Crosslinking of UHMWPE without Radiation

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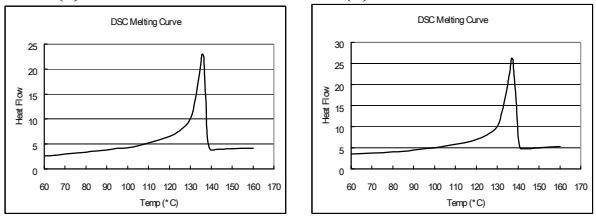
Statement of Purpose: Improvement in wear by radiation-induced crosslinking has been confirmed in recent clinical studies. Studies on silane-crosslinked UHMWPE also showed marked *in vitro* and *in vivo* wear improvement[1]. The major drawback of these crosslinking treatments is loss of ductility, as exemplified in reduced elongation and toughness. In this series of studies[2], we made an attempt to develop an alternative means of crosslinking with the objective to gain wear improvement without loss of mechanical properties. **Methods:** GUR1050 UHMWPE was treated in nitrogen gas purged oven from room temperature up to 250°C followed by slow cooling at about 1°C/min back to room temperature for a total time of 10 hours. The resultant material was evaluated for gel content/swell ratio, tensile, free radical, oxidation, melting/crystallinity, and wear. Gel content and swell ratio analysis followed ASTM D2765 using hot xylene at 130°C for 3 hours. Tensile tests followed ASTM D638. Free radicals were measured using ESR. Oxidation index (OI) was measured by FTIR (ASTM 2102). Melting curves and crystallinity were obtained by DSC. Hip wear simulator was employed to measure wear against a cobalt-chromium-molybdenum alloy head (diameter 28 mm) at 1Hz following ASTM F1714. A virgin GUR1050 UHMWPE was tested as control. **Results:** Data for gel content, swell ratio, tensile, free radical, OI, melting point, crystallinity, and wear rate are presented in Table 1. Figures 1(a) and 1(b) show DSC melting curves for the virgin and heat-treated UHMWPE. **Discussion and Conclusion:** Polymer scientists are taught not to overheat a polymer beyond its melting point to avoid thermal degradation where de-polymerization or decomposition reactions readily occur. The high temperature treatment employed in this study up to 250°C (about 110°C above melting) deviates severely from such conventional wisdom. However, judged from the melting curves in Figure 1 (virtually identical before and after treatment) and the melting points (136°C before and 137°C after), the material remained as UHMWPE. The melting point would have been much lower (100-130°C) if the material had become HDPE or LDPE. The increased gel content (from 65% before to 94% after) and reduced swell ratio (from 10.1 before to 6.2 after) suggest that the extent of crosslinking was enhanced in the treated material. Improved wear was another benefit observed (from 80-120 typical for the virgin polymer (see example in literature [3]) down to 40 mg/million cycle after treatment). What's more striking is that tensile elongation, ultimate strength, and toughness were all improved (by 40, 39, and 75% respectively). A tentative theory was developed to interpret the observation. UHMWPE consists of C-C and C-H bonds only. The associated bond energies are 80 and 98 kcal respectively. At sufficiently high temperatures (such as 250°C used in the study), C-C bonds are expected to break, creating chain-end alkyl free radicals. The majority of C-H bonds might remain intact at such temperatures due to much higher bond energy. Upon subsequent cooling, all free radicals would react with each other to form crosslinks. Note that ESR data showed no residual free radicals. In radiation or chemical agent induced crosslinking, rigid crosslinks are formed between neighboring molecules. They are chemical crosslinking in nature and often act against molecular extension, resulting in elongation and toughness reduction. Since free radials are located primarily at broken chain ends during this study, "branching" type of crosslinking between molecules is highly improbable. Three other mechanisms are more plausible: (1) broken chain ends re-connect back to form linear long molecules (2) the two chain ends of the same molecules recombine to form rings (cyclic polymers), and (3) such molecular rings form interlocks in the "spaghetti-like" polymer melt during cooling. In either probable case, the crosslinks are physical and non-rigid. That would explain the observed improvement in crosslinking and tensile toughness. Future studies are planned to elucidate further the molecular structure.

Table 1: Material property for virgin and heat-treated UHMWPE

Material Property	Before treatment	After treatment
Gel content (%)	65%	94%
Swell ratio	10.1	6.2
Yield Strength (MPa)	18 ± 3	19 ± 2
Tensile strength (MPa)	44 ±5	61 ± 2
Elongation (%)	488 ± 41	683 ± 17
Tensile toughness (MPa)	137 ± 24	240 ± 11
Free radical (spin/g)	undetectable	undetectable
Oxidation index	0.02	0.02
Melting point	136 °C	137°C
Crystallinity	53%	54%
Wear rate (mg/MM cycle)	80 – 120 (from literature)	40.4 ± 1.4

Figure 1: DSC melting curves

(a) before treatment **(b)** after treatment



References: (1) Wroblewski, B.M. et al., J Bone Joint Surg., 81-B:54-55, 1999 (2) Sun, DC, US patent applications 11/463,423 and 12/076,969 (3) Wang, A et al., US patent 6,849,224.

Acknowledgement: Authors are grateful to Dr. H. McKellop and Dr. Zhen Lu of UCLA, Los Angeles, CA. for conducting the hip wear work. Special thanks are given to Meditech Inc. for providing UHMWPE material.