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Effect of irradiation on the cryogenic mechanical characteristics of polyurethane foam

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Abstract
The present study investigated thermal and mechanical characteristics of irradiated polyurethane foams (PUFs) according to the irradiation does under various temperature conditions, including low/cryogenic temperatures. Fourier transform infrared analysis was performed to obtain information on the PUF molecular structure. In addition, Macro- and microstructural investigations were carried out to determine the relationship between thermal and mechanical characteristics and irradiation dose. The test results were quantitatively presented, and it was found that the irradiated PUF has potential for application in industrial structures.

Keywords Irradiation · Irradiation dose · Polyurethane foam · Compressive behavior · Fourier transform infrared analysis · Thermal conductivity

Introduction

Research and practical applications of using radiation has been actively pursued in various industrial fields, since Charlesby discovered that polyethylene was cross-linked owing to radiation, in the 1950s [1]. Radiation does not require the application of a harmful catalyst, as contrasted with reactions with other general chemical additives; it is a clean means, and can cause chemical reactions even in solid state or at low temperatures. In addition, energy consumption is low because it can be processed in a short time [2]. Currently, radiation with these characteristics has a variety of important applications in medicine, industry, agriculture, food, diagnosis, and sterilization, as well as inspection and instrumentation. Among them, improving the performance of polymeric materials is the most popular application that utilizes radiation.

With the irradiation, high-energy radiation promotes various types of chemical reactions in the structure of the polymer. Electron-beam processing was often used in the irradiation of polymers to enhance their thermal and mechanical performance through electron-beam-induced polymer reactions, including cross-linking, scissioning, grafting, and curing, as shown in Fig. 1. *Cross-linking* is a technique in which the monomers are covalently bonded onto the polymer chain in the position of cross linkers, and *scissioning* is a degradation reaction that can be applied to biopolymers and occurs when the radicals that are terminated by reactions with oxygen/hydrogen and are formed fail to recombine. *Grafting* is a polymer reforming method in which different monomers react and attach onto the polymer chain to add the feature of the monomer to the polymer. Finally, *curing* is a polymerization reaction in low molecular weight molecules that occurs when the radicals that are formed initiate the polymerization of monomers and oligomers; it usually is associated with a coating or adhesive on the polymer. The result of these reactions is a change in the properties of the polymer. The effect of irradiation may also include changes in arrangement of molecular bonds as well as microstructure [3–8]. As a result of these changes, many recent studies have

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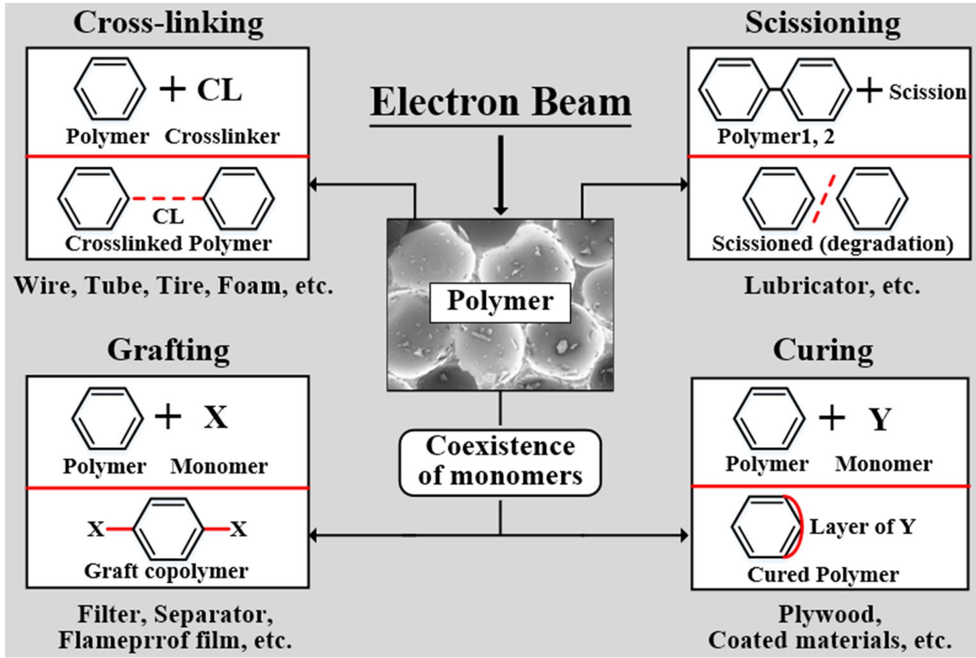


Fig. 1 Electron-beam-induced polymer reactions: cross-linking, scissioning, grafting, and curing

reported that chemical changes of the polymeric materials occur, affecting thermal and mechanical performance [9–11].

Because irradiation was reported to effect a difference in the thermal and mechanical properties of the polymer, in this study, the effect of irradiation on polyurethane foam (PUF) was investigated. PUFs have been extensively used in many fields, because PUF has many advantageous characteristics such as low thermal conductivity, good mechanical properties, and light weight [12]. PUF has been mainly used for the insulation of pipes that are used to transfer low-temperature materials in various types of power plants, and in liquefied petroleum gas (LPG) and liquefied natural gas (LNG) tank structures. Generally, LNG tanks in LNG carriers are operated in cryogenic conditions, and the insulation systems of these tanks are made of the polymeric material PUF. When the thermal and mechanical performances of the PUF are improved using irradiation, the thickness of the PUF layer is reduced. Accordingly, the amount of material to be stored or transported could be increased in accordance to the reduction in the insulation material density, thus leading to an overall increase in the economic efficiency [13].

Many studies have been conducted on the thermal and mechanical performance of irradiated PUF. In the past, mechanical properties (tensile properties) of polyurethane irradiated by gamma rays were investigated [14, 15], as well as the mechanical properties (tensile properties) of thermoplastic polyurethane irradiated with electron beams [16]. In addition, an experimental study of irradiated PUF under quasi-static and dynamic strain rates was conducted [17]; thermal characteristics and changes of irradiated PUF were investigated [16, 18, 19], and the thermal conductivity measurement of original PUF from room temperature to cryogenic temperatures was conducted [20]. The microstructure of radiation cross-linked polymer and microscopic characteristics of irradiated PUF by Fourier transform infrared analysis (FT-IR), Thermogravimetric Analysis (TGA), and scanning electron microscopy (SEM) were investigated [21–23]. However, no studies have been conducted on the mechanical behavior and thermal characteristics of irradiated PUFs under various temperature conditions including low/cryogenic temperatures. Therefore, in this study, to investigate the effect of irradiation on PUF, compression tests at quasi-static rates of loading and the thermal conductivity measurement of the irradiated PUF were performed and investigated according to the irradiation dose in various environments. In addition, FT-IR analysis was performed to obtain information on the PUF molecular structure. Macro- and microstructural investigations by SEM were carried out to determine the relationship between mechanical behavior and irradiation dose. The test results are quantitatively presented, and it was verified that the irradiated PUF has potential for application in industrial structures despite the relatively difficult irradiation process.

Experiments

Experimental preparations

In order to improve the thermal and mechanical performance of PUF, irradiation was conducted. The parameter set to investigate the effect of irradiation on the PUF was the irradiation dose. To irradiate the PUF, gamma-ray radiography equipment (MDS Nordion) with ^{60}Co as the source was used to irradiate the samples at various doses up to 900 kilo-gray (kGy) at an approximate dose rate of 10 kGy/h at room temperature. The irradiation time rate and the maximum irradiation time for one side were unified; a PUF irradiation process was conducted through the electron-beam-induced chemical reactions shown in Fig. 1. The irradiation doses by sample were 0, 150, 300, 500, 700, and 900 kGy, as shown in Fig. 2. The irradiation dose level including the highest dose and interval were set by referring to the previous studies on the mechanical performance of PUF according to irradiation dose [14, 24, 25]. The same intervals were set up to 900 kGy, simply centering on 500 kGy. Moreover, 150 kGy was set as the intermediate between 0 and 300 kGy. As shown in the figure, the difference in the irradiation dose of the specimens can be seen with the naked eye. The density of the original PUF used in this study was 140 kg/m^3 on average, and the density of the irradiated PUF was approximately 155 kg/m^3, an increase of approximately 10%.

