

Degradation diagnosis of ultrahigh-molecular weight polyethylene with terahertz-time-domain spectroscopy

Kohji Yamamoto,^{a)} Mariko Yamaguchi, Masahiko Tani, and Masanori Hangyo

Institute of Laser Engineering, Osaka University, 2-6 Yamadaoka, Suita, Osaka, 565-0871, Japan

Satoshi Teramura and Toshiro Isu

Graduate School of Material Science, Nara Institute of Science and Technology (NAIST), 8916-5, Takayama, Ikoma, Nara, 630-0101, Japan

Naohide Tomita

International Innovation Center, Kyoto University, Yoshida-Hon-machi, Sakyo-ku, Kyoto, 606-8501, Japan

(Received 28 May 2004; accepted 27 September 2004)

We investigated ultrahigh-molecular-weight-polyethylene (UHMWPE) samples prepared by various conditions with terahertz-time-domain spectroscopy (THz-TDS). Degradation of the virgin UHMWPE samples by γ irradiation induced a drastic increase of the absorption ranging continuously over the THz region. The increase of the absorption continuum is interpreted to originate in the oxidation of the amorphous region within the sample. Only slight THz spectral changes induced by the γ irradiation were, however, observed for the UHMWPE samples doped with 0.1 and 0.3 wt % vitamin E. This result agrees with the earlier indication that vitamin E has an antidegradation effect on UHMWPE. The present result shows that the THz-TDS can be used for the quality control of UHMWPE by monitoring the absorption continuum in the THz region. © 2004 American Institute of Physics. [DOI: 10.1063/1.1827332]

The terahertz-time-domain spectroscopy (THz-TDS) has made great progress owing to recent advances in the THz generation and THz detection techniques by using ultrashort laser pulses.^{1,2} The THz transmission technique has been applied to plastic-package imaging and inspection of an inner IC chip.³ It is the key point of this inspection that plastics are transparent to the THz radiation, although they are opaque for infrared and visible light. For this reason, the THz-TDS can be a useful tool for a nondestructive diagnosis of inner parts of plastics.

Polyethylene ($-\text{[CH}_2-\text{CH}_2\text{]}_n-$) is one of the polymer plastics which are widely used in versatile applications. Among various types of polyethylene, ultrahigh-molecular-weight polyethylene (UHMWPE) is used as medical polymers in contact with living tissues or biological fluids.^{4,5} For example, UHMWPE is, at present, implanted to human bodies as artificial acetabular cup components and as artificial knee joint components. Prior to surgical implants of UHMWPE, the γ irradiation is widely used for sterilization. Free radicals formed by the γ irradiation cause aging oxidation, resulting in degradation of UHMWPE.⁶ Because the life of implanted UHMWPE is dependent on degree of degradation,⁴ investigation of γ irradiation effects on UHMWPE is critical for success in the implants. Mid-IR absorption has been applied to measuring degree of oxidative degradation by monitoring the carbonyl band ($\sim 1720\text{ cm}^{-1}$).⁶ For this inspection it is necessary to cut out a thin slice from test objects. A nondestructive method for inspecting inner UHMWPE is, therefore, beneficial for the quality control of UHMWPE as source materials.

In this study we examined the applicability of the THz-TDS to the degradation diagnosis of UHMWPE. This inspec-

tion method is in a nondestructive and contactless manner. To investigate the influences of the γ irradiation we carried out the THz-TDS of UHMWPE samples with and without the γ irradiation. We also examined the changes of the THz spectra induced by the γ irradiation for the UHMWPE samples doped with vitamin E (α -tocopherol), which additive is known to be highly effective in reducing the oxidative degradation.⁷

