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전자빔을 이용한 Poly(dimethyl siloxane)의 개질

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Electron Beam-Induced Modification of Poly(dimethyl siloxane)

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초록: 본 연구에서는 전자빔을 이용하여 poly(dimethyl siloxane)(PDMS)을 개질하였으며 그 특성 변화를 분석하였다. PDMS 시트를 기존의 열경화법을 통해 제조한 후 20에서 200 kGy의 흡수선량으로 전자빔을 조사하였고, 조사된 시트들의 특성을 팽윤도 및 접촉각 측정, 만능시험분석기(UTM), 열중량분석기(TGA), X선 광전자 분광기(XPS)들을 이용하여 분석하였다. 팽윤도 측정, UTM 및 TGA 결과, 전자빔 조사에 의해 PDMS 시트의 가교 밀도가 증가함에 따라 조사된 PDMS 시트의 팽윤도는 순수한 것에 비해 최대 24%까지 감소하였고 압축강도와 열분해온도는 순수한 것에 대비 각각 최대 2.5 MPa와 10 ℃까지 증가함을 확인하였다. 또한, 접촉각 측정과 XPS 분석 결과를 토대로 전자빔 조사에 의한 산화 반응에 의하여 PDMS 표면에 친수성 관능기들이 형성되기 때문에 PDMS 표면의 젖음성은 순수한 것에 비해 최대 24%까지 향상됨을 확인하였다.

Abstract: In this paper, poly(dimethyl siloxane) (PDMS) was modified using electron beam irradiation and its property was investigated. PDMS sheets prepared using a conventional thermal curing method were irradiated by electron beams at absorbed doses between 20 and 200 kGy and their properties were characterized using swelling degree and contact angle measurements, universal testing machine (UTM), thermogravimetric analyzer (TGA), and X-ray photoelectron spectrometer (XPS). The results of the swelling degree measurements, UTM, and TGA revealed that the swelling degree of the irradiated PDMS sheets was reduced down to 24% in comparison to the control sheet, and their compression strength and thermal decomposition temperature increased up to maximum 2.5 MPa and 10 ℃, respectively, due to the increase in crosslinking density by irradiation. In addition, on the basis of the results of contact angle measurements and XPS, the wettability of the PDMS sheets was enhanced up to 24% owing to the generation of hydrophilic functional groups on the PDMS surface by oxidation during electron beam irradiation.

Keywords: electron beam, modification, poly(dimethyl siloxane), thermal and mechanical properties, wettability.

Introduction

Poly(dimethyl siloxane) (PDMS) has been extensively utilized in a wide range of academic and industrial applications owing to its strengths such as chemical inertness, non-toxicity, easy handling, and commercial availability.[1,2] Recently, PDMS has been used in the construction of microelectromechanical system and microfluidic devices for its biological and medical applications.[3-5] However, its use in versatile applications has been limited due to its low mechanical strength and hydrophobicity.[6] Thus, the modification of PDMS has been carried out by using a variety of physicochemical methods based on

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oxidation, composites, and surface coating to enhance its surface and mechanical properties.[6,7]

Among these methods, electron beam irradiation technique is a fascinating method to alter the physicochemical properties of PDMS. It offers several advantages over other modification methods such as an eco-friendly process, precise controllability, no additives, temperature-independence, low energy consumption, and so on.[8,9] Thus, this technique has been widely used to modify various materials.[10-13] Nonetheless, the modification of PDMS through electron beam irradiation to enhance its physicochemical properties has been little studied.

In this research, PDMS sheets were irradiated using electron beams to improve their physicochemical properties. PDMS sheets, prepared using a conventional thermal curing method, were modified by electron beam irradiation under various absorbed doses and their properties were investigated.

Experimental

Sylgard 184 (Dow Corning) was supplied in two separate kits with a pre-polymer (base resin) in one kit and a cross-linker (curing agent) in another kit. To prepare PDMS sheets, the base resin and its curing agent were well-mixed into different mixing weight ratios of 5:1, 10:1, and 15:1. The resulting mixture was degassed for 15 min to remove air bubbles, poured into a customized mold (150 mm (L)×150 mm (W)×3 mm (H)), and then cured at 100 ℃ for 2 h to complete the crosslinking.

For electron beam irradiation, the PDMS sheets prepared at a mass ratio of 10:1 were irradiated at room temperature using an UELV-10-10S linear electron accelerator installed at Korea Atomic Energy Research Institute (Jeongeup, Korea). The energy and current density of the electron beams were 10 MeV and 1 mA/cm^2, respectively. The total absorbed dose ranged from 20 to 200 kGy.