Thermal conductivity measurement

To investigate the effect of irradiation on the thermal performance of PUF, the thermal conductivity measurement was performed according to the irradiation dose. For the experiment, laser flash analysis (LFA) was used; LFA is the most common method to determine the thermal diffusivity and specific heat of a variety of solid materials according to ASTM E1461 [26]. Figure 3 shows the experimental equipment (LFA 467) used to measure thermal conductivity.

An efficient method for determining thermal conductivity was used. As shown in the figure, one side of a sample was heated by a short energy light pulse. From the resulting temperature excursion of the rear part measured with a detector, both thermal diffusivity and specific heat were determined. The higher the thermal diffusivity of the sample, the faster the energy reaches the back side. Accordingly, the thermal conductivity of the sample was determined from the thermal diffusivity, which was measured by LFA, specific heat, and density as follows:

$$\lambda(T) = \alpha(T) * C_p(T) * \rho(T) \quad (1)$$

where λ is thermal conductivity, α is thermal diffusivity, C_p is specific heat, and ρ is bulk density. The specimens used in the thermal conductivity measurement were cut into rectangular parallelepipeds with dimensions of 10 mm × 10 mm × 2 mm. The experiments were carried out at room temperature. Each experiment was conducted five times (total number of experiments was 30) to ensure the reliability of the experimental results, and the experimental results were obtained by removing the maximum and minimum values to reduce experimental error.

FT-IR analysis

To obtain the spectroscopic characteristics of irradiated PUF, FT-IR analysis was performed by using the experimental equipment Spectrum GX. It was possible to determine the type of functional group present in the molecule through the position of the absorption band of the sample or qualitatively determine the concentration of the sample. Figure 4 shows a schematic diagram of the FT-IR spectrometer.

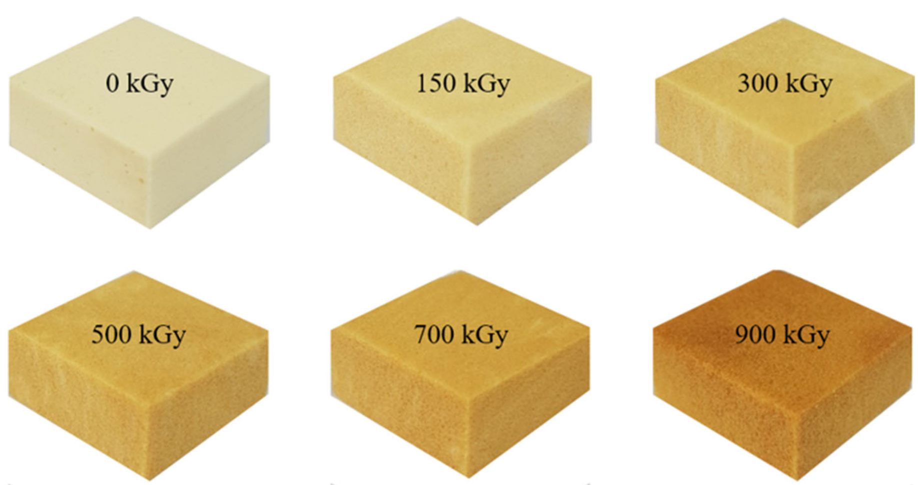


Fig. 2 Photographs of polyurethane foam specimens

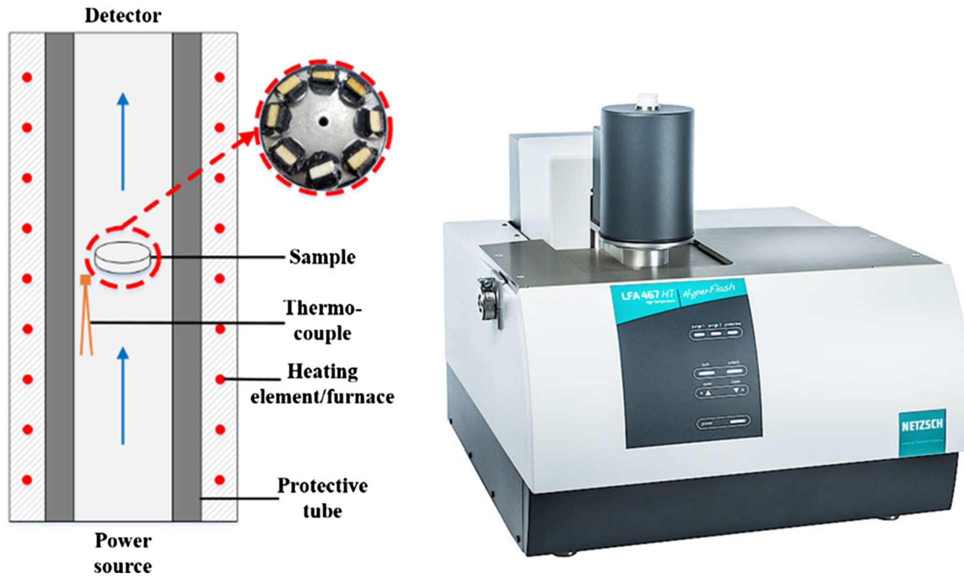


Fig. 3 Schematic and photograph of laser flash analysis used to measure the thermal characteristics of PUFs

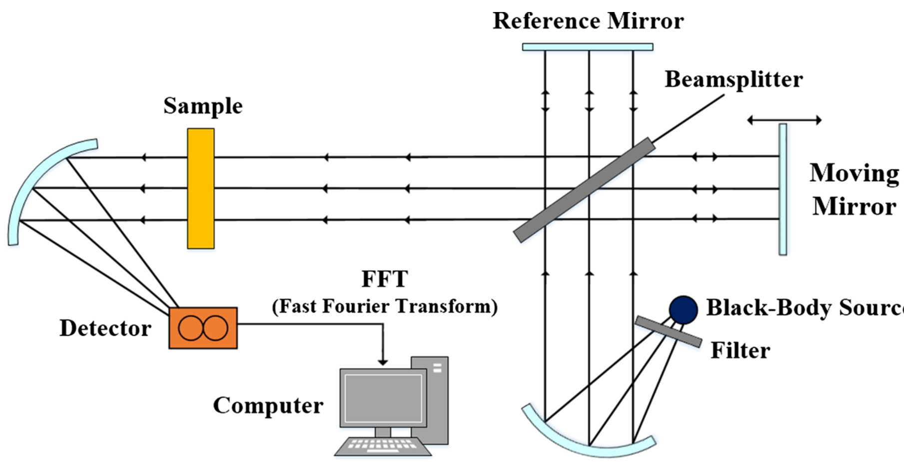


Fig. 4 Schematic diagram of FT-IR used to measure the spectroscopic characteristics of PUFs

The FT-IR spectrometer offers a fingerprint of the chemical bonds present within the materials. The mechanism of the chemical reaction and the detection of unstable substances can be investigated by reflecting infrared light on the sample. As shown in Fig. 4, an FT-IR spectrometer consists of a source, sample compartment, beam splitter, detector, and computer. The source generates radiation that passes through the beam splitter and the sample, and then reaches the detector. Then, the signal is converted to digital data by the detector. Eventually, the signal is transferred to a computer in which fast Fourier transform (FFT) is carried out. Accordingly, the spectra for the PUF were obtained by the FT-IR analysis. The analysis was conducted using mid-infrared light (wavelength of 4000–650 cm^{-1}) and setting the number of scenes to 32 to reduce noise.