We prepared UHMWPE plates with 9.5 mm in thickness under various conditions; virgin UHMWPE, γ -irradiated virgin UHMWPE, UHMWPE doped with vitamin E, γ -irradiated UHMWPE doped with vitamin E. The additive amounts of vitamin E were 0.1% and 0.3% in weight ratio (hereafter shown as 0.1 wt % and 0.3 wt %, respectively). Details of the sample preparation method have been described in Ref. 4. We prepared two pieces of plates for each sample and carried out the THz-TDS measurements twice for each plate. The data of four independent measurements were averaged to give the THz spectra shown in this letter. The THz-TDS measurements were carried out with a conventional system with photoconductive emitter and receiver antennas,⁸ which were pumped by 50 fs pulses from a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics). We conducted the THz analysis by the standard procedure^{8,9} to extract the complex refractive index ($\tilde{n}=n+i\kappa$), where n and κ are the refractive index and the extinction coefficient, respectively. The absorption coefficient α was calculated from the relation $\alpha=4\pi\tilde{\nu}\kappa$, where $\tilde{\nu}$ is wave number in cm^{-1} . α is represented by the logarithm to the base e (Napier number) in this letter. Dielectric permittivity ($\epsilon=\epsilon'+i\epsilon''$) was calculated from the relations, $\epsilon'=n^2-\kappa^2$ and $\epsilon''=2n\kappa$.

Figure 1 shows n and α spectra in the THz region for the UHMWPE samples. The γ -irradiated virgin UHMWPE sample shows the spectral features significantly different from the other UHMWPE samples. It is especially outstand-

^{a)} Author to whom correspondence should be addressed; electronic mail: kohji@ile.osaka-u.ac.jp

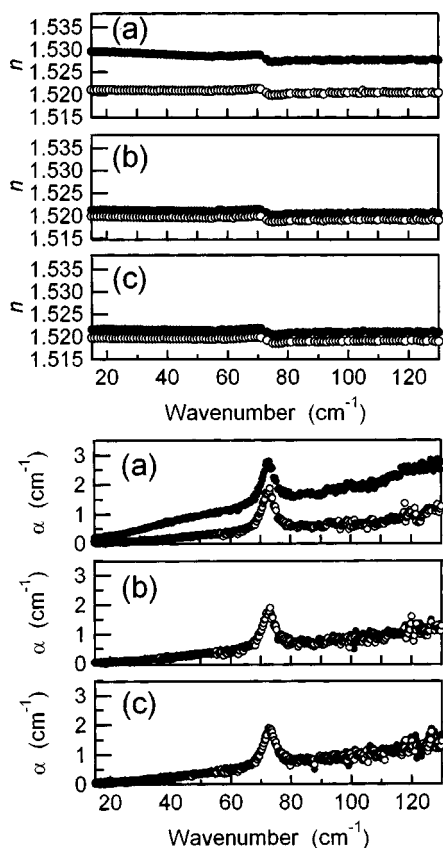


FIG. 1. THz spectra of the various UHMWPE samples; refractive indices in the upper panels, and absorption coefficients in the lower panels. (a), (b), and (c) correspond to the virgin UHMWPE samples, the UHMWPE samples doped with 0.1 wt % vitamin E, and the UHMWPE samples with 0.3 wt % vitamin E, respectively. Open and closed circles mean the nonirradiation and the γ irradiation, respectively. The open and closed circles of panels (b) and (c) almost overlap in the lower panels.

ing that the γ -irradiated virgin UHMWPE sample shows a drastic increase of an absorption continuum (α -continuum) ranging over the THz region. On the other hand, the γ -irradiated UHMWPE samples doped with 0.1 wt % and 0.3 wt % vitamin E show very small spectral changes in the THz region compared with the respective nonirradiated UHMWPE samples. The UHMWPE samples doped with vitamin E are suggested to be almost unaffected by the γ irradiation. This result agrees with the antidegradation effect of vitamin E doped in UHMWPE.⁶ We, therefore, conclude that the increase of the α -continuum over the THz region reflects the degradation of UHMWPE. In the practical use, the broadband feature of the α -continuum over the THz region enables us to inspect UHMWPE in a wide range of thickness by selecting an appropriate THz frequency in detection.

