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# Micro and macroscopic mechanical behaviors of high-density polyethylene under UV irradiation and temperature



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# A R T I C L E I N F O

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# ABSTRACT

The macroscopic mechanical behavior of high-density polyethylene (HDPE) during photodegradation is characterized by decreases of tensile elongation-at-failure. An apparent linear relation between the elongation-at-failure and the molar mass indicates that the decrease of the elongation of HDPE over time is highly dependent on the decrease of the average molar mass. Possible preferential scission of the high molar mass observed for HDPE exposed to ultraviolet (UV) irradiance higher than 40% (61 W/ $m^2$ ) of the full intensity at 50 °C. Tensile modulus of HDPE exposed at 50 °C increased with the exposure time until reaching the complete loss of ductility except the 5% UV. For 40% UV/30 °C as well as for 5% UV/ 50 °C, the young modulus trend cannot be evaluated with performed (small) duration. Nanomechanical test results suggest that the increased tensile modulus is due to stiffening of the entire cross-section. Furthermore, HDPE showing the complete loss of ductility excluding whibited significantly higher modulus in the surface regions than the core regions particularly for the UV intensity higher than 40% (61 W/ $m^2$ ), which increased crack sensitivity to cause embrittlement of the entire specimens.

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## 1. Introduction

High-density polyethylene (HDPE) is used around the world in various industrial areas such as water distribution pipes, geomembranes, and construction liners [1–3]. The usage of HDPE in these applications requires maintaining high mechanical performance and environmental resistance. For this reason, various aspects of their weathering behavior have been studied over the years. Reports on the degradation of HDPE in a hot natural environment showed a decrease of tensile elongation-at-failure and molar mass accompanying with an increase of crystallinity [4], and embrittlement associated with increasing carbonyl formation [5]. In a cold natural environmental study, Pages et al. exposed HDPE during the Canadian winter and reported a significant decrease in impact energy of HDPE due to a loss of crystallinity and daily thermal fluctuations [6], behavior which is in contrast with that observed for the hot environments.

During weathering tests in the natural environment, several variables play an important role including sunlight, heat, moisture, and thermo-mechanical stresses. In a solar radiation study Satoto et al. reported higher carbonyl index growth (from 0.6 to 1.7) at higher average temperatures (from 5 °C to 25 °C) for HDPE exposed in two different latitudes (Tsukuba in Japan and Bandung in Indonesia), but no clear relationship between carbonyl index and solar radiation [7]. For natural weathering conditions, the spectral energy distribution and intensity of the solar radiation vary with geographic location, altitude, time of day, and season [8], so the effect of UV irradiation on degradation behavior of HDPE is difficult to distinguish from other environmental factors (daily changes of temperature and humidity). Alternatively, artificial weathering tests are often carried out to use UV irradiation simulating solar irradiation with temperature and relative humidity conditions. Artificial aging of HDPE exposed to UV irradiation with a wavelength near 350 nm exhibited similar degradation in oxidation and the loss of elongation as observed in natural aging of HDPE [9]. In terms of the effect of UV intensity, a study using two different commercial UV sources (UVA 340: 0.35 W/m<sup>2</sup> at 340 nm and UVB 313: 0.60 W/m<sup>2</sup> at 313 nm) found that the higher UV intensity



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accelerates the increase of carbonyl index in HDPE [10]. This finding could be affected not by irradiance alone, but also due to different UV spectral characteristics of the two UV sources, which could influence the photochemical reactions [11]. Moreover, it is apparent that degradation studies for HDPE under various UV intensities are rarely reported, which is vital information to predict performance under various outdoor weathering conditions.

Several degradation studies have demonstrated that UV exposed HDPE exhibits a reduction of elongation via embrittlement [4,12]. Embrittlement of HDPE which exhibits a transition from a ductile to a brittle behavior is a critical issue in structural applications since it occurs abruptly and catastrophically. In semi-crystalline polymers, embrittlement is known to be caused by the decrease of molar mass resulting from a quasi-homogeneous chain scission process with the following possible mechanism: chain scission  $\rightarrow$  reduction of molar mass  $\rightarrow$  chemicrystallization  $\rightarrow$  reduction of the interlamellar spacing (or, reduction of the tie-macromolecule concentration)  $\rightarrow$ embrittlement [13]. Since chain disentanglement allows for chain plastic deformation during tensile loading [14], destruction of the entanglement network due to the chain scission prohibits plastic deformation, and HDPE essentially becomes embrittled. Considering UV irradiation, the degradation behaviors mentioned above occur differently through the thickness, showing changes of carbonyl index in-depth profiles of HDPE [10], and this heterogeneous oxidation behavior can cause different mechanical properties throughout the thickness and ultimately cause the brittle failure of the entire material. Therefore, it is important to investigate the effects of weathering parameters on the mechanical degradation processes to avoid catastrophic failure of HDPE during use, and the material properties measured under multiple weathering parameters ultimately provide a useful guide for optimally designing and selecting HDPE that are intended for use in various outdoor environments.

