Depth-Gradient and Photoinitiator-Free Photocrosslinking of Poly(ethylene oxide)

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ABSTRACT: Poly(ethylene oxide) (PEO) films are photocrosslinked by continuous UV irradiation without photoinitiators. Maximum gel fraction and swelling of the photocrosslinked PEO films reach up to about 38.8% and 2824%, respectively. From NMR analysis, the photocrosslinking mechanism of PEO can be attributed to recombination between methine radicals, which are generated from the polymer chain by hydrogen abstraction. However, the relatively low degree of crosslinking is attributed to more facile photooxidation of the generated radicals and concomitant photo-scission of the crosslinks. Depth-gradient crosslinked structure can be formed by inherent UV absorption and successive photoscission of the crosslinked polymer surface, which can be made uniform by adjusting UV energy. The photocrosslinked PEO shows the higher glass transition temperature as much as 7.3°C coupled with significantly enhanced storage modulus and thermal stability. The lower crystallinity causes by the reduced recrystallizability of the crosslinked polymer chains in melt. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2659–2667, 2012

Key words: poly(ethylene oxide); photocrosslinking; gel fraction; swelling; hydrogen abstraction; depth-gradient crosslinking

INTRODUCTION

To obtain functional properties such as thermal stability, mechanical strength, degree of swelling, and permeability, polymers can be modified by various photon related methods such photoirradiation, photocrosslinking, and photografting.[1] The photocrosslinking usually requires that the polymers contain photoreactive side groups or photosensitizer or photoinitiator, which can induce photogeneration of radicals. Photocrosslinking of macromolecules usually form three dimensional polymer gels structures, which can be swellable but insoluble by solvents.

Poly(ethylene oxide) (PEO) or poly(ethylene glycol) (PEG) are biocompatible, nonionic, water-soluble polymers of considerable industrial significance. Water insolubility of crosslinked polymer is required for various application fields such as wound dressings, controlled release drugs delivery systems, phase transfer catalysts, semipermeable membranes, solid electrolytes and separators for batteries, and many others. An essential drawback of PEO or PEG

hydrogels is the inevitable decrease in mechanical strength observed in the water-swollen state due to the inherent water solubility. An attempt to improve the gel strength is to introduce a hydrophobic component in the polymer structure, which reduces the hydrophilicity and usually results in an unacceptable drop in the equilibrium water content. Polymer hydrogels can be obtained by some crosslinking methods including thermal or chemical crosslinking and radiation crosslinking under ionizing or noninonizing electromagnetic irradiation.

The thermal crosslinking methods were carried out by the reaction of two hydroxyl terminal groups of PEO with crosslinkers such as aromatic triisocyanate, or diepoxide.[2,3] Their demerits were the low degree of crosslinking, high crosslinking temperature, the miscibility of crosslinkers and organic solvents in PEO. The PEO can be crosslinked in the molten state with dialkyl peroxide at 160°C for 15 min by the coupling of the abstracted polymer radicals by the peroxide.[4] However, the thermally crosslinked PEO can give low crosslinking efficiency and phase separation of the peroxide and PEO due to high temperature treatment. In the chemical crosslinking methods, the PEG were derivatized to 4-arms-PEG-vinylsulfone and PEG-diester-dithiol for the preparation of hydrogel scaffolds.[5] The crosslinkable triblock copolymer such as poly(lactide-*co*-ethylene oxide-*co*-fumarate) and poly(amidoamine-ethylene glycol-amidoamine) has been crosslinked with methylene bisacrylamide or diacrylamide crosslinker

for the enzymatically degradable or sensitive hydrogels.[6,7] A polyacrylate/PEG interpenetrating network hydrogel was also prepared.[8] The thermal or chemical polymer crosslinking may have some limitations such as high temperature miscibility of crosslinkers, heat-sensitivity of polymers, the need to separate synthesis of copolymer derivatives and crosslinking, uniform heat transfer requirement and removal of unreacted chemicals such as crosslinker or byproducts.

In radiation crosslinking, ionizing radiations are known to lead to either the structurization of polymers or radiation degradation. The PEO is classified as predominantly crosslinkable polymer on exposure to ionizing radiation.[9,10] The gamma and electron beam radiation were used with aqueous PEO solutions. The adsorption capacity and release of active substance have been used for drug delivery system, wound dressing or metal sorption and separation.[11–13] The crosslinked PEO hydrogels under gamma irradiation can give a gel fraction of 70% or more and a swelling of 16,000%. Hydrogels for wound dressing or superabsorbent, having 70–92% gel fraction and 2000–24,000% maximum swelling, have been prepared using gamma or electron beam irradiation by blending poly(vinylpyrrlidone) (PVP), poly(ethylene glycol) (PEG), or poly(vinyl alcohol) (PVA) with agar, kappa-carrageenan, or tragacanth.[14–18] When aqueous solution of PEO is subjected to the ionizing radiation, the hydroxyl radicals is produced by radiolysis of water, which can abstract hydrogen atom from the polymer chains leading to the formation and recombination of PEO macroradicals.