Compression tests

In order to investigate the effect of radiation on the mechanical performance of irradiated PUF, compression tests were carried out by using a universal testing machine (KSU-5 M) in accordance with Korean standard KS M 3809 [27]. Figure 5 shows the schematic design of the experimental setup for the cryogenic compression tests. During the test, specimens were compressed between the top and bottom jigs in the cryogenic chamber after a 1-h pre-cooling process.

Because the mechanical behavior of foam materials depends strongly on the test temperature and strain rate, the compression tests under four temperature conditions including low/cryogenic temperatures (20, − 50, − 110, and − 163 °C) were conducted at two quasi-static strain rates (0.001 and 0.0001 s^{-1}) to investigate the mechanical properties of irradiated PUF. The test temperatures were selected to investigate the temperature-dependent failure

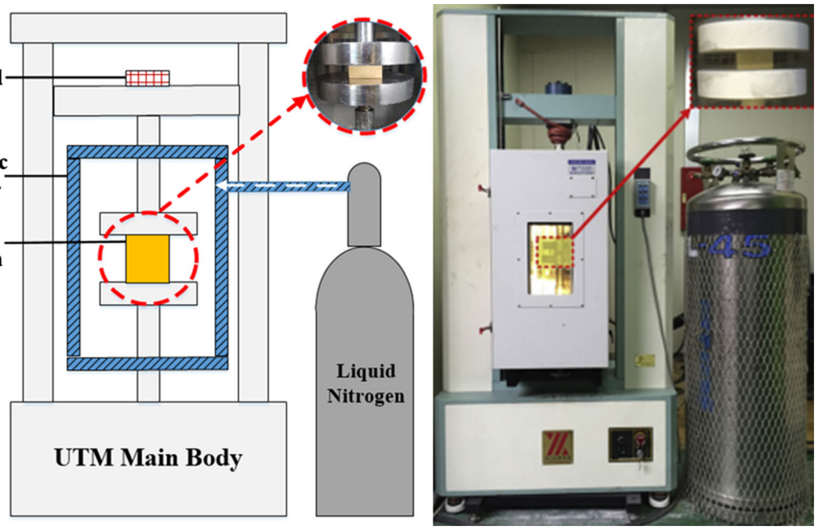


Fig. 5 Schematic design and photograph of universal testing machine used to measure the mechanical characteristics of PUFs

characteristics of PUF under room temperature (20 °C) and the operating temperatures of LPG (− 50 °C) and LNG (− 163 °C), which are representative cargoes that are stored or transported with PUF insulation, and a temperature (− 110 °C) between them.

The compressive stress–strain behavior of general polymeric materials, as shown in Fig. 6, was considered to reflect the hysteresis of the load element. As shown in the figure, compressive stress–strain behavior of polymeric materials simply consist of three regions: a linear elasticity region, a plateau region, and a densification region.

Prior to testing, the specimens were cut into rectangular parallelepipeds with dimensions of 50 mm × 50 mm × 25 mm. In addition, in the compression test, each experimental case was repeated five times (total number of experiments was 30) for reliability of the results, and the experimental results that had the maximum and minimum values were removed to reduce experimental error. In addition, a scanning electron microscope (SEM, Supra 25) at 1-μm scale was used to observe the PUF microstructure.

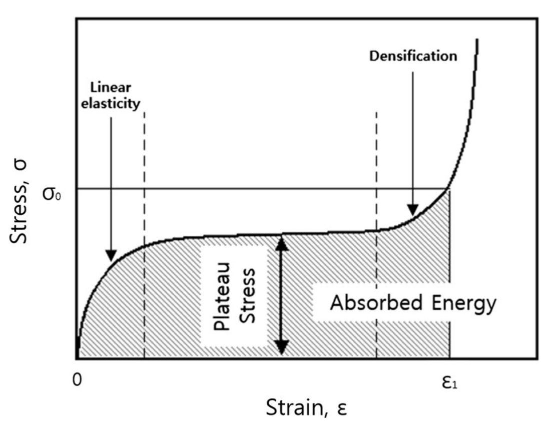


Fig. 6 Typical stress–strain behavior for porous foam material under compression

Results and discussion

Thermal characteristics of the irradiated PUF in thermal analysis

The thermal conductivity measurement of irradiated PUF was performed to investigate the thermal performance. Table 1 and Fig. 7 show the quantitative thermal conductivity results for irradiated PUF according to irradiation dose. The standard deviations of the data samples estimated from the five repetitions of the conducted tests have been inserted as error bars in the figure. As shown in the figure, it can be seen that these deviations are significantly low. For this reason, thermal analyses results are discussed and evaluated based on the elicited mean values. When the irradiation dose was increased from 150 to 500 kGy, the thermal conductivity gradually decreased and the performance was found to be excellent. At 500 kGy, the thermal conductivity was not better than that of the original specimen, exhibiting the same value of 0.03 W/mK. Above 500 kGy, the thermal conductivity increased again as the irradiation dose was increased. In particular, the ratio of thermal conductivity for the PUF irradiated with 150 kGy to that of the original PUF was 140%, and the ratio for the PUF irradiated with 900 kGy to that of the original PUF was 127%. This was a large increase in terms of thermal conductivity. In general, it is known that materials having a cell structure such as a PUF have different thermal characteristics depending on bulk density. However, the density of the irradiated PUF was only approximately 10% higher than that of the original PUF.

As a result, it was found that the irradiated PUF exhibited higher thermal conductivity than that of the original PUF. These results suggest that the change of molecular bonding through irradiation may improve the

Table 1 Thermal conductivity and ratios according to each tested irradiated PUF

Irradiation dose (kGy)	Thermal conductivity (W/mK)	Irradiated/original
0	0.03	1
150	0.042	1.4
300	0.033	1.1
500	0.03	1
700	0.036	1.2
900	0.038	1.27

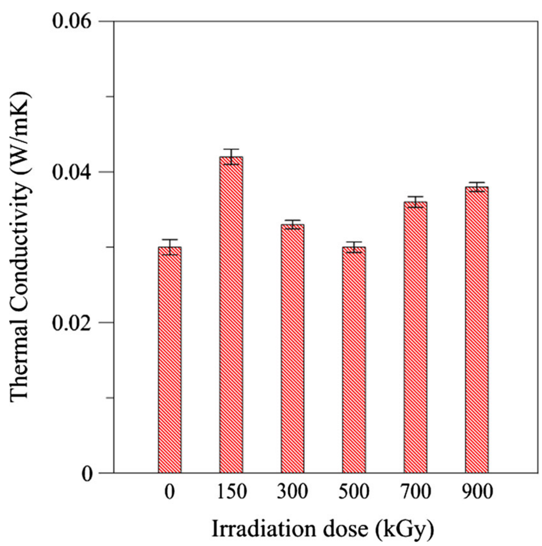


Fig. 7 Thermal conductivity of PUF at a room temperature for different irradiation doses

mechanical performance, but it may result in heat transfer resistance in the interior and obstruct thermal conduction. It is considered that the influence of the strut, cell size, and arrangement of PUF affect the thermal conductivity. Moreover, it was described in detail in the microscopic characteristics chapter. It is important to find the optimum point that is more economical because the deterioration of the thermal performance of the insulation system means that the amount of material to be transported or stored is reduced.

Spectroscopic characteristics of the irradiated PUF in FT-IR analysis

FT-IR analysis of the PUF was performed to investigate spectroscopic characteristics such as the molecular structure of irradiated PUF. Figure 8 shows the results of FT-IR spectra for irradiated PUF according to irradiation dose. In the figure, it was confirmed that the compound was a carboxylic acid compound having C=O and O–H bonds, and the presence of the urethane bond was observed in all the FT-IR spectra of the original and irradiated PUF. In addition, the region below 1500 cm^{-1} is the fingerprint portion of the IR spectrum because peaks due to stretching and bending vibration overlap, and the spectrum is much more complicated than in other regions. Thus, this region was not considered because it is used eventually to identify a substance or to determine whether two compounds are identical.

