

THz and Mid IR Fourier Transform Spectroscopy on Polyethylene Irradiated with γ -Co⁶⁰ Radiation

J. Beckmann¹, U. Schade², K. von der Ehe¹, M. Jaunich¹, D. Wolff¹, E. F. Aziz^{2,3}
¹BAM Federal Institute for Materials Research and Testing, 12200 Berlin, Germany
²HZB Helmholtz-Zentrum Berlin für Materialien und Energie, 12498 Berlin, Germany
³Freie Universität Berlin, Fachbereich Physik, 14195 Berlin, Germany

Abstract— THz and mid IR spectroscopy of high molecular PE (HMW) and ultra high molecular PE (UHMW) reveals modifications of the molecular structure induced by γ -Co⁶⁰ radiation. UHMW-PE and HMW-PE can be distinguished. The integral absorption in the B_{1u} THz-region can quantitatively describe the amorphization of crystallinity. The formation of trans vinylene unsaturations and the decay of vinyl can be followed by mid IR spectroscopy

I. INTRODUCTION

Today, casks for storage and transportation of used fuel rods of radioactive material are equipped with polyethylene (PE) roads to improve neutron flux shielding of nuclear waste. The embedded PE material is not only exposed to neutrons but also to gamma radiation and, in addition, to heat due to the specific high activity of the fission products. The gamma-radiation introduces free radicals into PE which in turn can lead to cross-linking and chain scissions of the polymer chains. An aging process accompanied by observable changes in PE such as oxidization, changes in the crystallinity as well as density can be observed known to be a dominant response to high energy irradiation [1].

Unfortunately, radiation induced degradation can often lead to unexpected and dramatic failures. It is the question if in the worst case PE aging processes can yield to the loss of the neutron shielding function in nuclear waste containers. The understanding of the radiation induced aging process at the molecular level seems to be necessary to clarify the details of the inherent material structure changes, especially the material requirements must be defined to fulfill the functioning of future nuclear waste containers.

There is still a demand on mobile inspection systems of such containers and the question arises whether THz and MIR spectroscopy can help to distinguish PE and to quantify the effect of gamma irradiation to the molecular structure. Systems either utilizing the THz time domain technique or modern quantum cascade lasers (QCL) are promising.

We studied the radiation induced aging process in PE by means of THz and mid IR Fourier transform spectroscopy on the molecular level. Our results may contribute to the understanding of radiation induced degradation of above mentioned containers and may help in developing stand-alone inspection systems.

II. EXPERIMENTS

High molecular PE (HMW) and ultra-high molecular PE (UHMW) samples have been exposed with different doses of gamma Co⁶⁰ radiation up to 600 kGy. After the irradiation the PE samples have been tempered for 2 hours at 160° C and subsequently cooled down to room temperature for recrystallization. THz and mid IR spectra were measured with

a FT-IR Bruker 80/v spectrometer at 300 K before and after the tempering. In addition, the irradiated PE samples were investigated by means of DSC measurements to gain information on their melting and crystallization behavior.

III. RESULTS

Representative absorption spectra in the THz and mid IR region are shown in case of HMW-PE in Figures 1 and 2.

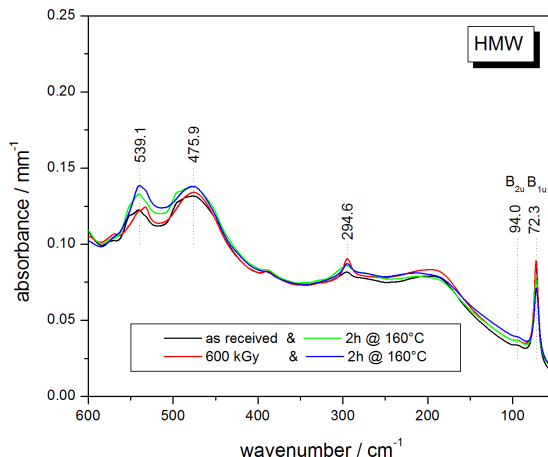


Fig. 1. Absorbance of HMW-PE, as received and exposed with 600kGy γ -Co⁶⁰ radiation in the THz-region before and after recrystallization.