In this study, environmental degradation behaviors of HDPE were characterized under multiple weathering conditions. Since it is difficult to control critical environmental parameters such as UV and temperature in outdoor weathering tests, an accelerated laboratory test methodology was used. Recently, we have reported first part of the study [15] focusing the photothermal kinetics (activation energies) and UV dose-damage relationships (Schwarzchild p-coefficients) for various mechanical, chemical (carbonyl and vinyl group formation), and structural (surface crystallinity) properties and UV dependences from accelerated laboratory exposures. The study also showed that embrittlement of HDPE was concurrent with increases in yield strength, stiffness, oxidation, and crystallinity. A comparison to FL outdoor exposure also shows a similar magnitude of material change up to the point of embrittlement. This observation indicates that the underlying chain scission mechanism is more relevant to embrittlement than the specific degradation chemistry (i.e. degradation products). For above reasons, it is vital for a more detailed study to focus on the molecular level changes (molar mass distribution) and tensile mechanical properties during the UV exposures to understand mechanisms of embrittlement. Therefore, morphological changes of HDPE after the UV exposures and their relationships with the tensile properties, molar mass averages and distributions were the focus of this continue study. Homogeneities in the mechanical property change of the entire specimen after the UV exposure were monitored by measuring the elastic modulus on the cross-section



**Fig. 1.** (a) An array of HDPE Dumbbell specimen in the specime holder (b) the layout of the environmental chamber for UV exposure.

of the specimens using an instrumented indentation technique.

# 2. Experimental procedures

# 2.1. Sample preparation and UV exposure conditions

Commercially available HDPE (DOW HDPE DGDB-2480  $\text{NT}^2$ ) was used in this study. It is a crystalline thermoplastic with a density of 0.944 g/cm<sup>3</sup> with no UV stabilizers and a small mount antioxidant (less than 0.5% by mass) according to the manufacturer's technical information.

Approximately 12.5 g of HDPE pellets were compression molded in a 13 cm by 13 cm mold cavity area at 160 °C. When the temperature reached 160 °C, a 5 min holding step was applied without a compressive load. After the holding step, 10 kN of compression was applied for 3 min and subsequently increased to 50 kN and maintained for 3 min. After the mold was cooled to 60 °C under the compressive load, the molded HDPE sheets were removed from the hot press and then die cut to fabricate the dumbbell tensile test specimen for accelerated weathering tests.

HDPE dumbbell specimens were mounted on a Teflon sheet in a sample holder with 10 cm long cavity using aluminum bars (Fig. 1a) so one side of the specimen surfaces was facing toward the UV source. Accelerated weathering tests were carried out in the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure), for which detailed information can be found elsewhere [16]. A WG295 filter [SCHOTT glass] cuts off most of the UV with wavelengths < 295 nm to give a spectral power distribution (SPD) shown in Fig. S1. Most visible and IR radiation is removed by cold mirrors before entering the chamber.

The UV spectral radiance level were controlled by placing a UV neutral density filter in the beam path (Fig. 1b) and selected for 5% (8 W/m<sup>2</sup>), 25% (38 W/m<sup>2</sup>), 40% (61 W/m<sup>2</sup>), 100% (153 W/m<sup>2</sup>) based on the integral intensities from 290 nm to 400 nm, and UV intensities for 5%, 25%, 40% were estimated using the measured 100% UV irradiance. Typical full irradiance through a quartz disk was  $\approx$  153 W/m<sup>2</sup> (295 nm–400 nm). UV exposures with four different irradiance were carried out under dry conditions (<5% RH) at 50 °C. Additional exposures at 30 °C were carried out under dry conditions and 40% UV intensity. All irradiance values (W/m<sup>2</sup>) reported in this paper were measured by NIST-calibrated radiometer in the wavelength range from 295 nm to 400 nm.

Uniformity of the UV irradiation on spatial sample locations and temporal intervals is an important factor for weathering tests. Fig. 2 displays the UV irradiance  $(W/m^2)$  for 10 sample locations across the sample holder at various UV exposure conditions (5% UV to 100% UV) with less than 3% variations between the highest and

<sup>&</sup>lt;sup>2</sup> Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

lowest intensity. This result indicates the good uniformity of UV flux across the all samples. The averaged daily UV dose (standard deviation) were 0.63 MJ/m<sup>2</sup> ( $\pm$ 0.01 MJ/m<sup>2</sup>) for 5%, 3.52 MJ/m<sup>2</sup> ( $\pm$ 0.10 MJ/m<sup>2</sup>) for 25%, 5.90 MJ/m<sup>2</sup> ( $\pm$ 0.14 MJ/m<sup>2</sup>) for 40%, and 13.67 MJ/m<sup>2</sup> ( $\pm$ 0.33 MJ/m<sup>2</sup>) for 100% for all the chambers used for the during of the study.

### 2.2. Tensile test and fractography

Tensile tests for the HDPE dumbbell-shaped specimens based on ASTM standard D638 (Type V specimen) were carried under the strain rate of 0.083 s<sup>-1</sup> at room temperature. Typical width and thickness of the specimens were 3.24 mm  $\pm$  0.01 mm (standard deviation), and 0.74 mm  $\pm$  0.03 mm (standard deviation) respectively. Pneumatic grips were used for applying a constant gripping force to the specimen. The engineering stress was obtained by measuring tensile loads and the original cross-sectional area of the sample in the gauge length region. The gauge length was set to be 25.4 mm due to extensive deformation including the neck, and elongation was determined by measuring the displacement of the cross head of a screw driven tensile test machine. To assess the change of mechanical properties, changes of elongation-at-failure for the ductility and Young's modulus for the stiffness were measured.

