Changes of optical and mechanical properties of polycarbonate by ion beams

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1. Introduction

Ion irradiation of polymers produces changes in their physical and chemical properties associated with the breaking and the rearrangement of original bonds in surface. The modification of the chain structure occurs within well-defined ion fluence ranges that depends on the linear energy transfer(LET) and on the target materials. These modifications result from changes in the chemical bonding when the incident ions cut the polymer chains, break covalent bonds, promote cross-linking, unsaturated bonding and liberate certain volatile species.[1-2]

Polycarbonate(PC) which are increasingly used in automobile and electronic product industry because they offer better lightweight and mechanical properties, need to enhance the surface properties such as surface hardness including anti-scratch property and no color & glossiness changes under UV and visible light for long term.

As well known, the surface hardness enhancement of polymer by ion beam is due to the cross-linking of surface polymer chains depending on ion mass, ion fluence. Generally, heavy ion irradiation is efficient for surface hardness of polymer due to high LET. However, heavy ion irradiation of polymer has disadvantage for color changes of polymer.

Therefore, in this study, it is aimed to improve the surface hardness, weatherability and UV and visible light resistance for long term without changing color of PC through hydrogen ion implantation.

2. Methods and Results

The PC were irradiated with H^+, N^+, N_2^+ ions having energies from 90 to 200 keV at dose up to 1E17 ions/cm^2. The ions were generated using a DuoPIGatron ion source at current density up to 4 μA/cm^2.

The surface hardness, color changes and the modifications of the surface microstructures of ion irradiated PC were studied by using pencil strength test, nano-indentation test, color difference meter and FT-IR measurement.

2.1 Color changes after ion irradiation

After ion irradiation to PC, the color of surface was changed due to surface microstructural changes. We measured the color difference before between after ion irradiation by using color difference meter (ColorMate Co., Color Spectrophotometer). The equation of the color difference (ΔE) is as follows.

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

L : Lightness
a : red & green degree
b : yellow & blue degree

As shown in Fig. 1, ΔE of PC surface is increased with increasing the ion doses and ion mass after ion irradiations. Also, the lightness difference mainly affected to the color difference. The change of lightness of ion irradiated polymer concerned with surface roughness and scattering of light on the abundant π-electrons due to the formation of aromatic structures.[3-4] However, at above 5E16ions/cm^2 of ion dose, the color difference was saturated due to the limit of microstructural change in sub-surface. Also, Δb of PC is important for mechanical property. Yellow color of polymer means the formation of unsaturated C=C bonding due to the cross-linkage of polymer chain.[5-8] Therefore, The higher Δb of PC at the higher ion doses means the surface hardness enhanced with increasing the ion doses.

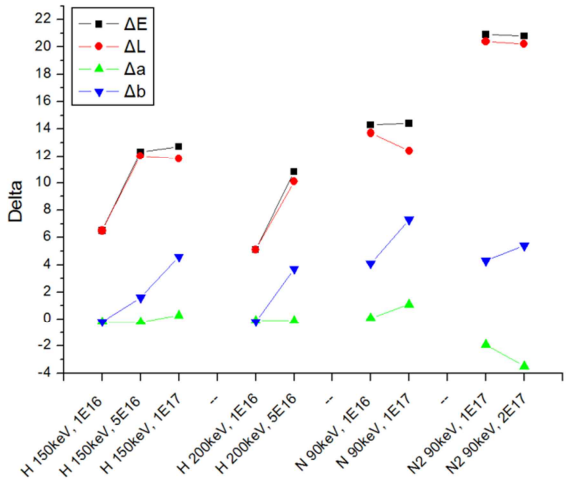

Fig. 1. Color Changes of PC after hydrogen ion irradiation

2.2 Surface Hardness Changes after Ion Irradiation

After ion irradiation to PC, the surface hardness was enhanced by formation of the cross-linkage of polymer chain. We measured the surface hardness after ion irradiation by using pencil strength test(ASTM D3363) and nano-indentation test(Ultra Nanoindentation Tester, Anton PAAR Co., Applied load : 1Mn, Static mode).