The liquid state crosslinking by gamma and electron beam radiation is relatively insensitive to the sample thickness even in the absence of photosensitive groups. Under ionizing radiation, the scission reaction of solid PEO in the presence of oxygen was dominated than in vacuum, where the competition between degradation and crosslinking under vacuum irradiation depended on the applied dose and material inhomogenity such as crystallinity and molecular weight.[19] However, the gamma and electron beam radiation was harmful to humans such as DNA damages due to potential radioactivity or high energy exposure requiring sufficient shielding. Also, the aqueous PEO solution must be prepared before crosslinking, resulting in low-density crosslinked materials such as sponges.

UV-induced crosslinking process may provide significant advantages for many applications in comparison with the high energy radiation crosslinking including easy shield, simple operation, and environmental friendliness. Also, the process can be carried out in solid state as well as in liquid state. Upon photon absorption, hydrogen-abstractable photoinitiators undergo several photophysical processes involving an excited triplet state, which proceeds to the reduction of photoinitiators and macroradical formation. The photochemical crosslinking of polymers mainly occurs by the recombination of two macroradicals producing bonds between the main chains.[20]

UV-induced crosslinking of solid PEO with benzophenone, under argon or vacuum, was investigated by Doycheva et al.[20–22] Especially, the efficient UV-induced crosslinking of PEO achieved 92% gel fraction and 2500% maximum swelling in water using various photoinitiators. Benzophenone was found to be the most efficient photoinitiator and both PEO samples prepared by solution casting or by press-molding can be crosslinked by UV irradiation.[20,21] The UV crosslinking of PEO without photoinitiators has been reported only in the presence of the additional crosslinking agent or synthesized PEO derivatives containing photoreactable groups, which suggested that the pure PEO cannot be UV-crosslinked due to the absence of photosensitive groups.[22,23] Recently, UV-based preparation of hydrogels containing ethylene oxide linkage has been reported by the photoreaction of poly(ethylene glycol) dimethacrylate with methacrylic alginate or 2-(hydroxylethyl methacrylate).[24,25] Photocured thiol-ene hydrogel coating was accomplished by changing PEG length, vinylic end-group, and thiol crosslinker where the antifouling properties improved with longer PEG lengths in the marine antifouling hydrogel coating.[26]

Until now, no in-depth study has been reported the photocrosslinking of pure PEO in the absence of any photoinitiators or crosslinkers. It seemed very attractive to obtain PEO hydrogels by the simple UV irradiation without using any photoinitiator or crosslinkable materials. Moreover, the photocrosslinked PEO containing photosensitive group, initiators or crosslinkers can be problematic in the biomedical application due to possible release of the fragmented and unreacted materials, which requires additional extraction and verification of the absence of possible carcinogenicity or mutagenicity of the crosslinked polymers.

The purpose of this study is to obtain the photocrosslinked hydrogel by UV irradiation of solid state PEO films in the absence of any additives such as photoinitiators and photosensitive additives. Until now, the photocrosslinking mechanism of pure PEO has not been suggested. The most probable crosslinking mechanism and depth-wise crosslink distribution of the crosslinked PEO is also elucidated.

EXPERIMENTAL

Materials

Poly(ethylene oxide) (PEO) powders with a viscosity-averaged molecular weight (M_V) of 300,000 and

molar absorptivity of 4.5×10^3 L/mol/cm were supplied by Aldrich Chemicals and used without further purification.

Preparation of PEO films and UV irradiation

The PEO powder was thoroughly spread on a dismountable mold. The mold was pressed between two heated brass plates at 200°C for 5 min under a pressure of 10 MPa. The mold was allowed to cool under pressure to ambient temperature. The thickness of the films was adjusted to 50, 100, 200, and 300 μm. The irradiation was carried out on both sides of films with a continuous UV irradiator containing D-bulb of a power of 80 W/cm. Fe-doped lamp was chosen to maximize deeper photocrosslinking effect compared with mercury lamps. UV energy was varied to find optimal treatment condition for the samples by changing the number of passing UV irradiation zone (2.5 J/cm² per pass) up to 211 passes. To confirm the depth-gradient photocrosslinking PEO film depending on UV energy, four 50 μm thickness PEO films were cast by the drying of aqueous PEO solutions for 48 h at room temperature on the casting plates. The four layered film was irradiated to verify the progressive depth-gradient photocrosslinking phenomenon for the simulation of a PEO film of 200 μm thickness.

Measurement of gel fraction and swelling

The irradiated PEO samples were weighed and then extracted with distilled water at the boiling for 24 h. After extraction the gels were dried to constant weight under vacuum and weighed gravimetrically. Gel fraction was calculated by the measured weight of samples as the following:

$$\%GF = \frac{W_2}{W_1} \times 100 \qquad (1)$$

where W_1 and W_2 are the weights of original and extracted samples, respectively. Crosslinked gels were equilibrated in distilled water at 30°C for 48 h and removed the excess surface water by placing the swollen gels on a 200 mesh sieve for 30 min and blotting with papers. The degree of swelling (DS) was determined at room temperature as the following:

$$\%DS = \frac{W_3 - W_2}{W_2} \times 100 \qquad (2)$$

where W_3 is weight of swollen hydrogels after the water extraction, respectively.

