

Development of UV absorbing PET through Electron Irradiation

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1. Introduction

Polyethylene terephthalate (PET) has become the most favourable packaging material world-wide for beverages. The reason for this development is the excellent material properties of the PET material, especially its unbreakability and the very low weight of the bottles compared to glass bottles of the same filling volumefilling volume. In comparison to other packaging polymers, PET has also a high clarity as well as good barrier properties towards moisture and oxygen[1]. However, liquids such as oil in PET bottles can be changed by photo-oxidation caused by UV lights. There are several methods to improve UV absorbance of PET such as coating and chemical mixture method. However, such a method can peel off the fabricated coated layer and requires a complicated process and time for manufacturing a chemical mixture.

In this study, experiment to increase UV absorbance through electron beam irradiation on PET was performed. Moreover, surface hardness and roughness of each sample were observed to find the key factor increasing UV absorbance. PET sheets were irradiated with an electron beam at various fluences. The irradiated samples, as well as pristine sample, were subjected to UV-visible spectral study(UV-Vis), pencil hardness test, and scanning electron microscopy(SEM) experiment.

2. Methods and Results

2.1 Methods

To prepare the sample, PET sample(1.1 x 2cm²) was cleaned in ethanol and was blown by nitrogen gas. As shown in Table I, the surface of the PET was irradiated with an electron beam under different irradiation conditions. The sample obtained after irradiation of UV absorbance was observed with UV-Vis spectrophotometer(produced by SCINCO, S-4100). The irradiated sample was also evaluated for pencil hardness through a pencil hardness tester(produced by Ocean Science, COAD 609). The surface of the irradiated sample was observed through the SEM equipment to examine the affects of the roughness of the sample surface. Before SEM measurements, each PET sample should be treated by plasma etching and Pt coating.

Table I: Condition of irradiated electron beam at each sample. The fluences of sample 3 and 5 were same.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Fluence (#/cm ²)	3.576×10^{16}	7.153×10^{16}	2.146×10^{17}	4.292×10^{17}	2.146×10^{17}
Current(μA)	40	40	40	40	20
Exposed Time(min)	30	60	180	360	360
Dose(MGy)	18.476	36.952	110.86	221.71	110.86

2.2 Results

2.2.1 UV-Visible spectroscopy Test

The respective spectra are shown in Figure 1. Decrease of transmittance of PET in UV-visible range compared with pristine sample was observed for all sheets after irradiation, which indicates a decrease in band gap after irradiation. Bond rupturing leading to scission, free radical formation, cross linking etc., resulting in the formation of new bonds affected decrease transmittance of PET[2]. Especially, It is estimated that chain scission reaction is dominant at irradiation process, because the average molecular weight of PET decreases as irradiation dose in γ -Irradiation increases. Besides, as the absorbed doses of PET increased, absorbance of PET was also increased. It means that the materials those are products of the electron-irradiation are better to absorb UV lights than original PET. It is suggested that these are the carbon oxides, and carboxyl end-groups.

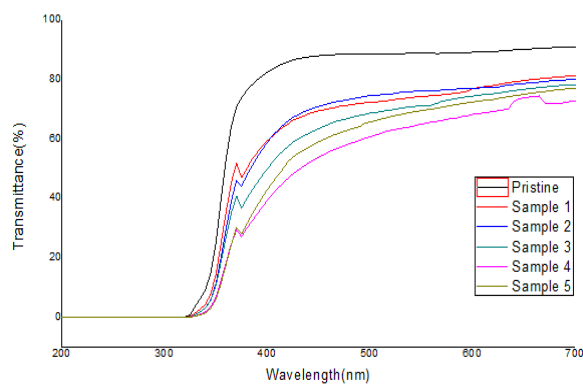


Figure 1. UV-visible transmittance spectra of PET. Decrease of transmittance of PET in UV-visible range compared with pristine sample was observed for all sheets after irradiation.

The irradiated samples and pristine sample are shown in Figure 2. The color of PET sheets became more yellow as irradiation doses increased. Similar observations in other polymers were reported by various papers such as experiments about polycarbonate, polystyrene and PMMA(Poly-methyl methacrylate). It is assumed that the change in color may be due to the removal of hydrogen atoms or due to increased carrier concentration as result of implantation effect or may be due to the production of defect levels in the band gap of polymers[3].

