

The Influence of Electron-beam Irradiation on the Chemical and the Structural Properties of Medical-grade Polyurethane

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Thermo plastic polyurethane (TPU) provides excellent bio-compatibility, flexibility and good irradiation resistance; however, extremely high irradiation doses can alter the structure and the function of macromolecules, resulting in oxidation, chain scission and cross-linking. In this study, the effects of e-beam irradiation on the medical-grade thermo plastic polyurethane were studied. Changes in the chain length and their distribution, as well as changes in the molecular structure were studied. The GPC (gel permeation chromatography) results show that the oxidative decomposition is followed by a decrease in the molecular mass and an increase in polydispersity. This indicates a very inhomogeneous degradation, which is a consequence of the specific course and of the intensity of oxidative degradation. This was confirmed by means of mechanical property measurements. Overall, this study demonstrated that medical-grade TPU was affected by radiation exposure, particularly at high irradiation doses.

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I. INTRODUCTION

Thermo plastic polyurethane (TPU) elastomers are flexible biomaterials that have many enduse applications, owing to the combination of excellent bio-stability, bio-compatibility, processability and desirable mechanical properties such as abrasion resistance, toughness, flexibility, durability and tensile strength [1]. TPUs are often referred to as segmented block copolymers as they consist of a hard and a soft phase which either mix or segregate due to their immiscibility and produce phase-mixed or phase-separated morphologies. Each of the hard and the soft segments is connected by means of urethane linkages, where the hard segment provides the physical crosslinks within the soft segment matrix [2,3]. Implant devices that contain such elastomers are significantly degraded in vivo after exposure to long-term biological environments as a result of hydrolytic or oxidative mechanisms [3–6]. Polyester TPUs are no longer used for devices that are required for long-term implantation due to poor hydrolytic stability. Polyether TPUs are hydrolytically stable, yet they can undergo oxidative degradation in several forms, including oxidation and environmental stress in the in-vivo environment [1,7,8].

A common type of medical-grade TPU is pellethane, which has been widely used as a biomaterial since its

introduction in 1977 [9–11]. This material is employed to manufacture medical devices, including those that are implanted, and for this reason, it is critical that the final product be sterilized before use. Conversely, such sterilization processes like dry steam, heat, and high-energy irradiation can have unfavorable effects, such as extensive material degradation and plastic deformation [12–14]. In terms of high energy radio sterilization, the susceptibility of TPU to these processes with respect to crosslinking and degradation depends highly on the chemical. With regards to the TPU material, different types of degradation processes can emerge subsequent to irradiation [15–18]. Furthermore, TPU elastomers can experience substantial structural changes when exposed to UV-irradiation, which causes deterioration in their morphology [19]. Little information in the literature identifies the effects of irradiation conducted in an air atmosphere on medical-grade PU (*e.g.*, pellethane 35D) or any systematic correlation between the segment composition and the resulting properties. The objective of this study is to quantify the effects of irradiation on the properties of TPU through gel permeation chromatography (GPC) and mechanical property analysis.

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Table 1. Materials and e-beam radiation dose information.

TPU type	E-beam condition
Elasthane 35D	control
	e-beam 35 kGy
	e-beam 50 kGy
	e-beam 50 kGy & aged 4 wks
Carbothane 40D	control
	e-beam 35 kGy
	e-beam 50 kGy
	e-beam 50 kGy & aged 4wks
Samples used for tensile test	
Pellethane 55D	control
	e-beam 80 kGy & aged 48 months
Pellethane 55D	control
	e-beam 80 kGy & aged 48 months
Pellethane 72D	control
	e-beam 80 kGy & aged 48 months

II. METHOD AND MATERIAL

The tubing was constructed with a 35D, 40D, 55D and 72D Thermo plastic polyurethane material. Elasthane and pellethane are polyether-base thermoplastic polyurethanes from the Polymer Technology Group and Lubrizol, respectively. Carbothane is a family of aliphatic and aromatic polycarbonate-based thermo plastic polyurethanes from Lubrizol. E-beam sterilization was performed by Nutek in Hayward, CA, by using a 10-MeV accelerator. Samples were irradiated in a serial fashion via a conveyance system for approximately 10 minutes per dose.