When irradiation doses were below 500 kGy, no significant changes were found in the IR spectra compared to the original PUF. However, as the irradiation doses increased after 500 kGy, changes took place in the IR spectra. Meanwhile, at irradiation doses of 700 and 900 kGy, the O–H bond (alcohols) observed near 3670 cm^{-1} and C–O bond (alcohols) observed between 1050 and 1070 cm^{-1} were considerably increased; the two bands distinctly observed between 2900 and 3000 cm^{-1} were attributed to symmetric and non-symmetric stretching of the C–H bond (alkanes), which is considered to affect the material properties. Furthermore, at higher irradiation doses, a decrease in the C=O stretch (carbonyl group) peak near 1700 cm-1 and an increase in the C–H stretch near 2900 cm^{-1} and the C–O–C syn-stretch peak near 1050 cm^{-1} indicate that the carbonyl group breaks and bonds to carbon in either form at other positions. As a result, these bonds also lead to the formation of a complex network with branches, which appears to influence the improvement in mechanical strength. Accordingly, irradiated PUF may have stronger bonds owing to gamma irradiation than bonds in unirradiated PUF.

It can also be seen that even if the strength of the double bonds was decreased, a stronger single-bond strength does not adversely affect the material performance. In addition, the C≡N stretching bond (nitriles) near 2250 cm^{-1} and C≡C bond (alkynes) near 3300 cm^{-1} were apparent. It is thought that these polymers can have better mechanical properties such as elastic modulus and compressive strength before the PUF is completely broken because the two peaks are relatively large, and the bonds are strong when irradiated at 300 kGy. In general, polymers with complex structures such as random branching and cross linking have higher strength and toughness than linear polymers. As the branched part increases in the polymer structure, the structure of the polymer becomes more complicated, leading to an improvement in mechanical

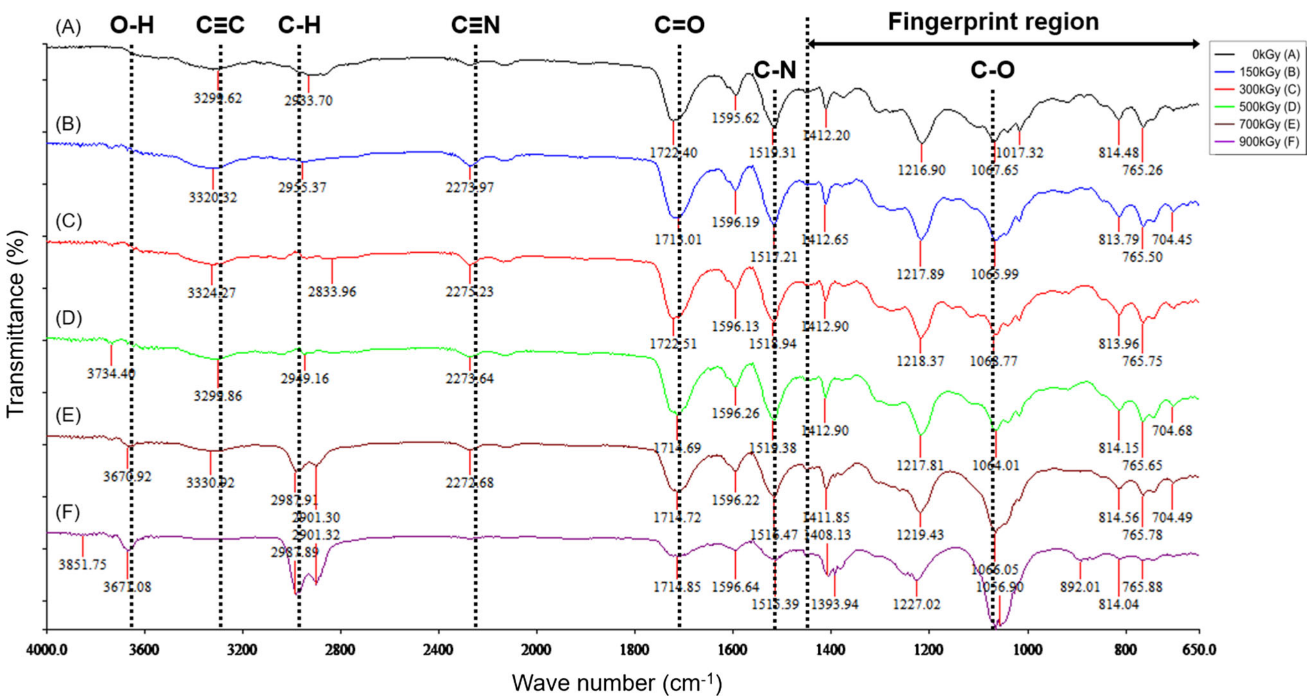


Fig. 8 FT-IR spectra for PUF at different irradiation doses

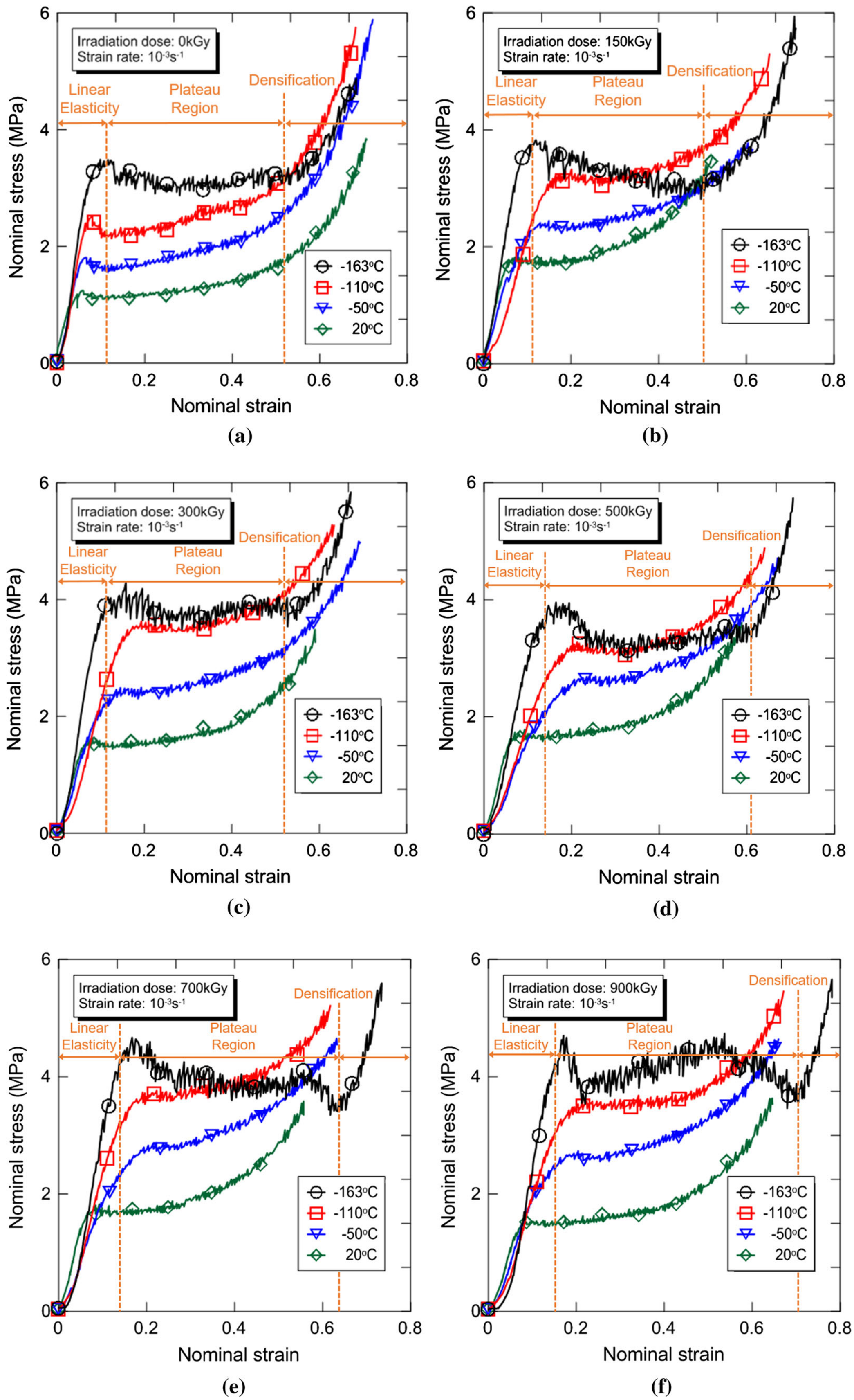
strength [28]. Studies using high-energy radiations, such as gamma-rays, have been reported for inducing branching in polymers. In these studies, a chain-branched polymer structure is formed by free-radical reactions through gamma irradiation [29, 30]. By a similar process, PUF is also expected to form a branched structure. When the irradiation does was increased to 300 kGy, an increase in the peak of 2275 cm^{-1} indicates an increase in the NCO group (cyanate group). It seems that the NCO group is regenerated owing to the breakage of bonds in PUF by irradiation, and seems to contribute to the formation of a branched structure by easily forming bonds with other parts because of the high reactivity of this group. Unlike the inferences of the other cited references, and although other peaks appeared in this study, the evoked results seem to have influenced the mechanical performance of the polymer, based on FT–IR analyses. Therefore, it is believed that the appropriate bond breakage induced by irradiation increases the complexity of the structure and contributes to an increased mechanical strength.