All the spectra of the UHMWPE samples in Fig. 1 present the 72.5 cm^{-1} band. This mode originates in the B_{1u} translational mode of the rhombic lattice, which has two ethylene groups in a unit cell.¹⁰ Polyethylene is actually known as crystalline polymers. The observation of the B_{1u} translational mode, therefore, indicates that all the UHMWPE samples contain the regions with a high degree of crystallinity. The peak frequencies of the B_{1u} -translational modes coincide within 0.1 cm^{-1} for all the samples. The differences in the absorption intensities of this band are also small (difference within 5%) between all the γ -irradiated and the corresponding nonirradiated UHMWPE samples. The 72.5 cm^{-1}

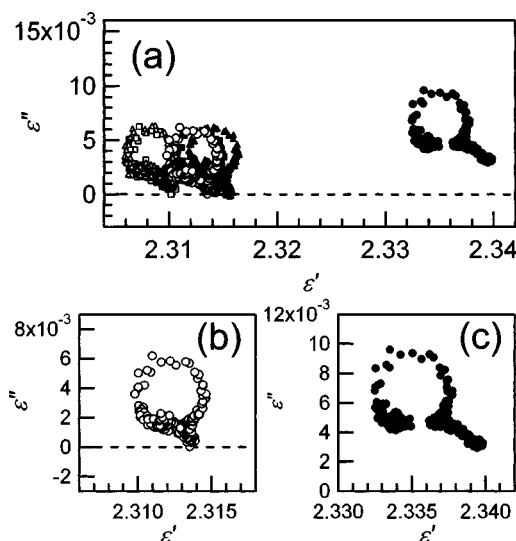


FIG. 2. Cole-Cole plots of the UHMWPE samples. (a) The virgin UHMWPE sample (open circle), the γ -irradiated virgin UHMWPE sample (closed circle), the UHMWPE sample doped with 0.1 wt % vitamin E (open square), the γ -irradiated UHMWPE sample doped with 0.1 wt % vitamin E (closed square), the UHMWPE sample doped with 0.3 wt % vitamin E (open triangle), and the γ -irradiated UHMWPE sample doped with 0.3 wt % vitamin E (closed triangle). (b) and (c) Enlarged illustrations of (a) for the virgin UHMWPE sample and the γ -irradiated virgin UHMWPE sample, respectively.

band is, therefore, not suitable for the degradation diagnosis of UHMWPE. The Cole-Cole plots ($\epsilon' - \epsilon''$ plots)¹¹ of the UHMWPE samples are shown in Fig. 2(a). The circular features of the plots represent the resonance absorption^{12,13} of the 72.5 cm^{-1} mode. The γ -irradiated virgin UHMWPE sample shows the curve which is distinctive and far away from those of the other UHMWPE samples. The Cole-Cole plots of the virgin and γ -irradiated virgin UHMWPE samples are enlarged in Figs. 2(b) and 2(c), respectively. The portion of the curves other than the circle (the portion of inclined line) correspond to the α -continuum. The positions in the $\epsilon' - \epsilon''$ space and the lengths of these linear parts present the large differences between the γ -irradiated virgin UHMWPE sample and the other samples. These differences indicate the significant change in the dielectric property of the virgin UHMWPE, which are induced by the γ irradiation.

UHMWPE samples consist of crystalline and amorphous regions. The 72.5 cm^{-1} band originates in the translational mode of the ethylene groups only in the crystalline phase but not in the amorphous phase.¹⁰ A very small influence of the γ irradiation on the crystalline region of UHMWPE is suggested from only small differences in frequency and intensity of the 72.5 cm^{-1} band between the nonirradiated and the γ -irradiated UHMWPE samples in Fig. 1. Therefore, the increase of the α -continuum induced by the γ irradiation should be attributed largely to modification in the amorphous region.⁶ Figure 3 shows the difference in ϵ'' , $\Delta\epsilon''_n$, between the γ -irradiated and nonirradiated UHMWPE samples. The value $\Delta\epsilon''_n$ is normalized to the density ρ of each nonirradiated UHMWPE sample ($\Delta\epsilon''_n = (\rho_{\text{non-}\gamma} / \rho_\gamma) \epsilon''_\gamma - \epsilon''_{\text{non-}\gamma}$), where the subscripts γ and non- γ represent the γ -irradiated and the nonirradiated UHMWPE samples, respectively. This normalization compensates the difference in ϵ'' due to density differences. The only virgin UHMWPE sample shows the substantial difference in Fig. 3. Mallécol *et al.* suggested that the oxidation processes in polyethylene produce the ketone