Samples used for the molecular weight analysis were placed in an oven for an accelerated aging simulation at 55°C with 50% relative humidity. Table 1 summarized the used TPU materials with different hardness grades, e-beam irradiation condition and the simulated accelerated aging time.

The GPC system used for this work was calibrated using Agilent/Polymer Laboratories Easi Vial polymethyl methacrylate (PMMA) calibrants. The highest molecular weight calibrant was considered to be 'excluded' and was not used in the calibration. The results are expressed as the 'PMMA equivalent' molecular weights and the reader should appreciate that there could be considerable differences between these PMMA equivalents and the true molecular weights of the polymer. Data were analyzed to determine the average number molecular weight (Mn), the weight average molecular weight (Mw), and the polydispersity (Mw/Mn).

All materials were evaluated by using mechanical testing. A Criterion Universal Testing Systems from MTS was used to mechanically test all materials in the tensile

Elasthane TPU 35D

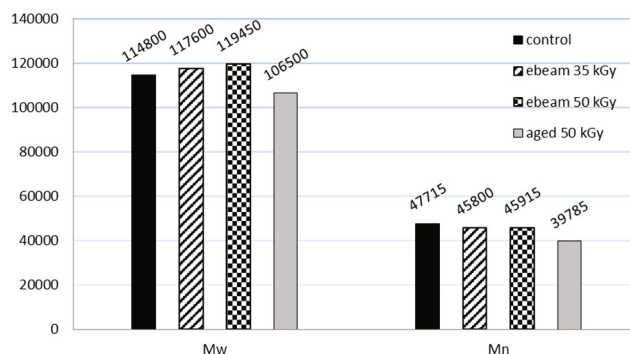


Fig. 1. Molecular weight analysis summary of elasthane 35D.

mode. A 2/G MTS loadframe was used to mechanically test the materials in the tensile mode. For each sample condition, 10 specimens were tested, and a single average datum point is reported in figures from 4 to 9.

III. RESULTS AND DISCUSSION

1. GPC Molecular Weight analysis

An electron-beam irradiation may be used on a material to induce effects such as chain scission (which makes the polymer chain shorter) and cross linking. The result is a change in the properties of the polymer which is intended to extend the range of applications for the material. Irradiation with an electron-beam can degrade the polymers, breaking chains and, therefore, reducing the molecular weight. Chain scission is the breaking apart of molecular chains to produce required molecular sub-units from the chain. Electron-beam processing provides chain scission without the use of the harsh chemicals usually utilized to initiate chain scission. Polymer can be cross-linked as well by using high-energy ionizing radiation, *i.e.*, electron-beam (or e-beam, e beam), gamma, or X-ray irradiation.

E-beam irradiation creates free radicals, which will often chemically react in various ways, sometimes at slow reaction rates. The free radicals can recombine to form crosslinks. The degree of crosslinking depends upon the polymer and the radiation dose. One of the benefits of using irradiation for crosslinking is that the degree of crosslinking can be easily controlled by using the amount of dose. Furthermore, oxidation can continue after irradiation, causing changes in the properties with time. Electron-beam processing of thermoplastic material also results in an array of enhancements, such as an increase in the tensile strength when polymers are cross-linked.

Figure 1, where shows GPC measurements of the molecular weight distributions of elasthane TPU 35D

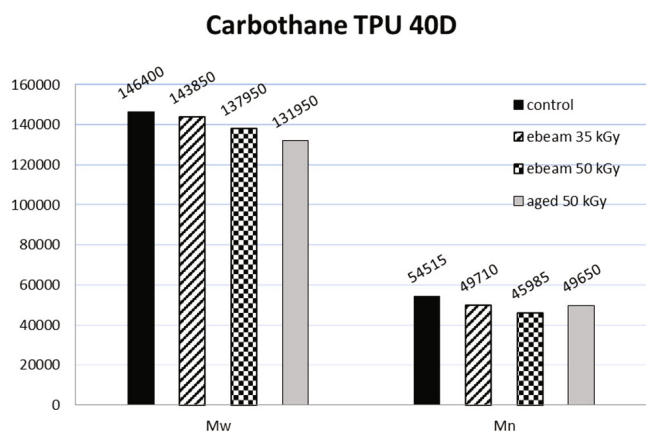


Fig. 2. Molecular weight analysis summary of carbothane 40D.