Mechanical characteristics of the irradiated PUF in compression testing

Compression tests was conducted under various temperatures to investigate the effect of irradiation dose. The stress–strain behavior according to irradiation dose was investigated. The results reveal a significant change in the mechanical properties of irradiated PUF. Figures 9 and 10 show the temperature-dependent stress–strain relationships of the tested PUFs at strain rates of 0.001 and 0.0001 s^{-1} at different irradiation doses. In addition, the compressive stress, defined as the maximum value between 0 and 15% deformation, and the elastic modulus were obtained by a linear regression at different temperatures and irradiation doses, as summarized in Tables 2 and 3 and Figs. 11 and 12 [31].

The mechanical performance of irradiated PUF improves as the temperature approaches the cryogenic temperature, as it does for a general PUF, because the bonding between cells becomes more rigid as the temperature decreases. Several interesting results were found through the calculation of compressive stress and elastic modulus of the irradiated PUF according to irradiation dose. The most prominent result is that the mechanical properties of the irradiated PUF were better than those of the general PUF except for two cases at − 110 °C, as shown in Fig. 11.

The ratios of strength of irradiated PUF and original PUF are shown in Table 4 when the rate of strength increase was a maximum value at each temperature. The data obtained from each test were obtained through several steps to ensure reliability and consistency; thus, it is considered that additional uncertainty analysis is not necessary. As shown in the table, the maximum rates of increase were observed for the specimens irradiated at 300 kGy at all temperatures except − 110 °C. When the samples were irradiated at 300 kGy, the strength increased by 172%


Irradiation dose: 0kGy
Strain rate: 10-3s-1
Linear Elasticity
Plateau Region
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(a)
Irradiation dose: 150kGy
Strain rate: 10-3s-1
Linear Elasticity
Plateau Region
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(b)
Irradiation dose: 300kGy
Strain rate: 10-3s-1
Linear Elasticity
Plateau Region
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(c)
Irradiation dose: 500kGy
Strain rate: 10-3s-1
Linear Elasticity
Plateau Region
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(d)
Irradiation dose: 700kGy
Strain rate: 10-3s-1
Linear Elasticity
Plateau Region
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(e)
Irradiation dose: 900kGy
Strain rate: 10-3s-1
Linear Elasticity
Plateau Region
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(f)

◀ **Fig. 9** Temperature-dependent stress–strain behaviors of PUF at a strain rate of 0.001 s^{-1} at different irradiation doses. **a** 0 kGy. **b** 150 kGy. **c** 300 kGy. **d** 500 kGy. **e** 700 kGy. **f** 900 kGy

compared to the original PUF in the cryogenic compression test at − 163 °C. The increase rate of this strength was a remarkably high value in terms of mechanical performance, and it is expected that it would be highly economical if it were applied to actual industrial structures.

It can be seen that an increase in irradiation doses does not always improve the mechanical properties, and there were several cases of irradiation doses that improve performance for each temperature. For example, as shown in the stress–strain behavior obtained by the cryogenic compression test, the PUF irradiated at 900 kGy showed the second-best strength at − 163 °C, compared to the results at other irradiation doses, but nearly the worst performance in cases of other temperatures. In addition, for specimens irradiated at 900 kGy, the thermal conductivity was relatively good compared to that of irradiation at 300 kGy, but the strength in the cryogenic environment was also similar to that for irradiation at 300 kGy. It was a highly interesting result in that the most effective performance was obtained at the temperature of − 163 °C when irradiated at 900 kGy. As a result, while the thermal performance of irradiated PUF is deteriorated owing to the influence of irradiation, the mechanical performance is relatively enhanced. Thus, irradiated PUF may be an attractive substitute for existing insulation materials.

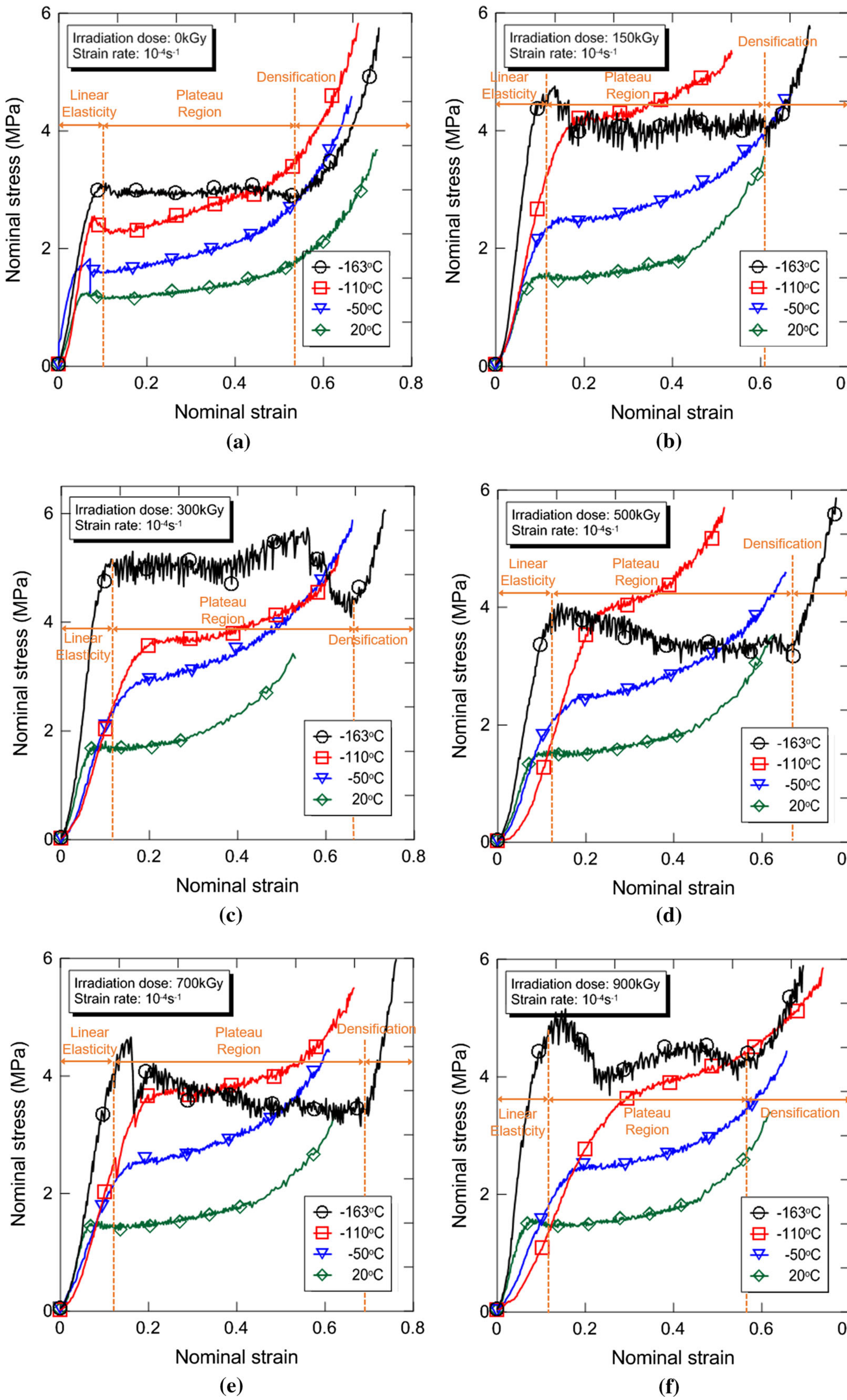
In terms of overall trends, both strength and elastic modulus tended to be lowest at 500 kGy of radiation and gradually increased before and after it. Even at the inflection point, although the thermal conductivity at 500 kGy was the same as that of the original PUF, the strength increased to 134% at room temperature and 133% at cryogenic temperature. As a result, it can be seen that irradiation certainly helps to prevent fragmentation of the polymer chain. In addition, it can be known that the mechanical properties of irradiated PUF are not improved unconditionally as the irradiation dose increases, and the performance up to the inflection point of a certain density becomes worse and improves considerably before and after this point. The performance before and after this point differs depending on the temperature, and it is important to use the most efficient irradiation dose according to each temperature. Furthermore, the elastic modulus of the original PUF was the smallest at room temperature, whereas it was much more easily deformed in the linear elasticity region at − 50 and − 110 °C. Because the elastic modulus of the original PUF was greater than that of irradiated PUF, it was considered that the design should be appropriate for the characteristics of the structure according to the allowable stress design.