The swelling degree was quantified by measuring the weights of the samples before and after immersing in toluene at room temperature for 24 h. The swelling degree was calculated from the following equation:

$$\text{Swelling degree}(\%) = (W_s - W_d)/W_d \times 100$$

where, W_d and W_s are the weights of the dry and swollen samples, respectively. Each value was taken as an average of three different measurements.

The compression strengths of the control and irradiated PDMS sheets were measured using a universal testing machine (UTM, Instron Model4210, Instron Engineering Co., USA) according to the ASTM Standard D575-91.

Thermogravimetric analysis (TGA) was carried out on a SDT Q600 analysis system (TA Instrument, USA) between 50 and 700 ℃ at a heating rate of 10 ℃/min under a nitrogen atmosphere. The decomposition temperature (T_d) in this measurement was defined as the temperature at which a 5% loss in mass was achieved.

Water contact angle measurements of the control and irradiated PDMS sheets were carried out using a contact angle analyzer (Pheonix 300, Surface Electro Optics Company). Redistilled water (10 μL) was gently placed on the samples. Each value of the contact angle was taken as the average value measured from five different samples fabricated under the same experimental conditions.

The surface chemical compositions of the control and irradiated PDMS sheets were characterized using an X-ray photoelectron spectrometer (XPS, MultiLab 2000, Thermo Electron Corporation, England) employing MgKα radiation. The applied power was 14.5 keV and 20 mA, and the base pressure in the analysis chamber was less than 10^{-9} mbar.

Results and Discussion

To investigate the effects of the mixing ratio of the base resin/curing agent on the swellability and wettability of PDMS sheets, the swelling degree measurement and water contact angle analysis were carried out and the results are shown in Figure 1. The swelling degree of the PDMS sheets varied from 84 to 145% based on the mixing ratio of the base resin/curing agent, and was the lowest at a mixing ratio of 10:1, which was proposed by Dow Corning. Thus, the optimized mixing ratio of the base resin/curing agent to obtain the most rigid PDMS in this study was 10:1. This effect of the base resin/curing agent ratio on the swellability may be attributed to the crosslinking density formed on PDMS sheets.[14] On the

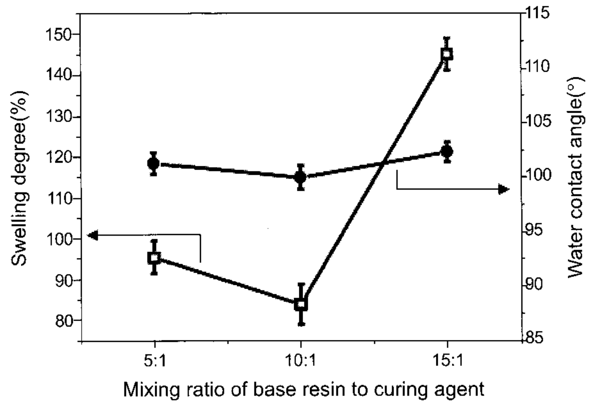

Figure 1. Swelling degree and contact angle of PDMS sheets with various mixing ratios of base resin/curing agent.

other hand, the contact angles were not changed significantly regardless of the mixing ratio, indicating that the mixing ratio did not affect the wettability of the PDMS. Thus, the PDMS sheets prepared with a common ratio of the base resin/curing agent (10:1) was selected for this experiment. The PDMS sheets were then modified using electron beam irradiation to enhance their physicochemical properties.

Changes in the swelling degree of PDMS sheets based on the absorbed dose are shown in Figure 2. The swelling degree of the control PDMS was 90%. For the irradiated PDMS sheets, the swelling degree was gradually decreased up to 66% with an increasing absorbed dose when compared to the control PDMS. This reduction in swellability of the PDMS sheets by electron beam irradiation may be explained by the fact that the crosslinking density of the PDMS suppressing its physical extension is further increased by the electron beam irradiation.[15]

The compressive strength of the PDMS sheets based on the absorbed dose is shown in Figure 3. The compressive strength of the control PDMS sheet was 2.9 MPa. On the other hand, for the irradiated PDMS sheets, the strengths were gradually increased up to 5.5 MPa with an increasing absorbed dose. This increase in the compressive strength may be ascribed to the formation of higher dense networks in the irradiated PDMS sheets, which may make the PDMS more rigid than the control PDMS.[16]

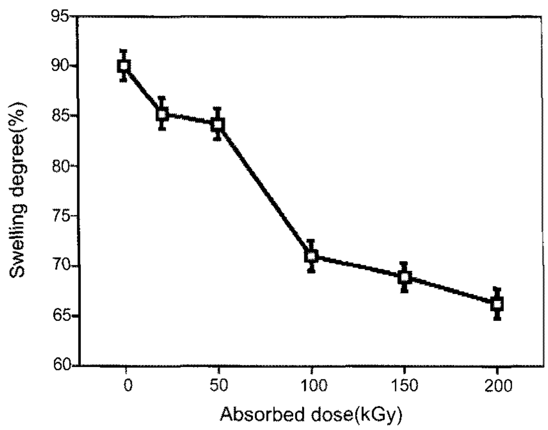

Figure 2. Swelling degree of PDMS sheets as a function of absorbed dose.

