Degradation and Stabilization of Cosmetic Polyetherurethane in Alcoholic Solution

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ABSTRACT: A polyetherurethane (PEU) was synthesized for potential cosmetic applications by coupling poly(tetramethylene oxide) (PTMO, M_n = 2000 g mol^{-1}) and poly(ethylene oxide) (PEO, M_n = 2000 g mol^{-1}) with 4,4'-diphenylmethane diisocyanate (MDI), without using a chain extender. The PEU polymer, synthesized with PEO and PTMO in the ratio of 1:3 by weight, was soluble in ethanol–water mixed solvents. The solution formed a thin film *in situ* on the skin by coating, which was flexible and elastomeric with appropriate skin adhesiveness. However, PEU was susceptible to degradation when it was exposed to an ethanol–water (80/20 v/v %) mixed solvent and stored in an air-filled and sealed bottle at 60°C for 4 weeks. These conditions resulted in deterioration of PEU molecular weight (M_n), viscosity, and mechanical properties. Peak analysis of the Fourier transform infrared spectrum of the aged PEU revealed that >97% of the urethane carbonyl bonds remained, whereas ether bonds were significantly reduced (~82% of initial value). The degraded PEU contained ester bonds, which were confirmed by proton and carbon-13 nuclear magnetic resonance spectroscopy. This observation suggests that oxidative chain cleavage rather than hydrolysis was the dominant reaction in the degradation process. Two approaches were adopted to minimize oxidative degradation of PEU dissolved in an ethanol–water (80/20 v/v %) mixed solvent; they were, applying a nitrogen environment and adding an antioxidant (1.8 wt % dry PEU). The results indicate that reduction of oxidative degradation produced a synergistic effect. Vitamin E was a more effective antioxidant than butylated hydroxytoluene (BHT), which is a typical antioxidant for commercial polyurethanes. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2270–2276, 2003

Key words: polyurethanes; degradation; additives; antioxidants

INTRODUCTION

Hydrophilic polymers, such as poly(hydroxyethyl methacrylate),[1] poly(acryl amide),[2] poly(acrylic acid),[3] cellulose derivatives,[4] poly(vinyl pyrrolidone),[5] and poly(vinyl alcohol),[6] are often employed for the cosmetic purposes of skin hydration and supplying nutrients. However, these polymer films have a glassy characteristic that is not appropriate for movement of the human body.

Polyurethane (PU) is composed of a variety of polyols for soft segments and diisocyanates and chain extenders for hard segments. The resulting PU offers a great versatility in physical properties and solubility,[7] but poor water solubility due to the presence of hard segments. In cosmetic applications, repetitive or prolonged topical exposure of human skin to organic solvents induces skin irritation, which restricts using PU in cosmetic applications. Ethanol has been used for various marketed transdermal delivery systems of nitroglycerin,[8] estradiol,[9] and fentanyl[10] because of its skin penetration-enhancing effect. Polyetherurethane

(PEU), a polyurethane (PU) based on the coupling of poly(ethylene oxide) (PEO) and poly(tetramethylene oxide) (PTMO) with 4,4'-diphenylmethane diisocyanate (MDI) without using any chain extender, demonstrated unique characteristics of high elasticity, high water content, low glass transition temperature in dried state, and solubility in ethanol–water mixtures.[11] However, PEU was found to be vulnerable to oxidative degradation. Current approaches to improve the stability of PU have centered on adding proper antioxidants, such as butylated hydroxytoluene (BHT), aminic antioxidant, and Irganox®.[12] These synthetic antioxidants may adversely influence skin biocompatibility.[13] In this research, Vitamin E (α-tocopherol), a nontoxic antioxidant, was tested as an antioxidant for PEU, which has good solubility in PEUs.[14, 15] Vitamin E is widely used as a commercial food additive and generally recognized as a safe compound by the Food and Drug Administration.[15] Vitamin E has also been used in many skin care products that are claimed to have anti-aging and moisturizing effect,[16] and to protect human skin fibroblasts against ultraviolet ray-induced harm.[17]