After tensile tests, fracture surfaces were examined in a scanning electron microscope (SEM). To avoid charging of the fracture surface, the fractured specimens were coated with gold prior to SEM observation. SEM images were taken at an acceleration voltage of 15 kV with a working distance range between 10 mm and 11 mm.

#### 2.3. Size-exclusion chromatography (SEC) measurements

Samples were cut from the regions between the neck and the gripping areas of the dumbbell-specimen after the tensile tests for gel permeation chromatography (GPC) SEC analysis. The samples were sectioned vertically with a razor blade to include the entire depth of each sample. High temperature SEC was performed using a Polymer Char GPC-IR instrument with an IR4 detector, a Wyatt Technology Dawn Heleos II multi-angle light scattering detector (18 angles), and 4-capillary differential viscometer, as well as separate analysis on a Tosoh HT-Eco SEC instrument with differential refractive index detection. For the Tosoh instrument, narrow dispersity polyethylene standards were used for calibration. For the Polymer Char instrument, narrow dispersity polystyrene standards were used for column calibration, as well as NIST SRM ® 1475A (linear, broad, HDPE), and NIST SRM ® 1478 (to determine interdetector delay and normalize photodiode response of the MALS detector), and 6 octene LLDPE standards (Polymer Char) to calibrate the IR response from the methyl and alkyl absorption bands.



**Fig. 2.** Distributions of UV irradiance levels across the sample holder for the  $100\% (\bullet)$ ,  $40\% (\bullet)$ ,  $25\% (\bullet)$ , and  $5\% (\bullet)$  intensities. The rradiance of the 5%, 25% and 40% were calculated by the measured transmission of ND filters multiplying the direct measured irradiance of 100% UV.

Calibration and data analysis was performed by proprietary software from each instrument vendor. Runs were performed at 160 °C using 1,2,4-trichlorobenzene as the mobile phase (300 mg/kg Irganox 1010 was added as antioxidant to the solvent). The stationary phase for both systems was a set of 3 Tosoh HTs columns (2 Tosoh TSKgel GMHhr-H (S) HT2, 13  $\mu$ m mixed bed, 7.8 mm ID  $\times$  30 cm columns and 1 Tosoh TSKgel GMHHR-H (20) HT2, 20  $\mu$ m, 7.8 mm ID  $\times$  30 cm column with an exclusion limit  $\approx$  4  $\times$  108 g/mol). The relative uncertainty (standard deviation) in the molar masses obtained by this measurement is  $\pm$ 1.5%.

### 2.4. Nanoindentation test

Stiffness of cross-sections for HDPE was measured by a nanoindentation technique. To prepare mirror-like flat surfaces for the cross-sections of the HDPE, specimens were embedded in epoxy, and then the whole piece of the epoxy and HDPE were cut at - 80 °C using a diamond knife in a cryomicrotome set-up. When both sides of HDPE (e.g. UV exposed and opposite sides for the exposed specimen) in the epoxy were clearly visible at the surface during the microtoming, the microtomed specimens were removed from the cryomicrome set-up and adhered to the aluminum cylindrical stage for nanoindentation tests at a room temperature. Instrumented indentations were performed on the cross-sections of HDPE specimens using a nanoindenter G200 (Keysight systems) with a 1 µm radius, 90° diamond cone probe (manufacture specification). Load was applied under a strain rate of  $\approx 0.05 \text{ s}^{-1}$  with a superimposed 2 nm oscillation amplitude at 45 Hz, which enables a continuous stiffness measurement [17]. The elastic modulus at individual locations was continuously determined until the probe penetrated approximately 1000 nm into the surface to ensure that constant modulus is reached as a function of depth. The mean elastic modulus was obtained at the range of the displacement into surface from 600 nm to 700 nm.

### 3. Results and discussions

# 3.1. Tensile stress-strain (elongation) behavior of HDPE after UV exposure

The typical tensile stress-strain behavior of HDPE aged at 50 °C under 40% UV for 0 d (unexposed), 2 d, 4 d, and 7 d is shown in Fig. 3. For the HDPE exposed for 2 days, yielding occurred around 10% strain and a strain-hardening like stress-strain behavior after yielding was observed until rupture at approximately 700% strain. As the exposure time increases, a significant decrease of the strainhardening like region was observed in the stress-strain behavior (4 days), and further exposure (7 days) led to failure around the yielding region. As seen in the yielding region (Fig. 3b), the initial slope of the stress-strain behavior and vield stress increased with increasing exposure time, but the magnitude of the changes observed in this region are relatively smaller than the change of the strain-at-failure. Hiss et al. [14] measured true stress-strains of HDPE to avoid the influence of the necking on the engineering stress-strain and suggested four stages in the tensile behaviors of HDPE, which may be associated with, (1) the onset of isolated interand intralamellar slip processes at initial loading region, (2) a change into a collective activity of slips at yielding, (3) the beginning of crystallite fragmentation after passing yielding, and (4) extent of chain disentanglement deforming near failure. From different roles of the internal structures to the tensile stress responses in the individual stages, one can assume that the increased slopes of the initial stress-strain curves and the higher yield stresses indicate the increased resistances of inter-and intralamellar slip processes, and the decreased strain-at-failure indicate