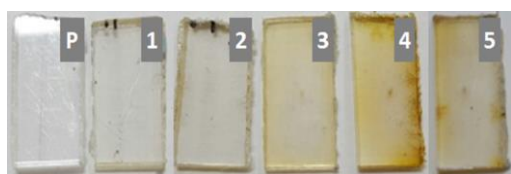


Figure 2. Pristine and irradiated sample. The color of PET sheets became more yellow as irradiation doses increased

The notable comparison is sample 3 and 5. These are exposed at same fluence of electrons, but exposed current of sample 5 is half of those of sample 3, and exposed time of sample 5 is double of sample 3. However, UV-visible spectrums of each sample are different. In graph, UV transmittance of sample 3 at peak is 40.83%, but UV transmittance of sample 5 at same wavelength is 30.18%. Moreover, the slope of UV transmittance of sample 5 from 300nm –UV lights region- is higher than those of sample 3. It is estimated that the UV transmittance of PET is affected by irradiated time. The specific cause to improve UV absorption should be revealed by next study. However, in visible lights region, UV transmittance of sample 3 and 5 are not so different[4].

2.2.2 Pencil hardness Test

Results of pencil hardness test are shown in Fig.3. Except for sample 4, all samples' pencil hardness values were HB. The pencil hardness of sample 4 was B, and it is assumed that chain scission reaction affected this change of pencil hardness. Cross-linking over scission increases polymer's hardness. But, as stated in 3.1, products formed after irradiation is caused by chain scission reaction for PET. In addition, sample 4 was exposed at electron beam for the longest time among the irradiated samples. Therefore, its surface hardness didn't increase, but rather decreased. However, pencil hardness test is not the most exact measurement method to measure the surface hardness of polymer. Therefore, a more exact measurement to measure surface hardness such as nano-indentation hardness test should be performed.

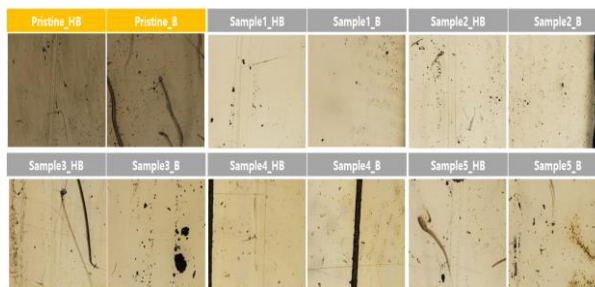


Figure 3. Results about pencil hardness test of each sample. Except sample 4, pencil hardness of all sample were same.

2.2.3 Scanning electron microscopy (SEM)

The results of SEM of the irradiated samples are shown in Figure 3. In Figure 3, there are no any symptom of changed roughness at irradiated sample compared with pristine sample. Other case of polymer like PMMA, polymer's roughness is changed during irradiation and it could be changed by heat energy from irradiation. It means that change of roughness is not the important reason of change of UV transmittance, and surface of PET didn't changed easy by heat energy. Because property that is hard at thermal energy is the one of main properties of PET. The big change of UV transmittance of irradiated PET sample was caused by materials produced through chain scission reaction. Thus, UV absorption of irradiated sample increased than pristine sample although their roughness were not changed.

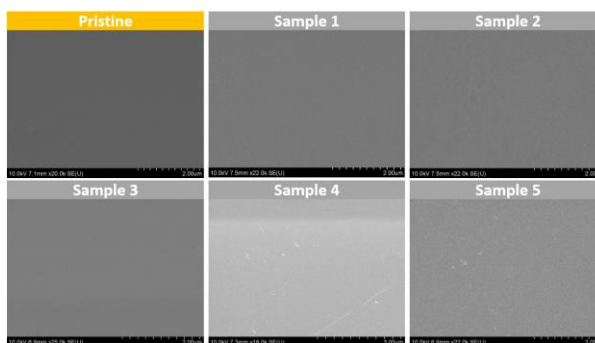


Figure 4. SEM images of each sample. There are no any symptom of changed roughness caused by irradiation.

3. Conclusions

In this study, PET samples irradiated at several conditions were analyzed through various measurements. UV absorbance-another meaning of transmittance in this study- of irradiated PET sample increased compared with pristine sample as fluence was increased in UV-Visible spectroscopy experiment. In pencil hardness test, pencil hardness of all samples, except sample 4, were HB.

Pencil hardness of sample 4 was only decreased to B.

In Scanning electron microscopy (SEM) measurements, surface roughness of irradiated PET samples was not different from that of pristine sample. These results meant that it was caused by materials produced through chain scission reaction during irradiation not the change of surface roughness. Furthermore, although the irradiated fluences were the same, UV absorbance of sample was increased. Thus, improved UV absorbing PET can be made through this process.

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