Fabrication of Non-toxic and UV Absorbing PMMA Particles by Irradiation of 50keV Electron Beam

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1. Introduction

Ultraviolet radiation is a sort of electromagnetic wave and it is classified as UV-A, B, and C. Among them, UV-A and B can penetrate atmospheric layer. They therefore can reach to the human skin. The interaction between UV and skin cells can have both positive and negative effects. Firstly, as for beneficial effects, an appropriate amount of exposure to UV-B induces production of vitamin D. on the other hand, excessive or cumulative exposure can cause skin aging, sunburn, or even skin cancer through direct DNA damage. Melanoma is one of the worst skin cancer and the number of patients suffering from melanoma is gradually increasing. In order to prevent the harmful effect of UV, sunscreens are widely used. However, there is a safety controversy on use of the conventional sunscreens. First, sunscreens are mainly classified into two types according to their screening method. Chemical sunscreen absorbs the UV while physical sunblock reflects the UV. But recently, the facts that both sunscreen and sunblock are actually toxic have been revealed by other researchers [5]. So, children and pregnant women are generally cautioned when they use those sunscreens. Therefore, researches on developing non-toxic material that screens the UV is highly required. Poly (methyl methacrylate) (PMMA) has repeated structure of its monomer MMA and its one important feature is that it has a great degree of tissue compatibility. The repeating unit of PMMA molecular structure is shown in Fig. 1. By virtue of its biocompatible property, PMMA has lots of medical application. For instance, some hard contact lens, dentures, and bone cement consist of PMMA. When energetic electron beam is irradiated on the PMMA, some molecular bonds in the PMMA can be broken and this dissociation is called scissioning. The sample becomes radical after the bond scissioning. Furthermore, two radical combinations in the sample is also possible. As a result, new bonds can be formed in the PMMA and chemical characteristics of irradiated PMMA will be different from the pristine due to the structural change. It is known that results of the irradiation experiment on the PMMA can vary from whether what types of radiation or what energy is used [1]. Generally, during the irradiation of radiation such as gamma ray, electron beam or ion beam on PMMA, gases such as CO_2 and H_2 are generated and new carbon double bonds are created [2][3][4]. As a result, UV absorption property is created to the irradiated PMMA. The two main goals of the research are the assessment of skin compatibility test of the irradiated PMMA powder and the evaluation of sun protection factor of the reference sunscreen homogenized with the irradiated PMMA powder.

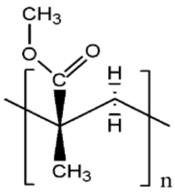


Fig. 1. Chemical structure of PMMA.

2. Experiments

Irradiations were conducted with 50keV electron beam under the pressure of less than 10-5Torr. The PMMA sheets with thickness of 3㎜(ME303031) and powder with diameter of 6㎛(ME306006) used in this experiments were purchased from Goodfellow Advanced Materials Company, Malvern, PA. 50keV electron beam generator used in this experiment is shown in Fig. 2 and schematic diagram in 3. Electron dose is controlled by changing irradiation time.

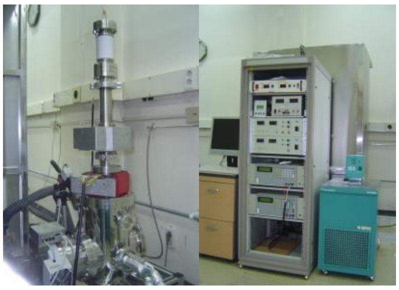


Fig. 2. Electron beam generator used in this work.

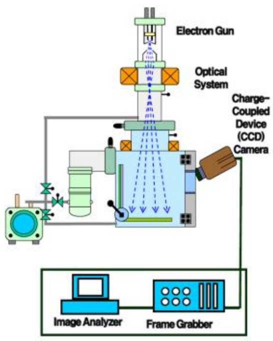


Fig. 3. Diagram of the electron beam generator.