Fig. 3. Typical tensile stress-strain behaviors (a) and enlarged yielding regions (b) of HDPE after exposure under 40% UV at 50  $^{\circ}$ C for unexposed (0 d), 2 d, 4 d, and 7 d.

increased chain disentanglements as the aging time increases. These tensile deformation processes depend on morphological structures of HDPE. To investigate overall trends of the initial and final stress-strain responses during the exposure, modulus and elongation-at-failure were determined for the individual exposure times.

# 3.2. Effect of UV intensity on elongation-at-failure and Young's modulus

Fig. 4 shows the changes of elongation-at-failure and Young's modulus for the UV exposed HDPE at 50 °C as a function of exposure time. Overall higher UV intensities increase the rate of the embrittlements. For the HDPE exposed with the UV intensity of 5%, the elongation-at-failure started to decrease after 15 days of the UV exposure (i.e. a ductile-brittle transition) while the elongation-at-failure for the UV intensities of 25%, 40%, and 100% started decreasing after 2 days of the exposure. The modulus obtained from all UV intensities increased with the exposure times. For the modulus exposed with the UV intensities of 25%, 40%, and 100% nearly superimposed during 7 days of the UV exposure compared to the 5% UV exposure. Reductions in the modulus were observed for the 25% and 40% UV intensities nearest the end of the exposures probably due to loss of the load bearing capability for internal structure of HDPE.

For photodegradation of polymers, if the degradaton kinetics depend only on the total absorbed energy, the same photoresponse should be observed when UV exposure is made at a high radiant flux for a short period time, or at a low radiant flux for a long period time. This hypothesis is often referred as the reciprocity law which yields Schwarzschild *p*-coefficients of approximately 1 for agreement. The *p*-coefficient of HDPE is reported to be 0.54 for



**Fig. 4.** Elongation-at-failure vs exposure time (a) vs dose (b) and Young's modulus vs exposure time (c) for HDPE specimens exposed at 50 °C with 5% ( $\bullet$ ), 25% ( $\blacksquare$ ), 40% ( $\bullet$ ), and 100% ( $\bullet$ ) of the UV intensities. Dashed in (b) indicated the does = 17 MJ/m<sup>2</sup>. Error bars represent one standard deviation.

elongation-at-break, indicating that reciprocity (p = 1) is not observed [15]. This time-sensitive photoresponse in term of mechanical property vs. elongation-at-failure under different UV exposure conditions at various irradiance levels can be demonstrated in Fig. 4b. The values of elongation-at-failure at a dose of around 17 MJ/m<sup>2</sup> (Dashed-line in Fig. 4b) are  $64\% \pm 37\%$  for 5% UV after 25 days' exposure time,  $549\% \pm 221\%$  for 25% UV after 5 days,  $577\% \pm 185\%$  for 40% UV after 3 days, and  $715\% \pm 85\%$  for 100% UV after 1 day, respectively. The elongation-at-failure values at 5%, 25%, and 40% UV exposure conditions were significantly slower than those for the 100% UV, which might indicate that increasing the UV intensities appear not monotonically increasing the rate of the loss of the ductility. The different elongation-at-failure values obtained from the similar dose level at the different exposure times (5 days at 40% UV comparing to 1 day at 100% UV) indicate a significant contribution of time sensitive photoresponse for causing decreasing the elongation-at-failure of HDPE.

The molar mass of HDPE is known to decrease by chain scission

accompanied by crosslinking during UV exposure. Moreover, Craig et al. have reported that scission was the dominant at all depths from the exposed surface and scission/crosslink ratio as high as 9 was observed near the exposed surface [18]. Ultimately the chain scission of entanglements and tie chain molecules in HDPE lead to their reorganization into a crystalline phase resulting in an increase of crystallinity (i.e., chemicrystallization). In the case of thermal oxidation of PE, approximately 45 monomer units enter in the crystallization process is presumed to occur in this study due to presence of UV at the elevated exposure temperature (50 °C). Therefore, faster loss of ductility and overlapped increase of the modulus as shown in Fig. 4 can be due to UV induced morphological changes including chain scission.

# 3.3. Effect of temperature on elongation-at-failure and Young's modulus

Fig. 5 shows the variations of elongation-at-failure and Young's modulus exposed at 30 °C and 50 °C with the 40% UV intensity. A nearly two times faster reduction of the elongation-at-failure was observed for 50 °C of the exposure temperature compared to 30 °C until reaching the complete loss of ductility, and a relatively significant increase for the modulus was observed for 50 °C compared to 30 °C. The different behaviors of the tensile properties obtained at 30 °C and 50 °C indicate the temperature sensitivities.