Although many researchers have already reported that PU is degraded in water,[18–20] studies on PEU degradation in cosmetically important solvent sys-

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tems, such as in ethanol–water binary mixtures, have not been made available. This study evaluated the mechanisms of degradation and stabilization of PEU based on PEO and PTMO in ethanol–water binary mixtures. The degradation study was conducted at 60°C for 4 weeks in an ethanol–water (80/20 v/v %) solvent mixture. Degradation was investigated by monitoring molecular weight, viscosity, and tensile strength and by using Fourier transform infrared (FTIR) and proton (^{1}H-NMR) and carbon-13 (^{13}C-NMR) nuclear magnetic resonance spectroscopy. The results suggest that oxidative degradation is the major mechanism in degradation. The pharmaceutical antioxidant vitamin E was used for the stabilization of PEU, and its utility in PEU was analyzed by gel permeation chromatography (GPC) after an accelerated test in ethanol–water (80/20 v/v %) solvent mixtures at 20, 40, 60, and 80°C for 2 weeks.

EXPERIMENTAL

Materials

Poly(ethylene oxide) (PEO, M_n = 2000 g mol^{-1}) and poly(tetramethylene oxide) (PTMO, M_n = 2,000 g mol^{-1}) were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI) in a powder form and dried for 5 h at 80°C in vacuum before use. 4,4′-Diphenylmethane diisocyanate (MDI; Aldrich) was melted at 60°C, filtered through a filter paper (Whatman Ltd., Maidstone, England) to remove high molecular weight products formed by allophanate or biuret reactions, and recrystallized in anhydrous n-hexane (J. T. Baker, Philipsburg, NJ). Dimethyl acetamide (DMAc; Junsei Chemical Company, Ltd., Tokyo, Japan) was purified by vacuum distillation. Tetrahydrofuran (THF; J. T. Baker) was refluxed on calcium hydride. Ethanol (Merck KGaA, Darmstadt, Germany), vitamin E (α-tocopherol) in a liquid form (Aldrich), and butylated hydroxytoluene (BHT, Aldrich) were used as received without further purification (chemical structures are presented in Figure 1).

Synthesis

Polyetherurethane (PEU) was synthesized by a modification of a previously described one-step polycondensation reaction of PEO, PTMO, and MDI.[11] Briefly, PTMO (15 g, 0.0075 mol) and PEO (5 g, 0.0025 mol) were dissolved in a DMAc/THF (1:3 volume ratio) mixed solvent before adding MDI (2.5 g, 0.01 mol) in a 500-mL round-bottomed glass reactor equipped with a magnetic stirrer, a thermometer, a reflux condenser, and a nitrogen inlet and outlet (see Table I). The reaction temperature was adjusted at 60°C, and nitrogen atmosphere was maintained until the reaction was finished. The polymerization reaction pro-
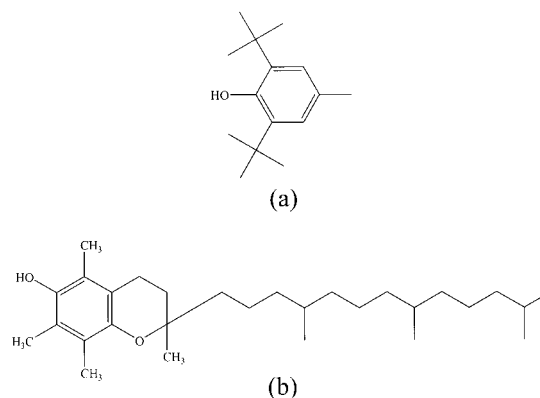

Figure 1 Chemical structures of (a) vitamin E (α-tocopherol) and (b) butylated hydroxytoluene (BHT).

ceeded for 7 h. The resulting PEU was precipitated in n-hexane. Any residual PTMO was removed by vigorously stirring with a mechanical stirrer for 10 h and dried under reduced pressure for 1 day. The remaining PEO was removed from PEU by first dissolving in THF, then precipitating in distilled water for 1 day, and finally filtering. The resulting PEU was dried in a freeze dryer for 1 day. The mechanical and thermal properties of this PEU have been previously reported.[11]

Sample preparation

For the degradation study, PEU was dissolved in an ethanol–water (80/20 v/v %) mixed solvent at a concentration of 5 w/v %. The resulting PEU solution in an air-filled and sealed bottle was stored at 60°C for 4 weeks.

