

## Improvement of Gas Barrier Property of Polyolefins by Diamond-Like Carbon Deposition and Photografting Polymerization

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**ABSTRACT:** The gas barrier properties of isotactic polypropylene (iPP) and high-density polyethylene (HDPE) are both significantly improved by diamond-like carbon (DLC) deposition and photografting polymerization using acrylic acid (AA) monomers. In fact, the gas barrier properties can be highly improved just by DLC or by AA-photografting polymerization. The improvement observed by AA-photografting polymerization is more pronounced than that by DLC deposition in our general experimental condition. In more detail, the oxygen barrier property of DLC-deposited and AA-grafted iPP is considerably improved by ~10 times when compared with that of neat iPP. As for HDPE, the oxygen barrier property is enhanced by nearly six times through DLC deposition and photografting polymerization. By observing the surfaces, 30 nm layer of DLC and 1.0  $\mu\text{m}$  of AA-grafted layer are firmly constructed on the polyolefins, which should contribute to the enhancement of the oxygen barrier property. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2591–2597, 2013

**KEYWORDS:** grafting; polyolefins; surfaces and interfaces; coatings; functionalization of polymers

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### INTRODUCTION

Polymers have become essential materials in our life because they possess plenty of prominent features such as flexibility, moldability, lightweight, and low cost. Polyolefins including polyethylene (PE) and polypropylene (PP) are two most widely used polymers with relatively low gas barrier property, which sometimes limited further applications of the polyolefins. Thus, enhancing the gas barrier property of polyolefins has been greatly desired especially in industrial fields such as automobile, medical, and beverage industries.<sup>1</sup>

There have been two major methods to improve the gas barrier property of polyolefins: composite and coating. A composite consists of two or more different materials with different physical or chemical properties. In fact, strictly speaking, coating is also one way of constructing composites. However, most of the cases, polymeric composites are composed of soft base polymers and hard microparticles dispersed in the polymers.<sup>2–14</sup> Villaluenga et al.<sup>2</sup> made isotactic PP (iPP) composites by dispersing montmorillonite clays into iPP to improve the gas barrier property. The oxygen transmission rate (OTR) of the resulting iPP composites decreased from 919 to 164  $\text{cm}^3/\text{m}^2/\text{day}$ . Nanocomposites of iPP with carbon nanoparticles exhibiting enhanced gas barrier property have also been reported.<sup>3</sup> Among the nanocomposites,

the maleic anhydride-grafted PP composite with phosphate glass (Pglass) particles exhibited highest reduction in OTR from 880 to 0.60  $\text{cm}^3/\text{m}^2/\text{day}$ .<sup>1</sup> The result of OTR is indeed very impressive, whereas the method itself was relatively complicated as they used “layers of a poly-(propylene-*graft*-maleic anhydride) (PP-*g*-MA) alternating with layers of PP-*g*-MA containing 20 vol% of phosphate glass (Pglass) upon biaxial orientation,” which would end up with higher production costs. The mechanical properties of the resulting materials were not discussed, which may be degraded due to rather higher concentration of the Pglass.

The improvement of the gas barrier property of polyolefins by surface coating has also been reported by several groups.<sup>15–22</sup> SiO<sub>x</sub>-based gas barrier coating for iPP by atmospheric pressure plasma jet deposition improved the gas barrier property from 550 to 320  $\text{cm}^3/\text{m}^2/\text{day}$  in OTR.<sup>23</sup> 3-Aminopropyltriethoxysilane-coated PP films exhibited 14  $\text{cm}^3/\text{m}^2/\text{day}$  of OTR, while the original OTR of neat PP films was 282  $\text{cm}^3/\text{m}^2/\text{day}$ .<sup>24</sup> Inagaki et al.<sup>15</sup> reported that the OTR through the silicon oxide (SiO<sub>x</sub>) coating on PP films using plasma polymerization of the tetramethoxysilane (TMOS)/O<sub>2</sub> was decreased from 2230 to 37–52  $\text{cm}^3/\text{m}^2/\text{day}$ .