Considering the effect of temperature, thermal oxidation of HDPE (without UV irradiation) is reported to induce predominantly chain scission of the carbon-carbon backbone to form secondary alkyl radicals in the presence of oxygen and increase of crystallinity via chemicrystallization throughout the bulk of the sample [12,19,20]. In the case of photooxidation (oxidation with UV



**Fig. 5.** Elongation-at-failure and Young's modulus for HDPE sample exposed at 30 °C ( $\blacksquare$ ) and 50 °C ( $\bullet$ ) with the 40% UV intensity. Note that Young's modulus for the samples exposed at 50 °C after 11 days of exposure was omitted due to high non-linearity in the initial stress-strain curves. Error bars represent one standard deviation.

irradiation), the processes can be synergistic with temperature level through complex mechanisms [21], which is experimentally found in the rates of carbonyl formation of pigmented low density polyethylenes showing lower activation energies (from 43 kJ/mol to 31 kJ/mol) for photooxidation than those (from 192 kJ/mol to 128 kJ/mol) for thermal oxidation over the temperature range 50 °C–90 °C [22]. (note that  $\approx$  86 kJ/mol as activation energy was determined in carbonyl formation for the 40% UV exposed HDPE as a part of the current study). Since the activation energy of typical PEs (HDPE and LDPE) decreases with increasing UV exposure time with thermal degradation and photodegradation as reported by Corrales et al. [19], the higher exposure temperature range applied here.

### 3.4. Molar mass distribution of UV exposed HDPE

Photooxidation studies of PE often use Fourier-transform infrared spectroscopy (FTIR) to measure the chemical changes such as vinylidene and carbonyl groups in reaction mechanisms [21]. Although the presence of carbonyl groups provides a certain extent of oxidation, it is difficult to explain how degradation progresses in HDPE using FTIR alone, especially when physical changes such as polymer molar mass and branching content have a direct influence on mechanical properties of HDPE. Therefore, changes of molar mass were investigated to understand the effects of the UV intensities on tensile behaviors of HDPE.

To measure molar mass changes of the exposed HDPE, hightemperature size exclusion chromatography was performed on a subset of the exposed samples to determine changes in molar mass averages, molar mass distribution (MMD), and intrinsic viscosity upon aging. The samples that failed in the transition (elongationat-failure  $\approx$  200%–400%) and complete loss of the ductility (elongation-at-failure < 50%) regimes for the tensile tests were selected for molar mass measurements. Representative SEC traces of the unaged HDPE are shown in Fig. S2 of the supporting information. The commercial HDPE used in this study is multi-modal, as evidenced by the multiple peaks observed in the light scattering and specific viscosity data. The differential MMD curves ( $\partial W/\partial \log$ M versus Log M, where W is weight fraction) for HDPE and all exposed samples are shown in Fig. 6a-c. For all exposure conditions, there is a distinct shift in the MMD to lower masses overall and a narrowing of the breadth of the distribution, as evidenced by the decrease in dispersity,  $D(D = M_w/M_n$  (weight averaged molar mass/number averaged molar mass), as shown in Table 1. The unexposed HDPE has a D of 19.6, while significant decreases in dispersity are observed for all irradiation conditions. This may be due to preferential scission of higher molar mass chains, which would decrease the mass fraction measured at the high end of the MMD and increase the relative percentage of chains present at lower molar masses, as is observed in Fig. 6.

A comparison of MMD across all exposure conditions and times was conducted (Fig. S3). Despite differences in UV intensity and duration, the final percent decrease in  $M_w$  is consistent across all samples at 57.4%  $\pm$  1.6% (relative uncertainty-standard deviation). The short chain branching distribution, measured as CH<sub>3</sub>/1000 total C (carbons), is determined by the area ratio of the methyl to alkyl content in the polymer measured at each slice of the MMD. CH<sub>3</sub>/1000 total C is consistent across the MMD curve and does not change within the limits of detection on the IR detector ( $\pm$ 10 CH<sub>3</sub>/1000 total C), indicating that significant fractions of short chain branching, however, is indicated by changes in the slope of the Mark-Houwink plot, which increases with time and relates the change in intrinsic viscosity ([ $\eta$ ]) of the polymer across the MMD (Fig. 6.,



**Fig. 6.** Differential MMD ( $\partial W/\partial$  Log M versus Log M, line) and Mark-Houwink plots (Log [ $\eta$ ] versus Log M, points) for the exposed HDPE with (a) 25% for 6 d (-, ....) and 10 d (-, ....), (b) 40% for 6 d (-, ....) and 10 d (-, ....), and (c) 100% for 4 d (-, ....) and 7 d (-, ....). The unexposed HDPE (-, ....) plots are shown for a comparison purpose.

right axes). This is defined by the relationship,  $[\eta] = KM^a$ , where M is molar mass, and K and a are empirically determined constants. Unexposed HDPE has a linear slope, consistent with HDPE standard NIST 1475A (Fig. S4). Upon irradiation, however, a decrease in the

slope is observed especially at higher molar masses (Fig. 6). Furthermore, the slope consistently decreases with further irradiation, as shown in Fig. 6. The average molar mass of the long chain branches can be measured by applying a power law to the two distinct regions of the exposed HDPEs and measuring the intersect of the two curves; this analysis has been previously measured for other branched polymers [23,24]. The average molar mass of the long chain branches for all samples does not vary significantly, where  $M_{segment} = 55,200 \text{ g/mol} \pm 8550 \text{ g/mol}$  (standard deviation).

