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Effects of electron beam irradiation on tribological and physico-chemical properties of Polyoxymethylene copolymer (POM-C)

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ABSTRACT

Polyoxymethylene copolymer (POM-C) is an attractive and widely used engineering thermoplastic across many industrial sectors owing to outstanding physical, mechanical, self-lubricating and chemical properties. In this research work, the POM-C blocks were irradiated with 1 MeV electron beam energy in five doses (100, 200, 300, 500 and 700 kGy) in vacuum condition at room temperature. The tribological and physico-chemical properties of electron beam irradiated POM-C blocks have been analyzed using pin on disk tribometer, Raman spectroscopy, FTIR-ATR, gel content analysis, SEM-EDS (scanning electron microscopy-energy dispersive spectroscopy), surface profiler and contact angle analyzer. Electron beam irradiation at a dose of 100 kGy resulted in decrease of the friction coefficient of POM-C block due to well suited carbonization, cross-linking, free radicals formation and partial physical modification. It also showed the lowest surface roughness and highest water contact angle among all unirradiated and irradiated POM-C blocks. The irradiation dose at 200 kGy resulted in increase of friction coefficient due to less effective cross-linking, but the irradiation doses at 300, 500 and 700 kGy resulted in increase of the friction coefficient as compared to unirradiated POM-C block due to severe chain scission, chemical and physical structural degradation. The degree of improvement for tribological attribute relies on the electron beam surface dose delivered (energy and dose rate).

1. Introduction

Polyoxymethylene copolymer (POM-C) is the most prominent engineering thermoplastic consisting of repeating carbon-oxygen bonds in the form of oxymethylene groups (OCH_2) [1]. It has been a focus of major attention in the field of polymer due to its promising properties i.e. low coefficient of friction, high abrasion resistance, high heat resistance and self-lubricating [2]. It is widely used to make small gear wheels, ball bearings, precision parts, automotive and consumer electronics [3,4]. To expand POM-C applications in low and high tech areas with good processibilities into valuable products, it has been ever-rising interest in the surface modifications of the tribological and physico-chemical properties [5]. Many reactions occur during desired surface modification of POM-C in the molecular structure level [6–12]. Several methods have been used to get the best surface modifications, varying from usual flame treatments, "wet" chemical treatments, electrical treatments (corona discharge) and plasma treatments, to particle beam irradiation (electrons, ions, photons and neutrons) method [12,13].

The application of ionizing radiation on polymers introducing energy into materials to create useful changes will sustain to attract great attentions in polymers field due to flexibility, effectiveness and environmentally friendly nature compared to usual methods [12–17]. The degradation reduction mechanism of POM-C polymer was observed in the 1960s. Reduction of friction coefficient for polyether- ketone with a cardo group (PEK-C) in the process of electron beam bombardment was reported by few researchers, which resulted in the formation of carbonated solid thin film layer on PEK-C surface during irradiation process [18]. Effects of low and medium energy electron beam irradiation on different polymers have been observed by several researchers [19–26]. Electron beam (EB) irradiation system is becoming an opti-

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mistic process to improve the tribological and physico-chemical properties of polymers at a large scale [23–26]. Modified polymers are leading materials for a vast range of useful applications e.g. light- emitting diode, solid state battery, optical display and electronic devices [27].

Electron beam irradiation causes modification on polymer surfaces as a result of cross-linking (electronic stopping), chain scission (nuclear stopping) and evolution of gases (CO_2, CH_4, CO and H_2) leading to physical and chemical properties changes on a molecular scale e.g. carbonization, generation of highly reactive intermediates (free radicals) and cyclization through the formation of intermolecular bonds and ionization [20–26,28–31]. Cross-linking creates three dimensional strong chemical networks, strengthens rigidity of the backbone structure, contributes to anchoring parts for the chain and refrains chain displacement, thus promoting dimensional durability with creep resistance [12,18,21–26,28,30]. Chain scission reduces molecular weight and it breaks the chemical bonds of polymers, which subsequently degrades the polymers surface. The radiation not only modifies the desired tribological and physico-chemical properties of polymer, but it can create flaws with deformation on the polymer materials [9,28–31]. The cross-linking becomes more dominant in vacuum condition, while the availability of oxygen increases the chain scission and gas formation during electron beam irradiation [8,9,18]. The cross-linking and chemical free radicals formation on polymeric surfaces lead to better tribological, mechanical, morphological and chemical properties [20–22,28–31]. However, the optimum improvement level relies on the electron beam bombardment parameters and polymeric structure [7,12,18,23,26].

The principal objective of this work is to study the effects of electron beam dose irradiation on the friction coefficient, chemical structure, surface roughness and water contact angle of POM-C polymer with correlation among tribological, morphological and chemical properties.

