Wear 297 (2013) 742–751

Contents lists available at SciVerse ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

Study on tribological properties of UHMWPE irradiated by electron beam with TMPTMA and TPGDA as crosslinking agents

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ARTICLE INFO

Article history:
Received 20 March 2012
Received in revised form
19 August 2012
Accepted 15 October 2012
Available online 2 November 2012

Keywords:
Wear testing
Bio-tribology joint
Prostheses
Polymers

ABSTRACT

Trimethylolpropane trimethacrylate (TMPTMA) and tripropylene glycol diacrylate (TPGDA) used as crosslinking agents were blended with ultra-high molecular weight polyethylene (UHMWPE or UPE) in alcohol, respectively. Then UPE plates were made by compression molding and electron beam (EB) irradiation crosslinking methods. FTIR, Soxhlet extractor, DSC, Wear tester and SEM were used for the characterization of all specimens. FTIR analyses show that *trans*-vinylene (965 cm^{-1}) absorption increases in all specimens and the $>C{=}C<$ stretching absorption decreases after irradiation. Soxhlet experiments reveal that gel fraction increases with the increasing dose. DSC results indicate that X_c of all the irradiated UPEs are higher than that of unirradiated UPEs because of the free radical and small molecular which can promote the crystallization. Wear rate of 100 kGy 1%TMPTMA/UPE and 1%TPGDA/UPE are $1.89\times10^{-7}\ \text{mm}^3/(\text{N m})$ and $4.28\times10^{-7}\ \text{mm}^3/(\text{N m})$, about 44.2% and 100% of that of 100 kGy UPE, respectively, illustrating that TMPTMA is beneficial to reduce the wear rate of UPE and TPGDA almost has no effect to reduce the wear rate of UPE before 100 kGy. SEMs of irradiated specimens are more smooth than that of unirradiated specimens. These can give some advice to improve tribological properties of UPE used in the friction field.

1. Introduction

UPE is a linear and highly entangled polyethylene with an average molecular weight more than 1.5×10^6 g/mol. Excellent properties such as high resistance to physical abrasion and low fiction coefficient have made UPE used in the replacement of damaged articulating cartilages [1–7]. However, the structure of UPE makes its creep weak and the strength fatigue. So the wear resistance and anti-creep properties of UPE must be improved to prolong the life of the replaced joint. Adding particles and crosslinking are the two main methods to improve the tribological properties of UPE.

The most advantage of adding particle additives (such as fiber, Pt–Zr, Cu, MoS_2) [8–11] is the avoidance of free radical generation and accelerated oxidation. But the toxicological effect on the body and the dispersion of the filling phase and the interfacial adhesion between various composite components restrict the particles use in the wear resistance.

Although radical crosslinking method (dicumyl peroxide, benzoyl peroxide, 2.5-dimethyl-2.5-di-(*t*-butyl-peroxy)hexyne-3) [12–14] and silane crosslinking [15] method used in UPE have caught great attentions, but little information is available on the clinical experiments. Now crosslinking of UPE is done in commerce through the use of gamma or EB irradiation under certain atmospheres along with a thermal treatment with doses range from 50 to 105 kGy [16–18]. The irradiation creates free radicals to produce the crosslinked structure. But the consumption of free radicals by crosslinking at room temperature is a slow process and the free radicals are consumed more through oxidative reactions to form carbonyl groups ($C{=}O$) to cause scission of UPE [19–26]. Although post-irradiation thermal processing [27,28] can be used to reduce free radicals to minimize the potential for post-irradiation oxidation, but it can also change the semicrystalline structure which may affect fracture toughness and other mechanical properties.

The main problem is to prevent the oxidation in and after irradiation process through the analysis above. So some scientists use inert atmospheres (nitrogen, a vacuum) [27,29] or add radical scavengers (vitamin E [4,30–33], hindered amine [34]) to catch the free radicals. Plasma/ion treatment [35,36] is also used to modify polymer surfaces without changing the bulk composition. Recently, someone irradiated UPE in the presence of acetylene or 1,7-octadiene to increase the molecule crosslinking density [37,38].

But the methods above need long time to process and also the processes are complicated. In addition, the high molecular weight and linear highly entangled structure (melt flow index=0) make

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http://dx.doi.org/10.1016/j.wear.2012.10.017

it difficult to mix additives with UPE in a mixing mill. In this paper, one method is issued to reduce the irradiation dose of UPE through adding TMPTMA or TGPDA as crosslinking agent which can increase the crosslinking density. When the irradiation doses reduce, the residual free radicals trapped in the amorphous region drop, the oxidation probability of UPE during use can be reduced. The method is simple, fast and can make crosslinking agent well dispersed in the UPE. The structure, gel fraction, X_c, tribological properties of TMPTMA/UPE, TPGDA/UPE, UPE are compared each other in this paper in order to find the best method to improve the tribological properties of UPE.