In this work, the diamond-like carbon (DLC)-coated PP films were investigated. DLC possessed notable characteristics, such as

**Table 1.** Sample Preparations

Sample	Thickness of DLC (nm)	Grafting polymerization conditions			AA-grafted amount ( $\mu\text{mol}/\text{cm}^2$ )
		Monomer concentration	Temperature	Grafting time	
iPP					
DLC/iPP	30				
iPP-g-PAA		0.75 M	60°C	40 min	3.5
DLC/iPP-g-PAA	30	0.75 M	60°C	40 min	3.5
HDPE					
DLC/HDPE	30				
HDPE-g-PAA		0.75 M	60°C	40 min	5.0
DLC/HDPE-g-PAA	30	0.75 M	60°C	40 min	5.0

high gas barrier property, high abrasion resistance, high biocompatibility, and high chemical stability. Tsubone et al.<sup>25</sup> carried out DLC deposition on poly(ethylene terephthalate) (PET) surface and improved the gas barrier property of PET from 25 to 12  $\text{cc}^3/\text{m}^2/\text{day}$  in OTR. Previously, our group deposited DLC onto high-density PE (HDPE), linear low-density PE (LLDPE), LDPE, iPP, and syndiotactic PP (sPP), which significantly enhanced the adhesion force between DLC and polyolefins by photografting polymerization of acrylic acid (AA) as an interlayer.<sup>26</sup> Herein, we investigated the gas barrier property of PP and PE by depositing DLC on AA-grafted polyolefins. Since the thickness of the DLC layer and the AA-grafted layer was  $\sim 50$  nm and  $\sim 1.0$   $\mu\text{m}$ , respectively, the two layers were relatively very thin when compared with the thickness of the base polyolefins ( $\sim 0.1$  mm). Thus, the bulk polyolefin properties were not affected by these thin layers, keeping original prominent features of the polyolefin after the coating processing.

## EXPERIMENTAL

### Materials

Polyolefins (iPP and HDPE) have been purchased in the form of pellets from Sigma-Aldrich. The molecular weights and the melting points of iPP and HDPE were  $M_w$ : 190,000 and  $m.p.$ : 166°C for iPP and  $M_w$ : 125,000 and  $m.p.$ : 130°C for HDPE. Pellets of each material were thermally pressed and molded for 15 min into thin films with a thickness of 0.1 mm at temperatures 10°C higher than each melting point of the polymers with the molding pressure of 5 MPa, using heat press equipment (A-H2003, As One Corp.). The polymeric samples were then cut into 35 mm squares before the photografting polymerization.

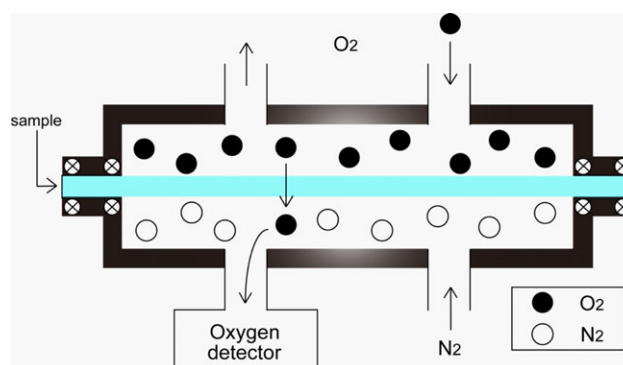
### Photografting Polymerization

The photografting polymerization of AA onto polymer substrates was carried out using photografting equipment (Riko rotary photochemical reactor RH400-10W; Science and Technology Industry Co., Ltd). First, benzophenone, the polymerization initiator, was dissolved in acetone for a sensitizer at the concentration of 0.0275M. Each polymer substrate was then immersed in the benzophenone solution for 1 min to generate radicals on the polymer substrate. AA-monomer solution was prepared at the concentration of 0.75M. iPP and HDPE substrates immersed

in the benzophenone solution was then dipped into the AA-monomer solution using Pyrex reaction tubes. The reaction tubes with each monomer solution and the polymer substrates were irradiated by the ultraviolet (UV) ray emitted from a 400-W high-pressure mercury lamp at 60°C for 40 min. The photografted polymer substrates were rinsed with pure water to remove unreacted monomers and homopolymers and dried at 50°C. Finally, the AA-grafted iPP (iPP-g-PAA) and the AA-grafted HDPE (HDPE-g-PAA) were prepared to observe the gas barrier properties and the mechanical properties. In Table I, the condition of the photografting polymerization as well as the AA-grafted amount and the thickness of DLC were listed. The AA-grafted amount was calculated by dividing the mass difference before and after photografting by AA molecular mass of 72.06 g/mol. The AA-grafted amounts of iPP and HDPE were different, as the grafting efficiency of HDPE was slightly higher than the grafting efficiency of iPP, due to the higher polar character of iPP.

### Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy (FT/IR-4200, JASCO) was carried out to analyze the chemical structures of grafted polymer substrates by analyzing the changes in the FTIR spectra from the polymer surfaces before and after the photografting polymerization. The film samples were set on the



**Figure 1.** Oxygen transmission measurement using MOCON. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

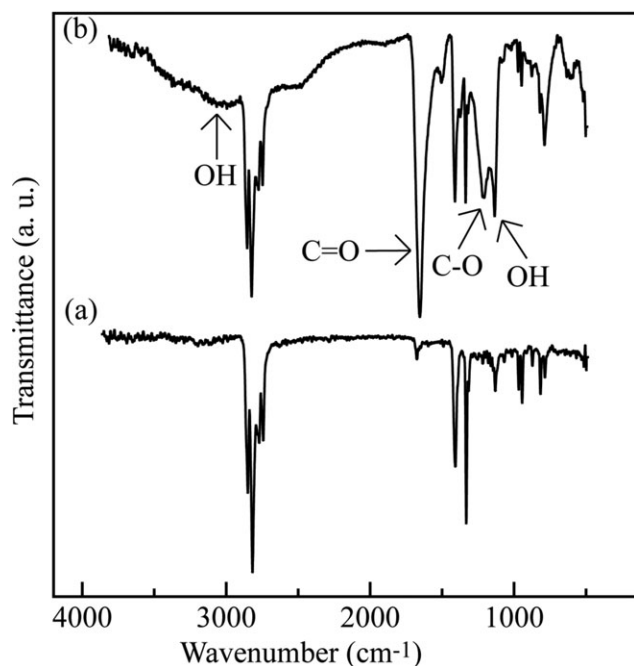


Figure 2. FTIR spectra of (a) non-grafted iPP and (b) iPP-g-PAA.

sample stage, and the IR spectra ranging from 400 to 4000  $\text{cm}^{-1}$  in wavenumbers were analyzed. The averaged data of 16 scans were collected to construct each FTIR spectrum at a resolution of 2  $\text{cm}^{-1}$  by the attenuated total reflectance method. The peak of the carboxyl groups ( $-\text{COOH}$ ) should be observed at 1720  $\text{cm}^{-1}$ , which can be used as an indicator of the progress of the AA-photografting polymerization. In addition, by observing the IR peaks at 1250  $\text{cm}^{-1}$  and 3000–3600  $\text{cm}^{-1}$ , hydroxyl groups in the materials could also be detected.

#### Deposition of DLC

The deposition of DLC was carried out at the pressure of 13.3 Pa with the output of 200 W using a high-frequency plasma CVD device (Hiranokoh-on Corp.). First, the polyolefin films were placed between the two electrodes in the plasma CVD device, and the pressure was reduced to 0.3 Pa using a rotary pump and a mechanical booster pump.  $\text{C}_2\text{H}_2$  gas was inserted as a source of DLC with the pressure of 13.3 Pa. DLC was then deposited on the polymer surface for 8 s under the condition of 13.56 MHz and 200 W. The thickness of the deposited DLC was  $\sim 30$  nm.

#### The Oxygen Transmission Measurement

The OTR was measured under 100% of oxygen atmosphere using the MOCON, OX-TRAN permeability testing technique. Figure 1 described the oxygen transmission test equipment in detail. Nitrogen gas ( $\text{N}_2$ ) was gently injected to the lower part of the chamber while oxygen gas ( $\text{O}_2$ ) was injected to the upper part of the chamber. Some of the oxygen that penetrated through the test specimen with 0.1 mm in thickness will be detected by the oxygen detector set at the lowest part of the equipment. The test temperature was 23°C and the humidity was kept at 90% RH with the oxygen concentration at 100%. At the lower part of the chamber, the transmitted oxygen was

collected and measured for 30 min.<sup>25</sup> All DLC-deposited samples were cut and shaped into a square sheet (35×35 mm) so that the sheet can cover the entire hole (30 mm in diameter) of the chamber.