2. Experimental

Natural color POM-C round blocks of 10 mm thickness and 30 mm diameter were used for all the experiments. The blocks of POM-C used were supplied from DYNEX engineering plastic company (Korea), with a melt flow rate of 3 g/10 min (ISO 1133) and density of 1.41 g/cm^3 (ISO 1183). The molecular chain and 3D model structure of POM-C blocks are shown in Fig. 1. The POM-C blocks were polished by grinder polisher (TwinPrep 5, ALLIED high tech. products Inc.) machine using 1200 (P4000) grit of SiC abrasive paper at 200 RPM speed with abundant water. All POM-C blocks surfaces were cleaned in ultrasonic bath in distilled water and 96% ethanol and, then placed in a dry desiccator, consecutively.

Electron beam (EB) dose irradiation was performed under vacuum condition at room temperature with an ELV-8 (electrostatic, coreless DC and induction coupling) electron accelerator at a voltage of 1 MeV in EB Tech Co., Ltd. (Daejon, Korea). The blocks of POM-C (numbered as a-f) were irradiated to doses of 0, 100, 200, 300, 500 and 700 kGy, respectively. The electron beam current was 40 mA and the dose rate was 25 kGy per pass. The schematic diagram of EB dose irradiation is shown in Fig. 2(a).

Friction coefficient was tested on a J&L Tech tribometer using a ball on disk method, in which the disk was fixed and the ball (SUJ 52100, bearing ball) was rotated at a sliding speed of 100 mm/s unidirectionally. The contact schematic diagram of ball on disk method is shown in Fig. 2(b). Sliding was observed under a load of 10 N during 228 m sliding distance over a period of 38 min. The chemical structural modification of unirradiated and irradiated POM-C blocks was observed by micro Raman spectrometer system (LABRAM HR EV) with laser excitation source of 514 nm from laser diode. The Fourier transform- infrared (FTIR) spectra of unirradiated and irradiated POM-C blocks were measured by Nicolet 6700 FTIR system using an attenuated total reflectance (ATR) accessory with a resolution of 8 cm^{-1}.

All the specimens, each weighing ~0.5 g, were collected after cutting off 0.3 mm from the surface of different EB dose irradiated POM-C samples. Extraction of gel content for each specimen was conducted by boiling in toluene at 160 °C for 48 h using a Soxhlet apparatus. The extracted specimen was then dried at 80 °C in a vacuum oven for 24 h. The gel content for each specimen was calculated from the ratio of the dried extracted specimen weight (W_2) to its initial weight (W_1).

$$\text{Gel content }(\%) = \frac{W_2}{W_1} \times 100 \tag{1}$$

The morphology and elemental composition analysis of unirradiated and different EB dose irradiated POM-C blocks (a-f) were studied by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) facility (S-4300, Hitachi). Changes in surface roughness of POM-C blocks surfaces were studied with 3D nano surface profiling system (Non-contact white light scanning interferometer system, WT-250), and a 10x objective was used. The wettability of unirradiated and irradiated POM-C polymer blocks was observed using contact angle analyzer (SEO Phoenix 300T). The average contact angle was measured according to 10 points for each POM-C block.

3. Results and discussion

3.1. Friction coefficient

In this research work, reduction of friction coefficient in extreme operating environment was considered among all parameters. It is feasible to draw attention on such implementations which are connected to high tech operations and, the usual systems of lubrication cannot be applied. The variation of friction coefficient for both unirradiated and irradiated POM-C blocks as a function of EB dose irradiation is demonstrated in Fig. 3. It is explicitly demonstrated that the value of friction coefficient had

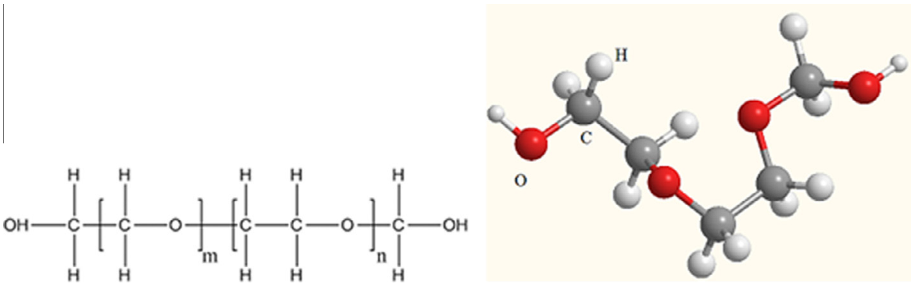

Fig. 1. Molecular chain and 3D model structure of POM-C.