Conformation plots (Fig. S5)., demonstrating the change in radius of gyration with molar mass (on a log-log scale) can also be used to measure long chain branching. The conformation plot follows a similar trend to the Mark-Houwink plot, where irradiation results in a decrease in radius of gyration and long chain branches with average long chain branch molar masses of  $M_{segment} = 68,000 \text{ g/mol } \pm 10,000 \text{ g/mol } (standard deviation)$ among all samples. Further analysis of viscosity and confirmation plot data has been previously used to calculate long chain branching frequency across the MMD [24,25]. These calculations were not performed in this study due to a priori knowledge required regarding branching topography because measuring quantitatively whether branching is trifunctional (3 arms per branch site) or tetrafunctional (4 arms per branch site) is difficult for PE branching induced by radical mechanisms.

As seen in Table 1, several UV exposure tests for the M<sub>w</sub> measurements have similar dosages due to a lower UV intensity with a longer time and vice versa (e.g. 25% UV for 10 days and 40% UV for 6 days, 40% UV for 10 days and 100% for 4 days). If a degradation process to change M<sub>w</sub> depends only on the intensity of UV, the M<sub>w</sub> values should be the same for the same dosages, and HDPE can be considered to obey reciprocity as indicated by photodegradation study of coatings [26]. When comparing the HDPE samples with the similar accumulated dosages, Mw values are significantly higher for the samples exposed for the shorter period of time under the high UV intensities. This indicates that not only the UV dosage level but also a time-dependent process influences on the change of the M<sub>w</sub>. High UV irradiance can cause rapid photooxidation of the surface resulting in diffusion-limited oxidation, so a more detailed kinetic study needs to be carried out to explain the relationship between M<sub>w</sub> and UV intensity since the change of M<sub>w</sub> is caused by multiple chemical processes [27].

As discussed previously, the molar mass of HDPE is known to decrease by chain scission accompanied by crosslinking during UV exposure. To explore the relationships between chain scission and crosslinking during the exposure, the ratio for the number of chain scission (n)/crosslinks (x) per mass unit at three different UV intensities over exposure times were calculated listed in Table 1. Using the Saito relationships, we calculated the "ratio for the number of chain scission/crosslinks per mass unit" and incorporated into Table 1. The ratios ranges from 4.6 to 5.8. For similar accumulated UV dose:  $\approx 35.2 \text{ MJ/m}^2$  to 35.4 MJ/m<sup>2</sup>, the ratio is around 4.8 for (25%, 10 d) and 4.9 (40%, 6 d). However for a higher accumulated UV dose:  $\approx 59 \text{ MJ/m}^2$ , the ratios are very different 5.8 for (40%, 10 d) versus 4.6 for (100%, 4 d). Note that the relative uncertainty in the molar masses obtained by SEC measurement is  $\pm 1.5\%$  (Table 1) and the molar mass distribution and dispersity (D) also changed significantly from D = 10.8 to D = 16.6. Therefore, the difference in ratio of n/x for a higher accumulated UV dose of  $\approx$  59 MJ/m<sup>2</sup> is significant (a 26% in difference). In general, the ratio should increase as increasing accumulated UV dose if the degradation pathway is the same. In this case, a lower ratio of 4.6 implies more crosslinks events occurred at 100% UV exposure conditions at similar accumulated UV dose while exposed at 40% UV. This results is consistent with the observation of significant contribution of time sensitive photoresponse on elongation-at-failure values

Table 1

UV doses, number averaged molar mass<sup>\*\*\*</sup> ( $M_n$ ) and weight averaged molar mass<sup>\*\*\*</sup> ( $M_w$ ), dispersity (D) of HDPE, Ratio for number of chain scissions (n)/crosslinks (x) per mass unit at three different UV intensities over exposure times.

	Accumulated UV dose (MJ/m <sup>2</sup> )	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)	Đ	Ratio n/x
HDPE, unexposed	0	12000	235100	19.6	_
25% UV, 6 d	21.1	9200	123000	13.3	5.3
25% UV, 10 d	35.2	6960	94000	13.5	4.8
40% UV, 6 d	35.4	8930	130300	14.6	4.9
40% UV, 10 d	59.0	8300	89400	10.8	5.8
100% UV, 4 d	58.8	8900	147000	16.6	4.6
100% UV, 7 d	88.9	8100	113500	14.0	4.8

\*\*\* Note that the relative uncertainty (standard deviation) in the molar masses obtained by this measurement is  $\pm 1.5\%$ .

obtained from the similar dose level at the different exposure mentioned in the "Effect of UV intensity on elongation-at-failure and Young's modulus" section.