The storage modulus is assumed to be proportional to the crosslinking density of crosslinked poly-

mers. The molecular weight between crosslinks (M_C, g/mol) can be derived using from the storage modulus measurement of the irradiated films[26]:

$$M_C = \frac{3\rho RT}{E} \qquad (3)$$

where ρ is the density of PEO ($\rho = 1.13$ g/cm³), R is the gas constant (8.32 J/mol/K), and T is the temperature fixed at 335 K to evaluate M_C from the rubbery modulus values of the crosslinked polymers.

Crosslinking density of the crosslinked gels and films is calculated by the following equation[26]:

$$d_x = \frac{1}{\upsilon M_C} \qquad (4)$$

where υ is the specific volume of PEO polymer.

Characterizations

A soluble fraction of the crosslinked samples was obtained by drying the fraction dissolved within a dissolution time from 15 min to 30 min under boiling and D_2O is used for the dissolution of the fraction at 90°C for 60 min. ¹H-NMR spectra of a 0.1% solution of unirradiated PEO and the soluble fraction of the irradiated PEO were acquired by 400 MHz NMR spectrometer (Avance Digital 400, Bruker). The quantitative analysis was carried out to find out the photocrosslnking mechanism and degree of crosslinking of the PEO. The ¹³C solid-state NMR spectra of the pristine and the crosslinked PEO gel were measured to identify the photocrosslinking mechanism using a 600 MHz solid-state NMR spectrometer (UnitylNOVA600, Varian). FT-IR analysis was carried out using a KBr pellet with a Tensor 27 spectrophotometer (Bruker). The subtracted spectra were obtained by subtracting the absorbance of treated samples by that of the untreated after standardization. Dynamic mechanical properties were investigated using a dynamic mechanical analyzer (DMA-Q800). Samples in the form of strips (25 mm × 3 mm × 0.2 mm) were measured in tensile mode at a constant frequency of 1.0 Hz as a function of temperature from −100°C to 80°C at a heating rate of 2°C per minute under nitrogen atmosphere. The DSC curves were obtained with a Perkin–Elmer Diamond DSC thermal analysis system at standard heating and cooling rates of 10°C/min. Samples of about 8 mg were run in an nitrogen atmosphere over a temperature range of −80°C to 80°C. Indium ($T_m = 156.6$°C) was used for temperature calibration. The degree of crystallinity was estimated as the ratio of the experimental melting enthalpy to melting enthalpy of a 100% crystalline PEO (8.276 J/mol).[15] Thermal behavior of the
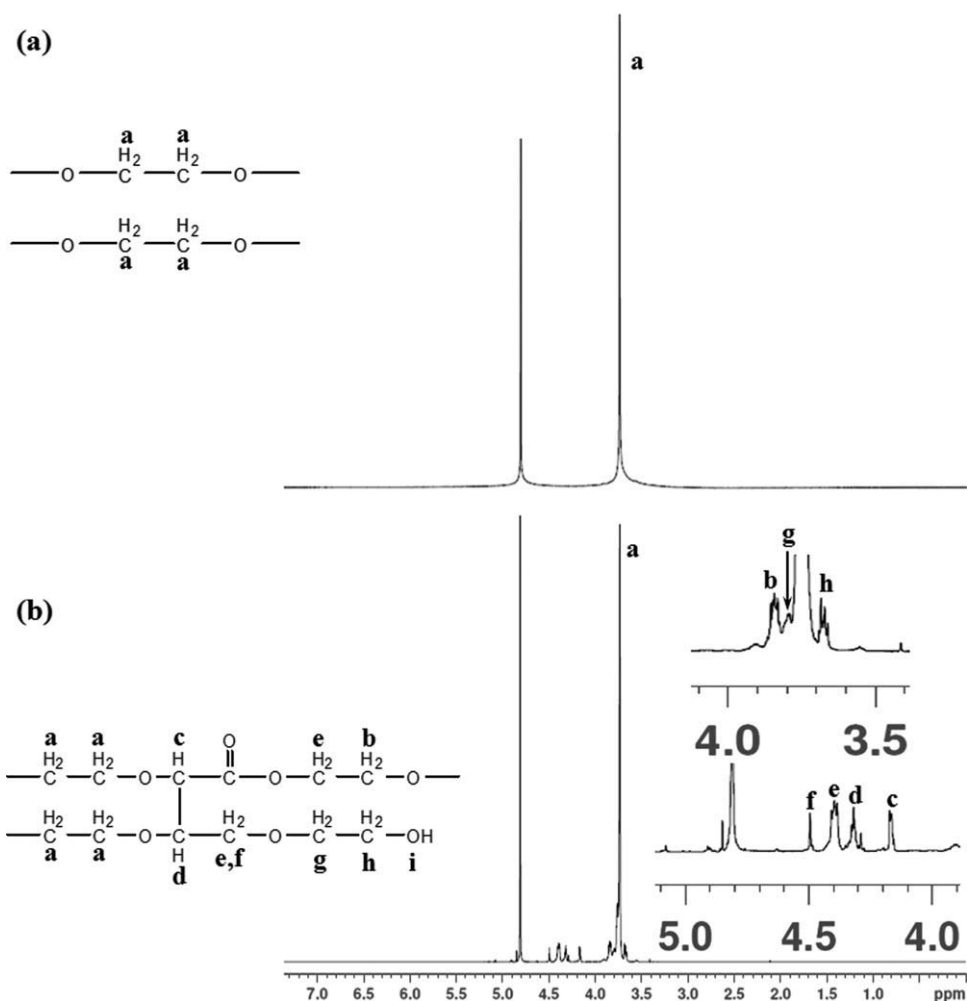
Figure 1 The ^{1}H-NMR spectra of untreated and crosslinked PEO (a). Untreated and (b) crosslinked PEO with a gel fraction of 38.8%.