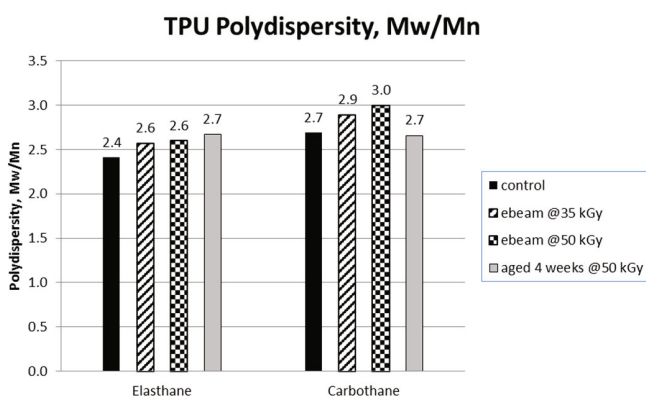


Fig. 3. Polydispersity summary of polyurethane post e-beam irradiation & aging.

samples, reveals an increase in the number average molecular weight. A conceivable reason for the molecular weight increase caused by the higher dosage is the crosslinking between free monomers or polymer chains. While the Mn value of the elasthane samples did not change, the increased MW was attributed to crosslinking of the polymer and might reflect the loss of low-molecular-weight fragments. This suggests degradation, in the absence of stress, at the surface, but not in the bulk, of the polymer.

For carbothane TPU 40D, there was a decrease in molecular weight numbers for higher irradiation doses, with the exception of aged Mn, where the difference was not statistically significant. This can be explained by the prevalence of chain scissioning the carbothane TPU material.

In Fig. 3, the GPC results show that the oxidative decomposition is followed by a decrease in molecular mass together with an increase in polydispersity.

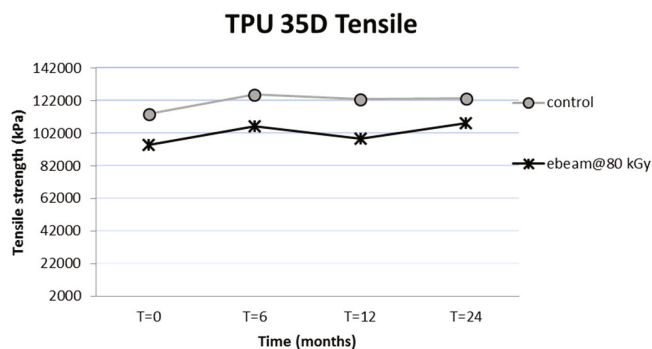


Fig. 4. Tensile strength property summary of pellethane 35D post e-beam irradiation & aging.

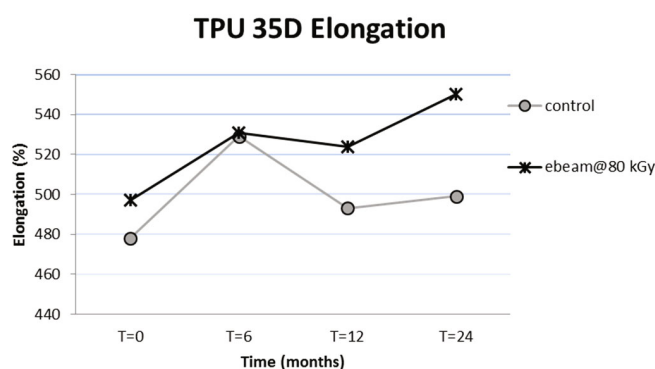


Fig. 5. Elongation property summary of pellethane 35D post e-beam irradiation & aging.