2.1 Sheet Experiment

In the interaction between electron and the PMMA sample, thermal damage could be induced with high beam current. Higher current means more electrons interacting in a unit area of the sample so more heat would be generated with higher current density. It is obvious that current density and heat have positive correlation. So in order to avoid overheating or thermal damage on the surface of the sample, current density should be optimized. Four examples are shown in Fig. 4. From the four experimental results, it is observed that thermal damage is more dependent on current density than on total fluence. In order to investigate only radiation-induced effects, thermal damage should be excluded and so current density should be optimized. With this experimental condition, current density of 0.17 ㎂/㎝ ^{2} is determined as the optimum value.

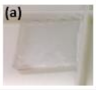
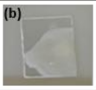
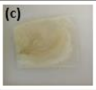
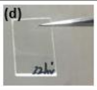
Samples	(a) 	(b) 	(c) 	(d) 
Fluence [electrons/cm^2]	0	3.2E+16	1.6E+16	7.0E+16
Current density [μA/cm^2]	0	0.53	0.71	0.17

Fig. 4. Irradiated PMMA sheet with various current.

The absorption spectra from UV-Vis spectroscopy carried out on pristine and irradiated PMMA samples are presented in Fig. 5.

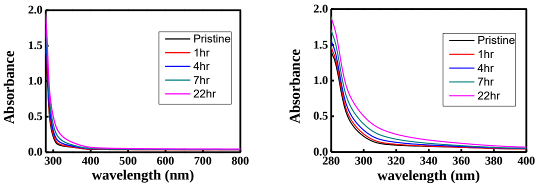


Fig. 5. Absorption spectra of pristine and irradiated PMMA sheets(left) and magnified spectra with respect to the wavelength in the UV region of interest(right).

The absorbance of the irradiated sample is increased with higher electron dose and the samples tend to have UV absorbing property. From the view point of being used as a cosmetic material, it is preferable to absorb UV and not to absorb visible light simultaneously. Monte Carlo simulation of electron trajectory in PMMA captured from CASINO software program is shown in Fig. 6. Beam energy used in this experiment is 50keV and ESTAR continuously slowing down approximation range is about 37 ㎛. Only surface is affected by the e-beam and 99% of the sheet sample remains pristine.

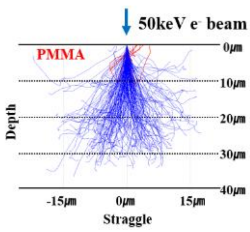


Fig. 6. Monte Carlo simulation of electron trajectory in PMMA.

FTIR measurements were carried out to investigate the structural changes by electron beam irradiation. The FTIR spectra of the PMMA sheets with and without irradiation are shown in Fig. 7 and the corresponding band assignments are presented in Table I. From Fig. 7, it is observed that the pendant groups are dissociated by irradiation generating gases such as H_2 and CO_2. All spectra exhibit the characteristic peaks at specific wavenumbers. Interestingly, there is a new bond generated by electron beam irradiation. Electron beam irradiation separates the pendant groups of the PMMA and irradiated PMMA tends to become carbonaceous.

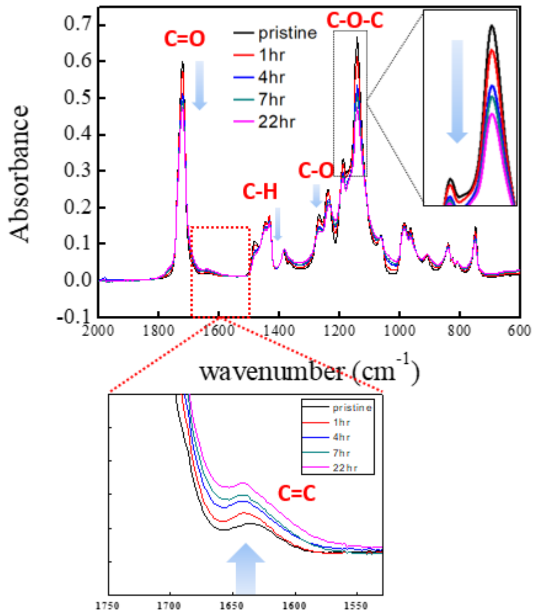


Fig. 7. FTIR absorption spectra of PMMA polymer samples: pristine and irradiated with 50keV electron beam.

