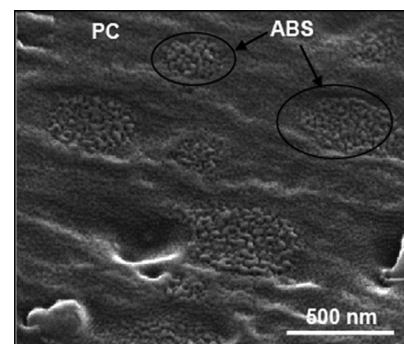


# The Morphology and Mechanical Properties of Polycarbonate/Acrylonitrile Butadiene Styrene Modified by Ar Ion Beam Irradiation

Sk. Faruque Ahmed, Jin Woo Yi, Myoung-Woon Moon,\* Yong-Jun Jang,\*  
Bong-Hyun Park, Seong-Hoon Lee, Kwang-Ryeol Lee

This study examined the surface morphological evolution of polycarbonate and acrylonitrile butadiene styrene (PC/ABS) irradiated with an Ar ion beam using an ion beam system. PC was not affected by the Ar ion beam treatment at a lower ion beam treatment times but the ABS portion formed a foam-like nanostructure at the surface. On the other hand, both PC and ABS formed nanostructures with length of 100 to 120 nm and a mean diameter of  $\approx 35$  nm at longer beam treatment times. The Raman and FTIR spectra revealed polymer chain scissioning. Nanoindentation showed that the hardness and elastic modulus of the PC/ABS decreases from 0.22 to 0.18 GPa and from 3.39 to 2.98 GPa, respectively with increasing Ar ion beam treatment time due to the surface nano-structures formed by Ar ion beam.



## Introduction

Polycarbonate and acrylonitrile butadiene styrene (PC/ABS) alloys are well-known commercial polymers. The advantage of the PC/ABS combination is that they form blends, where ABS helps to reduce the cost and PC contributes to heat resistance. Due to the appropriate combination of the two components, PC/ABS is widely used in engineering thermoplastics, such as aircraft interior trim, car wind-screens, automobile interior parts, safety helmets, and

display screens.<sup>[1–3]</sup> The major drawbacks of PC/ABS are its low hardness, low scratch resistance and degradation by ultraviolet radiation as well as permeability to gases. In order to overcome these drawbacks, functional coatings applied to the surface of the polymer can provide protection from scratching damage. A thin film coating can improve the mechanical, chemical properties and compatibility of PC/ABS, which are useful in protective optical materials or biomedical products. However, the direct deposition of hard thin film coatings on polymer substrates causes problems with film adhesion.<sup>[4–6]</sup>

From the standpoint of environment protection, plasma technologies play an important role in surface treatment of polymers through use of a low temperature glow discharge, ion beam bombardment. Surface treatments with Ar, N<sub>2</sub>, O<sub>2</sub>, CF<sub>4</sub>, Ga, CO<sub>2</sub>, and He ions, on a polymer can affect the structural properties, optical properties, electrical conductivity<sup>[7–11]</sup> as well as the chemical properties, i.e., wettability and biocompatibility for implants.<sup>[11–15]</sup> The mechanical properties such as the hardness and tribological properties of polymers can be also modified by high-energy,

Sk. F. Ahmed, J. W. Yi, M.-W. Moon, K.-R. Lee  
Future Convergence Technology Laboratory, Korea Institute of  
Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-  
650, Republic of Korea  
Fax: +82 2 958 5509; E-mail: mwmoon@kist.re.kr  
Y.-J. Jang, B.-H. Park, S.-H. Lee  
Polymeric Materials Research Team, Research & Development  
Division for Hyundai Motor Company & Kia Motors Corporation,  
Gyeonggi-Do, Republic of Korea  
E-mail: yjjang@hyundai-motor.com

low-dose ion implantation. In the last few years, many fundamental studies have explained these changes based on the cross-linking effect originating from the ionization effects of ion bombardment.<sup>[13,14]</sup> PC/ABS surfaces were modified with a low energy (300 eV) Ar and N ion beam to improve the adhesion of metal thin films.<sup>[15]</sup> Surface morphological evolution of PC/ABS by chemical etching was reported by Dong et al.<sup>[16]</sup> The PC in the PC/ABS blend was selectively etched by a NaOH solution while a strong acid solution selectively etched the ABS on the surface of the same blends. Nevertheless, wet chemical coating technologies involve several steps and produce toxic by-products.<sup>[17,18]</sup> UV irradiation inducing microstructural changes of PC/ABS have been studied extensively.<sup>[19]</sup> However, there are no reports on the detail effect of low energy Ar ion beam on the surface morphological evolution of PC/ABS. A study of the morphological evolution of PC/ABS at low ion energy is interesting due to its potential for use in biological applications and automobile components. A proper estimation of the mechanical properties of ion beam irradiated surfaces is essential for further applications of PC/ABS blends, such as automobile parts requiring long-term mechanical stability.