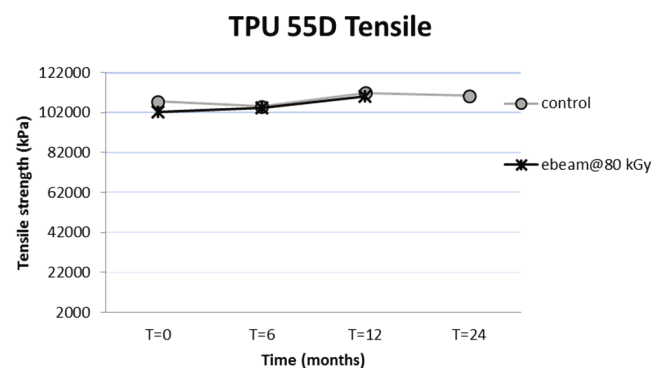


Fig. 6. Tensile strength property summary of pellethane 55D post e-beam irradiation & aging.

2. Mechanical Property Analysis

Figure 4 shows that significant tensile differences were observed between the pellethane 35D two-year e-beam results for time zero and a time of twelve months. Actual numerical differences between e-beam air groups were in line with differences observed between controls. When compared to two-year control data, two-year e-beam data showed a significantly different elongation. The numerical difference (499% versus 550%) is fairly

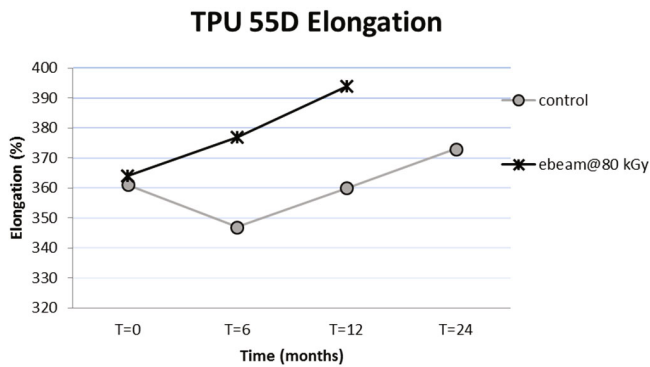


Fig. 7. Elongation property summary of pellethane 55D post e-beam irradiation & aging.

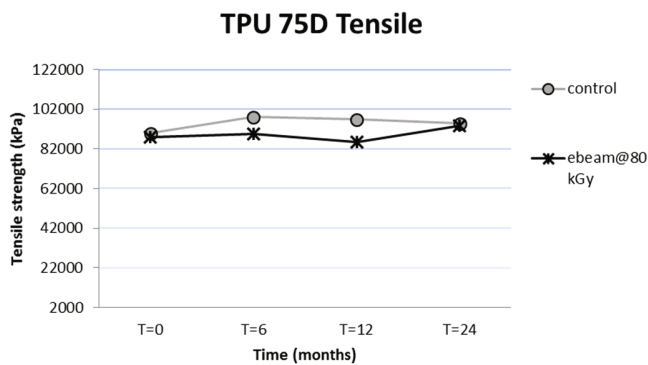


Fig. 8. Tensile strength property summary of pellethane 75D post e-beam irradiation & aging.

modest and likely reflects no practical significance. A minimum elongation specification of 400% was available for pellethane 35D tubing. Materials from e-beam sterilization groups exceeded this specification.

No significant differences were observed for pellethane 55D two-year E-beam data from other time points.

In Fig. 7, significant elongation differences were observed between pellethane 55D two-year e-beam materials for times zero and six months. However, two-year e-beam data was limited to $n = 4$ specimens, and actual numerical differences were modest and in line with those observed between controls.

No significant differences were observed for pellethane 75D two-year e-beam data compared to other time points.

At two years, pellethane 75D e-beam elongation was statistically significantly different from the respective two-year control elongation, but the actual numerical difference between the two-year control and the e-beam (350% versus 338%) data was quite modest, reflecting no likely practical significance.