crosslinked films was observed using a thermogravimetric analyzer (TGA Q500) at a heating rate of 20°C/min under nitrogen gas atmosphere.

RESULTS AND DISCUSSION

Photochemical crosslinking

The NMR analysis was shown in Figure 1. The pristine PEO showed well-defined spectrum where methylene protons appeared at 3.74 ppm, respectively. The soluble fraction of UV-irradiated PEO samples with a gel fraction of 38.8% showed various new peaks. The UV irradiation may generate methine radicals from PEO main chains. The crosslinked methine protons by recombination between the two methine radicals showed at 4.15 and 4.33 ppm. When the radicals recombined to form covalent crosslinks between chains, the methylene protons adjacent to the crosslink appeared at 4.50 and 4.39 ppm. The radicals generated by abstraction and/or chain scission may participate in the hydro-

gen abstraction of PEO chain again or be oxidized by oxygen in air resulting in generation of carbonyl or hydroxyl group.[27–30] Consequently, the methylene linked to the hydroxyl and carbonyl groups peaks were shifted at 3.68, 3.76, and 3.82 ppm. The peak area calculation of the ^{1}H-NMR spectra of the soluble fraction at a gel fraction of 38.8% indicated a degree of crosslinking of 14.0%. Among the crosslinking types, the crosslinked PEO without (I) and with oxidation (II and III) were estimated to 8.0% and 5.9%, respectively. The total oxidation of PEO was calculated to 10.3%. Therefore, the photocrosslinking in the crosslinked PEO dominated over the oxidation. The ^{13}C solid-state NMR analysis was carried out to identify the crosslink structure as shown in Figure 2. The methylene carbons pristine PEO spectrum was located at 70.6 ppm. The crosslinked PEO showed new peaks of methine carbons at 80.1 and 84.2 ppm, which the corresponded crosslink without and with neighboring carbonyl groups. The carbonyl carbon and methylene with adjacent hydroxyl group were assigned to 168.4 and 67.9
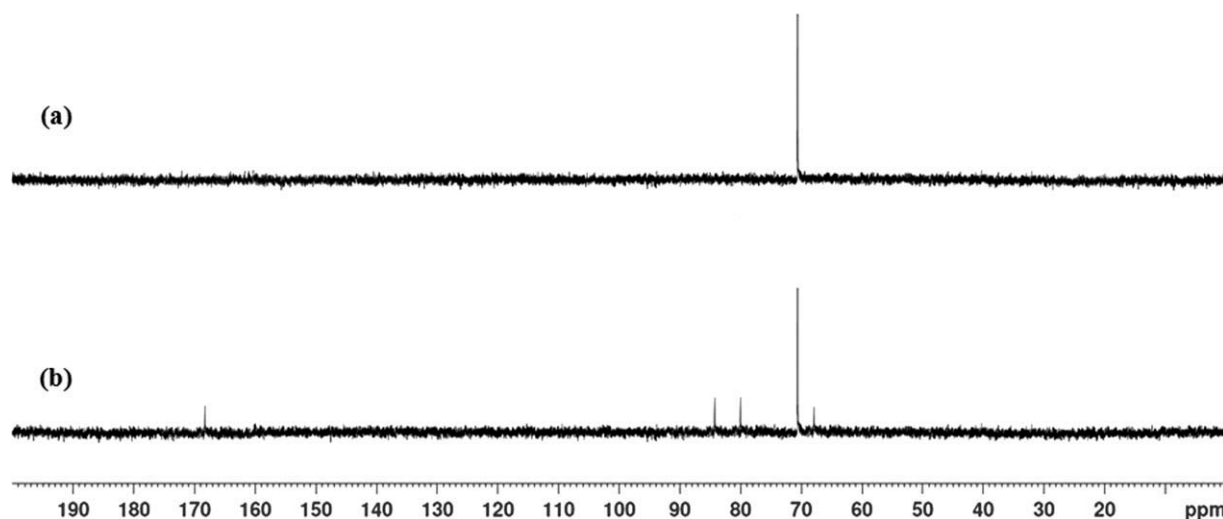
Figure 2 The ^{13}C solid-state NMR spectra of untreated and crosslinked PEO (a). Untreated and (b) crosslinked PEO with the gel fractions of 38.8%.