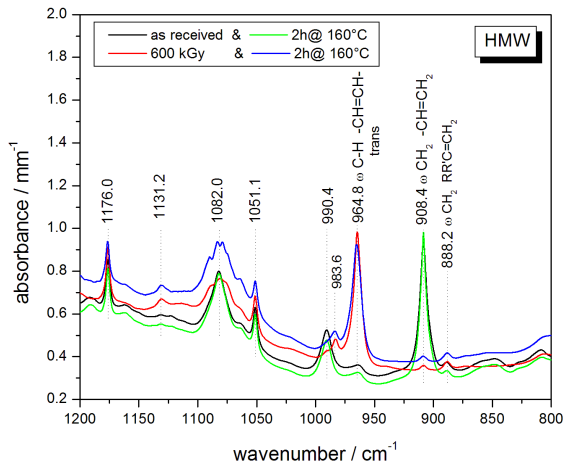


Fig. 2. Absorbance of HMW-PE, as received and exposed with 600kGy γ -Co⁶⁰ radiation in the MIR-region before and after recrystallization.

Both spectra indicate characteristic absorption regions for PE. Measurable changes of absorption regions are detectable for different modifications of PE initiated by γ -irradiation and/or subsequent additional melting and

recrystallization processes respectively. Generally, PE shows in the THz-region a pronounced background spectrum which arises from the normal vibrations of the random configured PE chain segments in the amorphous PE region. Additionally, portions of PE chains, located in the crystalline regions give rise to THz active lattice vibrations. One of them is the B_{1u} translation lattice mode located at $\nu=72.3 \text{ cm}^{-1}$ [2,3]. Absorption bands with intensity peak maxima far above the background intensities can be observed in the mid IR range. Dramatic changes of the absorption behavior can be observed at $\nu=964.8 \text{ cm}^{-1}$ and $\nu=908.4 \text{ cm}^{-1}$ in case PE was Co^{60} γ -irradiated. Similar behavior was observed at swift heavy ion irradiated polyethylene [4]. The two mid IR absorption bands were subjected to wagging vibrations of unsaturated double bonds of the CH group (trans-vinylene, 964.8 cm^{-1}) and of the CH_2 end group at the chain (terminal vinyl, $\nu=908.4 \text{ cm}^{-1}$). First, appropriated parameters were identified for a quantitative analysis of the PE material modifications.

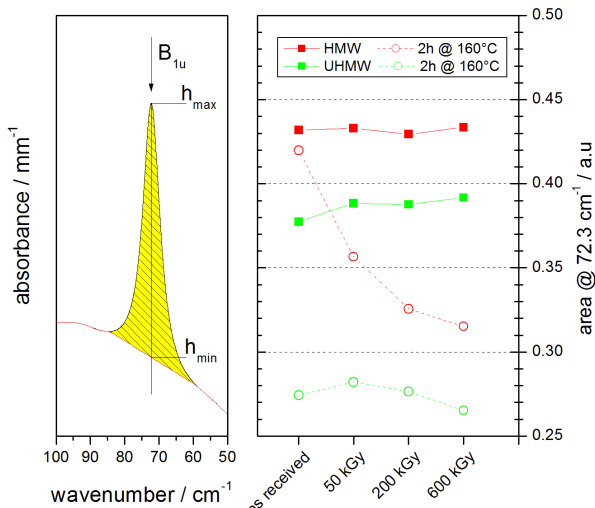


Fig. 3. Integral absorption of the translation lattice vibration mode located at $\nu=72.3 \text{ cm}^{-1}$ (yellow marked area on the left diagram) used to analyze the influence of Co^{60} γ -radiation dose and the effect of recrystallization on the crystalline portion of UHMW and HMW (right diagram).