This paper reports the evolution of the nanostructure surface morphology of PC/ABS and the change in the mechanical hardness and elastic modulus with increasing treatment time with a low energy Ar ion beam. Observation of the PC/ABS revealed that nanostructures like holes and foams evolved on the PC and ABS, respectively, under different ion exposure times. Alternation of the chemical bonds due to ion beam irradiation was explored by chemical analysis. The decrease in hardness and elastic modulus of PC/ABS was explained in terms of the changes in surface morphology induced by the Ar ion beam treatment.

## Experimental Part

Ar ion beam treatment of the PC/ABS blends were carried out in an ion beam system. Single PC and ABS were also prepared for comparison. The samples were placed in the ion beam chamber as described earlier.<sup>[20]</sup> The chamber was evacuated to a base pressure  $2 \times 10^{-5}$  mbar. The distance between the ion source and substrate holder was approximately 15 cm. The Ar gas was introduced into the end-Hall type ion gun to obtain Ar ions with flow rate of 8 sccm and the anode voltage was kept at a constant value of 1 kV with a current density  $50 \mu\text{A} \cdot \text{cm}^{-2}$ . A radio frequency (RF) bias voltage was applied to the substrate holder at a bias voltage of  $-600$  V with different exposure times varying from 5 to 50 min.

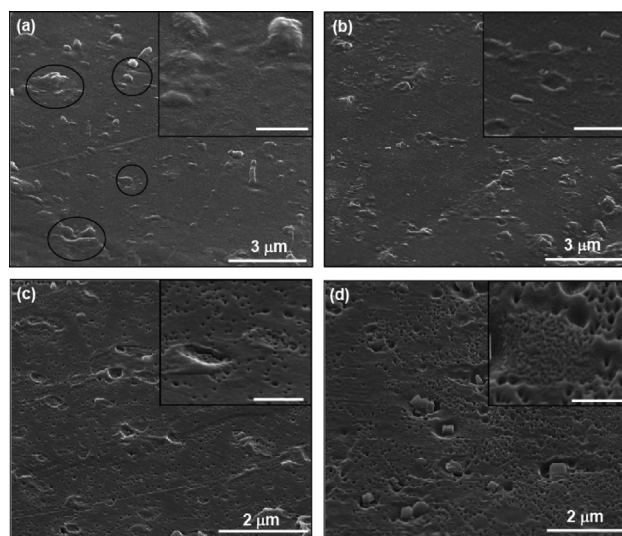
The surface morphology of the Ar ion beam treated PC, ABS, and PC/ABS blend (LG Chem) was studied by scanning electron microscopy (SEM, NanoSEM, FEI Company). The atomic bond structure of the Ar ion beam irradiated PC/ABS samples were analyzed by Raman spectroscopy (LabRAM HR, HORIBA Jobin-Yvon

Inc.) and Fourier transform infrared spectroscopy (FTIR, Infinity Gold FTIR, Thermo Mattson). Nanomechanical testing instruments (Triboindenter, Hysitron Inc.) were used to measure the mechanical properties of the ion beam treated surfaces. A Berkovich diamond tip with an approximate radius of curvature of 150 nm was used as the nanoindentation tip. Nano-indentation in continuous stiffness measurement (CSM) mode was used to characterize the hardness and elastic modulus of the PC/ABS with and without the ion beam treatment. The load and displacement curves were recorded continuously up to a maximum load at  $275 \mu\text{N}$  for a 5 s loading, held at that holding time for 5 s, and unloaded for 5 s. The measurements were carried out at six different points for each sample.