ppm, respectively. Therefore, the supposed mechanism of photocrosslinking by the recombination and oxidation could be proved to occur as indicated by Figure 3. Surface functional groups of the irradiated PEO depending on UV energy were estimated by the FT-IR and subtracted IR spectra (Fig. 4). In case of untreated PEO film, stretching vibration bands of C–H located at 2991 and 2947 cm^{-1} and bending peaks of C–H at 1452 and 1381 cm^{-1}, C–O stretching band was found at 1083 cm^{-1}. The CH$_2$ stretching of the untreated PEO diminished upon UV irradiation and new C–H stretching and C=O bonds appeared at 2887 cm^{-1} and 1724 cm^{-1}, respectively, presumably due to the photocrosslinking and photo-oxidation of the PEO. UV irradiation can cause two

photo-scission reactions of carbon–carbon or carbon–oxygen links of main PEO chain as well as hydrogen abstraction. The photo-scission reactions are expected to occur much easily compared to the hydrogen abstraction due to lower bond energy for scission (345–380 kJ/mol) than that for abstraction (400–415 kJ/mol). Therefore, the crosslinking can require a large amount of UV energy due to competition with scission and result in low gel fraction compared to the photoinitiator-containing systems.

Gel fraction and degree of swelling

The gel fraction (GF) and degree of swelling (DS) of PEO films depending on UV energy were shown in
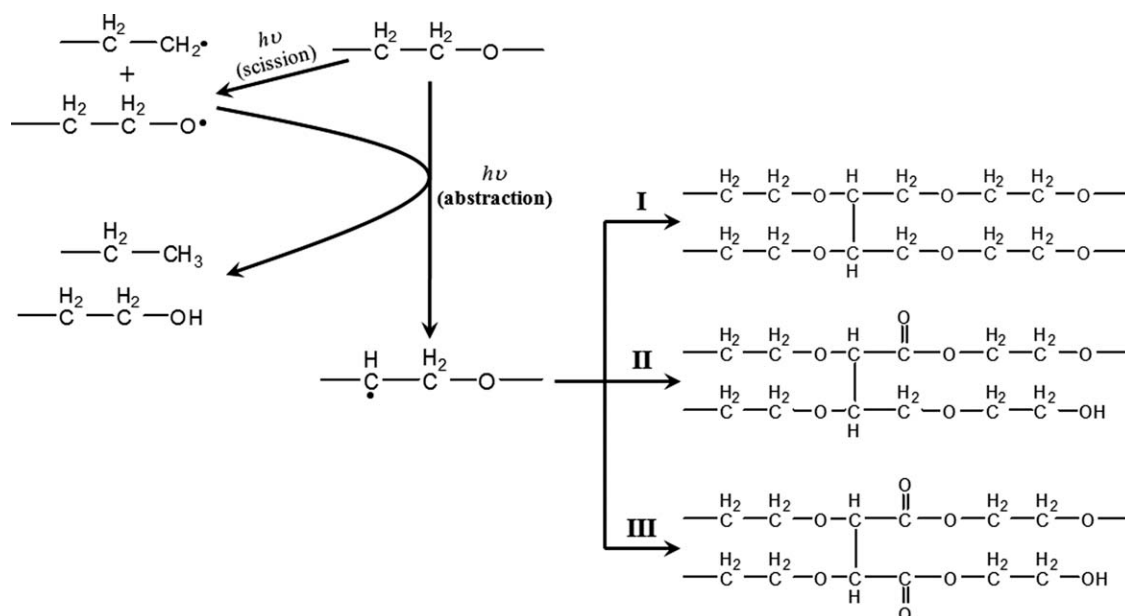

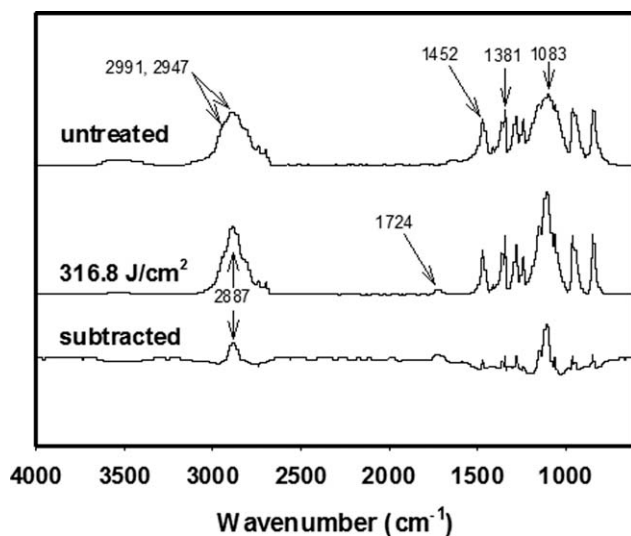**Figure 3** The proposed photocrosslinking mechanism of PEO.