Vitamin E (1.8 wt % of dry PEU) was added as an antioxidant to the PEU solution, and the same amount of BHT was added in a control sample. The bottles containing the solutions were then filled with nitrogen or air, sealed, and stored at 20, 40, 60, or 80°C for 2 weeks.

The aged samples were poured into a Teflon plate and dried at room temperature for 3 days under vacuum to remove the mixed solvent. After drying, the samples were redissolved in THF at a concentration of 10 w/v %. Clear films were obtained by using the solvent casting method. The films were then dried at 50°C under vacuum for 3 days and analyzed.

Characterization

The polymer particle size in ethanol–water mixtures in varying mixing ratios was measured by dynamic light scattering (DLS; Malvern 4700) at 30°C. The wavelength of the unpolarized incident beam (He/Ne laser) was 488 nm. The measuring angle was fixed at 90°.

TABLE I
Materials in PEU Synthesis

Sample ID	Ingredient[a]				
	PEO	PTMO	MDI	DMAc	THF
PEU	5 g	15 g	2.5 g	300 mL	100 mL

[a] Molar ratio of NCO group to OH group = 1.

Viscosity was measured with a Cannon-Ubbelohde type viscometer, following the procedures of ASTM D 445 and ISO 3104 at 23 ± 0.2°C. Predetermined amounts of dried PEU were weighed accurately and dissolved in DMAc. The solutions were filtered carefully through a 0.2-μm syringe filter (Whatman Ltd., Maidstone, England).

The molecular weights and molecular weight distribution of PEU were determined by GPC with a Waters LC system coupled with a Waters 410 differential refractometer. Dried polymer samples were dissolved in THF (0.2 w/v %). The solution (200 μL) was injected into μ-Styragel columns. The flow rate of eluant (THF) in operation was 1.0 mL/min at 35°C.

Uniaxial tensile analysis was performed with an Instron model 5567. Dog-bone type films (thickness, 0.25 mm; width, 3.26 mm; sp.length, 14 mm) that corresponded to ASTM D638M were prepared. The crosshead speed was 508 mm/min, and the experiment was conducted at 23°C and in 65 % relative humidity (RH).

PEU was qualitatively characterized with a FTIR spectrometer (Perkin Elmer IR-200). A KBr pellet coated by the PEU solution was dried at 60°C in a convection oven to remove the solvent. The FTIR spectra were collected under nitrogen environment at a resolution of 4 cm^{-1}. The peak at 1730 cm^{-1} was assigned to an urethane carbonyl bond that is free from hydrogen bonding, and the 1100 cm^{-1} peak was assigned to the ether bond (C—O—C) of polyols. The reference peak to which other peaks were normalized was 1600 cm^{-1}, representing the aromatic (C=C).

^{1}H-NMR and ^{13}C-NMR spectra of the degraded PEU were obtained in the 10% solution of DMSO with a JEOL JNM-LA 300WB FT-NMR spectrometer at ~25°C.

