

**PHOTO-OXIDATIVE DEGRADATION OF
RECYCLED, REPROCESSED HDPE:
CHANGES IN CHEMICAL, THERMAL AND
MECHANICAL PROPERTIES**

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Abstract. Weathering degradation of thermally stabilized recycled and reprocessed high-density polyethylene (HDPE) was monitored by naturally exposing the HDPE dumbbells on the aluminum exposure racks. The HDPE dumbbells were prepared in the injection-molding machine using small percentage of anti-oxidants and slip agent to protect the thermo-oxidative degradation of the material. Four types of HDPE material were used under this study such as: virgin HDPE, 50/50 mixture of recycled and fresh HDPE, virgin HDPE with thermal stabilizers and recycled HDPE with thermal stabilizers. The performance characteristics of the weathered recycled HDPE material was monitored by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and the mechanical properties. The results clearly revealed the deterioration of virgin and recycled mixed HDPE formulations as compared to thermally stabilized recycled HDPE material under the hostile outdoor weather conditions of Dhahran, Saudi Arabia. A significant drop in the mechanical, thermal and the chemical properties was observed for all the exposed HDPE formulations in terms of drop in elongation, increase in the percent crystallinity and percent carbonyl index. The photo-stability of recycled and reprocessed HDPE materials can be enhanced by incorporating appropriate amount of photo stabilizers in the base formulations.

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1. Introduction

The photo-degradation of polymers has been studied from the early years due to its commercial production. Most plastics are affected by exposure to sunlight in conjunction with other natural weathering forces such as oxygen, water and heat. Synthetic polymers are now often used in applications where the service life is short and the use of long-lived plastics has resulted in criticism because of their non-degradability after they are discarded.

Due to superior properties of plastics they have been used in many outdoor applications such as packaging. These products elude the garbage collection system and become litter. The longevity of these plastics in the litter is semi-permanent and is highly visible. The waste products arising from plastics packaging, which accounts for about 30 % of the total plastics consumption, has contributed to the perception of the plastics as a major environmental problem and to the introduction of legislation prescribing targets for recycling.

The recycled high-density polyethylene (HDPE) can be utilized in too many consumer plastics products, which needs shorter photostability in their service lifetime. These recycled plastics can be made more useful for the commodity products by adding small percentage of virgin resins, processing agents and thermal stabilizers and can save lots of environmental problems arising due to plastics waste material [1].

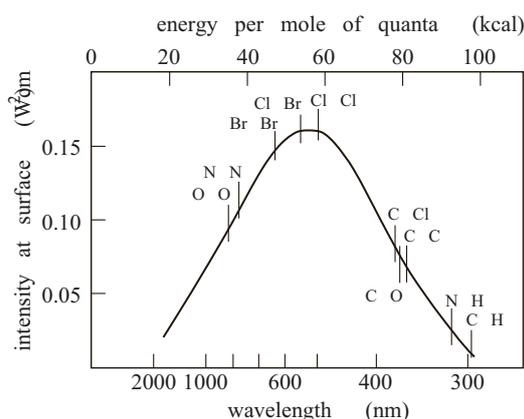


Fig. 1. The wavelength distribution of the radiation reaching the earth from the sun

The polymer undergoes photochemical degradation in an outdoor environment must absorb sunlight. The wavelength distribution of the radiation reaching the earth from the sun is presented in Fig. 1. The strengths of the bonds commonly found in commercial plastics are also shown in the figure. It is

observed that the most useful wavelengths are those in the UV region below 350 nm. Natural sunlight has a low wavelength cut-off at about 300 nm and there is sufficient energy in the photons of the UV range 300–350 nm to break a wide variety of bonds. A photon of the light at 313 nm has enough energy to break a C–C bond, but an alkane will not absorb in this region and in fact, does not absorb down to about 200 nm. However, a carbonyl group will absorb in this region and it can cause the breaking of the C–C bond adjacent to the carbonyl bond.

Oxygen plays a dominant role in the degradation of polymers in the presence of solar radiation. The oxidation of olefins generally leads to a complex mixture of products, in which the oxygen may be combined in a number of different ways. The general mechanism of photo-degradation of polymers is given in Fig. 5 [2]. Polymer UV stability should be evaluated by outdoor exposure, which will allow prediction of performance under conditions of end use [3].

