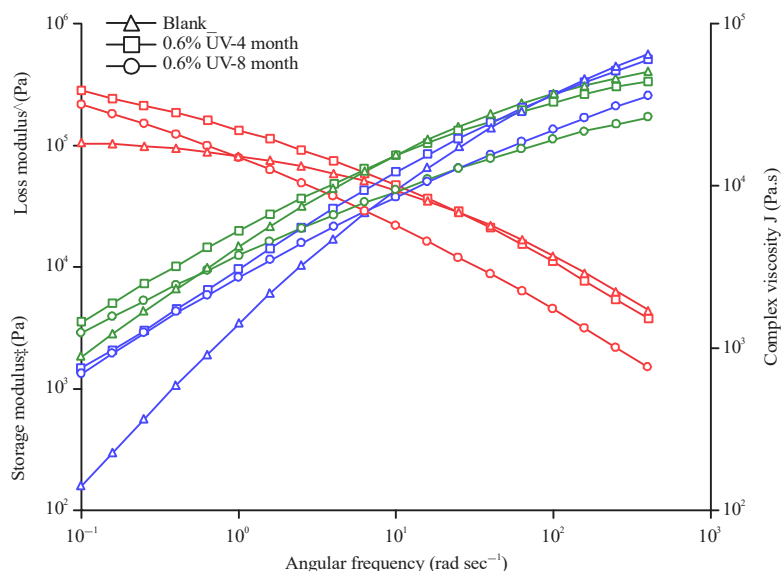


Fig. 8: Rheological analysis of LLDPE/UV 0.6% for exposure period 4 and 8 months
Storage modulus (Pa) (blue lines), Loss modulus (Pa) (green lines), Complex viscosity (Pa.s) (red lines)

material under a shorter process of time has a negative effect on its process ability and is linked to creep and stress relaxation.

Different behaviors were observed for samples with UV stabilizers when compared to blank samples. Figure 7 and 8 show a variation of moduli and complex viscosity with an angular frequency for the samples containing UV stabilizers. The samples containing UV stabilizers show higher zero shear viscosity compared to the pure resin. Samples without UV stabilizers undergo chain scission and there by reduction in molecular weight. The viscosity is also influenced by the molecular structure of the polymer. There is a sharp decrease in the complex viscosity of samples with stabilizers at high angular frequencies. The effect of UV stabilizers was further confirmed by the results of the storage and loss of modulus, which is less value for the virgin resin.

CONCLUSION

Thermo gravimetric analysis (TGA), morphological analysis and rheology were carried out to evaluate ultraviolet stabilizer additive influence on linear low density polyethylene under sever conditions. The samples were subjected to outdoor exposure under severe Kuwait desert climate conditions to study the thermal stability of LLDPE/UV stabilizer formulations. The results suggest significant effects of outdoor exposure and additives (UV absorbers) on thermal stability as indicated by the temperature at initiation of decomposition. It was found that longer exposure is associated with more TGA weight

loss of the sample. However, decomposition temperatures of outdoor weathered samples are higher for samples containing the chemical additives, particularly after 4 month of exposure period. The balance of depolymerization and cross linking reactions occurring during ultraviolet exposure might determine the decomposition temperature of the material. The SEM observation show visual evidence of surface and morphological changes associated with prolonged outdoor exposure (8 months). These changes probably reflect erosion and abrasion effects, in addition to chemical changes due to combined thermal and photo degradation of LLDPE. Overall, the results indicate that the overall thermal stability of LLDPE, especially containing UV absorbers of 0.3% has improved. The rheology part of the study showed that the samples containing UV stabilizers have higher zero shear viscosity compared to the pure resin. Samples without UV stabilizers undergo chain scission and there by reduction in molecular weight. Dominance of viscous behavior is preferable in this case as the elastic behavior of the material under shorter process times has a negative effect on its processability and linked to creep and stress relaxation.

SIGNIFICANCE STATEMENT

This study revealed the impact of the gulf desert severs conditions on the thermal and rheological behavior of LLDPE protected with UV additives. Also, the study uncovers the processability and suitability of the enhanced LLDPE for recycling after usage.