#### Mechanical Properties

Stress–strain curves were established by the tensile tester (AG-50NIS MS of Shimadzu Co., Ltd.) on each specimen that was cut into a dog-bone shaped film with 16.5 mm in length and 3 mm in width, which was defined by Japanese Industrial Standards. The two edges of the testing sample were fastened by two clamps of the tensile tester, and the sample was then stretched at a constant tensile rate of 10 mm/min up to the fracture point to create the stress–strain curve. The values of the Young's modulus, the yield stress, and the fracture strain were analyzed from each stress–strain curve.

#### The Evaluation of the Transparency of the Specimens

The light transmittance of untreated, AA-grafted, DLC-deposited, and AA+DLC treated specimens was measured using the spectrophotometer U-3310 (Hitachi High-Technologies Corporations). Each specimen was set up on the sample stage in the equipment, followed by the UV and visible light scanning ranging from 320 nm to 680 nm in wavelength. The light transmittance of a PET film was also measured for comparison.

## RESULTS AND DISCUSSION

#### Photografting Polymerization Confirmed by FTIR Spectroscopy

The results of the IR spectra of neat iPP and iPP-g-PAA were shown in Figure 2. The IR spectra of neat HDPE and HDPE-g-PAA were shown in Figure 3. From these spectra, it was found that IR signals of hydroxyl groups from iPP-g-PAA or HDPE-g-PAA was indeed observed at 1250  $\text{cm}^{-1}$ , and that the signals

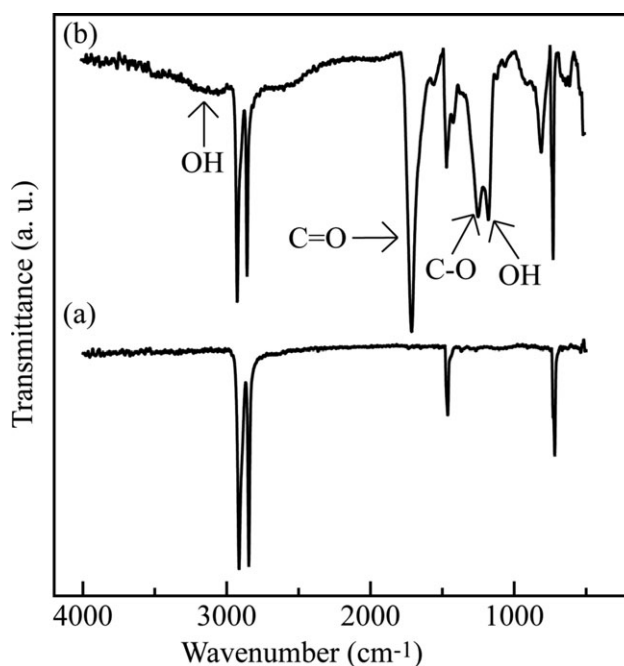
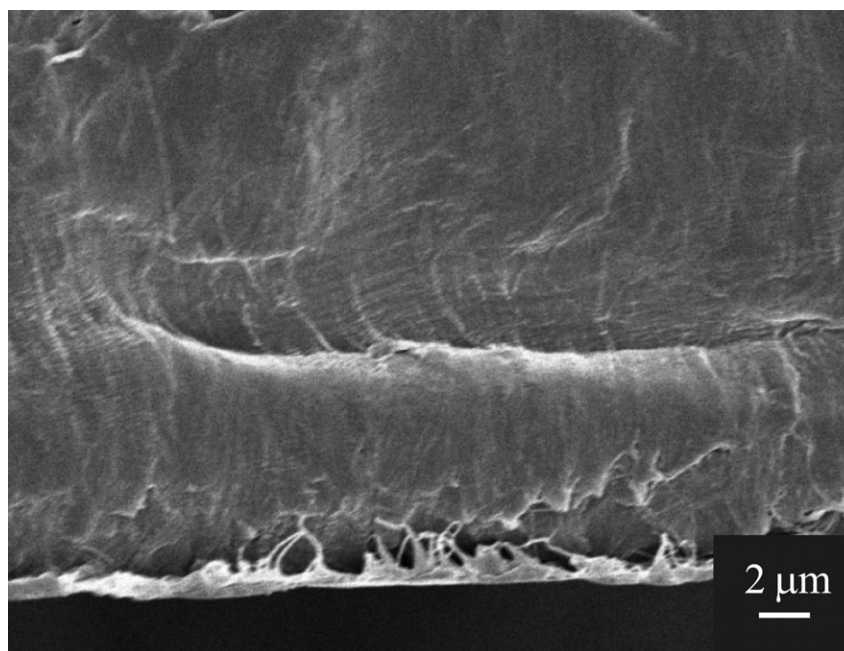