Figure 4 FT-IR spectra of PEO gels depending on UV energy.

Figure 5 and Table I. UV irradiation caused both GF and DS of the crosslinked PEO films to increase proportionally with increasing UV energy up to 317 J/cm^2 in case of 200 μm thickness film. Although the obtained DS was 2785% comparable to swelling capacity of other photoinitiator containing systems, maximum GF was limited to 39%. The decrease in GF and DS above the UV energy of 317 J/cm^2 may be due to dominant photo-degradation of the crosslinked PEO rather than additional crosslink formation above the UV irradiation. Since the penetration of ultraviolet light into the thick films was rather limited by the inherent light absorption of the polymer, the degree of crosslinking was low in spite of high UV energy. The intensity of transmitted light is known to decrease with increasing film thickness as
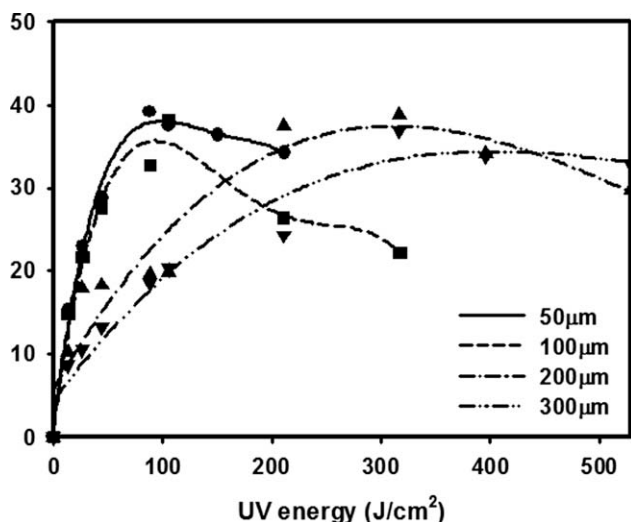
TABLE I
The Degree of Swelling (%) of the Crosslinked PEO Hydrogels of Different Film Thickness Depending on UV Energy

UV energy (J/cm^2)	Film thickness			
	50 μm	100 μm	200 μm	300 μm
13.2	1346	1359	1338	932
44.0	2018	1918	1458	1358
88.0	2811	2463	1527	1469
105.6	2617	2824	1589	1611
211.2	2502	1783	2451	1678
316.8	–	1597	2785	2574
396.0	–	–	2241	2451

suggested by Lambert's law. Therefore, the crosslinking efficiency can be maximized by lowering the film thickness. A third of UV energy was required to obtain the same gel fraction of the crosslinked PEO films of 50 or 100 μm thickness samples in comparison with the samples of 200 or 300 μm thickness ones. The depth-dependent photocrosslinking of PEO film was investigated by irradiating the four layers of 50 μm thickness film to simulate a depth profile of crosslinking structure within the 200 μm film (Fig. 6). Unsurprisingly, the first and fourth layers were crosslinked more quickly due to higher absorption of the surface layers compared to that of the second and third intermediate layers. With larger irradiation the gel fractions of the outer two layers reached a maximum at 211 J/cm^2, whereas those of the inner layers required a UV energy of 317 J/cm^2 to reach a maximum crosslinking. Therefore, depth-wise uniform crosslinking structure can be achieved by adjusting the UV energy between 211 and 317 J/cm^2. The photocrosslinking of the optically thick films occurs primarily at the outer film surface with successive increase in the crosslinking of the inner film region, which resulted in a
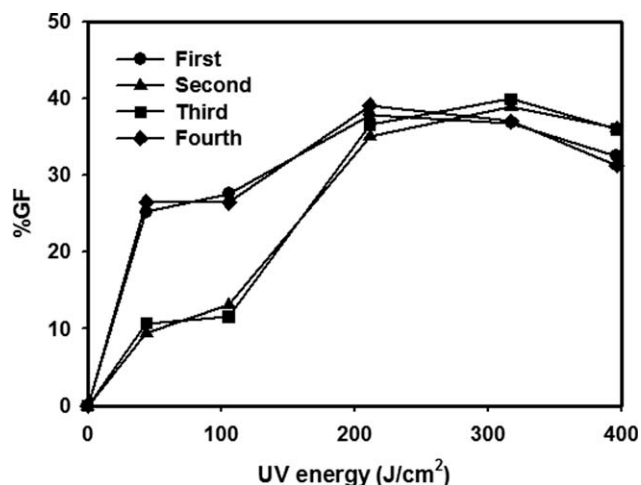

Figure 5 %GF of PEO films depending on UV energy and film thickness.

