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# Microscopic structural changes during photodegradation of low-density polyethylene detected by Raman spectroscopy



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## ABSTRACT

Raman spectroscopy has been used to reveal the microscopic structural changes of low-density polyethylene under ultraviolet irradiation. The fraction of non-crystalline consecutive trans chains (the molecular chains in the trans conformation separate from the orthorhombic crystalline phase) drastically decreases at  $\sim 600$  h, together with a decrement in the molecular weight and an increment in the crystallinity owing to chemicrystallization. This suggests that short trans chains are prolonged to form consecutive trans chains before chemicrystallization. Moreover, gradual increases of the stretching and compression stresses are observed on the trans and amorphous chains, respectively. These conformational changes are detected by Raman spectroscopy even in the early stage of photodegradation. Chemicrystallization at  $\sim 600$  h is accompanied by structural changes, such as shortening of the interchain distance of the lamellar crystals and thinning of the amorphous layer, which induce formation of surface cracks on the macroscopic specimen.

#### 1. Introduction

Degradation of polymeric materials is induced by various environmental factors, such as sunlight, heat, and humidity, which result in deterioration of the physical properties, such as the color change, gloss, and impact strength. The chemical aspects of the degradation processes [1] and the stabilization mechanisms [2,3] have been intensively investigated [4]. The mechanism of deterioration of these physical properties during degradation in various environments has also been discussed [5–14]. For example, because of the growing importance of low-density polyethylene (LDPE) in the agricultural industry, degradation and stabilization of LDPE have been intensively investigated [15,16] based on standard testing methods [17]. However, the molecular mechanisms that induce modification of the hierarchical structures are still unclear.

It has been demonstrated that degradation of polymeric materials is accompanied by structural and morphological changes at various levels [9–12]. Chemical modifications of the polymer chains such as chains scission, branching and crosslinking, as well as formation of carbonyl groups owing to oxidation, are also accompanied by appreciable changes in the superstructures such as the increase of crystallinity [18] and decrease of the amorphous thickness. Although the relation of these structural modifications to the deterioration of the mechanical properties such as the drastic decrease of the toughness has been investigated, a clear correlation has not been established yet [10]. Spectroscopic techniques are used to evaluate the molecular and structural changes of polymeric systems during degradation. Infrared absorption spectroscopy has been extensively applied to evaluate degradation [19,20]. The carbonyl index [21], which is the relative intensity of the absorption of the C=O stretching mode at ~1700 cm<sup>-1</sup>, is used as a measure of degradation caused by oxidation reactions [22,23]. The limitations of using the carbonyl index to predict physical deterioration have been recently discussed [24]. Raman spectroscopy has also been used to investigate degradation of polyethylene (PE) and PE blends [25,26]. The increase in the crystallinity of photodegraded PE has been measured by Raman spectroscopy [27]. Ultra-high molecular-weight PE is used for biomedical purposes, such as artificial bones and joints [26,28]. Its physical and chemical characteristics, such as the crystallinity and degree of oxidation, have been evaluated by Raman spectroscopy [29–32].

In this work, we applied Raman spectroscopy for photodegradation of LDPE, and found that the Raman spectral shifts, as well as the intensities, are useful to provide structural insight into photodegradation of LDPE. Spectroscopic analysis revealed the microscopic structural changes during photodegradation, including in the early stage before the onset of chemicrystallization.

#### 2. Materials and methods

LDPE (Prime Polymer Co., Ltd.) with a density of 0.92 g/cm<sup>3</sup> and a

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melt index of 4 g/10 min was used in this study. We have confirmed that the LDPE contained 0.2 wt% of dibutylhydroxytoluene as the antioxidant. To simulate the rotational molding process, LDPE sheets with a thickness of 0.5 mm were prepared as follows. LDPE powder was preheated in a hot press at 150 °C for 3 min and then degassed at 150 °C for 2 min. The sample was pressurized at 10 MPa for 1 min. The sample was then heated to 200 °C in 8 min and gradually cooled to 180 °C in 8 min, followed by quenching to room temperature.