Peak assignment	Absorption peak(cm^{-1})
C-CH_3 Bending vibrations	1442
CH_2 bending vibration	1484
C-O stretching vibrations	1241
C-O asymmetric stretching(C-O-C)	1147
C=O stretching vibrations	1728
C=C stretching vibrations	1636

Table I. FTIR peak assignments for pristine and irradiated PMMA samples.

2.2 Powder Experiments

Experiments on powder were successfully carried out. In order to prepare the powder in the vacuum chamber, self-designed powder mold was used. The sample was prepared by drop-casting a powder suspension dispersed in DI water into the powder mold, followed by solidification through a drying process. The solidified powder film placed on the powder mold is shown in Fig. 8 and its thickness is about 3 ㎛ which is less than the CSDA rage of the 50keV electron in the PMMA. UV-Vis absorption spectra are shown in Fig. 9.

Fig. 8. Aqueous suspension (PMMA powder dispersed in the DI water) on the powder mold(left) and dried powder film(right): thresholds are prepared to minimize non-uniform distribution.

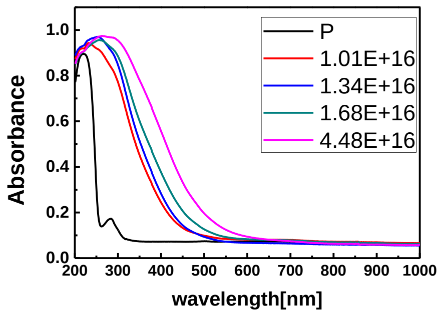


Fig. 9. UV-Vis absorption spectra of pristine and irradiated PMMA powder.

The increase in absorbance is clearly observable compared to the results of sheet experiment since the thickness of the powder film is thinner than CSDA range. Absorption of the light in the range of 380-460nm make the visibly observed color of the irradiated powder yellow and the yellowing coloration is shown in Fig. 10.

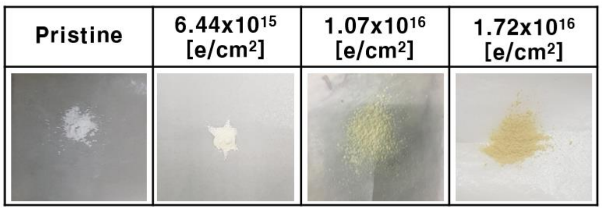


Fig. 10. Coloration of the PMMA powder according to the total electron dose.

3. Discussion and future works

This study is ongoing and there are plenty of works to do in the future. To sum up, the severity of UV exposure and toxicity of existing sunscreens are already known and researches to solve this problem are underway. Meanwhile, bio-compatible PMMA particles can have UV absorbing property through a chemical change by electron beam irradiation. Combining these facts, there is a possibility that Development of bio-compatible and UV absorbing material for the purpose of being used as non-toxic sunscreen ingredient is feasible. Depending on which radiation or which energy is used to irradiate the sample, the results can be significantly different. In this work, 50keV electron beam was irradiated to the PMMA powder. For the future works, some skin compatibility test should be carried out to the irradiated powder such as toxic test, skin irritation test, etc. Furthermore, UV shielding contribution of irradiated powder should be evaluated when it is added to sunscreen. S2 reference sunscreen is prepared to evaluate the enhancement of sun protection factor(SPF) by the irradiated powder. Last but not least, the mechanism of increase in absorbance of UV should be analyzed more clearly. In addition to UV-Vis and FTIR spectroscopies, additional analytical method such as Raman spectroscopy should be conducted to clearly figure out the mechanism. It is expected that it will make a great contribution to society from the development of non-toxic sunscreen by analyzing optimal irradiation condition.

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