Electron-beam induced graft polymerization to improve the surface hydrophilicity of medical grade elastomer

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1. Introduction

Surface functionalization of polymeric materials are essential which are used for semiconductor, biomaterial and medical applications. Therefore, researchers are conducting massive researches to modify the surface of polymers by using plasma, ozone treatment, or irradiation of ion beam, gamma ray, and electron-beam [1-3]. Among those, electron-beam irradiation has advantages such as simple process, easily scalable, and ability of grafting various functional groups by using different monomers [4]. In this study, we attempted to modify the surface hydrophilicity of a medical elastomer, polyether block amide (PEBA) by electron-beam induced graft polymerization using acrylic acid (AAc) monomer. We analyzed the change of surface hydrophilicity as a function of various electron-beam irradiation parameters.

2. Experimental methods

2.1 Electron-beam irradiation

Typical medical grade PEBA (denoted as PEBAX-7 and PEBAX-4) resins purchased from Arkema (France) were used for preparation of elastomer films. The as-prepared PEBA films were irradiated by an electron-beam at the facility of Korea Institute of Industrial Technology (KITECH). The beam energy, beam current and dose-rate were fixed at 5 MeV, 1.90 mA, 1.7 kGy/s for all irradiation experiments under air atmosphere. The total absorbed dose was controlled as 10, 30, and 50 kGy.

2.2 Graft polymerization

The AAc graft polymerization on PEBA films were conducted via the pre-irradiation method. For grafting polymerization, 30 wt% of AAc monomer and 1 wt% of Mohr's salt were added to distilled water and stirred for 30 minutes, followed by injecting Ar gas and stirring for 30 minutes. The prepared solution and the irradiated PEBA films were contained in a PE bag and sealed immediately. The PE bag was placed in an oven at 70 ℃ for 4 hours for graft polymerization reaction. After the reaction, PEBA films were thoroughly washed with distilled water for 24 hours to remove any residual monomer and homopolymer. Finally, the washed PEBA films were vacuum-dried at 50°C overnight.

2.4 Characterization

The grafting yield of grafted PEBA films was calculated by the following equation,

$$\text{Grafting yield} = (W_f - W_o)/W_o \quad (1)$$

where, W_o and W_f are the weight of pristine and grafted PEBA films, respectively.

To confirm the existence of poly(AAc) of grafted PEBA, Fourier transform-infrared (FT-IR) spectroscopy (IS-50, Thermo Fisher Scientific, USA) was performed in attenuated total reflection (ATR) mode with a resolution of 4 cm^{-1} and 32 scans. Surface and cross-sectional morphology of poly(AAc) grafted PEBA were observed using a scanning electron microscope (SEM, SU8220, Hitachi, Japan). The hydrophilicity was estimated by measuring the static contact angle on the surface of poly(AAc) grafted PEBA surface with 2 μm droplets using a contact angle geometer.

3. Results

3.1 Radiation graft polymerization of AAc onto PEBA

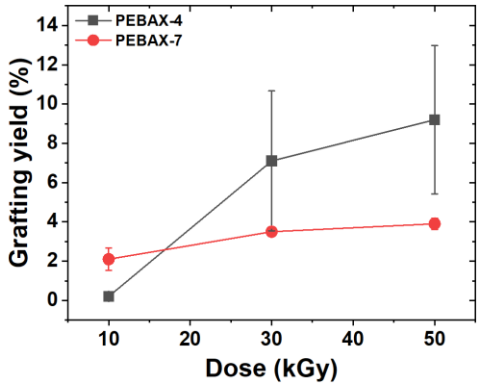

Fig. 1. Effect of absorbed dose on grafting yield of poly(AAc) grafted PEBA.

Figure 1 shows the grafting yield obtained after grafted polymerization of AAc onto PEBAX-4 and PEBAX-7 irradiated at absorbed doses. The range of the grafting yield obtained in this study is from 0% to 7.1%. Overall, the grafting yield tends to increase as the absorbed dose increases. In case of PEBAX-4, grafting yield remains as 0% at 10 kGy, but increases

significantly to 9.2% at 50 kGy. PEBAX-7 displayed a grafting yield less than 4% even at an absorbed dose of 50 kGy. When the absorbed dose is high during electron beam irradiation on the PEBA substrate, PEBA has many active sites, which increases the amount of AAc monomers participating in the graft polymerization reaction, thus greatly increases the grafting yield.