The influence of processing (extrusion, molding, etc) in terms of exposure to shear forces, temperature, oxygen can also add in the degradation process of the polymers. During the end use application polymers are exposed to different environments, which eventually affect polymer lifetime [4].

The consequences of photo-degradation depend on the nature of the polymer and can cause polymer chain scission and cross-linking leading to changes at the molecular level. These irreversible processes eventually change the physical or visual properties of polymer to such extent that the end product cannot serve its purpose [5].

The purpose of this work was to evaluate the outdoor stability of pure, recycled and reprocessed HDPE mixed material with the addition of small percentage of thermal stabilizers in the base formulations. Proper mixing of recycled HDPE and virgin HDPE material was also observed during sample preparation in the injection-molding machine. No additional photo stabilizers were added in the base formulation of material under study.

2. Experimental

2.1. Materials

The recycled shredded material (high-density polyethylene crates) was collected from a local plastics recycling company. SABIC unstabilized HDPE grade M-80064 was used as a virgin HDPE material for mixing with the recycled HDPE.

2.2. Preparation of Samples

Different mixtures were used for preparing the HDPE samples for this study. A total of four types of samples were prepared in the injection-molding machine. Certain percentage of processing agents in the form of antioxidants and slipping

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agents were added to protect the polymer material from thermal degradation during injection molding. The following four combinations of HDPE virgin and HDPE/recycled were extruded with the addition of thermal stabilizers, 0.2 % Irgafos 168, 0.2 % Irganox 1010 and slipping agent 0.1 % Ca stearate.

- Sample MB00 Virgin HDPE (M-80064)
- Sample MB0 50/50 (virgin HDPE/Recycled HDPE + 0.2 % Irgafos 168 + 0.2 % Irganox 1010 + 0.1 % Ca stearate)
- Sample MB1 virgin HDPE + (0.2 % Irgafos 168 + 0.2 % Irganox 1010 + 0.1 % Ca stearate)
- Sample MB2 recycled HDPE + (0.2 % Irgafos 168 + 0.2 % Irganox 1010 + 0.1 % Ca stearate)

The weathering trials for the HDPE samples were done in the hot and humid climate of Dhahran, Saudi Arabia. This region has high level of temperature, humidity and solar radiation and proved to be more aggressive to the plastics material. The HDPE dumbbells were exposed on the aluminum exposure racks. The exposure racks were designed according to ASTM standard D-1435. The samples in the form of dumbbells were mounted on 45-degree racks, facing south direction. The dumbbells were exposed for the period of six months and samples were withdrawn with the predetermined interval. The hostile environmental conditions in terms of average total and UV radiation of Dhahran area are shown in Fig. 2 and the average monthly temperature and relative humidity are shown in Fig. 3. Useful service lifetime of weathered plastics can only be predicted, when all aspects of the anticipated environment are considered.

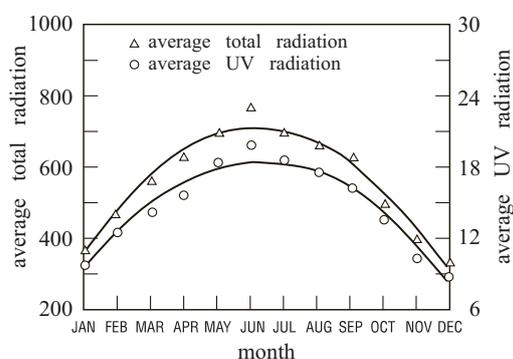


Fig. 2. The environmental conditions in terms of average total and UV radiation of Dhahran area

2.3. Materials Characterization

The naturally weathered HDPE samples were characterized using Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and mechanical testing.

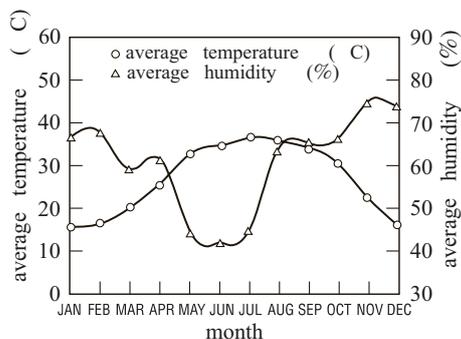


Fig. 3. Relative humidity in Dhahran area

Spectra were recorded by using Perkin-Elmer FTIR model 1650 purged with dry air, with 4 cm^{-1} resolution and at least 16 scans. The integrated area between 1730 and 1710 cm^{-1} of the absorption band at 1715 cm^{-1} was used to determine the oxidation degree, carbonyl index at different exposure month. The instrument was calibrated using standard polystyrene thin film.