Figure 3. FTIR spectra of (a) non-grafted HDPE and (b) HDPE-g-PAA.



**Figure 4.** Cross-sectional view of AA-grafted layer on HDPE-g-PAA.

from carbonyl groups were also detected at  $1730\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ) and  $1450\text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ). Thus, the existence of the AA-grafted layer (PAA) on the surface of iPP and HDPE was confirmed by FTIR spectroscopy.

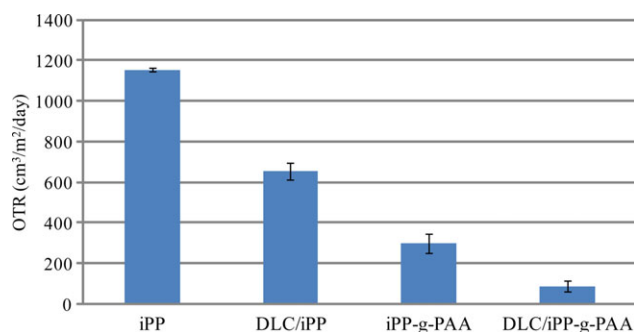
#### Grafted PAA Layer Observed by Scanning Electron Microscopy

The grafted PAA layers on iPP and HDPE were observed by scanning electron microscopy (Hitachi High-Technologies Corporations). The thickness of PAA layer formed on the specimens was detected by observing the cross-section from the frozen sample of the AA-grafted specimen photografted under the same conditions as listed in Table I. Figure 4 shows the result of AA-grafted layer on HDPE (HDPE-g-PAA). From Figure 4, it was found that the thickness of PAA layer was  $\sim 1.0\ \mu\text{m}$ .

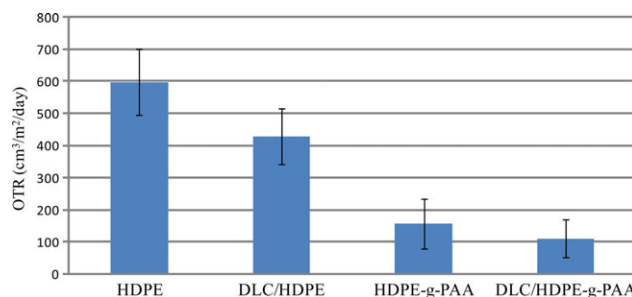
#### The Oxygen Transmission Measurement

Figures 5 and 6 show the OTR results of iPP and HDPE, respectively. According to Figure 5, it was found that the neat iPP

with highest OTR (i.e., lowest gas barrier property against oxygen) improved in its gas barrier property by coating DLC, grafting AA, and applying both DLC and AA-grafting, in that order. In more detail, the oxygen barrier property nearly doubled up by DLC coating, while becoming approximately four times in oxygen barrier property by AA-grafting, eventually becoming  $\sim 10$  times by both DLC deposition and AA-grafting. The initial OTR was  $1153\text{ cm}^3/\text{m}^2/\text{day}$ , which became  $86\text{ cm}^3/\text{m}^2/\text{day}$  by DLC and AA-grafting. Similar enhancement could be observed in HDPE specimens. According to Figure 6, it was found that the neat HDPE with highest OTR also presented stepwise improvement in the oxygen barrier property by coating DLC, grafting AA, and applying both DLC and AA-grafting as it was shown in the iPP case. Eventually, in the HDPE case, the gas barrier property has improved approximately six times by both DLC and AA-grafting. The OTR was  $598\text{ cm}^3/\text{m}^2/\text{day}$  at the initial stage, which became  $111\text{ cm}^3/\text{m}^2/\text{day}$  after DLC deposition and AA-grafting. It was concluded that the gas barrier property of polyolefins was remarkably improved by introducing