The photodegraded LDPE sheets were prepared with a Xenon Weather Meter (SX2-75, Suga Test Instruments). A Xenon fade lamp was used as the light source. The LDPE sheets were irradiated at 60 W/m<sup>2</sup> in the wavelength range 300–400 nm at a black panel temperature of 89 °C under the no rain condition. Note that the present condition has recently been employed for interior components of automobiles, in accordance with increasing demands for harsh conditions such as in the desert area. The irradiation time was set at 120–1200 h.

High-temperature gel permeation chromatography (HT-GPC) was performed at 140 °C using a Viscotek Triple Detector HT-GPC (Model-SG system, Malvern Instruments Ltd., Worcestershire, UK) containing refractive index, light scattering, and viscometer detectors. *o*-Dichlorobenzene with 0.05% dibutylhydroxyltoluene as an antioxidant was used as the solvent. The samples were dissolved at 140 °C to obtain a concentration of 1.0 mg/ml. A polystyrene standard sample was used for column calibration.

A Raman spectrometer previously applied to rheo-Raman measurements [33,34] was used. A DPSS laser (RLK-640-200, LASOS) and a CCD camera equipped with a monochromator (PIXIS100 and SpectraPro 2300i, Princeton Instruments) were used as the light source and detector, respectively. Each Raman spectrum was accumulated 20 times with an exposure time of 2 s. The Raman spectrum was fitted with the sum of Voigt functions using the nonlinear Levenberg–Marquardt method, and the peak positions and areas were determined. The uncertainty of the peak positions and areas for the Raman bands were less than  $\pm 0.32$  cm<sup>-1</sup> and  $\pm 6.2\%$ , respectively, except for the 1080 cm<sup>-1</sup> band ( $\pm 10\%$  uncertainty for the peak area).

The peak shift of each Raman band  $\Delta \nu$  is defined as the deviation of the peak position during ultraviolet (UV) irradiation:

$$\Delta \nu = \nu(t) - \nu(0), \tag{1}$$

where  $\nu(0)$  and  $\nu(t)$  are the peak positions before and after irradiation.

The Raman bands at 1298 and  $1305 \text{ cm}^{-1}$  are assigned to the CH<sub>2</sub> twisting modes of the trans and amorphous conformers, respectively (Table 1). It has been suggested that 3–5 consecutive trans chains contribute to the intensity of the Raman band at 1298 cm<sup>-1</sup> [35]. Therefore, the mass fractions of the trans and amorphous conformers were determined using the following equations [36,37]:

$$\chi_{\rm t} = \frac{I_{1298}}{I_{1298} + I_{1305}},\tag{2}$$

$$\chi_{\rm a} = \frac{I_{1305}}{I_{1298} + I_{1305}} \tag{3}$$

#### Table 1

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Vibrational modes and phase assignments of the Raman bands of PE [42-45].
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Peak position/cm <sup>-1</sup>	Vibrational mode <sup>a</sup>	Phase
1063 1080 1130 1298 1305 1418 1440	$\nu_{as} (C-C)$ $\nu (C-C)$ $\nu_{s} (C-C)$ $\tau (CH_{2})$ $\tau (CH_{2})$ $\delta (CH_{2}) + \omega (CH_{2})$ $\delta (CH_{2})$	Trans chain Amorphous Trans chain Trans chain Amorphous Crystalline (orthorhombic) Amorphous trans
1460	δ (CH <sub>2</sub> )	Amorphous

<sup>a</sup>  $\nu$ , stretching;  $\nu_{as}$ , anti-symmetric stretching;  $\nu_{s}$ , symmetric stretching;  $\tau$ , twisting;  $\delta$ , bending,  $\omega$ , wagging.