## Results and Discussion

### Surface Morphology Studies

Figure 1 shows the  $50^\circ$  tilted view SEM images on the PC/ABS samples treated with Ar ions for different times. Figure 1(a) clearly shows that the PC/ABS substrate contains softer ABS within the PC matrix and the ABS forms a convex structure on the surface. In PC/ABS blends the PC and ABS could be etched separately using a chemical etching technique.<sup>[16]</sup> After 5 min Ar ion beam irradiation, some holes began to form on the PC but the ABS part appeared concave in nature. After 10 min Ar ion beam irradiation, holes formed over the surface of the PC/ABS with a mean diameter  $\approx 30$  nm. For 30 min, the softer ABS part exhibited a foam-like structure while the holes in the PC counterpart became larger with a mean diameter of  $\approx 80$  nm. After 50 min Ar ion beam irradiation, nanostructures of the



**Figure 1.** SEM images of the PC/ABS surfaces a) untreated, b) 5 min., c) 10 min. and d) 30 min. treated with an Ar ion beam. The black circles indicate the ABS part surrounded by PC.

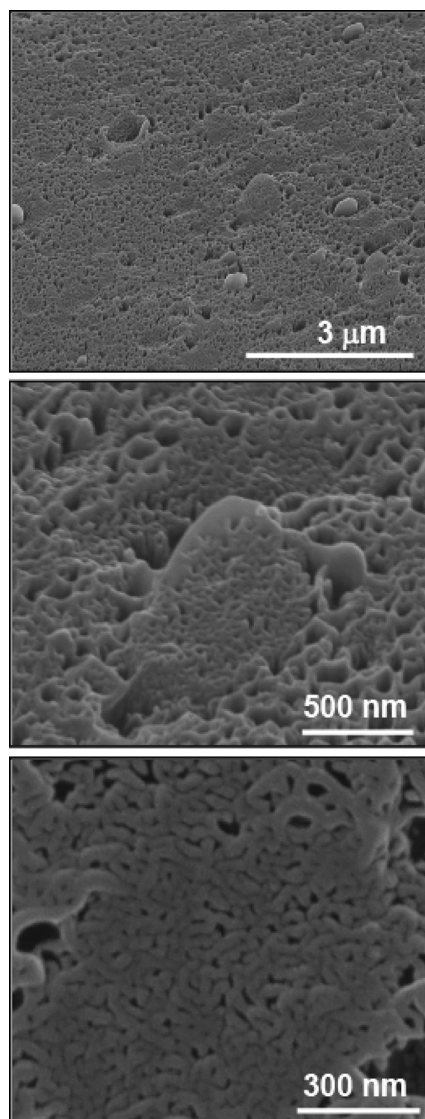


Figure 2. SEM images of the PC/ABS surfaces treated with an Ar ion beam for 50 min.

nanofiber forms on PC and also on the ABS part shown in Figure 2. The length of the nanofiber ranged 100–120 nm and a mean diameter of  $\approx 35$  nm. To identify the PC and ABS on the PC/ABS sample, PC and ABS sample was treated separately by an Ar ion beam for 30 min. Figure 3 shows the surface morphology of PC and ABS after 30 min Ar ion beam irradiation. Holes were formed on the PC sample with a mean diameter of  $\approx 90$  nm, and a foam-like structure formed on the ABS sample, which is similar to the PC/ABS surface after 30 min Ar ion beam irradiation, as shown in the inset of Figure 1(d). From this observation it is clear that the convex part of the PC/ABS surface (marked as black circle) in Figure 1(a) was ABS and remaining part was PC.

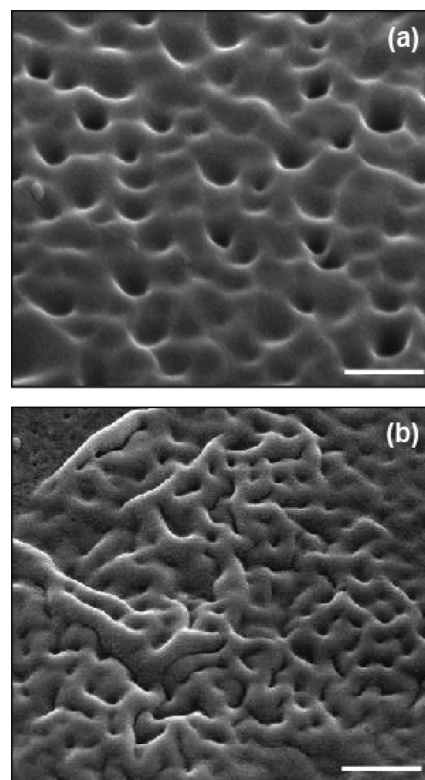


Figure 3. SEM images (a) PC and (b) ABS surfaces irradiated with 30 min Ar ion beam.