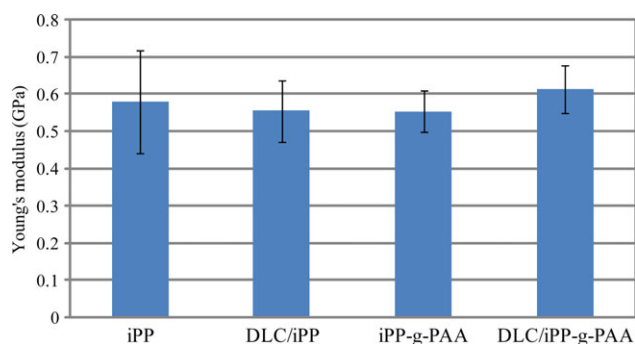


**Figure 5.** OTR results on iPP, DLC-deposited iPP, iPP-g-PAA, and DLC-deposited iPP-g-PAA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** OTR results on HDPE, DLC-deposited HDPE, HDPE-g-PAA, and DLC-deposited HDPE-g-PAA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



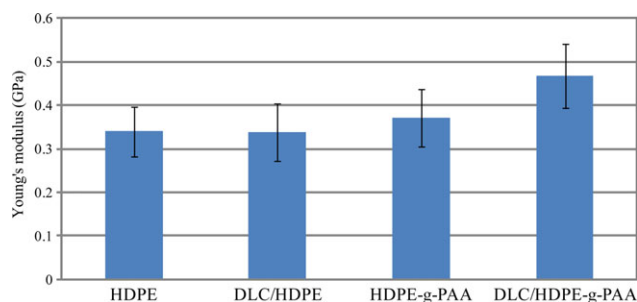


**Figure 7.** Young's moduli of iPP, DLC-deposited iPP, iPP-g-PAA, and DLC-deposited iPP-g-PAA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

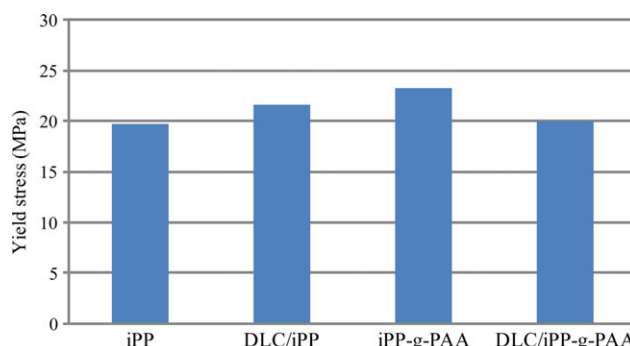
AA-grafting and DLC. The surface modification methods are particularly promising in that the methods are both cost effective and innocuous for the polyolefin materials since they are extremely thin-layer surface modification.

### Mechanical Properties

The mechanical properties of surface modified samples were investigated by measuring Young's modulus, yield stress, and fracture strain through each stress-strain curve of the specimens. The Young's moduli of iPP-related samples and HDPE-related samples were presented in Figures 7 and 8, respectively. The results of the yield stress and the fracture strain were presented in Figures 9 and 10 for the yield stress of iPP and HDPE, and in Figures 11 and 12 for the fracture strain of iPP and HDPE. The Young's modulus and the yield stress of iPP samples were almost constant even after the surface modifications. However, the Young's modulus of HDPE samples was slightly increased by each surface modification, where the Young's modulus was increased by  $\sim 1.4$  times after DLC deposition and AA-photografting when compared with that of the neat HDPE. The yield stress of HDPE samples were almost the same. These results indicated that the DLC deposition and the AA-grafting could effectively increase the gas barrier property of polyolefins without any influence on the Young's modulus and the yield stress (or even an enhancement in the Young's modulus could be observed for HDPE samples). The fracture strain was found decreased especially for the DLC-coated and AA-grafted specimens for both iPP and HDPE. Considering the



**Figure 8.** Young's moduli of HDPE, DLC-deposited HDPE, HDPE-g-PAA, and DLC-deposited HDPE-g-PAA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