In general, the closer it is to cryogenic temperatures, the more delayed is the starting point of densification and the greater the amount of energy absorbed at the starting point of densification. Here, densification indicates that after the flat region ends, the cell collapses and stress begins to increase with the strain. Consequently, it can be seen that the energy absorption characteristics of irradiated PUF increased as the temperature approached a cryogenic environment regardless of the strain rate. As contrasted with other temperatures, the behavior at − 163 °C show an unprecedented phenomenon in that densification occurs after the stress decreases in the plateau region, and the plateau region was not clearly visible; even the stress decreased during strain increase. It was considered necessary to consider other environmental variables for compression behavior at the cryogenic temperatures. For polymeric materials, deformation and fracture under compression were mainly controlled by the following main reasons: bending of the cell and stretching of the membrane windows [32]. As the deformation gradually increases at low temperatures, the cell under bending and the thin membrane window under stretching can be more easily ruptured because these are more easily deformed and more susceptible to brittle crushing and fracture at a faster deformation rate.

Macroscopic characteristics of irradiated PUF

The macrostructure of the test specimens was observed after testing because it was expected that the breakage pattern of the surface of the PUF would be different after the test. Figure 13 presents images of irradiated PUF specimens after the compression test from room temperature to cryogenic temperature. As shown in the previously described test results, the irradiated PUF specimens were deformed without any breakage or failure at 20 and − 50 °C. On the other hand, the specimens were broken at − 110 and − 163 °C in all cases. In particular, at − 163 °C, the structures of all specimens were completely broken and crushed. As a result, it can be confirmed that the embrittlement of PUF having a cell structure easily occurs on the surface and interior of the specimens as the temperature decreases to cryogenic temperature.

When the sample was irradiated, embrittlement occurred noticeably at -110 °C as the irradiation dose increased. It can be seen that the embrittlement became worse even as the irradiation dose increased. In particular, in the case of a irradiation dose of 900 kGy, significant breakage occurred because of the brittle crushing of structures at cryogenic temperature. The reason is explained for the behavior where densification occurs after the stress decreases in the


Irradiation dose: 0kGy
Strain rate: 10-4s-1
Linear Elasticity
Plateau Region
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(a)
Irradiation dose: 150kGy
Strain rate: 10-4s-1
Linear Elasticity
Plateau Region
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(b)
Irradiation dose: 300kGy
Strain rate: 10-4s-1
Plateau Region
Linear Elasticity
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(c)
Irradiation dose: 500kGy
Strain rate: 10-4s-1
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Linear Elasticity
Plateau Region
Densification
-163°C
-110°C
-50°C
20°C
Nominal stress (MPa)
Nominal strain
(f)

◀**Fig. 10** Temperature-dependent stress–strain behaviors of PUF at a strain rate of 0.0001 s^{-1} at different irradiation doses. **a** 0 kGy. **b** 150 kGy. **c** 300 kGy. **d** 500 kGy. **e** 700 kGy. **f** 900 kGy

plateau region, and the plateau region was not clearly visible in the stress–strain behavior in the case of 900 kGy at cryogenic temperatures.

Microscopic characteristics of the irradiated PUF in SEM analysis

The microstructure of the test specimens before testing was observed because it was predicted that the cell structure would be changed by irradiation with respect to the mechanical characteristics of the polymer. As mentioned previously, the polymeric materials were mainly fractured

Table 2 Compressive stress for each tested specimen

Compressive stress (MPa)												
Irradiation dose (kGy)	0		150		300		500		700		900	
Strain rate (s^{-1})	0.001	0.0001	0.001	0.0001	0.001	0.0001	0.001	0.0001	0.001	0.0001	0.001	0.0001
Temperature (°C)												
20	1.33	1.29	1.86	1.59	1.61	1.84	1.79	1.61	1.83	1.59	1.59	1.62
− 50	1.82	1.83	2.47	2.55	2.49	2.76	2.22	2.29	2.48	2.49	2.55	2.27
− 110	2.58	2.55	3.07	3.97	3.37	3.15	2.79	2.47	3.42	3.09	3.97	2.05
− 163	3.52	3.11	3.87	4.80	4.21	5.34	3.91	4.17	4.45	4.70	4.80	5.12

Table 3 Elastic modulus for each tested specimen

Elastic modulus (MPa)												
Irradiation dose (kGy)	0		150		300		500		700		900	
Strain rate (s^{-1})	0.001	0.0001	0.001	0.0001	0.001	0.0001	0.001	0.0001	0.001	0.0001	0.001	0.0001
Temperature (°C)												
20	25.6	25.6	36.9	25.5	31.4	35.1	34.5	26.0	35.1	32.8	27.4	29.0
− 50	40.7	38.9	21.7	27.1	23.8	26.8	17.2	20.3	21.1	20.3	22.9	17.2
− 110	51.6	51.1	25.0	34.4	28.7	25.5	19.7	25.0	28.6	23.9	24.7	16.9
− 163	56.5	49.9	47.0	65.3	48.9	63.8	36.7	42.6	43.5	43.1	41.8	70.4