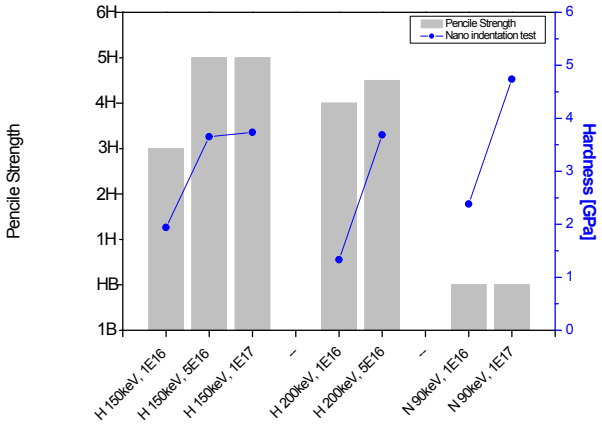

Fig. 2. Surface hardness Changes of PC after ion irradiation

As shown in Fig. 2, the surface hardness of PC is increased with increasing the ion doses after ion irradiations. But, ion energy and ion mass do not affect to surface hardness due to skin depth and the limit of microstructural change at specific depth. As a result of pencil strength test, hydrogen ion irradiation of PC was more efficient for mechanical property comparing with nitrogen irradiation due to affected depth. The tendency of the surface hardness enhancement is in agreement with the changes in the color difference.

2.3 Microstructure Changes after Ion Irradiation

After ion irradiation to PC, we measured the microstructural changes by using FT-IR measurement(Cary660 model, Agillent Co., ATR mode).

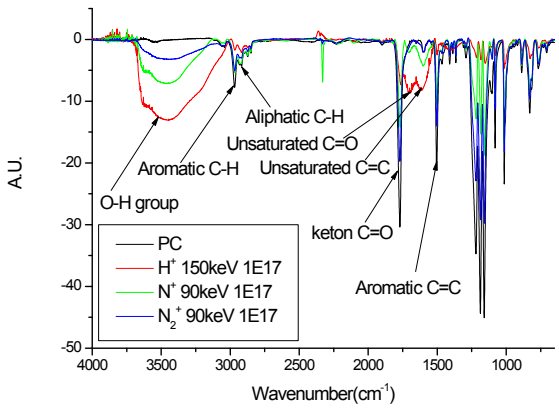

Fig. 3. Microstructral Changes of PC after ion irradiation

Fig. 3 shows the variation in the absorbance intensity of various functional groups of ion-irradiated PC with ion species. The observed chemical changes of PC are as follows: (i) increase in the concentrations of O-H (3000-3900 cm^{-1}), unsaturated C=C(1600-1650 cm^{-1}) and C=O (1728 cm^{-1}) with decreasing the ion mass, (ii) decrease in the concentrations of keton C=O (1680-1750 cm^{-1}) cm–1), aromatic C=C (1500-1700 cm^{-1}) and C-H (2900-3100 cm^{-1}) with decreasing the ion mass. This absorption band is concerned with the change in micro structure. [9-10]. As a result of IR spectra, hydrogen ion irradiation of PC was more efficient for mechanical property comparing with nitrogen irradiation due to the increase of unsaturated bonding of C=C, C=O bond concerning with cross-linkage of polymer chain.

2.4. Surface Changes after weatherability test

Since along lasting hardened surface is the major concern, the ion-beam-irradiated PC were subjected to weatherability test to evaluate the weather resistance of the optical and mechanical properties. Commercially, the hardened surface is required not to degrade for at least 58 days for UV light of 2,500kJ/m2 at 38-70 ℃ under 50-95% humidity (industrial standard).

As shown in Fig. 4, The sample irradiated with low dose hydrogen ion beam showed degradations with delamination and color change on the surface of PC(right) before 58 days, while the sample irradiated with high dose hydrogen ion beams maintained appreciable color with no delamination even after 58days (left).

These result are concerned with surface hardness due to microstrutral changes such as cross-linkage of polymer chain.

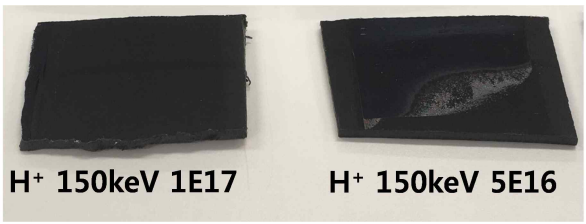

Fig. 4. Hydrogen irradiated PC Sample after weatherability test for 58 days

3. Conclusions

Hydrogen ion irradiated PC is successfully achieved the higher hardness with small color changes.

- After hydrogen ion irradiation, the pencil strength of PC enhanced up to 6H from 6B of original PC.
- At 6H pencil strength hardened PC, the color change (ΔE) limited under 13 after hydrogen ion irradiation.
- As a result of nano-indentation test, the surface hardness of PC enhanced up to 4 GPa after hydrogen ion irradiation.
- In FT-IR measurement of ion irradiated PC, hydrogen ion irradiation of PC was more efficient for mechanical property comparing with nitrogen irradiation due to the increase of unsaturated bonding of C=C, C=O bond concerning with cross-linkage of polymer chain.
- After weatherability test of hydrogen irradiated PC with high dose, the PC sample maintained appreciable color with no delamination.

4. Acknowledgments

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