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Radiation cross-linking in ultra-high molecular weight polyethylene for orthopaedic applications

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Abstract

The motivation for radiation cross-linking of ultra-high molecular weight polyethylene (UHMWPE) is to increase its wear resistance to be used as bearing surfaces for total joint arthroplasty. However, radiation also leaves behind long-lived residual free radicals in this polymer, the reactions of which can detrimentally affect mechanical properties. In this review, we focus on the radiation cross-linking and oxidative stability of first and second generation highly cross-linked UHMWPEs developed in our laboratory.

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1. Introduction

The most accepted bearing couple in joint arthroplasty today is a cobalt/chromium/molybdenum alloy (CoCr) articulating against UHMWPE. This articulating couple is based on the original design of Dr. Charnley developed in the 1960's comprising a 'hard' metallic component articulating against a 'soft' polymeric component. Although total joint arthroplasty using this bearing couple has been one of the most successful operations of the last century, long-term resorption of the bone around the implants (osteolysis) was observed, limiting the longevity of the arthroplasty. One major cause of this phenomenon is the immune reactions associated with the wear debris primarily generated from the UHMWPE component [1,2].

UHMWPE has a composite structure with highly ordered crystalline lamellae embedded in a randomly oriented amorphous matrix (Fig. 1). Due to its high molecular weight, typically on the order of 2–6 million g/mol, it has high crystallinity (50–60%) and shape memory. Its high mechanical strength under load and its favorable fatigue resistance are attributed to its composite structure, where, in addition to the crystalline content and associated strength, the mobility of the chains in the amorphous phase provides ductility and plasticity to the polymer. The stresses to which the polymer is exposed are easily dissipated through plastic deformation. On the other hand, polyethylene wear is associated with increased plasticity. Increased plasticity allows the chains to be oriented in the direction of the applied stresses, and weakens the material in the transverse direction, leading to the breakup of particles, especially under the multi-directional motion of the joints [3].

Radiation cross-linking by high dose irradiation was proposed to increase the wear resistance of the polymer in general. Cross-linking of the polymer chains, which only occurs in the amorphous phase in polyethylene, introduces

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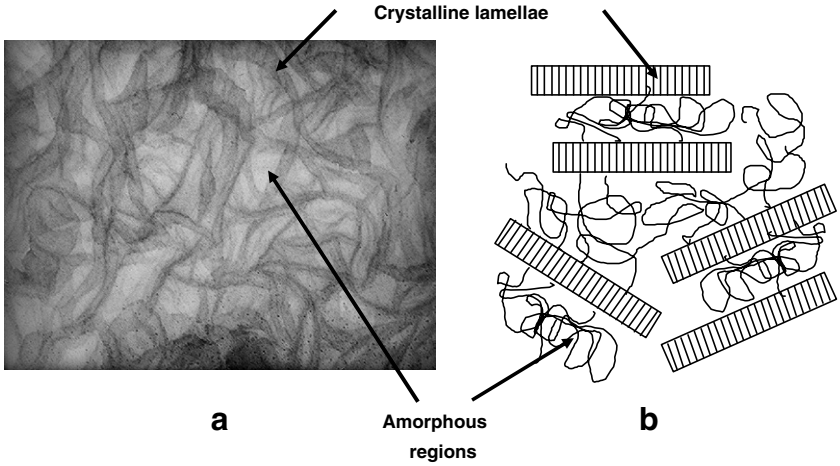

Fig. 1. A transmission electron micrograph (a) and schematic (b) depicting the semi-crystalline morphology of UHMWPE.

junctions between the polymer chains, reducing the mobility. Thus, it was hypothesized that wear would be reduced through a decrease in plasticity and thus orientation of the polymer.

Adhesive/abrasive wear properties of joint materials are typically tested in vitro using wear simulators. For the hip, the motion of the femoral neck on the acetabular surface in the joint is simulated on a bidirectional pin-on-disc machine (POD), where pins of UHMWPE are loaded on polished CoCr surfaces in a rectangular crossing pattern and the wear of the pins are determined gravimetrically at certain number of cycles [4,5]. In a more clinically relevant test, joint simulators are used where the load and kinematics patterns are superimposed and actual implant devices are tested under these conditions [6–9]. Most of these tests are done in a synovial fluid analog (bovine serum) [10–12]. The results of these tests have been a good predictor of in vivo behavior. Clinically, wear is most often determined by calculating the penetration of the hard component in the soft polymeric surface from X-rays [13–15].

Early attempts were made at using gamma radiation to cross-link UHMWPE for bearing surfaces in total joint arthroplasty by using very high dose irradiation (1000 kGy; [16–19]). The wear rate of these surfaces was reduced compared to conventional UHMWPE (gamma sterilized in air). Radiation cross-linking in the presence of a sensitizing gas environment such as acetylene was also shown to increase the efficiency of cross-linking [20–22].

Alternative to ionizing radiation, cross-linking by silane chemistry was also proposed as a means to decrease the creep of the UHMWPE [23–25]. Typically, hip implants undergo a 'bedding in' period of one to two years, where the observed penetration of the femoral head into the acetabular socket is mainly due to the creep of the polymer. After this period, a steady wear rate is the major cause of further penetration. The average clinical penetration rates of 22-mm diameter acetabular cups made of silane cross-linked UHMWPE [26] articulating against ceramic femoral heads was 0.022 mm/year after the initial creep was complete. This value was significantly lower than the wear rate observed with conventional UHMWPE.

Thus, the hypothesis tested positive that cross-linking increased the wear resistance of UHMWPE and presented an improvement to address one major limitation of total joint arthroplasty.

2. First generation cross-linked UHMWPE

Most UHMWPE medical devices are terminally sterilized by gamma irradiation (25–40 kGy). Ionizing radiation induces radiolytic cleavage of the polymer chains throughout the polymer with the formation of C and H free radicals. Because of the high molecular weight of UHMWPE, recombination reactions along the backbone are favored limiting chain scission. The decay of the remaining free radicals is through recombination of the free radicals on different chains to form cross-links. However, some free radicals become trapped in the crystalline regions or in the folds of the crystalline lamellae for prolonged periods of time [27,28]. Due to the fixed distance between the crystal chains and the immobility of the chains in the crystallites, these free radicals are thought to migrate along the chains to the crystalline/amorphous region and react with the diffused oxygen over time.

The primary alkyl and allyl free radicals on the polymer chains react with oxygen to form peroxy free radicals. These very reactive free radicals then stabilize themselves by abstracting hydrogens from nearby chains and becoming hydroperoxides. The decay of the hydroperoxides over time degrade the molecular weight. In addition, the abstraction of hydrogens creates a new primary alkyl free radical that feeds the oxidation reaction, leading to more severe degradation and more free radicals [29,30]. This cascading oxidative reaction of the free radicals is the cause of oxidative embrittlement through the local re-crystallization of the newly formed degraded short chains (Fig. 2). The molecular weight degradation accompanying embrittlement manifests itself in increased wear [31] and also