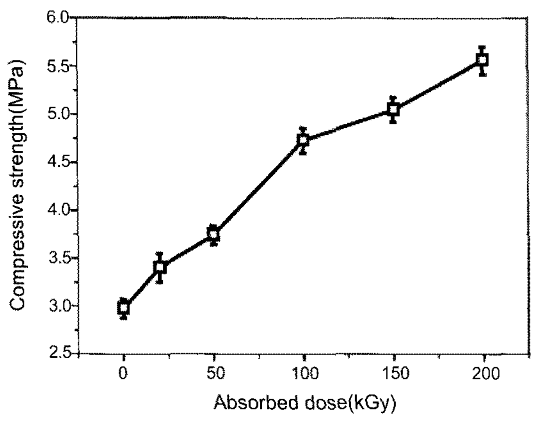

Figure 3. Compressive strength of PDMS sheets as a function of absorbed dose.

To investigate the influence of electron beam irradiation on the thermal decomposition, the control and irradiated PDMS sheets were investigated using TGA in a nitrogen atmosphere and the results are shown in Figure 4. The thermal degradation of all the samples created a one-stage weight loss. The T_d of the control PDMS sheet was 388.6 ℃. For the irradiated PDMS sheets, the T_d was increased up to 398.8 ℃ with an increasing absorbed dose in comparison to that of the control sheet. This increase in the T_d of the irradiated PDMS sheets can be attributed to a further increase in the crosslinking density of the PDMS sheet by electron beam irradiation, which could retard the thermal decomposition.

In order to examine the changes in the wettability of the PDMS sheets by electron beam irradiation, the control and irradiated PDMS sheets were analyzed by contact angle measurements and the results are shown in Figure 5. In comparison to the contact angle of the control PDMS sheet, 101°, the angles of the irradiated PDMS sheets were gradually decreased up to 75° with an increasing absorbed dose. This improved wettability of the irradiated PDMS sheets means that the PDMS surface becomes more hydrophilic due to the formation of hydrophilic groups caused by oxidation during the electron beam irradiation.[12]

The effects of electron beam irradiation on the chemical compositions of PDMS sheets were investigated by using a high resolution XPS and the results are shown in Figure 6. In comparison to the control PDMS sheet, the [O]/[Si] and [C]/[Si] atomic ratio of the irradiated PDMS surfaces increased with an increase in absorbed dose. The increase in

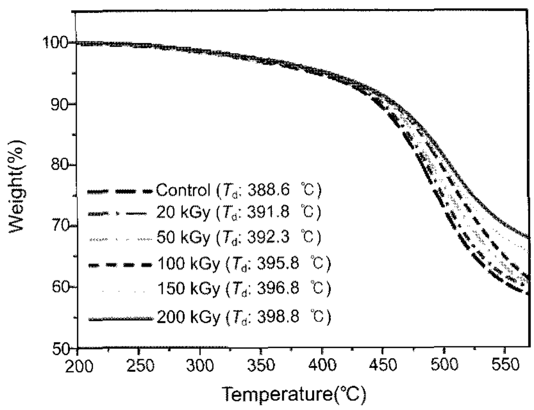

Figure 4. TGA curves and thermal decomposition temperatures (T_d) of the control and irradiated PDMS sheets.

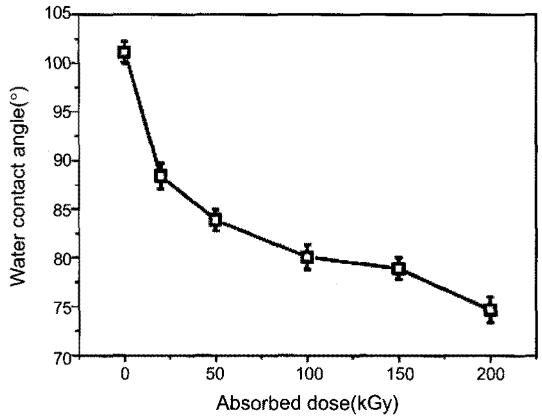

Figure 5. Contact angle of PDMS sheet as a function of absorbed dose.