The thermal properties were evaluated using Perkin-Elmer DSC-4 differential scanning calorimeter. The thermo grams were recorded in the temperature range of $50\text{--}150\text{ }^{\circ}\text{C}$. The calibration of the instrument was done using Indium, having melting point $156.6\text{ }^{\circ}\text{C}$, transition energy 6.8 cal/g and atomic weight 114.82 .

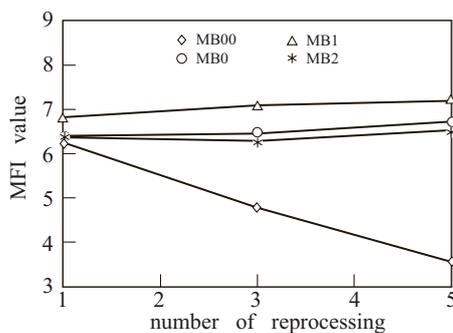


Fig. 4. Melt flow index of recycled polymer at different moldings

Many reactions and pathways of the polymer photo-degradation are similar with those of thermal degradation. The mechanism of the photo-oxidative reactions is presented in Fig. 5. The basic propagating reaction is a free radical chain reaction, which ends up with the formation of carbonyl group and causes chain scission reactions in the polymer backbone. Photo-excited ketone chromophores usually undergo reaction by the Norrish I and II. Both paths lead to polymer backbone cleavage.

Deterioration of the physical and mechanical properties of the polymer takes place, due to combine effect of weather parameters. The test methods commonly used for determining the oxidative stability of the polymers are percent elongation, tensile strength and impact strength. Determination of percent elongation is more effective measurement of oxidative degradation than tensile strength. Tensile strength may not be markedly affected by sample embrittlement, whereas elongation is much more sensitive to photo degradation. It is evident from the literature that chain scission and crosslinking reactions in the polymer backbone are the direct cause of mechanical failure [10].

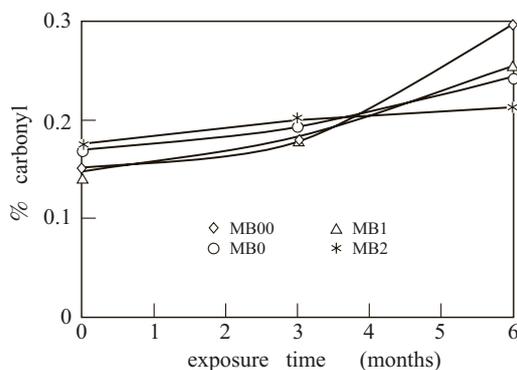


Fig. 6. Effect of weathering on the carbonyl formation in polyethylene

The effect of photo-oxidative degradation on the recycled and reprocessed HDPE has been monitored for the six month exposed samples. The oxidative chemical changes in terms of carbonyl absorbance were monitored through FTIR. Figure 6 and Table 1 present the changes in percent carbonyl for four types of HDPE formulations with different number of molding, as a function of outdoors exposure period. The higher value of carbonyl absorbance in the exposed material indicates severe photo-oxidative reactions in the polymer matrix. The result shows the highest carbonyl index for the virgin HDPE material reprocessed five times with no thermal or photo-stabilizers. Although the gradual increment in the carbonyl index has been observed for all the four

formulations exposed outdoor for the period of six months. The lowest carbonyl formation has been observed for the recycled HDPE formulation MB2. The five times reprocessed sample of MB2 has shown the carbonyl increase of only 21.38 % from its initial value, while the MB00, MB0 and MB1 have shown the higher increase in the range of 97.33 %, 42.35 %, and 75.17 %. The formulation MB2 has shown better weather resistance as compared to other formulations due to the presence of certain percentage of photo-stabilizers in the recycled base material. The other two formulations MB1 and MB00 have shown poor weatherability due to the absence of photo-stabilizers. It could be attributed from these findings that these two formulations MB1 and MB00 have received higher thermo-oxidative degradation during five times reprocessing in the injection molding and were unable to survive in the outdoor. The formulation based on 50/50 HDPE and recycled material MB0 has shown some stability in the outdoor weather due to the presence of small percentage of photo-stabilizers. The addition of virgin unstabilized HDPE in this formulation has further diluted the concentration of available photo-stabilizer in the base material.