The relationship between M<sub>w</sub> and the elongation-at-failure of the HDPE exposed at 50 °C with the different UV intensities is shown in Fig. 7 (a) as a function of the exposure time.  $M_w$  decreases with increasing exposure time for individual UV intensities, and a similar observation as uniform decreases of Mw for HDPE after the UV exposure using 40 W fluorescencent UV lamps was also found by Jabarin and Lofgren [4]. A similar linear relation was observed between M<sub>w</sub> and elongation-at-failure in Fig. 7b. Note that the slope, dM<sub>w</sub>/d(elongation-at-failure), is quite low, which implies that a small decrease in Mw may induced a drop in elongation-atfailure. This clearly demonstrates the loss of the load bearing capability of the entire HDPE due to the decreased M<sub>w</sub>. M<sub>w</sub> of the exposed HDPE exhibiting the complete loss of the ductility was around 100 kg mol<sup>-1</sup> in this study, which is a similar range with the reported  $M_w$  range (50 kg mol<sup>-1</sup> < Mw < 100 kg mol<sup>-1</sup>) causing embrittlement of HDPE in thermal aging [12]. Furthermore, chain



**Fig. 7.** Molar mass average  $(M_w)$  values for the unexposed ( $\blacklozenge$ ) and exposed HDPE samples at 50 °C with 25% ( $\blacklozenge$ ), 40% ( $\blacksquare$ ), and 100% ( $\blacktriangle$ ) as a function of the aging times (a) and elongation-at-failure (b). Error bars represent one standard deviation.

scission is known to induce a decrease of the interlamellar space  $(l_a)$ by increasing lamellar thickness during chemicrystallization (i.e. increase of crystallized region) [13]. The increase of crystallinity ratios from 0.55 to 0.81 with a constant M<sub>w</sub> is known to decrease the elongation at failure from  $\approx$  2200% to  $\approx$  20% in the case of linear PE [28] and similar influence of the crystallinity on embrittlement of PE is presumed to occur in the current study. In a micromechanical interpretation for chain scission during chemicrystallization, small amorphous domains might not be able to sustain large deformations [13], or can cause a stress concentration effect for a size of cavity radius in evolution of cavitation [29]. Considering the decrease of  $M_w$  (and the likelihood of increases in the crystallinity), the embrittlement process of UV exposed HDPE should be governed by the interaction of these two parameters in terms of global load bearing capacity and crack sensitivity. A magnitude of their contributions per UV conditions can alter fracture processes during the ductile-brittle transition of tensile properties, which should be reflected in the fracture surfaces.

### 3.5. Tensile fracture surface of aged HDPE

Fracture surfaces were examined to observe the failure process of HDPE before and after the UV exposure. Fig. 8 shows typical tensile fractography of the unexposed (a, b, c) and exposed HDPE (d, e, f) at 50 °C with 100% UV for 7 days observed by scanning electron microscopy. The fracture surfaces of the unexposed HDPE exhibit the extensive fibrillation oriented in the inner region (Fig. 8a-b) and the surface (Fig. 8c) in a parallel direction with tensile loading. The fracture surface of the exposed HDPE exhibits no significant fibrillation but a brittle surface (Fig. 8d). The surface region (0 µm to  $\approx$  100 µm from the exposed surface) of the cross section of the UV exposed specimen exhibits a more brittle fracture surface compared to the inner core region (Fig. 8e), and only limited fibrillations in a layer below the superficial layer were observed as shown in the enlarged image (Fig. 8f). In addition to overall morphological changes for M<sub>w</sub> and crystallinity as discussed previously, it is known that embrittlement at the UV exposed surface is caused by the higher crystallinity as a self-notching mechanism by generating sharp surface cracks at a low tensile strain [30]. Furthermore, fracture toughness of a medium density polyethylene is reported to decrease with the time at a rate between 0.108 MPa $\sqrt{m}$ /year and 0.373 MPa $\sqrt{m}$ /year exposed under central-European climate conditions [31] and behavior of fracture toughness of HDPE is expected to be similar. Therefore, one can assume that the decrease of the fracture toughness of the entire specimen also contributes to forming the fracture surface shown in Fig. 8e.

# 3.6. Modulus variation across the cross-section of aged HDPE

To probe the effects of the morphological changes on



Fig. 8. Tensile fracture surfaces of HDPE before the UV exposure (a, b, c) and after the UV exposure (d, e, f) with 100% intensity at 50 °C for 7 days.

mechanical properties inside of the UV exposed HDPE, elastic modulus was measured across cross-sections of the specimens listed in Table 1 using nanoindentation. The modulus measured across the cross-section of the UV exposed HDPE with 25%, 40%, and 100% of the UV intensities are shown in Fig. 9 as well as those for the unexposed specimen ranging around 1.5 GPa without showing a significant spatial variation. Overall, the modulus of the cross-sections of the exposed specimens was higher than the unexposed specimen. Regional variations were observed for the exposed specimens by showing relatively higher modulus at both surface regions than the core regions. Similar modulus values for the front and backside of the specimen may be caused by reflected UV irradiation from shiny surface of the Teflon sheet in the samples holder and/or the UV transmission through the thickness.