Figure 6 %GF of PEO films depending on 200 μm film depth.

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TABLE II
T_C and T_m Data of UV-Irradiated PEO Gels

UV energy (J/cm^2)	T_C (°C)	ΔH_c (J/mol)	T_m (°C)	ΔH_m (J/mol)	Crystallinity
0	30.7	5.736	60.6	5.876	0.71
44.0	34.5	5.570	59.3	5.545	0.67
105.6	31.8	5.623	61.5	5.607	0.69
316.8	35.1	5.513	58.8	4.800	0.58

TABLE III
TGA Data of UV-Irradiated PEO Gels

UV energy (J/cm^2)	%GF	$T_{0.5}$	$T_{5.0}$	T_{50}	T_{max}	Char (%)
Untreated	–	191.0	245.9	385.8	404.8	1.8
44.0	18.3	229.6	312.8	410.3	423.8	2.8
105.6	20.2	236.3	294.1	413.4	424.8	4.0
316.8	38.8	244.6	274.5	414.8	425.3	2.7

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maximum crosslink formation with optimal UV energy. The higher UV energy than 211 J/cm^2 or more seemed to cause the predominant photodegradation of the crosslinked networks at outer film surfaces and further progressive crosslinking at inner layers, implying that the limited crosslinking of the PEO film without photoinitiators may be resulted from the dominant photoscission and photooxidation reactions of the uncrosslinked and crosslinked PEO over the hydrogen abstraction and radical recombination (Fig. 2). The photooxidized segment may not participate in further hydrogen abstraction due to compact crosslink structure, which is indispensible for the depth-wisely uniform photocrosslinking.

Thermal properties of the crosslinked PEO gels

Phase transition temperatures and calorimetric data of PEO gels depending on UV energy were shown in Table II. The crystallization temperature (T_C) and crystallization enthalpy (ΔH_C) of the untreated PEO were 30.7°C and 5.736 J/mol respectively. The T_C of the crosslinked PEO gels increased up to 35.1°C and ΔH_C decreased to 5.513 J/mol with increasing UV irradiation maybe due to the more facile nucleation and lower degree of crystallization in the crosslinked polymer network. With increasing UV energy both the melting temperature (T_m) and melting enthalpy
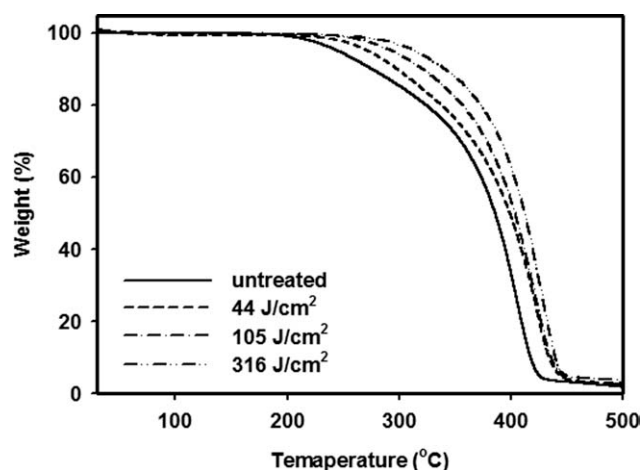
(ΔH_m) of the crosslinked PEO decreased to 58.8°C and 4.800 J/mol from 60.6°C and 5.836 J/mol for the untreated, respectively. Also, the crystallinity of the recrystallized PEO decreased from 0.71 to 0.58 accordingly implying that recrystallization was limited by the crosslinked polymer chains in melt with increase in the degree of crosslink.

The thermal degradation behavior of the crosslinked PEO gels determined by thermo-gravimetric analysis in nitrogen was shown in Figure 7 and Table III. The thermal decomposition behavior of the untreated PEO occurred in two steps, where the first and second pyrolysis could be related to successive decompositions of amorphous and crystalline regions. The first decomposition of the crosslinked PEO gels disappeared because the amorphous region may be crosslinked dominately. In addition, the maximum decomposition temperature of the
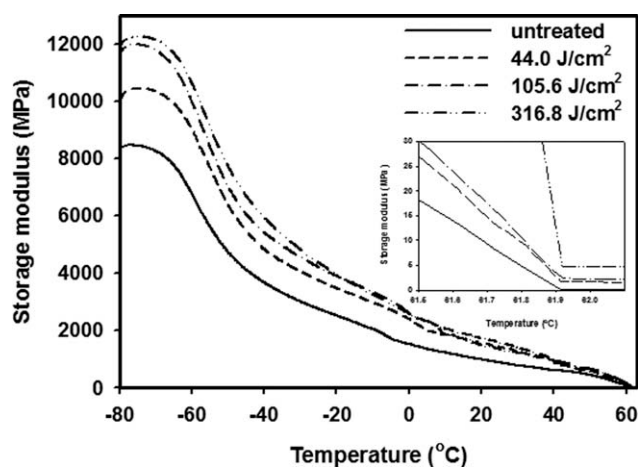
Figure 8 Storage modulus of untreated and crosslinked PEO films.