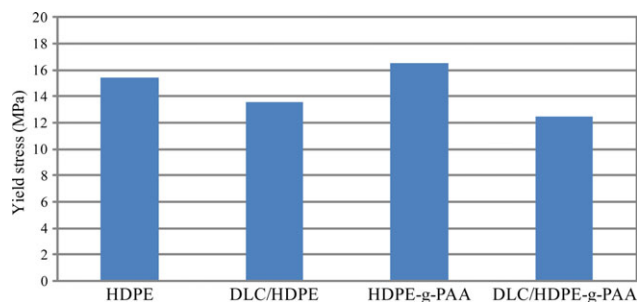


**Figure 9.** Yield stress of iPP, DLC-deposited iPP, iPP-g-PAA, and DLC-deposited iPP-g-PAA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

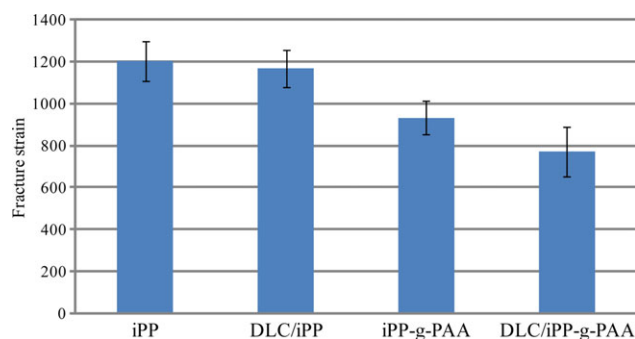
application of polyolefin materials to the materials used in the gas barrier systems such as plastic containers and plastic caps for bottles, the decrease in the fracture strain would not cause much serious damage to the systems, because the polyolefin materials should be used mechanically in a linear region or below yield points. In such cases, Young's modulus and yield stress should be more important, which should work as two key parameters in material characteristics for the gas barrier systems.

### The Light Transmittance of the Samples

Light transparency is one of the important factors for the materials to be used practically, e.g., containers and caps with high gas barrier properties. Figures 13 and 14 are the results of the light transmittance measurements of neat sample, DLC-deposited sample, AA-grafted sample, DLC-deposited AA-grafted sample, and PET. Figure 13 shows that the transparency of each sample was quite close to each other. In fact, as the color of DLC was brownish, the transparency of DLC-coated specimens was relatively slightly lower than that of AA-photografted samples or neat polyolefins and PET. AA-photografting would not lower the transparency, or in fact, the transparency of AA-photografted iPP was similar to that of neat iPP or even better than that of PET, since PET has significant light absorption starting at 320 nm. The transparency of neat HDPE used in this experiment was originally lower than that of PET. The transparency of AA-grafted HDPE became slightly lower than that of neat HDPE. As mentioned above, the light transmittance of DLC-



**Figure 10.** Yield stress of HDPE, DLC-deposited HDPE, HDPE-g-PAA, and DLC-deposited HDPE-g-PAA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

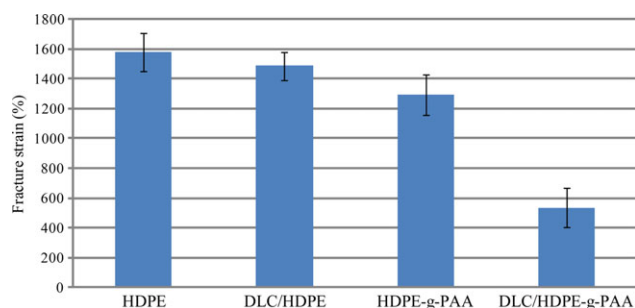


**Figure 11.** Fracture strains of iPP, DLC-deposited iPP, iPP-g-PAA, and DLC-deposited iPP-g-PAA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