### Compositional Analysis

Figure 4 shows the Raman spectra of the Ar ion beam treated PC/ABS samples at different times. There was a significant change in the Raman spectra near  $1500\text{ cm}^{-1}$  after Ar ion beam irradiation. The dominant peak at approximately  $1605\text{ cm}^{-1}$  corresponds to the ring stretching bond. The Raman peaks at  $1880$  and  $1112\text{ cm}^{-1}$  were assigned to the CH in-plane wagging mode and the peak at  $885\text{ cm}^{-1}$  CH was assigned to the out of plane wagging mode.<sup>[21]</sup> There were broad peaks in the  $1200\text{--}1600\text{ cm}^{-1}$  region, which are attributed to the C–O stretching and C–H deformation mode, respectively.<sup>[21,22]</sup> The broadness of the peak is an indication that there are several polymer conformations that contribute to the morphological changes giving rise to an aging mechanism.

Figure 5 shows the FTIR spectra of the Ar ion beam treated PC/ABS samples at different times. The broad peaks at approximately  $2950$  and  $3200\text{--}3400\text{ cm}^{-1}$  were assigned to the stretching modes of different C–H<sub>n</sub> group and O–H vibrational mode,<sup>[22,23]</sup> respectively, and the peaks at  $1400\text{--}1600\text{ cm}^{-1}$  were assigned to the vibrations due to the C–C stretching mode.<sup>[23]</sup> The peaks centered at  $1780$  and  $1000\text{ cm}^{-1}$  were attributed to the C=O and C–O stretching modes, respectively. The dominant peak at

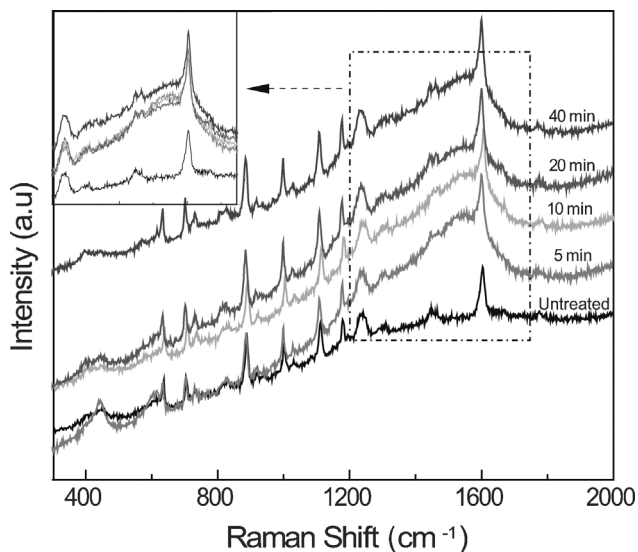


Figure 4. Raman spectra of PC/ABS irradiated for different Ar treatment times and in inset magnified Raman spectra in the 1200–1600  $\text{cm}^{-1}$  region merged together.

approximately 1200  $\text{cm}^{-1}$  corresponds to the C–H<sub>3</sub> bending, and the medium peaks at 830  $\text{cm}^{-1}$  were assigned to the C–H wagging modes.<sup>[22,24]</sup> It has been found that with the increase of Ar ion beam irradiation time, there was a decrease in the intensity of the C–H absorption band around 2950  $\text{cm}^{-1}$ , intensity of the C=O band at approximately 1780  $\text{cm}^{-1}$ , and the intensity of the C–H<sub>3</sub> band at approximately 1200  $\text{cm}^{-1}$ , which is indicative of the chain scission of PC/ABS.<sup>[24]</sup>

High-energy ion irradiation can modify the structure, composition, and properties of a polymer surface in two ways: (i) by introducing ion species (doping or chemical