RESULTS AND DISCUSSION

PEU degradation

The PEU synthesized in this study was soluble in various organic solvents such as THF, DMAc, methylene chloride, chloroform, benzene, and dimethylformamide. However, PEU was not soluble in water, ethanol, methanol, n-hexane, and ether, but became soluble in ethanol–water binary mixtures. PEU started to disintegrate when the ethanol solution was 50 vol %, but a clear solution was only obtained when the
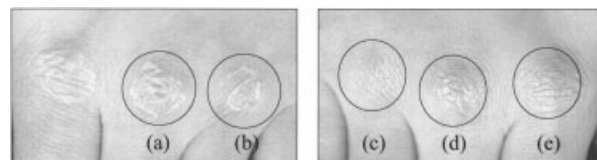

Figure 2 Film formation on the back of hands within 5 min after spreading solutions of various ethanol–water binary mixtures: (a) 50%, (b) 60%, (c) 70%, (d) 80%, and (e) 90% (ethanol vol %).

ethanol solution was 80–90 vol %. Photographs demonstrating the film-forming capability of alcoholic PEU solution on the back of hands are shown in Figure 2. Within 5 min, adhering clear films were formed on the skin when the ethanol content of the solution was 70, 80, or 90% (Figures 2c, 2d, and 2e, respectively). The films tolerated moving and skin stretching. However, when ethanol content was 50% (Figure 2a) and 60% (Figure 2b), the films formed on the skin were turbid and easily peeled off from the skin. The particle sizes of PEU in different mixed solvents with various ethanol contents are listed in Table II. A clear solution was observed when the particle size was <200 nm. As the ethanol content decreased, the particle became larger and its solution became opaque. At 60%, the particle size sharply increased and reached 3000 nm at 50% ethanol. These results indicate that the ability to form films perhaps depends on the particle size in the binary mixture, because smaller particles (<600 nm) possessed stronger driving force for film formation due to high surface energy.[21]

The time-dependent intrinsic viscosity of the PEU solution in an ethanol–water (80/20 v/v %) solvent mixture stored in an air-filled bottle at 60°C is shown in Figure 3. The data clearly indicate that heating PEU in air leads to a marked decrease in the intrinsic viscosity as the exposure time increases. The number-average molecular weight (M_n) also showed a consid-

TABLE II
Particle Size of PEU in Water and Ethanol Binary Mixture

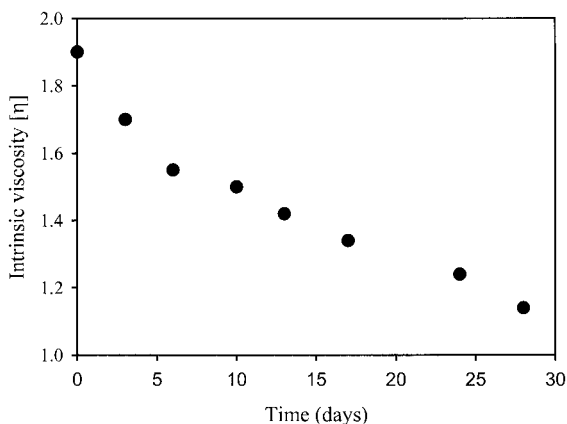| Ethanol content (vol %)	Particle size (nm)[a]
0	—
10	—
20	—
30	—
40	—
50	3245
60	2980
70	572.2
80	198.4
90	118.8
100	—

[a] Particle size was measured by dynamic light scattering.

Figure 3 Intrinsic viscosity change with time with air conditioning at 60°C for 4 weeks in ethanol–water (80/20 v/v %) solvent mixture.
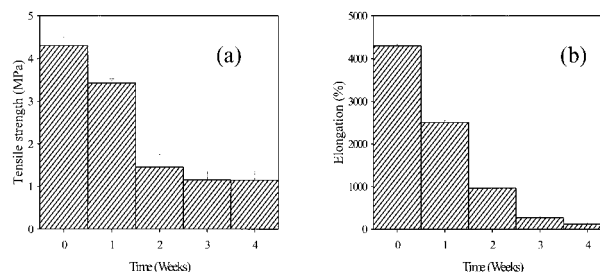

Figure 4 Mechanical properties change with time with air conditioning at 60°C for 4 weeks in ethanol–water (80/20 v/v %) solvent mixture ($n = 3$): (a) tensile strength and (b) elongation at break (%).

erable decrease (Table III) resulting from the production of low molecular weight species.