REFERENCES

1. Gewert, B., M.M. Plassmann and M. MacLeod, 2015. Pathways for degradation of plastic polymers floating in the marine environment. *Environ. Sci.: Process. Impacts*, 17: 1513-1521.
2. Fabiyi, J.S. and A.G. McDonald, 2014. Degradation of polypropylene in naturally and artificially weathered plastic matrix composites. *Maderas. Ciencia Tecnol.*, 16: 275-290.
3. Batista, N.L., M.C. Rezende and E.C. Botelho, 2018. Effect of crystallinity on CF/PPS performance under weather exposure: Moisture, salt fog and UV radiation. *Polym. Degrad. Stab.*, 153: 255-261.
4. Wang, G., X. Yang and W. Wang, 2019. Reinforcing linear low-density polyethylene with surfactant-treated microfibrillated cellulose. *Polymers*, Vol. 11. 10.3390/polym11030441.
5. Nguyen, V., J. Hao and W. Wang, 2018. Ultraviolet weathering performance of high-density polyethylene/wood-flour composites with a basalt-fiber-included shell. *Polymers*, Vol. 10. 10.3390/polym10080831.
6. Martinez-Romo, A., R.G. Mota, J.S. Bernal, C.F. Reyes and I.R. Candelas, 2015. Effect of ultraviolet radiation in the photo-oxidation of high density polyethylene and biodegradable polyethylene films. *J. Phys.: Confer. Ser.*, Vol. 582. 10.1088/1742-6596/582/1/012026.
7. Lu, T., E. Solis-Ramos, Y. Yi and M. Kumosa, 2018. UV degradation model for polymers and polymer matrix composites. *Polym. Degrad. Stab.*, 154: 203-210.
8. Amin, R.M., P.A. Sreekumar, M.A. Al Harthi, S.K. De and B.F. Abu Sharkh, 2013. Natural weather ageing of the low density polyethylene: Effect of polystarch N. *J. Applied Polym. Sci.*, 127: 1122-1127.
9. Basfar, A.A. and K.I. Ali, 2006. Natural weathering test for films of various formulations of low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). *Polym. Degrad. Stab.*, 91: 437-443.
10. El-Tonsy, M.M., S.A.A. AlSaati and A.H. Oraby, 2015. Degradation of low density polyethylene due to successive exposure to acid rain and UV radiation. *Int. J. Sci. Eng. Applic.*, 4: 327-334.
11. Gogotov, I.N. and S.K. Barazov, 2014. The effect of ultraviolet light and temperature on the degradation of composite polypropylene. *Int. Polym. Sci. Technol.*, 41: 55-58.
12. Dana, M., G.H. Zohuri and S. Asadi, 2019. Improvement in volume resistivity and morphology of a blend of polyolefin elastomer with linear low-density polyethylene. *Iran. Polym. J.*, 58: 587-595.
13. Kahar, A.W.M., N. Sarifuddin and H. Ismail, 2017. Structural, thermal and physico-chemical properties of high density polyethylene/natural rubber/modified cassava starch blends. *Iran. Polym. J.*, 26: 149-159.
14. Wallis, M. and S.K. Bhatia, 2006. Kinetic study of the thermal degradation of high density polyethylene. *Polym. Degrad. Stab.*, 91: 1476-1483.
15. Bolbukh, Y., P. Kuzema, V. Tertykh and I. Laguta, 2008. Thermal degradation of polyethylene containing antioxidant and hydrophilic/hydrophobic silica. *J. Thermal Anal. Calorimet.*, 94: 727-736.
16. Aboulkas, A. and A. El Bouadili, 2010. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. *Energy Convers. Manage.*, 51: 1363-1369.
17. Fairbrother, A., H.C. Hsueh, J.H. Kim, D. Jacobs and L. Perry *et al.*, 2019. Temperature and light intensity effects on photodegradation of high-density polyethylene. *Polym. Degrad. Stab.*, 165: 153-160.
18. Anonymous, 2015. Rheology of polymer 2015: Report. TA Instruments, USA.
19. Pielichowski, K. and J. Njuguna, 2005. Thermal Degradation of Polymeric Materials. iSmithers Rapra Publishing, UK.
20. Mackay, M.E., 2018. The importance of rheological behavior in the additive manufacturing technique material extrusion. *J. Rheol.*, Vol. 62. 10.1122/1.5037687.
21. Bustos, M., 2017. Effect of selected additives on the mechanical and rheological properties of an amorphous poly (Hydroxyalkanoate). Master's Thesis, Department of Chemical Engineering McGill University Montreal, Quebec, Canada.
22. Climate-Data.Org, 2018. Data sources. Open Data Commons Open Database License (ODbL). <https://en.climate-data.org/info/sources/>