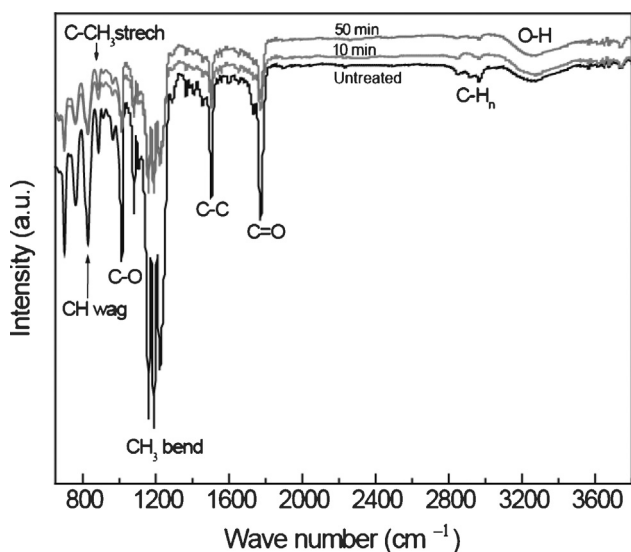


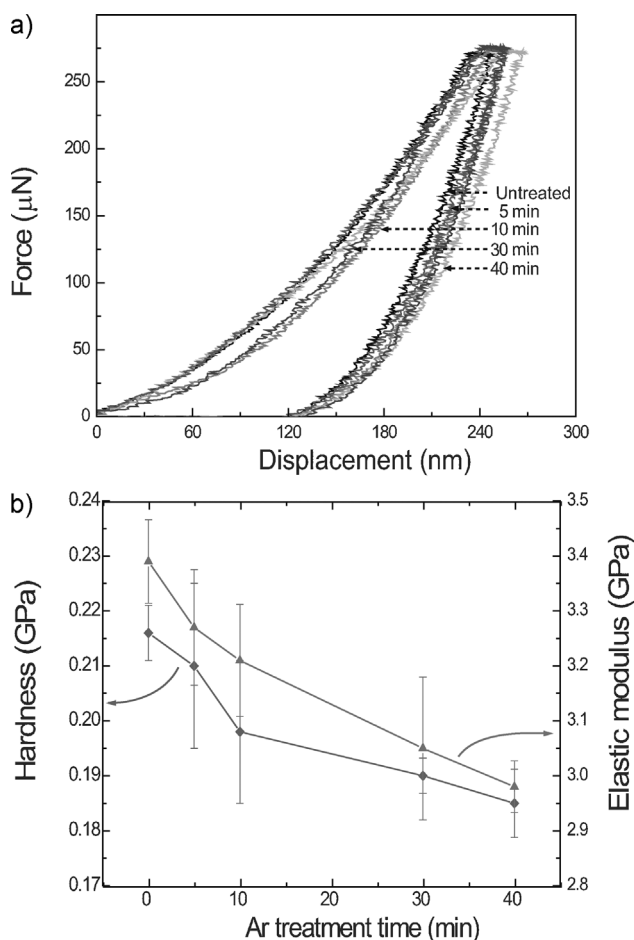
Figure 5. FTIR spectra of PC/ABS irradiated for different Ar treatment times.

effect) and (ii) through irradiation-induced defects (radiation or defect effect). However, the effect of defects is more important in surface modification of polymers than that for metals and ceramics. This is because the doping effect is an end-of-track phenomenon and the implanted ion concentrations are generally quite low. On the other hand, the radiation effect operates throughout the entire range of the ion track and produces a high yield, and the bond breakage of organic molecules results in the formation of an ensemble of smaller molecules, many of which may be volatile.<sup>[25]</sup> Ion beam irradiation leads to irreversible changes in polymers, and is important for understanding the damage mechanisms in polymers. Energetic ions are slowed down in materials by momentum transfer to the target atoms, which known as nuclear stopping, as well as by exciting the electronic system of the target, which is known as electronic stopping.<sup>[26,27]</sup> The displacement of the target atoms by energetic collisions can cause permanent damage to a polymer mainly in the form of chain scission by displacing the atoms from the polymer chains.<sup>[28]</sup> If a bond that makes up part of the backbone of the molecule (such as C–C in UHMWPE) breaks, main chain scission results in degradation to products with a lower average molecular weight. Alternatively, electronic excitation or the removal of valence electrons (ionization) can result in the formation of free radicals that may readily cross-link the polymer chains.<sup>[28]</sup> Depended upon the type of ion radiation, dose rate, and environment such as ion beam or plasma, either cross-linking or scissioning may dominate in the affected layer of polymer by ion irradiation. Her et al. showed that different morphologies, such as hole, cone or tunnel in nanoscale, were formed on a poly(methyl methacrylate) (PMMA) surface at a relatively lower energy of 5 or 10 kV by a Ga<sup>+</sup> focused ion beam.<sup>[29]</sup> The morphologies were induced from sputtering phenomena and degradation with chain-scissioning and fragmentation in the polymer by the ion irradiation, which leads to the formation of many vacancies or voids by over-saturated vacancies in a shallow subsurface layer of PMMA. Similarly, it can be explained that the nanoscale patterns of holes formed on the PC/ABS and PC in Figures 2 and 3a, respectively, would be induced with the mechanism of chain scissioning and fragmentation, which can be also confirmed with the decrease of a C–H band by FTIR analysis shown in Figure 5.