Table 1. Change in carbonyl percentage with exposure time

Samples	Exposure time (months)	Carbonyl (%)		
		1 st mold	3 rd mold	5 th mold
MB00	0	0.134	0.141	0.15
	3	0.143	0.172	0.178
	6	0.184	0.241	0.296
MB0	0	0.14	0.151	0.17
	3	0.181	0.19	0.191
	6	0.212	0.22	0.242
MB1	0	0.127	0.137	0.145
	3	0.151	0.164	0.183
	6	0.17	0.192	0.254
MB2	0	0.139	0.14	0.173
	3	0.151	0.155	0.199
	6	0.163	0.181	0.213

The thermal properties in terms of crystalline melt temperature T_m , and percent of crystallinity were monitored by using DSC technique. Figures 7, 8 and Table 2 present the change in crystalline melt temperature T_m and percent of crystallinity for the four HDPE formulations exposed six months in the outdoor.

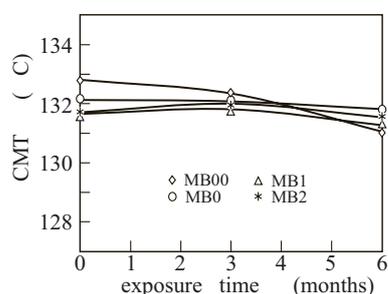


Fig. 7. Effect of weathering on the crystalline melt temperature

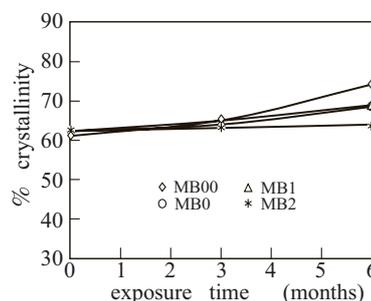


Fig. 8. Effect of weathering on percent crystallinity

Table 2. Change in thermal properties with exposure time

Samples	Exposure time (months)	Crystallinity (%)			CMT (°C)		
		1 st mold	3 rd mold	5 th mold	1 st mold	3 rd mold	5 th mold
MB00	0	59.88	60.05	61.22	132.04	133.39	132.34
	3	62.99	63.56	65.1	131.42	132.45	132.8
	6	68.49	69.06	74.25	132.97	131.84	131.1
MB0	0	61.55	61.9	62.4	133.97	132.93	132.15
	3	62.44	63.21	63.91	131.36	132.09	132.10
	6	64.22	66.33	68.5	133.62	132.22	131.85
MB1	0	60.11	61.43	62.31	131.83	132.82	131.69
	3	63.21	64.3	65.19	131.56	132.20	131.83
	6	65.55	63.51	69.22	131.86	131.97	131.31
MB2	0	61.79	62.11	62.5	133.43	132.12	131.74
	3	63.0	64.18	63.44	131.64	133.77	132.08
	6	64.11	65.9	64.12	132.07	132.28	131.57

The gradual increment in the percent crystallinity was observed for all the four exposed formulations from its initial value. The percent of crystallinity of five times reprocessed and weathered samples clearly indicates the lowest increase of 2.59 percent in crystallinity from its initial value for MB2 as compared to other formulations. The other formulations MB00, MB0 and MB1 have shown increase of 21.28 %, 9.77 % and 11.08 % from its initial value in the percent of crystallinity. The gradual addition in percent of crystallinity is due to oxidative crystallization and scission allowing the freed segments to crystallize in the polymer matrix. The results also present consistent behavior in crystalline melt temperature (CMT) for all the exposed samples. A downward trend was observed for the CMT from its initial value for all the weathered samples. The possible reason for this drop in CMT could be the secondary

crystallization, resulting in the creation of new intermolecular polar bonds due to formation of oxygen containing carbonyl groups [11]. In contrast, some studies have reported increase or constant behavior in T_m with the outdoor exposure time [12]. The percent crystallinity has a good synchronism with the increase in carbonyl absorbance.

The effect of weather on the HDPE material has also been evaluated by determining the percent of elongation and tensile strength of the exposed formulations. Figures 9, 10 and Table 3 present the change in the mechanical properties of six months exposed formulations. The result shows a drop in both the elongation and stress at break for all the exposed samples. The highest drop of elongation of 99.20 and 96.90 % were observed for the samples MB00 and MB1 while the drop in MB0 and MB2 was only 25.0 and 16.8 from its initial value. The reasonable explanation for this behavior in MB0 and MB2 is the prior existence of some percentage of photo stabilizers in the recycled HDPE material. The other formulations MB00 and MB1 were not having a trace of photo stabilizers in the base material to resist the outdoor UV induced degradation and drastically lost all its performance properties.