Comparing the specimen exposed with the same UV intensities, higher variations of the modulus were observed for the longer exposure times. Furthermore, the specimens with the longer times show higher modulus at the surface regions, compared to their core regions. Although the specimens showing the same tensile failure mode (i.e. complete loss of ductility) were measured, the cross-sectional variations of the modulus obtained from the 40% and 100% UV intensity conditions (Fig. 9b and c) increased with the time while relatively lower variations were observed for the 25% UV (Fig. 9a). This indicates that higher UV intensity created higher crystallinity on the surface regions and enhanced their contributions on the embrittlement of the entire specimens.

A reason for causing the variations of the modulus across the cross-sections in Fig. 9 can be attributed to a formation of a diffusion limited oxidation layer as approximated by  $(D/k)^{1/2}$  (D is the diffusion coefficient of oxygen and k is the rate constant for oxygen consumption during aging). Diffusion limited oxidation occurs when oxygen transport is lower than the oxygen consumption rate. For the same D value, the degradation depth is expected to be lower for more advanced degradation due to a relative increase of k value. The higher UV intensity can cause a fast reaction resulting in oxygen consumption at and near the surface and restricted diffusion into the deeper region. Oxidation in the surface region leads to chain scission more than the inner core region as observed by Craig

et al. [18], and this consequently causes more chemicrystallization for the higher crystallinity in the surface region. Therefore, the exposed HDPE with the UV intensities of 40% and 100% exhibit greater variations of the modulus on the cross-section compared to the 25% UV intensity, showing a relatively smaller variation (Fig. 9a versus Fig. 9b and c). This indicates an effect of the UV intensity causing the diffusion limited oxidation for HDPE, where the threshold UV intensity seem to reside between 25% and 40% intensities. Furthermore, since D across the specimen thickness depends on UV exposure time due to degradation, the variations of the modulus are more pronounced with the relatively longer exposed specimens within the same UV intensity conditions (see the filled and open circle symbols in Fig. 9a, 9b and 9c). These postulations are supported by Hoekstra et al. [32] that observed similar variations of carbonyl concentrations across the 620 µm thick HDPE film.

Through the modulus measurements on the cross-sections of the UV exposed HDPE, we found that the photo-oxidation induced by the UV irradiation increased the modulus on the surface region  $(\approx 100 \text{ }\mu\text{m} \text{ deep})$  by presumably increasing the crystallinity via chemicrystallization. Considering a higher modulus with a more brittle nature, a remaining question was why the crack initiated at the surface region was not arrested as it moved toward the inner core region. The inner core region should possess the higher toughness due to less chain scission as shown in a layer-by-layer oxidation study using multi stacks of polyamide 6 films [33]. Schoolenberg [34] explained a crack propagation from a brittle layer to a ductile layer using a concept of the crack speed effect. A crack initiated at the surface will propagate at high velocity as it reaches the brittle-ductile boundary region, and this will lower the fracture toughness of the ductile inner region, so the crack can continuously propagate into the further remained region. Based on the modulus measurements (filled symbols in Fig. 9), approximately 100 µm layers on both surface regions which occupy nearly 30% of the thickness of the tensile test specimen are presumed to cause a rapid crack propagation for HDPE and contribute on the embrittlement during the tensile tests. For a bulk specimen level, Gulmine [10] reported that increases in density and Durometer



**Fig. 9.** The mean modulus of the cross-sections of HDPE collected from the specimens exhibiting transitional ( $\bigcirc$ ) and complete loss of ductility ( $\bullet$ ) after exposing at 50 °C with 25% (a), 40% (b), and 100% (c) of UV intensities as well as those for the unexposed HDPE ( $\triangle$ ). The error bar indicates one standard deviation.

hardness of polyethylene with the accelerated aging tests (ASTM G26/95 and G53-96) are attributed to an increase in the crystallinity and/or the occurrence of cross-linking reactions. Further assessments of a crystallinity ratio and crack initiation-propagation in the surface and core regions will provide a refined explanation on UV induced fracture process of HDPE with a certain thickness.

# 4. Conclusions

The effects of UV intensity and temperature on the degradation behavior of HDPE were determined for the micro and macroscopic mechanical properties, and concentrations of macromolecules. The increase in the UV intensity caused the decrease in the tensile elongation-at-failure at the shorter exposure times, and an apparent UV intensity threshold exists at the 25% UV for the ductility loss of HDPE. The decrease in the molar mass averages suggest a sensitivity of the UV intensity and time on chain scission for causing the loss of the ductility, and the magnitude of the decrease were more significant with the longer exposure when compared with that at the similar dose levels. Furthermore, the increasing trends of the tensile modulus at the higher exposure temperature indicates temperature sensitivity on chemicrystallization during the UV exposure. The modulus profiles obtained from the cross-sections with various UV intensities suggest that the increased tensile modulus is due to formations of stiffer superficial layers as a result of diffusion limited oxidation led by chemicrystallization. Above the 40% UV (61 W/m<sup>2</sup>) intensity, the stiffer superficial layers are presumed to promote brittle crack propagations into the core regions at the stage of the complete loss of the ductility. The significant effects of UV and temperature on the mechanical performances and fracture process of HDPE can guide the onset of accelerated test conditions causing diffusion limited oxidation, which is important for the optimal design and selection of HDPE in various outdoor environments.

## **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.

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# Appendix A. Supplementary data

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