It is expected that the PC/ABS surface can be heated as the ion beam irradiation time increases, which may enhance the polymer degradation since the kinetic energy of ions is the main cause for the heating of target<sup>[30]</sup>. Even though the ion beam irradiation induced heating on PC/ABS was not considered to change the substrate temperature remarkably in this work, further analysis should be performed for the thermal heating effect on the pattern formation and degradation in the PC/ABS by varying the ion dose, energy, or ion source.

## Mechanical Properties

The force ( $P$ ) and displacement ( $h$ ) curves during the nanoindentation tests were obtained on the PC/ABS surfaces at different ion exposure times, as shown in Figure 6(a). The  $P$ - $h$  curve indicates full elastic deformation in PC/ABS during indentation under this load condition. Increasing the Ar ion beam irradiation time will increase the contact stiffness ( $S = dp/dh$ ). The hardness and elastic modulus were estimated by a computer program using the Oliver-Pharr method.<sup>[31]</sup> Figure 6(b) shows the relationship between the Ar ion beam irradiation time and the hardness and elastic modulus with a 275  $\mu\text{N}$  load. With increasing Ar irradiation time, the hardness of the PC/ABS decreased from 0.22 to 0.18 GPa, while the elastic modulus decreased from 3.39 to 2.98 GPa. Note that the range estimated for the hardness and elastic modulus for the untreated PC/ABS is comparable to those of the PC thin film, even though these values depend on the applied load, loading rate, and holding time.<sup>[32]</sup> The surface hardness of the PC/ABS surfaces after



**Figure 6.** (a) The force – displacement curve of the nanoindentation at an applied load of 275  $\mu\text{N}$  and (b) the changes in the hardness and elastic modulus of PC/ABS irradiated for different Ar treatment times.

more than 10 min irradiation decreased further than those of the pristine and 5 min irradiation samples, which is consistent with the morphological evolution of the holes and foams for PC and ABS after 10 min irradiation, respectively, as shown in Figure 1. This suggests that the nano-structures evolved due to Ar ion beam irradiation (see Figure 1 and 2) play a significant role in reducing the surface strength or hardness. In addition, the surface hardness would be underestimated in the ion beam irradiated region of the PC/ABS surfaces due to substrate effect during the indentation experiment.<sup>[33]</sup> For a proper evaluation of the substrate effect, further studies should examine the thickness affected by ion beam irradiation, which depends on the ion energy condition.

## Conclusion

The morphological evolution and mechanical properties of PC/ABS surface were examined after exposure to an Ar ion beam. SEM showed that PC was not affected by the Ar ion beam treatment at lower times but ABS formed nanostructures. On the other hand, at higher treatment times, both PC and ABS are affected by the Ar ion beam and formed nanostructures. Raman and FTIR spectroscopy showed changes in the composition of the PC/ABS surface by the ion beam with major changes in the C–O and C–H mode, resulting in aging and chain scissioning. Nanoindentation revealed a decrease in the hardness and elastic modulus of the PC/ABS with increasing Ar ion beam irradiation time due to a deterioration in the mechanical strength caused by the nano-scale holes and foams on the PC and ABS surfaces, respectively.

**Acknowledgements:** This study was supported financially in part by a grant from the *Hyundai Motor Company* and *Kia Motors Corporation* and in part by *Korea Institute of Science & Technology* project code of 2E20640.

Received: March 23, 2009; Revised: July 12, 2009; Accepted: August 26, 2009; DOI: 10.1002/ppap.200900043

**Keywords:** Ar ion beam; irradiation; mechanical properties; nanostructures; PC/ABS; plasma treatment; surface morphology

- [1] M. C. Choi, Y. Kim, C. S. Ha, *Prog. Polym. Sci.* **2008**, *33*, 581.
- [2] F. Samson, *Surf. Coat. Technol.* **1996**, *81*, 79.
- [3] H. J. Borg, R. V. Woudenberg, *J. Magn. Magn. Mater.* **1999**, *193*, 519.
- [4] M. Kemell, E. Farm, M. Ritala, M. Leskela, *Eur. Polym. J.* **2008**, *44*, 3564.
- [5] C. T. Guo, *Thin Solid Films* **2008**, *516*, 4053.
- [6] J. C. Damasceno, S. S. Camargo, Jr, M. Cremona, *Thin Solid Films* **2003**, *433*, 199.
- [7] R. M. Radwan, A. M. A. Kader, A. E. H. Ali, *Nucl. Instrum. Methods Phys. Res. B* **2008**, *266*, 3588.
- [8] M. Diepens, P. Gijsman, *Polym. Degrad. Stab.* **2007**, *92*, 397.