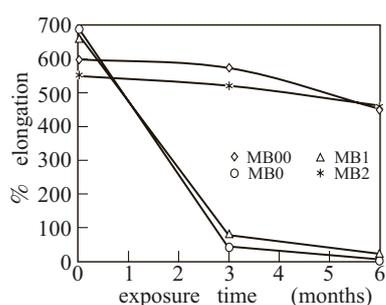


Fig. 9. Effect of weathering on percent elongation at break

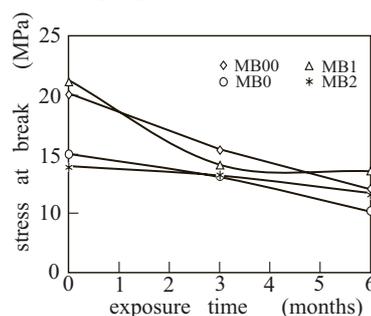


Fig. 10. Effect of weathering on stress at break (MPa)

The photo-oxidation of the polymers generally induces chain scission and crosslinking, the former being generally predominant in the presence of oxygen. In natural photo-aging the mechanical properties decreases rapidly [13].

The similar downward trend was also observed for the Stress at break for all the weathered samples. Figure 10 and Table 3 show the change in stress at break for the weathered samples. The highest drop of 39.6 % and 35.5 % were observed in the stress at break for the samples MB00 and MB1, while the samples MB0 and MB2 have shown the lower drop of 31.5 % and 16.7 % from its initial value after the exposure.

Table 3. Change in mechanical properties with exposure time

Samples	Exposure time (months)	Stress at break (MPa)			Elongation (%)		
		1 st mold	3 rd mold	5 th mold	1 st mold	3 rd mold	5 th mold
MB00	0	21.94	20.91	20.05	720.2	701.2	688.1
	3	19.66	18.21	15.53	59.1	51.1	40.2
	6	18.7	17.24	12.1	20.2	18.2	5.0
MB0	0	16.35	15.9	14.94	650.9	640.6	600.5
	3	14.88	13.96	13.1	613.2	592.2	575.3
	6	13.4	12.83	10.22	484.3	470.1	450.6
MB1	0	22.05	21.31	21.06	716	710.1	671.4
	3	19.26	18.56	14.19	100.2	91.2	80.5
	6	19.0	17.1	13.58	40.6	30.2	20.6
MB2	0	15.4	14.98	13.99	585.9	573.2	549.0
	3	14.91	14.26	13.16	572.3	564.8	520.2
	6	13.56	12.74	11.65	510.4	460.2	456.6

The drop in percent elongation reveals reduction in the strength of polymeric materials, resulting from chain scission and other complex reactions inside the polymer backbone.

4. Conclusions

1. The formulation MB2 has shown overall better performance in terms of lower gain in carbonyl index, percent of crystallinity and lower drop in mechanical properties even after the five times molding and six months of outdoor exposure.
2. The presence of certain percentage of photo-stabilizers inside the base recycled material in MB2 has well resisted the outdoor environment for six months.
3. The formulation MB0 a 50/50 mixture of HDPE and recycled material have also shown improved weatherability as compared to other formulations MB00 and MB1.
4. The addition of unstabilized virgin HDPE in the formulation MB0 has further diluted the available concentration of photo stabilizers in the base material and resulted in lowering weatherability of the material.
5. The two formulations MB00 and MB1 could not resist the outdoor weathering degradation due to the absence of any photo-stabilizers in the material. The material lost all its properties with in six months of exposure.
6. The poor photo-stability of the formulations MB00 and MB1 indicates higher thermo-oxidative degradation during five times extrusion of the material.

7. The incorporation of a small percentage of photo-stabilizers in the base materials leads to further increasing of photo-stability of MB2 formulation.
8. The addition of small quantity of virgin HDPE could enhance the mechanical strength of the MB2 material.
9. The formulation MB2 has retained its performance characteristics up to the second extrusion and could be very useful material for many commodity products, which demand shorter outdoor service life-time.

Acknowledgements

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