The Impact of Therapeutic Radiation on Crystallinity in Medical Polymers

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Statement of Purpose: Medical polymers are often exposed to ionizing radiation within the body as implants, coatings and bystander materials. How this might impact degradation rates, mechanical properties and chemical structure are currently unreported. High levels of ionizing radiation (eg. x-ray and gamma) have been reported to cause degradation and/or cross-linking in certain polymers (1). However, few studies report the effects that low levels of therapeutic radiation, commonly used in cancer treatments, have on medical polymers. This study investigated how therapeutic radiation affected the degradation and chemical structure (crystallinity) of two different porous polymeric scaffolds: polycaprolactone (PCL) and polyurethane (PU). PCL has been used in biomedical devices and high doses of gamma-radiation are known to initiate degradation. PU has shown little response to gamma radiation and was considered a non-degradable polymer in this study.

Methods: Porous scaffolds were fabricated using solvent casting and/or salt leeching techniques. Scaffolds were placed in phosphate buffered saline (PBS, pH = 7.4) and exposed to a typical radiotherapy schedule for cancer patients. A total dose of 50 Gy was broken into 25 dosages over a three-month period. PBS was collected every other treatment and tested for polymer leachants and degradation through high performance liquid chromatography (HPLC). Scaffolds were characterized by changes in microstructure using Environmental Scanning Electron Microscopy (ESEM), and crystallization using Differential Scanning Calorimetry (DSC). The as received and non-irradiated PU and PCL were used as controls.

Results: There were no visual changes in the microstructure of PCL samples. HPLC did not detect the presence of leachants or PCL monomers. PU displayed a slight change in pore shape and size, but HPLC did not indicate the release of leachants or PU monomers. Since little visual change is seen in PCL and PU, DSC was used to determine the crystallinity changes in these polymers. DSC scans (Figure 1) display a statistically significant change ($p < 0.05$) between irradiated samples compared to the as received and non-irradiated samples in both PCL's recrystallization curve (Figure 1A) and PU's melting (Figure 1B). However, PCL scans reveal no significant change in the first heat. Changes in crystallinity were calculated using reported heat of fusion for a purely crystalline material (139.5 J/g for PCL (3), and 136 J/g for PU (4)) and the heat of fusion calculated by DSC scans. There is a ~16% decrease in crystallinity after PU scaffolds were irradiated, and a ~8% decrease after PCL scaffolds were irradiated. Another critical change seen in PU DSC scans is the disappearance of Peak II after irradiation (Figure 1B). Peak (I) represents the beak up of short-range order hard segments, while Peak (II) is the break up of long-range hard segments (5).

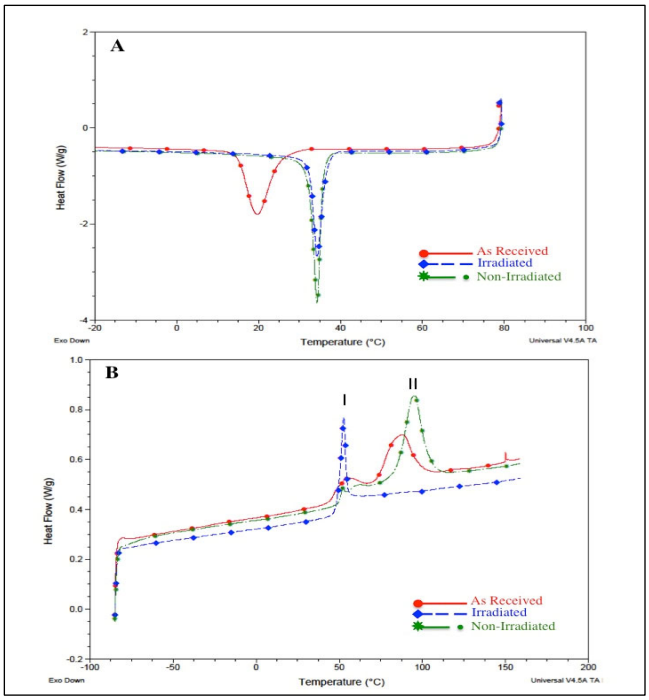

Figure 1. Differential Scanning Calorimetry scans comparing the as received (•), irradiated (◆), and non-irradiated (■) a) PCL, and b) PU

This suggests that irradiated is causing an alteration in the long-range order of PU.

Conclusions: While degradation of these polymers was not observed over three months, PCL and PU both display significant changes in crystallinity after irradiation. Notably, the disappearance of Peak II in PU could represent a break up of long-range order, or a conversion of long-range to short-range as a result of irradiation. These changes in crystallinity were unexpected and further analysis of the change in chemical structure will be investigated using Fourier Transform Infrared Spectroscopy (FTIR). FTIR should provide a better understanding of the crystallinity change in medical polymers, whether it is chain scission, molecular rearrangement or a different type of degradation.

References:

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