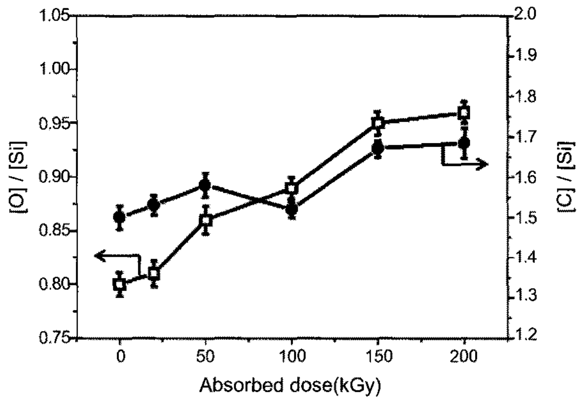

Figure 6. [O]/[Si] and [C]/[Si] atomic concentration ratio of PDMS sheet as a function of absorbed dose as obtained by XPS.

the [O]/[Si] atomic ratio of the irradiated PDMS means that hydrophilic groups were generated on the surface of the PDMS sheets during the electron beam irradiation. The formation of the hydrophilic groups could be attributed to the fact that the free radicals generated in the PDMS during the irradiation reacted with oxygen atoms in the air, and thus leading to oxidized PDMS sheets, which could be responsible for the improved wettability of the PDMS sheets.[13]

Conclusions

In this work, PDMS was successfully modified using electron beam irradiation. The swellability of the irradiated PDMS sheets was reduced and their compressive strengths and thermal decomposition temperatures were improved in comparison to those of the control sheet due to a further increase in the crosslinking density of the PDMS by the electron beam irradiation. Moreover, the wettability of the irradiated PDMS sheets was also enhanced owing to the generation of hydrophilic groups on the surface of the PDMS by oxidation during the electron beam irradiation. Therefore, this eco-friendly and simple technique can be a promising way to modify a PDMS for broader applications.

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References

1. Y. Wu, Y. Huang, and H. Ma, *J. Am. Chem. Soc.*, **129**, 7226 (2007).
2. H. Cong and T. Pan, *Adv. Funct. Mater.*, **18**, 1912 (2008).
3. Y. Zhang, E. A. Matsumoto, A. Peter, P.-C. Lin, R. D. Kamine, and S. Yang, *Nano Lett.*, **8**, 1192 (2008).
4. J. Tong, C. A. Simmons, and Y. Sun, *J. Micromech. Microeng.*, **18**, 037004 (2008).
5. P. Nandi, D. P. Desal, and S. M. Lunte, *Electrophoresis*, **31**, 1414 (2010).
6. H. Xu and J. Huskens, *Chem. Eur. J.*, **16**, 2342 (2010).
7. T. Kaufmann and B. J. Ravoo, *Polym. Chem.*, **1**, 371 (2010).
8. A. G. Chmielewski, M. Haji-Saeid, and S. Ahmed, *Nucl. Instrum. Methods Phys. Res. Sect. B*, **236**, 44 (2005).
9. J.-S. Lee, C.-H. Jung, S.-Y Jo, J.-H. Choi, I.-T. Hwang, Y.-C. Nho, Y.-M. Lee, and J.-S. Lee, *J. Polym. Sci. Part A: Polym. Chem.*, **48**, 2725 (2010).
10. H. M. Lee, Y. N. Kim, B. H. Kim, S. O. Kim, and S. O. Cho, *Adv. Mater.*, **20**, 2094 (2008).
11. I. Rezaeian, S. H. Jafari, P. Zahedi, M. Ghaffari, and S. Afradian, *Polym. Adv. Technol.*, **20**, 487 (2009).
12. S. Burkert, M. Kuntzsch, C. Bellmann, P. Uhlmann, and M. Stamm, *Appl. Surf. Sci.*, **255**, 6256 (2009).
13. A. M. Abdul-Kader, A. Turos, R. M. Radwan, and A. M. Kelany, *Appl. Surf. Sci.*, **255**, 7786 (2009).
14. S.-H. Choi, J.-H. Kim, and S.-B. Lee, *J. Membr. Sci.*, **229**, 54 (2007).
15. K. Yu and Y. Han, *Soft Matter*, **2**, 705 (2006).
16. A. S. Palsule, S. J. Clarson, and C. W. Widenhouse, *J. Inorg. Organomet. Polym.*, **18**, 207 (2008).