Overall, TPU degradation due to high dose e-beam irradiation is not as severe as it is for other medical-grade elastomeric materials such as PEBA. For PEBA, fair amounts of decrease in the molecular weight and the mechanical properties post irradiation have been re-

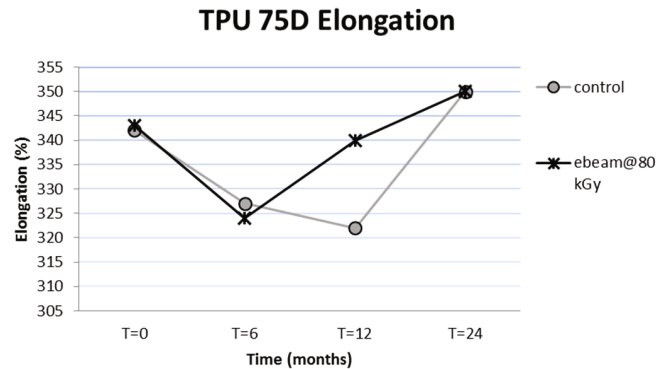


Fig. 9. Elongation property summary of pellethane 75D post e-beam irradiation & aging.

ported.

IV. CONCLUSION

Irradiation of medical-grade PU and its aging effect while using a commercially-available electron-beam irradiator resulted in considerable modifications to the materials properties by GPC analyses and tensile tests. The material modifications triggered by irradiation exposure were analyzed by using the molecular-weight change and mechanical properties. The GPC results show that the oxidative decomposition is followed by a decrease in molecular mass and an increase in polydispersity. This indicates a very in-homogeneous degradation, which is a consequence of the specific course and of the intensity of oxidative degradation. This was confirmed by means of mechanical property measurements.

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REFERENCES

- [1] A. Simmons *et al.*, *Biomat.* **25**, 4887 (2004).
- [2] G. Abraham, P. Frontini and T. Cuadrado. *J. of Appl. Polymer Sci.* **65**, 1193 (1997).
- [3] I. Khan, N. Smith, E. Jones, D. Finch and R. Cameron. *Biomat.* **26**, 621 (2005).
- [4] J. Boretos, D. Detmer and J. Donachy. *J. of Biomed. Mater. Res.* **5**, 373 (1971).

- [5] D. Wilson, N. Rhodes and R. Williams. *Biomater.* **24**, 5069 (2003).
- [6] E. Abdand, *Phys. Appl. Phys.* **40**, 6014 (2007).
- [7] A. Takahara, A. Coury, R. Hergenrother and S. Cooper, *J. of Biomed. Mater. Res.* **25**, 341 (1991).
- [8] J. Santerre, R. Labow, D. Duguay and D. Erfle, *J. of Biomed. Mater. Res.* **28**, 1187 (1994).
- [9] M. Szycher, *Biostability of polyurethane elastomer: Technomic Publishing* (1990), p. 33.
- [10] A. Coury, K. Stokes, P. Cahalan and P. Slaikou, *Life Support Systems.* **5**, 25 (1987).
- [11] K. Stokes, A. Coury and P. Urbanski, *Biomater. Appl.* **1**, 411 (1987).
- [12] I. Matthews, C. Gibson and A. Samuel, *Clinical Materials.* **15**, 191 (1994).
- [13] S. Gogolewski and P. Mainil-Varlet, *Biomater.* **18**, 251 (1997).
- [14] W. Skiens and J. Williams, *Ionizing Radiation's Effects on Selected Biomedical Polymers. Lancaster, PA: Technomic* (1983).
- [15] C. Wilhelm, A. Rivaton and J. Gardette, *Polymer.* **39**, 1223 (1998).
- [16] B. Ravat, R. Gschwind, M. Grivet, E. Duverger, A. Chambaudet and L. Makovicka, *Beam Interactions with Materials and Atoms.* **160**, 499 (2000).
- [17] B. Ravat, M. Grivet, Y. Grohens and A. Chambaudet, *Radiation Measur.* **34**, 31 (2001).
- [18] B. Ravat, M. Grivet, and A. Chambaudet, *Beam Interactions with Mater. and Atoms.* **179**, 243 (2001).
- [19] K. Zia, M. Barikani, I. Bhatti, M. Zuber and M. Barmar, *Carbohydrate Polymers.* **77**, 54 (2009).