The changes in the mechanical properties of the PEU during degradation are shown in Figure 4. Tensile strength and elongation at break are sensitive to the degradation of elastomeric materials. Tensile strength gradually reduced with time (Figure 4a). A 15% reduction of initial tensile strength was observed after 1 week. A 50% reduction occurred between the first and second weeks. After the first 2 weeks, the strength was maintained constant at ~30% of the initial tensile strength. The degradation effect on the elongation at break was even more significant (Figure 4 b). A reduction of elongation at break of ~50% was observed within 1 week and a reduction of ~90% was observed after 3 weeks. In contrast to tensile strength, a continuous reduction in elongation at break was observed. This result may be due to cleavage of ether bonds, because Hsieh et al.[22] reported that the soft segment matrix influences extension and elastic recovery, whereas the hard domains contribute to modulus and strength of polyurethanes.

To support this assertion, the urethane and ether bonds of PEU were monitored over time by FTIR

spectroscopy, and the results are shown in Figure 5. The major intensity changes appeared in the range 1800–1000 cm^{-1}. The peak intensity at 1100 cm^{-1}, which was identified as the ether bond in PEU, significantly decreased with time. The peak at 1730 cm^{-1} represents a nonhydrogen bonded carbonyl bond in urethane and the valley between 1730 and 1700 cm^{-1} indicates a new broad carbonyl, resulting from an increase in the weakly hydrogen-bonded carbonyls or carbonyl of degradation product.[22] The aromatic C—C stretching vibration was observed at 1600 cm^{-1}, which was a reference peak. The results of peak analysis with time are presented in Figure 6. The decrease in the height of the ether peak from 100 to 85% occurred in the first 1 week of aging. After 4 weeks of aging, the peak height decreased to 82% of the initial ether peak height. On the other hand, the nonhydrogen-bonded carbonyl peak at 1730 cm^{-1} was reduced from 100 to 98% after 4 weeks. These results clearly indicate that the ether bond is more vulnerable than the urethane bond to cleavage during aging.

The degradation products in an air environment were identified by ^{1}H- and ^{13}C-NMR spectroscopy and calculated with Chemdraw software. Before treatment of PEU, ^{1}H-NMR spectra showed a peak at 3.56 ppm that represents a methylene group in PEO

TABLE III
Number Average Molecular Weight (M_n), Weight Average Molecular Weight (M_w), and Molecular Weight Distribution (M_wD) of PEU[a] at 60°C for 4 Weeks under air condition

Time (weeks)	M_n[a]	M_w[a]	M_wD[a]
0	26500	38100	1.44
1	25000	35100	1.40
2	24500	32000	1.31
3	23700	33100	1.40
4	23000	30900	1.34

[a] Measured by GPC after storage for 4 weeks with air conditioning at 60°C
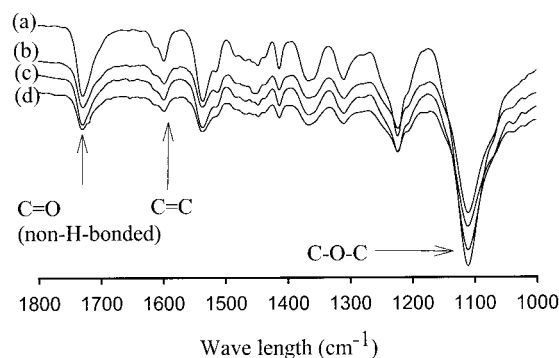