- [9] R. Sharma, E. Holcomb, S. Trigwell, M. Mazumder, *J. Electrostatics*. **2007**, *65*, 269.
- [10] M. W. Moon, J. H. Han, A. Vaziri, E. K. Her, K. H. Oh, K. R. Lee, J. W. Hutchinson, *Nanotechnology* **2009**, *20*, 115301.
- [11] C. Darraudt, B. Bennamane, C. Gagnadre, J. L. Decossas, J. C. Vareille, *Polymer* **1994**, *35*, 2447.
- [12] J. C. Varin, G. Levesque, E. Nakache, *Polymer* **1993**, *34*, 3727.
- [13] L. Zang, K. Takata, T. Yasui, H. Tahara, T. Yoshikawa, *Mater. Chem. Phys.* **1998**, *54*, 98.
- [14] H. Dong, T. Bell, *Surf. Coat. Technol.* **1999**, *111*, 29.
- [15] B. A. Ratchev, G. S. Was, J. H. Booske, *Nucl. Instrum. Methods Phys. Res. B* **1995**, *106*, 68.
- [16] L. Dong, R. Greco, G. Orsello, *Polymer* **1993**, *34*, 1375.
- [17] M. Herrero, R. Navarro, Y. Grohens, H. Reinecke, C. Mijangos, *Polym. Degrad. Stab.* **2006**, *91*, 1915.
- [18] M. Herrero, P. Tiemblo, J. R. Labarta, C. Mijangos, H. Reinecke, *Polymer* **2002**, *43*, 2631.
- [19] R. Ramani, C. Ranganathaiah, *Polym. Degrad. Stab.* **2000**, *69*, 347.
- [20] A. Y. Wang, K. R. Lee, J. P. Ahn, J. H. Han, *Carbon* **2006**, *44*, 1826.
- [21] D. L. Vien, N. B. Colthup, W. G. Fateley, J. G. Grasselli, "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules", Academic Press, Boston, MA 1991.
- [22] J. Dybal, P. Schmidt, J. Baldrian, J. Kratochvíl, *Macromolecules* **1998**, *31*, 6611.
- [23] C. Vree, S. G. Mayr, *J. Appl. Phys.* **2008**, *104*, 83517.
- [24] A. Torikai, T. Murata, K. Fueki, *Polym. Photochem.* **1984**, *4*, 255.
- [25] T. Venkatesan, L. Calcagno, B. S. Elman, G. Foti, "Ion Beam Modification of Insulators", P. Mazzoldi, G. W. Arnold, Eds., Elsevier, Amsterdam 1987.
- [26] E. H. Lee, G. R. Rao, M. B. Lewis, C. K. Mansur, *J. Mater. Res.* **1994**, *91*, 1043.
- [27] J. F. Ziegler, "Ion Implantation Physics", in: *Handbook of Ion Implantation Technology*, J. F. Ziegler, Ed., North Holland, Amsterdam 1992, p. 1.
- [28] A. Chapiro, "Radiation Chemistry of polymer System", Interscience Publishers, London 1962.
- [29] E. K. Her, H. S. Chung, M. W. Moon, K. H. Oh, *Nanotechnology* **2009**, *20*, 285301.
- [30] H. Kersten, R. Wiese, M. Hannemann, A. Kapitov, F. Scholze, H. Neumann, R. Hippler, *Surf. Coat. Technol.* **2005**, *200*, 809.
- [31] W. C. Oliver, G. M. Pharr, *J. Mater. Res.* **1992**, *7*, 1564.
- [32] T. H. Fang, W. J. Chang, *Microelectron. J.* **2004**, *35*, 595.
- [33] H. Bei, S. Shim, M. K. Miller, G. M. Pharr, E. P. George, *Appl. Phys. Lett.* **2007**, *91*, 111915.