2. Materials and methods

2.1. Sample preparation

The preparation of crosslinked UPE samples could be described in Fig. 1. UPE (M_c=2,000,000, SLL4020, Shanghai lianle industry science and technology Co., Ltd) powders were mixed with a previously prepared alcohol (CP) solution of TMPTMA (>98 wt%, Nanjing hand in hand chemical technology Co., LTD) or TGPDA (>99 wt%, Nanjing hand in hand chemical technology Co., LTD) in a high speed mixer. Alcohol in the uniform slurry was removed by evaporating the slurry in a vacuum oven at 60 °C for 1 h. The final concentration of TMPTMA or TPGDA in UPE was 1 wt%. The process had been proved to be effective in providing uniform TMPTMA or TPGDA dispersion on the surface of UPE powders, with negligible residual alcohol. The above mixture was compression-molded into plates with dimensions of 100 mm × 100 mm × 6 mm (or 1 mm thickness sheet for tension test, 100 μm thickness film for IR) under a pressure of 15 MPa at 200 °C for 30 min. Then the plates packed with a PE bag were irradiated by an EB generator (GJ-2E-EB, 2 MeV, 10 mA) by passing the oven with a dose rate of 5 kGy per pass. The oven had an aluminum foil window through which EB passed the oven to irradiate on the surface of the plates. The irradiation doses varied from 10 kGy to 200 kGy. The specimens on the transmission mechanism could transmit along with transmission rail which was 3 m long after every 5 kGy irradiation, and there was a forced air cooling machine blowing the specimens in irradiation process. So, the temperature of the specimens could be controlled and would barely affect the activity of the free radicals and the mobility of UPE chains.

2.2. FTIR

The materials were studied by FTIR spectroscopy (Spectrum 100, Perkin Elmer, Inc., USA). The FTIR spectrum was recorded in transmission mode with a 0.4 cm^{-1} resolution. In order to detect the occurrence of crosslinking, the region of the spectrum between 2000 cm^{-1} and 600 cm^{-1} was analyzed, especially in vinyl double bonds area ($>C{=}C<$ stretching for vinylidene group about 1632 cm^{-1}) and the *trans*-vinylene groups area (about 965 cm^{-1}). The peak at 720 cm^{-1}, a combination band associated with in-plane rocking vibration of $>CH_2$, was used as an internal standard, since it can be regarded as unaffected by minor changes in the polymer structure. The sample thickness is 100 μm.

2.3. Gel fraction

The percentage of crosslinking can be characterized by gel fraction [39]. Gel fraction experiments were performed in *o*-xylene with 0.1 mass% Irganox 1010 (Ciba Geigy) added as an antioxidant. The samples (w g) were kept at 130 °C for 24 h. After cooling to room temperature in the Soxhlet Extractor, the specimens were dried in a vacuum oven at 130 °C to reach a constant weight-w_1.

Gel fraction was calculated by formula (1):

$$\text{Gel fraction }(\%) = \frac{\text{extracted sample weight }(g)}{\text{sample weight }(g)} \times 100\% = \frac{W_1}{W} \times 100\% \tag{1}$$

2.4. Differential scanning calorimetry (DSC)

DSC measurements were conducted in a NETZSCH DSC-200 $F3$ instrument at a heating rate of 10 °C min^{-1} under dry nitrogen atmosphere. After they were quenched to an ambient temperature, the samples were heated from room temperature to 200 °C, and the results were recorded.

X_c of crosslinked UPE was calculated using the formula (2):

$$X_c(\%) = \frac{\Delta H}{\Delta H_\infty} \times 100\% \tag{2}$$

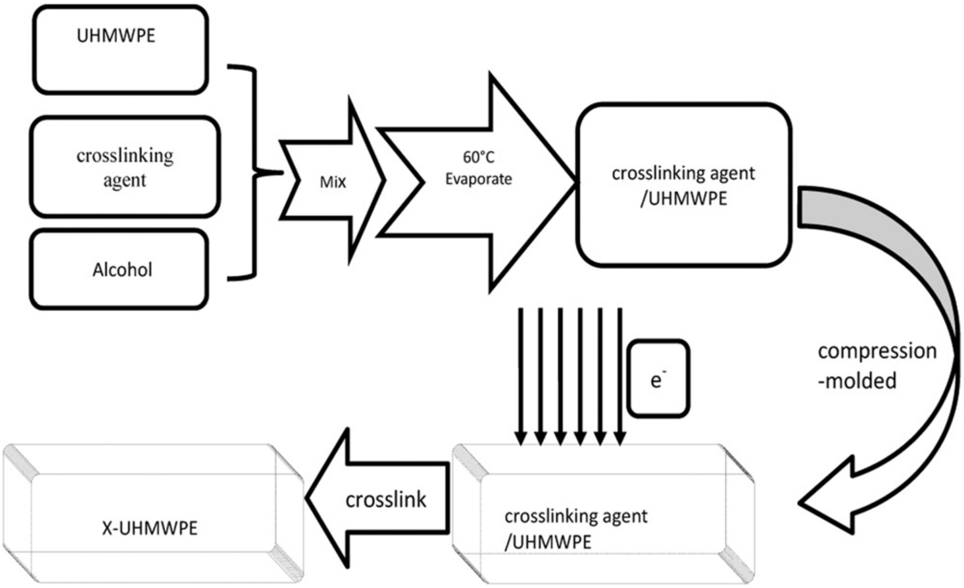

Fig. 1. Preparation process of crosslinked UPE specimens.