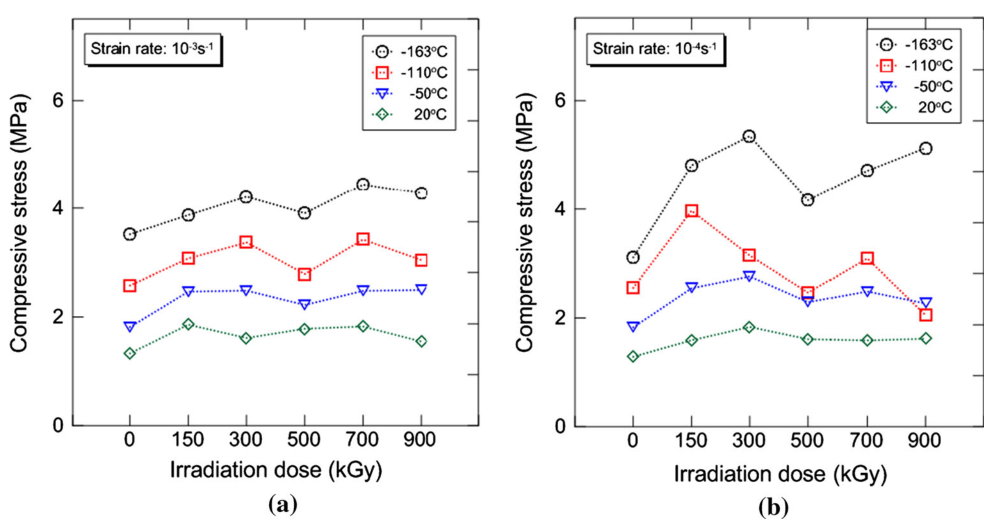

Fig. 11 Irradiation dose-dependent compressive stress of irradiated PUF at a different temperatures and strain rates. **a** 0.001 s^{-1}. **b** 0.0001 s^{-1}

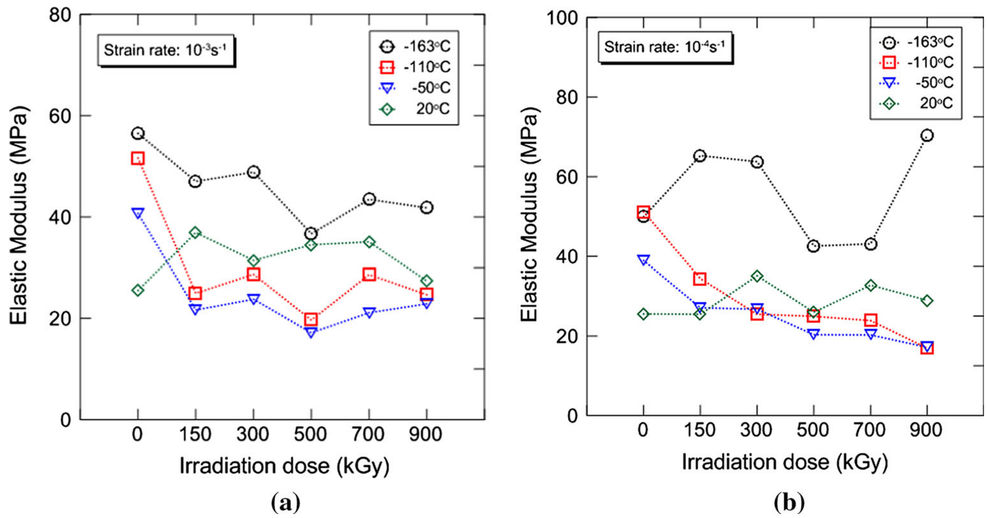

Fig. 12 Irradiation dose-dependent elastic modulus of irradiated PUF at a different temperatures and strain rates. **a** 0.001 s^{-1}. **b** 0.0001 s^{-1}

Table 4 Ratio of strength of irradiated PUF to original PUF when the rate of increase in the strength was the maximum value at each temperature

Temperature (°C)	Irradiation dose (kGy)	Irradiated/original
20	300	1.42
− 50	300	1.51
− 110	150	1.55
− 163	300	1.72

where the cell and membrane windows no longer could withstand a load.

Figure 14 shows SEM images of PUF at 50× magnification before the compression test with regard to the loading direction. As a representative feature, compared to the original specimen, as the irradiation dose increases, the cells become more rounded and intact, and less membrane window was formed. In the cases of 700 and 900 kGy, a large amount of strut connecting cell to cell was distributed. For this reason, it seems that the structure of the cell was modified by cross-linking according to irradiation. In general, as the number of struts increases, the thermal conductivity of the PUF increases as the thermal conductivity through the strut increases. In addition, the mechanical characteristics were different according to the cell size and arrangement and the formation of the membrane window.

In terms of thermal conductivity, a large amount of strut was distributed at 700 and 900 kGy, and the cell size and shape were different from those at 0–300 kGy. On the other hand, in the case of 500 kGy, a small amount of strut was distributed, and cell was small and dense compared with the SEM images of other cases. This result can be verified by thermal conductivity measurement, which shows the same level of thermal conductivity compared to the original specimen at 500 kGy with a significant improvement in strength.

In terms of mechanical properties, a large membrane window was formed, and the wrinkles are considerably large, and even the cells were broken or crushed at 0, 150, and 500 kGy. As a result, it can be seen that the deformation of the cell and the generation of the window due to the change of the molecular structure rapidly accelerate the rupture of the cell wall. Accordingly, as the compressive test progressed, holes were formed in the cell to cause brittle fracture, which can be seen from the experimental results. However, it was difficult to clearly identify the reason why the performance was excellent at 300 kGy compared with the other cases. In the case of 300 kGy, the membrane window was relatively less distributed and intact cells were formed because the strut was not distributed in large quantity compared with the other cases. The presence of struts can explain the improvement in the mechanical performance of PUF [33, 34]. In addition, the failure behavior of porous materials is also influenced by the distribution of struts [35]. In general, the process by which the cell structure collapses involves bending, compression, and other phenomena. The reason why the presence and distribution of the strut affect the mechanical performance seems to be because it prevents the collapse of cells by providing support and a connection between cells. For this reason, it was considered that it affected the improvement of the mechanical performance. Finally, in the cases of 700 and 900 kGy, although the cell was fairly intact, it was considered that the strut, which is distributed too much between the cells, adversely affected the mechanical performance.