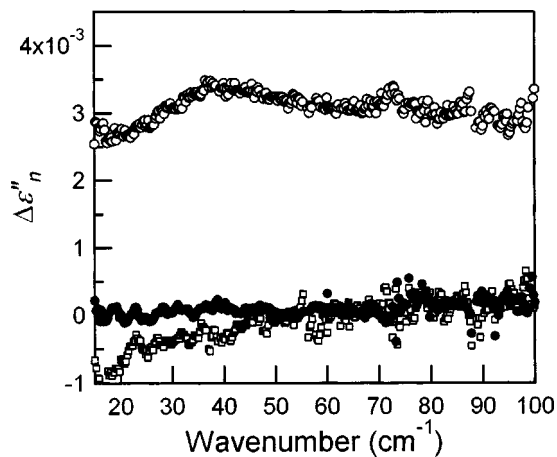


FIG. 3. Difference spectra in density-normalized ϵ'' , $\Delta\epsilon''_n$, between the γ -irradiated and corresponding nonirradiated UHMWPE samples. Open circle, closed circle, and open square represent $\Delta\epsilon''_n$ for the virgin UHMWPE samples, the UHMWPE samples doped with 0.1 wt % vitamin E, and the UHMWPE samples doped with 0.3 wt % vitamin E, respectively.

group ($>C=O$) and the carboxy group ($-COOH$) within the CH_2 chains.⁶ These polar groups have larger dipole moments compared with the CH_2 group. The bond moments of C-H and C=O are calculated to be 0.3 D and 2.4 D,¹⁴ respectively ($1 D = 3.34 \times 10^{-30}$ C m). The net dipole moment in UHMWPE sums up to zero, resulting from the *trans* conformation of the CH_2 chain, in which the dipole moments of adjacent CH_2 groups cancel with each other.¹¹ The oxidation due to the γ -irradiation, therefore, raises the dipole moments in UHMWPE owing to the increase of the polar groups in the amorphous region, leading to additional dielectric responses in ϵ'' in the THz region. Very broad band around 40 cm^{-1} of $\Delta\epsilon''_n$ in Fig. 3, is also observed for the virgin UHMWPE sample. The A_{1u} lattice mode of polyethylene chains at 40 cm^{-1} was theoretically derived from the force field calculation¹⁰ and it was experimentally observed with inelastic neutron scattering.¹⁵ This mode, which is both infrared-inactive and Raman-inactive, originates in the translational mode along the polyethylene chains.¹⁰ The modification from the methylene group to the ketone group would make this mode IR-active because of symmetry breaking. Dielectric loss due to an ultrafast dielectric relaxation is also considered as the origin of the 40 cm^{-1} band. According to the dielectric relaxation of the Debye model, the relaxation time τ is related to the peak frequency as $\tau = 1/(2\pi c\tilde{\nu}_{\max})$, where c is speed of light *in vacuo* and $\tilde{\nu}_{\max}$ is the peak frequency.¹¹ The dielectric relaxation time is calculated to be 0.13 ps when 40 cm^{-1} is substituted to $\tilde{\nu}_{\max}$. This relaxation time is, however, too fast for typical dielectric relaxation in condensed phase. Dielectric loss, therefore, seems unlikely for the origin of the 40 cm^{-1} band in Fig. 3. The boson peak, which is universally observed as a broad peak in the THz region for amorphous materials,¹⁶ is another candidate of the 40 cm^{-1} band. The boson peak is considered to be closely related to the disorder-induced absorption which is attributed to breaking of the translational symmetry in the solid phase.¹⁶ Further experiments are necessary to clarify the origin of this band.