3.2 Characterization of AAc grafted PEBA

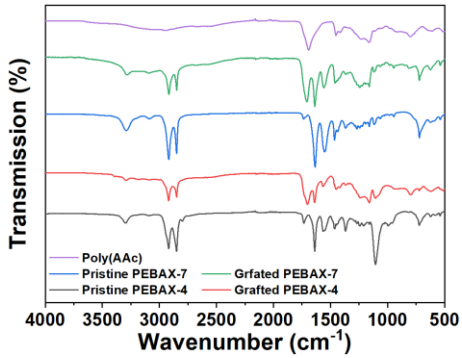

Fig. 2. FT-IR spectra of poly(AAc) grafted PEBA.

Figure 2 shows the FT-IR spectra of PEBAX-4 and PEBAX-7 before and after AAc graft polymerization, along with the spectrum of pure poly(AAc) film. Pristine PEBA has several strong characteristic absorption bands, such as NH stretching, C=O stretching, CO stretching, and NH bending at 3295 cm^{-1},1735 cm^{-1},1637 cm^{-1},1550 cm^{-1}, respectively [5]. In particular, PEBAX-4 has a remarkably observed ether group absorption band of the PE segment corresponding to 1100 cm^{-1}. In the case of pure poly(AAc), a strong carboxylic group band corresponding to C=O appears at 1694 cm^{-1}, C-O stretching at 1249 cm^{-1}, 1162 cm^{-1}, and OH stretching at 2400-3600 cm^{-1}. After graft polymerization, broad OH stretching was developed in both PEBAX-4 and PEBAX-7, and the C=O carboxylic group of AAc increased at 1637 cm^{-1}. In addition, the C-O group (1227 cm^{-1}, 1159 cm^{-1}) contained in AAc developed and the ether group of PEBA diminished. Therefore, it shows that a a sufficient layer of poly(AAC) brush due to graft polymerization of AAc on the PEBA surface was formed.

3.3 Morphology and hydrophilicity

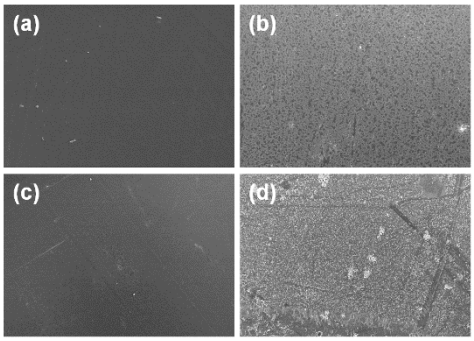

Fig. 3. SEM images of (a) pristine PEBAX-4, (b) grafted PEBAX-4 (c) pristine PEBAX-7 (d) grafted PEBAX-7.

Figure 3 shows the surface morphology of grafted PEBAX-4 and grafted PEBAX-7 by SEM formed at absorbed dose of 50 kGy. After graft polymerization of both PEBAX-4 and PEBAX-7, it can be observed that the white poly(AAc) brush is uniformly distributed.

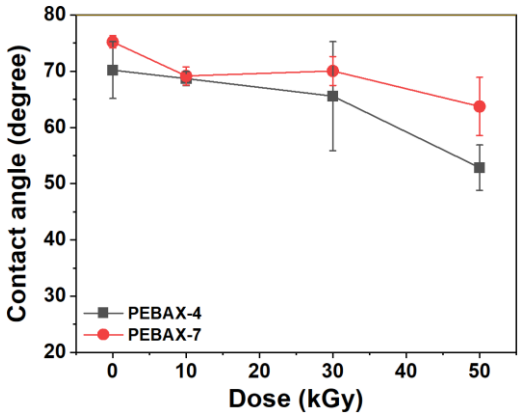

Fig. 4. Effect of absorbed dose on the grafting yield of poly(AAc) grafted PEBA.

Figure 4 shows the water contact angle according to the absorbed dose of PEBAX-4 and PEBAX-7. In both samples, it was found that hydrophilic poly(AAc) was grafted onto the surface, increasing the surface energy, thereby decreasing the contact angle. PEBAX-7 and PEBAX-4 showed a maximum reduction of 18% and 32%. Furthermore, it was observed that the contact angle decreased as the absorbed dose increased, which appears to improve hydrophilicity due to the increased poly(AAc) brushes formed on the surface as the grafting yield increased.

3. Conclusions

It was observed that the grafting yield increased as the absorbed dose increased during electron-beam irradiation for both types of PEBA. Accordingly, it was found that the wettability of modified PEBA surface was improved. On the other hand, if electron beam induced graft polymerization technology is introduced for various polymer surfaces, it is expected that it can be applied to various surface functionalization such as antibacterial and antifouling.

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