where  $I_{1298}$  and  $I_{1305}$  are the intensities of the Raman bands at 1298 and 1305 cm<sup>-1</sup>, respectively. It is noted that the CH<sub>2</sub> twisting modes at 1298 and 1305 cm<sup>-1</sup> were used as the internal reference [36]; the peak position of the prominent peak at 1298 cm<sup>-1</sup> was assumed to be unchanged, and the intensity of each Raman band was determined as its peak area divided by the sum of the peak areas of two CH<sub>2</sub> twisting bands at 1298 and 1305 cm<sup>-1</sup>. Using the intensity of the Raman band at 1418 cm<sup>-1</sup> assigned to the orthorhombic crystalline chains, the orthorhombic crystallinity was determined by Ref. [36].

$$\chi_{\rm c} = \frac{I_{1418}}{A(I_{1298} + I_{1305})},\tag{4}$$

where *A* (=0.46) is the experimental constant. It has been found that PE has an intermediate phase composed of amorphous trans chains separate from the orthorhombic crystals [36,38]. The fraction of the non-crystalline consecutive trans (NCCT) chains was determined by Ref. [37].

 $\chi_{\rm NCCT} = \chi_{\rm t} - \chi_{\rm c} \,. \tag{5}$ 

#### 3. Results and discussion

Photographs of the LDPE specimens before and after the UV exposure tests are shown in Fig. 1. While the LDPE specimen is semitransparent before UV irradiation, the transparency of the specimen decreases with increasing exposure time and the color becomes yellowish. From the optical microscopic images shown in Fig. 1(b), onset of crack formation is observed at 840 h. After 1080 h, surface cracks have propagated over the entire specimen. These macroscopic changes are commonly observed during the decrease of the gloss and the increase of the yellowness index, both of which are conventionally used as an indicator of polymeric material degradation.

GPC traces and intrinsic viscosities of LDPE at various exposure times are shown in Fig. 2. The molecular weight distributions are slightly broadened in the early stage of the photodegradation process up to 480 h, followed by an abrupt decrease of the molecular weight at 600 h indicative of scission of PE chains [9]. The lower shift of intrinsic viscosity with the exposure time suggests modification of chains structure such as the formation of branches and crosslinks. The slope in the low molecular weight region becomes more gradual after UV irradiation compared to those in the high molecular weight region, suggesting that short chains are more likely to be modified during photodegradation.

The Raman spectra of photodegraded LDPE at various exposure times are shown in Fig. 3. The assignments of the Raman bands of PE are listed in Table 1. The intensities of the Raman spectra were normalized by the intensity of the CH<sub>2</sub> twisting bands at 1298 and  $1305 \text{ cm}^{-1}$  [39,40]. The intensity of the broad  $1080 \text{ cm}^{-1}$  band assigned to the C-C stretching mode of the amorphous chains gradually decreases with increasing irradiation time, indicating an increase in the crystallinity. A similar decrease in the intensity of the amorphous band is observed in high-density polyethylene (HDPE) exposed in an aqueous solution of a surfactant [41]. The peak positions and areas of the crystalline C–C stretching modes at 1063 and 1130 cm<sup>-1</sup> slightly vary with the irradiation time. The spectral changes are more obvious in the 1400 cm<sup>-1</sup> region, as shown in Fig. 2(b). The crystalline (1418 cm<sup>-1</sup>) and amorphous (1460 cm<sup>-1</sup>) bands show clear red and blue shifts, respectively. Similar spectral changes have been observed during environmental stress cracking [30]. Although no obvious Raman peak is observed in the  $1700 \text{ cm}^{-1}$  range, the formation of carbonyl group on the surface is confirmed by the attenuated total reflection infrared (ATR-IR) spectra as shown in S-7. The variation of the peak areas and positions will be discussed in the following paragraphs.

The changes of the mass fractions of the chains in various phases with time are shown in Fig. 4. The crystallinity of the LDPE specimen remains almost constant in the early stage, followed by an increase at Download English Version:

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