Mallégol *et al.* stated that vitamin E is less effective in reducing the oxidation after the γ irradiation of high-density

polyethylene (HDPE) though it is effective during the γ irradiation.⁶ To examine the oxidative amount of our samples, we measured mid-infrared absorption of the UHMWPE plates, which were cut into slices with 50–200 μm in thickness. The total carbonyl content of the γ -irradiated virgin UHMWPE samples was much larger than that of the γ -irradiated HDPE in Ref. 6. In contrast, the differences in the total carbonyl content between the nonirradiated and γ -irradiated UHMWPE samples doped with vitamin E were very small. The oxidation due to the γ irradiation is, therefore, highly reduced in the UHMWPE samples doped with vitamin E. This result agrees with our conclusion that the THz absorption continuum increases owing to the oxidation of UHMWPE.

In summary, we carried out the THz-TDS of UHMWPE prepared by various conditions and observed the drastic increases of the α -continuum due to the UHMWPE degradation induced by the γ irradiation. The degradation was observed for the virgin samples and not observed for the samples doped with vitamin E. We showed that the α -continuum and the Cole–Cole plot in the THz region can be used as indicators for the degradation diagnosis of the UHMWPE. The THz inspection can be carried out in nondestructive and contactless manners, and it can be applied to the diagnosis for inner parts of UHMWPE. These features, which are difficult to attain with other methods using mid-IR and visible light, are significant advantages in a practical inspection. The degradation diagnosis of UHMWPE using the THz-TDS can contribute to medical applications as the quality control of UHMWPE in stock.

This work has been partly supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Sports, Science, and Technology, Japan.

- ¹M. van Exter, Ch. Fattinger, and D. Grischkowsky, *Appl. Phys. Lett.* **55**, 337 (1989).
- ²X.-C. Zhang, B. B. Hu, J. T. Darrow, and D. H. Auston, *Appl. Phys. Lett.* **56**, 1011 (1990).
- ³B. B. Hu and M. C. Nuss, *Opt. Lett.* **20**, 1716 (1995).
- ⁴N. Tomita, T. Kitakura, N. Onmori, Y. Ikada, and, E. Aoyama, *J. Biomed. Mater. Res.* **48**, 474 (1999).
- ⁵P. Bruni, C. Conti, A. Corvi, M. Rocchi, and G. Tosi, *Vib. Spectrosc.* **29**, 103 (2002).
- ⁶J. Mallégol, D. J. Carlsson, and L. Deschenes, *Polym. Degrad. Stab.* **73**, 269 (2001); *Nucl. Instrum. Methods Phys. Res. B* **185**, 283 (2001).
- ⁷G. W. Burton and K. U. Ingold, *J. Am. Chem. Soc.* **103**, 6472 (1981).
- ⁸M. Hangyo, T. Nagashima, and S. Nashimal, *Meas. Sci. Technol.* **13**, 1727 (2002).
- ⁹K. Yamamoto, M. Yamaguchi, F. Miyamaru, M. Tani, M. Hangyo, T. Ikeda, A. Matsushita, K. Koide, M. Tatsuno, and Y. Minami, *Jpn. J. Appl. Phys., Part 2* **43**, L414 (2004).
- ¹⁰S. Krimm, C. Y. Liang, and G. B. M. Sutherland, *J. Chem. Phys.* **25**, 549 (1956); M. Tasumi and T. Shimanouchi, *ibid.* **43**, 1245 (1965); M. Tasumi and S. Krimm, *ibid.* **46**, 755 (1967); M. I. Bank and S. Krimm, *J. Appl. Phys.* **39**, 4951 (1968).
- ¹¹H. Fröhlich, *Theory of Dielectrics*, 2nd ed. (Clarendon, Oxford, 1986).
- ¹²R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II: Nonequilibrium Statistical Mechanics*, 2nd ed. (Springer, Berlin, 1991).
- ¹³J. E. Boyd, A. Briskman, V. L. Colvin, and D. M. Mittleman, *Phys. Rev. Lett.* **87**, 147401 (2001).
- ¹⁴C. P. Smyth, *J. Phys. Chem.* **41**, 209 (1937).
- ¹⁵G. J. Safford, W. Naumann, and F. T. Simon, *J. Chem. Phys.* **45**, 3787 (1966).
- ¹⁶T. S. Grigera, V. Martin-Mayor, G. Parisi, and P. Verrocchio, *Nature (London)* **422**, 289 (2003), and references therein.