Figure 3 shows the integral signal intensities of the absorption band in the vicinity of 72.3 cm^{-1} after background correction for HMW and UHMW. Changes of the microstructure in the crystalline regions can be separated by this way. The two peaks at 964.8 cm^{-1} and 908.4 cm^{-1} are isolated and intense enough. As shown in Figure 4, the differences between the peak maxima and the background can clearly describe the influence of radiation dose and recrystallization on the material properties in the mid IR range. Irradiation causes a significant increase of the yield of chain scission. The now more movable chain sections located in the vicinity of the crystalline phase boundaries can attribute on a further crystal growth. As shown in Figure 3, a slight increase of crystallinity proportional to Co^{60} γ irradiation dose can be observed. The reduction of the polymer chain length results into a higher amorphisation of the PE in case a heat load and a recrystallization process were applied. The

influence of Co^{60} γ -radiation on the PE modification is also observable by the increasing number of trans-vinylene formed at in-chain unsaturations. The modification process is accompanied by the reduction of unsaturated vinyl end groups (terminal vinyl) as shown in Figure 4.

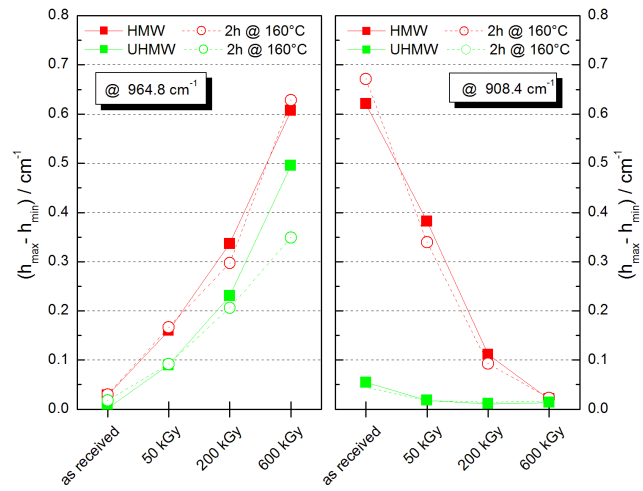


Fig. 4. Influence of radiation dose and recrystallization on the maximum of the absorption intensity after underground correction for the two absorption bands at $\nu=964.8 \text{ cm}^{-1}$ and $\nu=908.4 \text{ cm}^{-1}$ attributed to trans-vinylene and terminal vinyl groups.

The results point to the opportunity to distinct between HMW and UHMW if nondestructive THz- and mid IR measurements are applied on the materials.

IV. SUMMARY

THz- and MIR-IR reveals modifications in PE induced by γ -irradiation processes and subsequently applied thermal load cycle covering a temperature range above and below the melting temperature. Changes in the spectrum point towards chain scission and crosslinking formations. This results initially to a slight increase of the degree of crystallinity. An amorphization of the HMW and UHMW can be observed if recrystallization has been initiated by a thermal load cycle. UHMW shows a higher stability against Co^{60} γ -irradiation in comparison to HMW.

REFERENCES

- [1]. D. Wolff, K. von der Ehe, M. Jaunich, M. Böhning, H. Goering, "(U)HMWPE as neutron radiation shielding materials: impact of gamma radiation on structure and properties, in: Effects of radiation on nuclear materials", ASTM International (American Society for Testing and Materials), 2013, pp. 211-227.
- [2]. E. M. Amrhein and F. H. Müller, "Zur Absorption von Polymeren im Fernen Infrarot", Kolloid-Zeitschrift und Zeitschrift für Polymere, October 1969, Volume 234, Issue 2, 1078-1082
- [3]. W. Frank, "Far-infrared spectrum of irradiated polyethylene", J. Polym. Sci. B Polym. Lett. (1977) Ed., 15: 679-682.
- [4]. E. Balanzat, N. Betz, S. Bouffard, "Swift heavy ion modification of polymers", Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, Volume 105, Issues 1-4, 2 November 1995, Pages