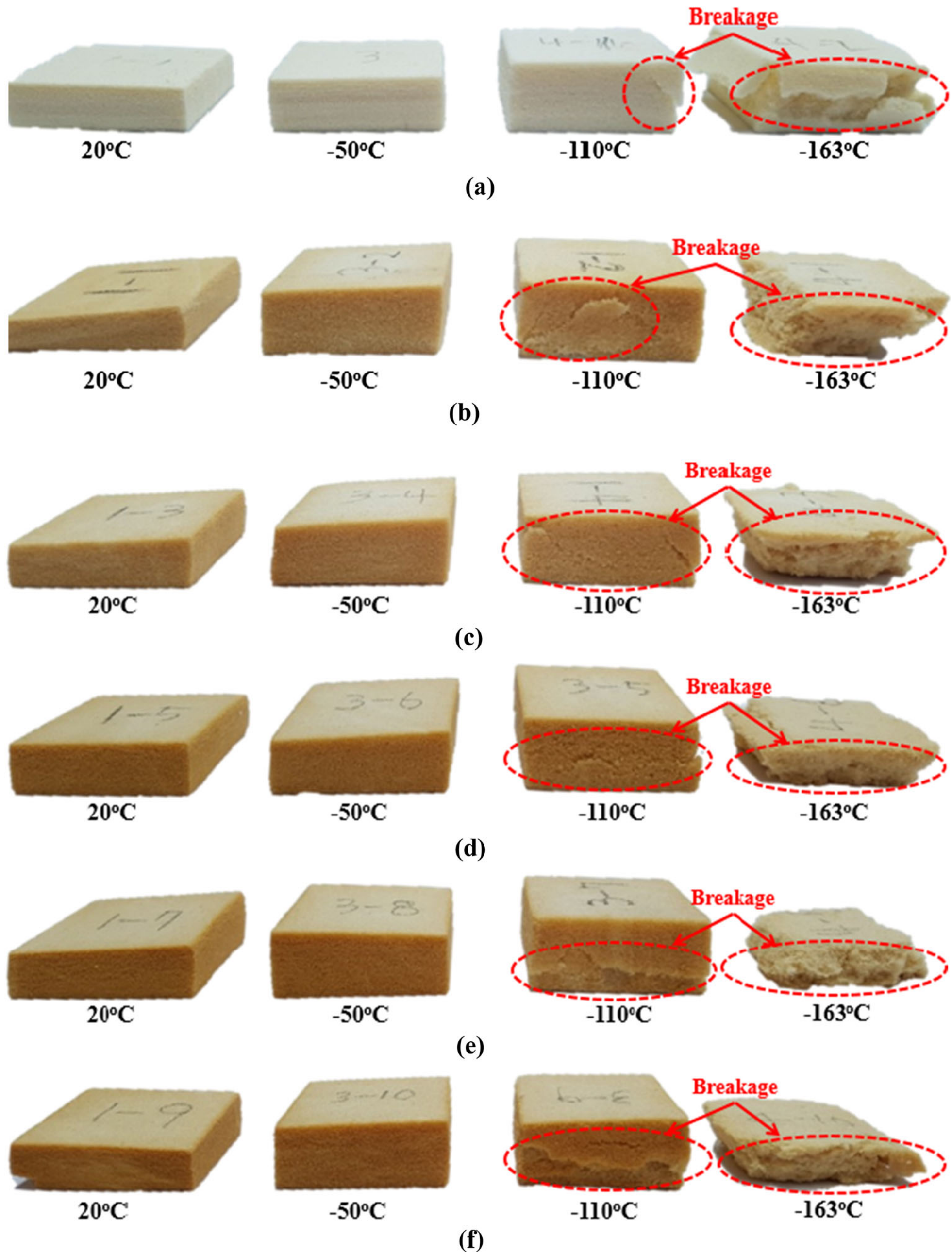

Fig. 13 Macrostructure of polyurethane foams at different irradiation doses after testing. **a** 0 kGy. **b** 150 kGy. **c** 300 kGy. **d** 500 kGy. **e** 700 kGy. **f** 900 kGy

Conclusions

In this study, to improve the thermal and mechanical performance of the PUF, irradiation was conducted. Accordingly, thermal conductivity measurement and compression tests at quasi-static rates of loading on irradiated PUF were performed to investigate its performance. In addition, information on the molecular structure of the samples was obtained through FT-IR analysis, and the macro- and microstructures of the test specimens were observed. The main results are summarized as follows:

- At higher irradiation doses, a decrease in the C=O stretch peak and an increase in the C–H stretch and the COC syn-stretch indicate that the carbonyl group breaks and bonds to carbon in either form at other positions. Accordingly, these bonds also lead to the formation of a complex network with branches, which appears to influence the improvement in mechanical strength.
- Mechanical properties of the irradiated PUF are better than those of the original PUF. The thermal conductivity slightly increases compared to the original PUF, but the strength increases considerably in the

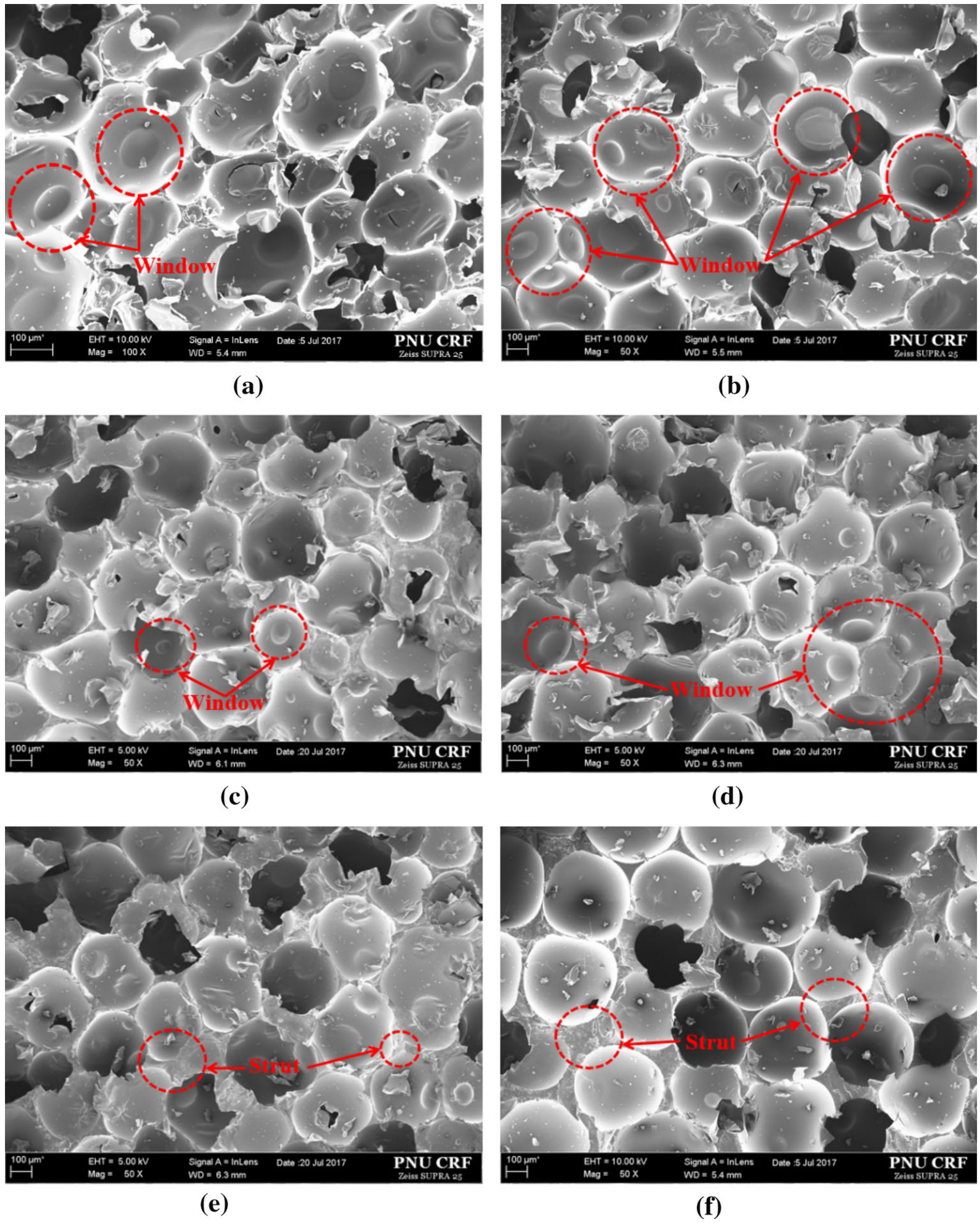

Fig. 14 Microstructure of polyurethane foams at different irradiation doses. **a** 0 kGy. **b** 150 kGy. **c** 300 kGy. **d** 500 kGy. **e** 700 kGy. **f** 900 kGy

compression tests performed from room to cryogenic temperatures. The increase rate of this strength is a remarkably high value in terms of mechanical performance, and it is expected that it will be highly economical if it were applied to actual industrial structures.

- As contrasted with other temperatures, the behavior at cryogenic temperatures show an unprecedented phenomenon that densification occurs after the stress decreases in the plateau region, and the plateau region is not clearly visible and even the stress decreases during strain increase. It was considered necessary to consider other environmental variables for compression behavior at cryogenic temperatures.
- When the irradiation was increased to 300 kGy, an increase in the peak indicates an increase in the NCO group (cyanate group). It seems that the NCO group is regenerated due to the breakage of bonds in PUF by irradiation, and seems to contribute to the formation of branch structure by forming bonds with other parts easily due to high reactivity of this group. Therefore, it is believed that the appropriate bond breakage by irradiation increases the structure complexity and contributes to high mechanical strength.

In conclusion, we examined the effect of the gamma irradiation dose in this study. As a future work, we will conduct a study using neutron rays and proton beam, and a comparative analysis of the radiation effects on the polymer to obtain the best source and dose will be performed.

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