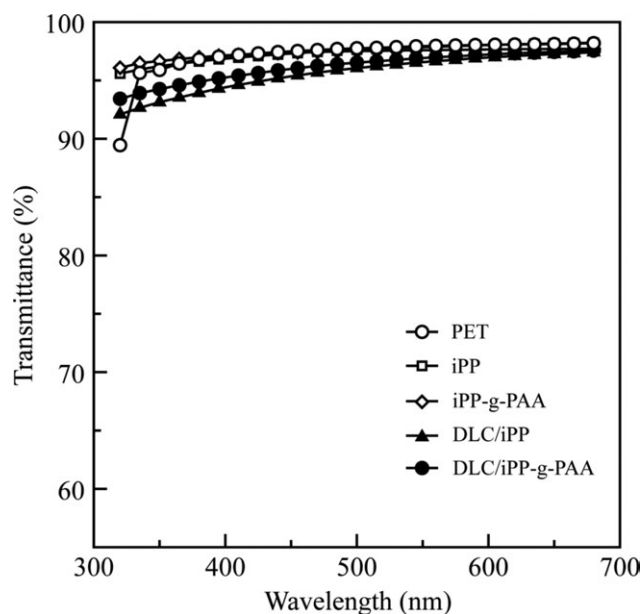
coated HDPE became even slightly lower due to the relatively brown color of the DLC nano-layer on polyolefins, originating from graphite component in DLC. However, the amount of reduction in the light transmittance was very limited that it can be disregarded for the industrial application.

## CONCLUSIONS

The improvement of the gas barrier properties of iPP and HDPE by DLC deposition and AA-photografting polymerization was discussed. The gas barrier properties of iPP and HDPE were both significantly enhanced by DLC deposition and AA-photografting polymerization on the surface of iPP and HDPE. The effects of both DLC deposition and AA-photografting polymerization were investigated separately, and it was found that the gas barrier properties could be highly improved just by DLC or by AA-photografting polymerization. The improvement observed by AA-photografting polymerization was greater than that by the DLC deposition in our experimental condition, which, as a matter of course, should be dependent on the thickness of the deposition layers. In more detail, the oxygen barrier property of DLC-deposited and AA-grafted iPP was increased by ~10 times when compared with that of neat iPP. As for HDPE, the oxygen barrier property was increased by nearly six times by DLC deposition and photografting polymerization. By observing the surfaces, it was found that 30 nm layer of DLC and 1.0  $\mu\text{m}$  of AA-grafted layer were firmly constructed on the

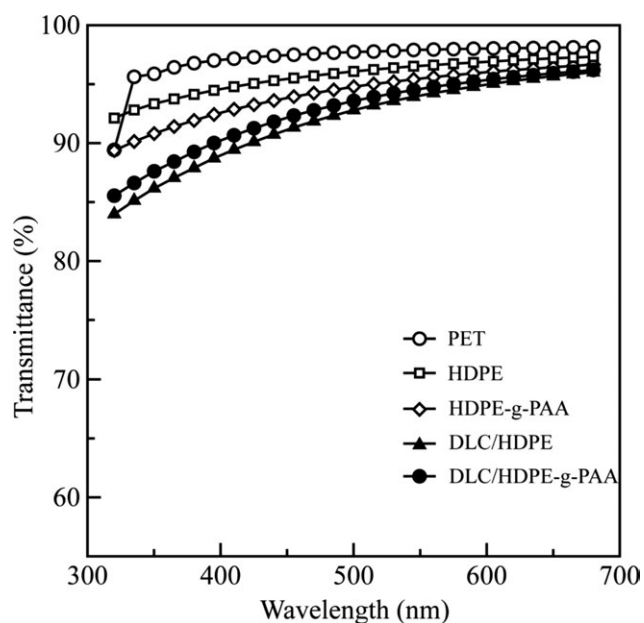


**Figure 12.** Fracture strains of HDPE, DLC-deposited HDPE, HDPE-g-PAA, and DLC-deposited HDPE-g-PAA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 13.** Light transmittance of PET, pure iPP, DLC-deposited iPP, iPP-g-PAA, and DLC-deposited iPP-g-PAA.

polyolefins, which should have contributed to the enhancement of the oxygen barrier property. Young's moduli and yield stresses were not changed by DLC-deposition and AA-photografting polymerization. The light transmittance after AA-photografting was unchanged, whereas the light transmittance after DLC deposition was slightly decreased, which, however, would not seriously affect the transparency of resulting materials for gas barrier systems. The methods may highly be applicable to other polymeric materials for the enhancement of the gas barrier property.



**Figure 14.** Light transmittance of PET, pure HDPE, DLC-deposited HDPE, HDPE-g-PAA, and DLC-deposited HDPE-g-PAA.

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