Figure 7 TGA curves of PEO gels depending on UV energy.

TABLE IV
M_C and d_X of Crosslinked PEO Films

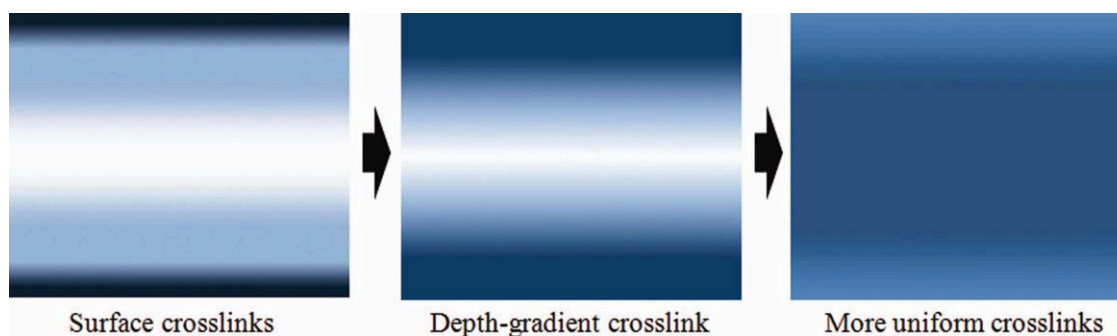| UV energy (J/cm^2)	Dynamic mechanical analysis			
	T_g (°C)	E' (MPa)	M_C (g/mol)	d_X (10^{-4} mol/cm³)
Untreated	−50.7	–	–	–
44.0	−49.6	1.80	5239	2.16
105.6	−48.1	2.34	4043	2.80
316.8	−43.4	4.65	2032	5.56

Figure 9 The schematized depth-gradient and uniform crosslink formation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crosslinked PEO gels increased significantly from 405°C to 425°C by 20°C with increased char residue. Furthermore, the onset (0.5% weight loss) decomposition temperature ($T_{0.5}$) also increased by 54°C from 191°C to 245°C. The higher thermal stability can also be attributed to the polymer network formation.

Dynamic mechanical analysis

Figure 8 and Table IV show storage modulus of the untreated and crosslinked PEO samples as a function of temperature. The storage modulus of the crosslinked samples increased from 8.3 to 11.8 GPa at −80°C. The crosslinked PEO has more energy stored elastically than the untreated during deformation, which can be explained by the reduced chain mobility of the crosslinked structure. The glass transition temperature (T_g) of PEO films can be obtained by the peak of tan δ. The T_g of PEO films increased significantly from −50.7 to −43.4°C by 7.3°C. This may be caused by the highly crosslinked PEO network, which inhibited segmental mobility during the heating. The photocrosslinked PEO films showed higher thermal and mechanical properties.

As shown in Tables I and IV (200 μm), the degree of swelling (DS) of PEO gels was closely related with number average molecular weight between crosslinks (M_C) and crosslinking density (d_x). It has been well known that M_C should decrease with increasing degree of crosslinking, which results in corresponding decrease in DS due to lower water absorption capacity. Under low UV energy irradiation the depth wise inhomogeneous crosslinking resulted in more compact surface crosslinks with a high d_x. On the contrary, the prolonged UV irradiation may produce more loosened and uniform bulk polymer network of a low d_x due to both concomitant scission of the surface crosslinks and new crosslink formation inside. The depth-gradient and uniform crosslink structure formation by optimizing UV energy can be schematized in Figure 9.

However, the M_C and d_x values of the UV-irradiated PEO films determined by dynamic mechanical measurement were inversely proportional to DS values apparently due to the inevitable influence of the water-soluble fraction as well as the gel fraction in the UV-irradiated PEO film. The modulus-based bulk evaluation may be more suitable for a uniformly crosslinked systems and the crosslink structure estimation based on rubber elasticity may not be useful to analyze the water absorption behavior of the present photocrosslinked hydrogel systems of depth-gradient crosslinks.

CONCLUSIONS

Press-molded PEO films can be continuously photocrosslinked by the recombination of PEO radicals generated under ambient UV irradiation without photoinitiators. The relatively low degree of crosslinking resulted from the limited radical recombination due to concomitant photo-scission and photooxidation of PEO chains as proved by NMR and FT-IR analysis. Maximum gel fraction and degree of swelling of 39% and 2824% can be achieved by adjusting UV energy and film thickness where thinner film required lower UV energy. The thermal stability and mechanical properties of the crosslinked polymers remarkably improved as shown by increases in onset and peak decomposition temperatures, T_g and storage modulus. The depthwise gradient crosslinking structure can be obtained under low UV energy and more uniform crosslinked polymer network can be generated under optimal UV energy, which can be indicated by larger M_C with higher gel fraction.

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