Physical and Optical Changes to Polymers after Electron Irradiation

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1. Introduction

Polymers are widely used in society for their diversity in application. They are present in items ranging from household appliances to industrial scale equipment. Recently, the polymer market has grown significantly in the automotive industry. Headlights and large portions of the inner frames of cars are now composed of polymers. However, even with their excellent properties, polymers are still not capable of replacing glass as the main windshield material. This is due to the thermal and mechanical property issues of polymers. If these problems can be solved through a polymer enhancement method, further polymerization of cars will be possible.

This research addresses a new way to fabricate hardened, UV-absorbing polymer for practical application. Polymers are currently coated and taken through convoluted chemical, thermal and mechanical processes to meet the requirements set by industries. These conventional methods are very sensitive to small condition changes, can cause environmental damage, are expensive, and pose limitations in design. Therefore, a simple single-step process in developing industrial-grade polymer-based materials will prove to be extremely lucrative.

Research has shown that polymethyl methacrylate (PMMA) could be mechanically enhanced significantly through the electron beam irradiation process. When the electron fluence was less than 1×10^{15} electrons/cm^2, PMMA showed heavy signs of deterioration, as expected, due to irradiation degradation. However, at a fluence higher than 1×10^{17} electrons/cm^2, PMMA samples were mechanically improved tremendously. The surface hardness of PMMA samples increased from a value of 0.26 to 2.8 GPa after electron irradiation [1].

Another research demonstrated that the light absorbing property of polymers could be altered through the electron irradiation process. Irradiating polystyrene (PS) with electrons caused a shift in the band gap, causing the polymer to absorb photons of differing wavelengths depending on the electron fluence [2]. This is most likely due to the production of polycyclic aromatic hydrocarbons (PAHs) after electron irradiation. According to "*Spectral Atlas Polycyclic Aromatic Compounds*", the presence of specific PAHs causes a specific photon absorption peak to appear [3].

Ultimately, this research focuses on developing a simple method of fabricating hardened, UV-absorbing plastics. With the development of such process, lucrative opportunities can be obtained due to the wide use of polymers.

2. Methods

In this research, polymers were hardened through the electron irradiation method. Commercial grade polystyrene (PS) and polymethyl methacrylate (PMMA) sheets with a thickness of 2 mm and 3 mm, respectively, (Goodfellow, United Kingdom) were used. Each sample was placed inside an electron irradiation device (custom made; 0.5 m×0.5 m×0.5 m), and then near vacuum of less than 10^{-5} torr was achieved within the device inner chamber using rotary and turbo pumps. Once the vacuum condition was achieved, the filament (Kimball Physics, Germany) was heated to generate electrons, while the voltage potential of 50 keV was applied between the top and the bottom of the device inner chamber to accelerate

the produced electrons. Integral doses of varying fluences were administered to the samples. The fluence values used were 1.9×10^{16} electrons/cm^2, 2.54×10^{17} electrons/cm^2, and 5.09×10^{17} electrons/cm^2.

Once all the samples were irradiated under appropriate conditions, they were tested for their properties with three different measuring devices: the pencil hardness device (Coretech, South Korea), the nano-indentation device (Keysight Technologies, South Korea), and the UV-Vis spectrophotometer (Scinco, South Korea).

The pencil hardness device scratched at an angle of 45˚ with a weight of 500 g. The samples were scratched at five different locations to check for consistency. The pencil hardness values were averaged to obtain the final hardness value.

The nano-indentation device used a diamond, Berkovich tip to press down on the samples. The tip was pressed to a depth of 1 μm for all samples to obtain the depth-hardness profiles. A total of nine different locations were tested for every sample to check for consistency. The average values were used for finalization.

The UV-Vis spectrophotometer measured the absorbance of the samples from the wavelength of 250 nm to 1100 nm, after the calibration was made in air.

3. Results

Fourier Transform Infrared Spectroscopy

To confirm what molecular changes occurred after irradiation, FTIR results were obtained for the pristine and the irradiated PS sheets, and the values are shown in Figure 1. Peak differences were found at following wavelength values of 694 nm, 758 nm, 1453 nm, 1494 nm, 1602 nm, 1700-2000 nm (3 peaks), 2850 nm, 2921 nm, and 3021 nm. Changes to the peak intensities indicate substantial increase in aromatic carbon sp^2 bonds, signifying the formation of aromatic structures in the PS samples.

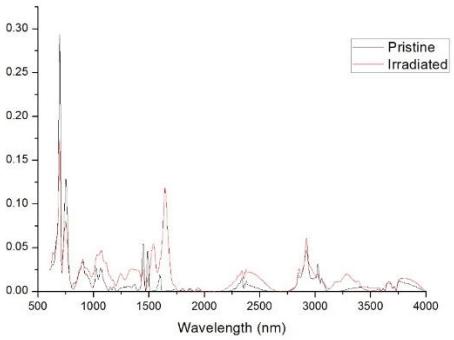

Figure 1. FTIR Results

Pencil Hardness

The pencil hardness results for both the irradiated and pristine PMMA samples are shown in Table 1. The values of the irradiated samples sufficiently surpassed those of pristine samples by four levels. This indicates significant improvement in surface scratch resistance through the irradiation process.

Material	PMMA	PMMA
Irradiated condition	Pristine	1.9×10^{16} electrons/cm^2
Pencil Hardness	4B	>B

Table 2. Pencil Hardness Results

Nano-Indentation Results

The nano-indentation results for both the irradiated and pristine PMMA samples are shown in Figure 2. Nano-indentation hardness clearly indicates significant improvement in surface indentation hardness as the values of irradiated samples more than tripled the values of the pristine sample.

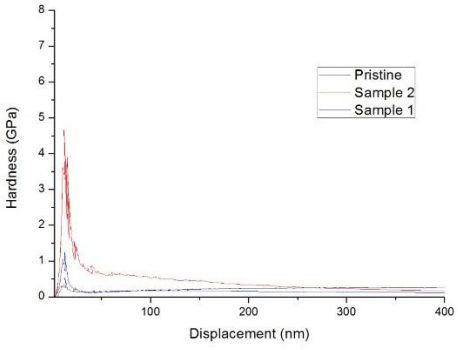

Figure 2. Nano-indentation Results

UV-Vis Spectroscopy

Figure 3 shows the absorption spectra of the pristine and irradiated PS sheets plotted within the wavelength range of 200 and 800 nm. Higher sample number implies greater electron irradiation dose received by the sample. It can be clearly observed that the increase in electron irradiation substantially increases the UV absorption of PS sheets. Clear peaks in absorption can be noticed at 4 different wavelengths of 284 nm, 325 nm, 380 nm, and 470 nm. It should be noted that increase in electron irradiation dose actually decreases the absorption of PS sheet at the first peak point of 284 nm.

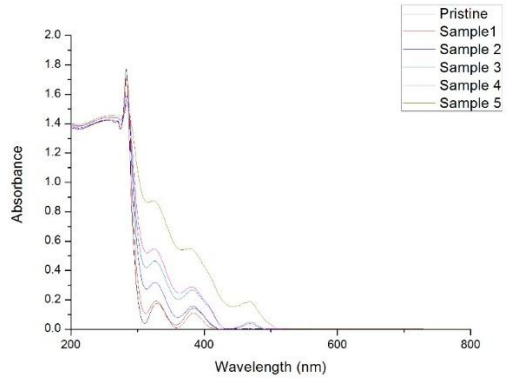

Figure 3. Absorption Spectra

4. Discussion and Conclusion

Optical Enhancement

In Figure 3, the absorption peak at 284 nm can be explained by the presence of PS monomers within the sheet. The monomers are known to peak in UV absorption at the value of 291.5 nm [1]. As PS is a crosslinking polymer under irradiation, increase in electron irradiation dose would promote the linking of the monomers causing a drop in the 284 nm UV absorption peak.

The other absorption peaks formed can be explained by the manifestations of polycyclic aromatic hydrocarbons (PAHs). From the FTIR analysis, it was determined that electron irradiation capacitates the formation of aromatic carbon sp^2 bonds. There are multiple types of PAHs, but it is with high certainty that the simplest of PAHs will materialize before the complex. Thus, it can be deduced that the peak formation is due to the presence of simple PAHs.

Mechanical Enhancement

The significant mechanical improvement displayed in the nano-indentation and the pencil hardness results can be attributed to crosslinking. Crosslinking is a process, where chains of polymeric structures become linked, possibly through the addition of heat, chemicals, pressure or radiation. The increase in hardness near the surface region results from the low energy of the electron beam. The low energy of the electrons made it possible to only travel few micrometers in the polymeric samples.

With the use of the electron irradiation enhancement method, significant polymerization of items can be achieved. However, further development of the procedure must be researched, as maintaining a vacuum condition during the enhancement process is impractical in mass production.

REFERENCES

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