Figure 5 FTIR spectra of PEU with air conditioning at 60°C for 4 weeks in ethanol–water (80/20 v/v %) solvent mixture: (a) 1 week; (b) 2 weeks; (c) 3 weeks; and (d) 4 weeks.
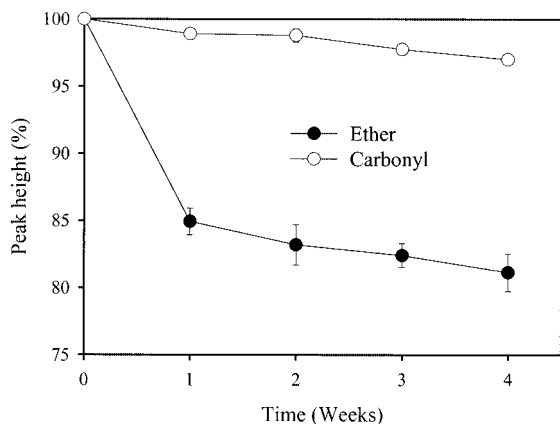
Figure 6 FTIR peak analyses of functional groups at 1100 cm^{-1} (C—O—C) and 1730 cm^{-1} (C=O) normalized to the 1600 cm^{-1} (C=C; n = 3). (a) Peak height (%) of initial carbonyl = [{transmittance (C=O)/transmittance (C=C) at a time}/{transmittance (C=O)/transmittance (C=C) at initial}] · 100. (b) Peak height (%) of initial ether = [{transmittance (C—O—C)/transmittance (C=C) at a time}/{transmittance (C—O—C)/transmittance (C=C) at initial ether}] · 100.

(—CH$_2$CH$_2$O—). The methylene groups in PTMO were at 3.37 ppm (—CH$_2$CH$_2$CH$_2$CH$_2$O—) and 1.58 ppm (—CH$_2$CH$_2$CH$_2$CH$_2$O—). The phenylene groups in MDI were at 7.26 and 7.06 ppm. Methylene groups in MDI were at 3.83 ppm. The ^{13}C-NMR chemical shifts associated with polyols were at 70.5 ppm (—CH$_2$CH$_2$O—), corresponding to the PEO methylene groups. PTMO methylenes were at 70.2 ppm (—CH$_2$CH$_2$CH$_2$CH$_2$O—) and 27.3 ppm (—CH$_2$CH$_2$CH$_2$CH$_2$O—). The chemical shifts of phenyl rings in MDI were located in the 118.7–136.1 ppm region, and those of carbonyl in urethane were at 155 ppm (—NHCOO—). After degradation, new peaks appeared in the ^{1}H- and ^{13}C-NMR spectra, indicating PEU degradation in air. In ^{1}H-NMR spectra, a triplet and some other peaks were identified at 4.2 and 3.9–4.1 ppm, respectively, and new peaks appeared at 2.2–1.38 ppm. The peaks at 3.1–4.1 and 2.2–1.4 ppm can be assigned to the methylenes of the ester in PEO and PTMO, respectively. In the ^{13}C-NMR spectrum, new peaks assigned to the carbon of the esters in PEO increased at 60–80 ppm and a new peak assigned to the carbon of the esters in PTMO appeared at 30.25 ppm. No other signals corresponding to aldehyde or carboxylic groups were observed in either ^{1}H- or ^{13}C-NMR spectra. These results indicate that the ester bond on the polymer chain or low molecular weight esters were produced as the main products of PEU.

A proposed mechanism of the PEU degradation is shown in Figure 7. Hydrogen peroxide (H$_2$O$_2$) has high solubility in water[23] and is known as a powerful oxidant in a liquid phase. In addition, H$_2$O$_2$ appears to be ubiquitous in air and thus plays a vital role in

determining the oxidizing capacity of the atmosphere.[24] The H$_2$O$_2$ concentration in air varies from 0.1 to 0.8 parts per billion by volume (ppbv) depending on temperature and ozone (O$_3$) concentration in air.[23] As shown schematically in Figure 7, degradation is initiated by H$_2$O$_2$ dissolved in the liquid phase. H$_2$O$_2$ creates alkyl radicals (R•) on the polymer chain by abstracting a hydrogen atom from the ether methylene, because α-carbon groups in ether are easily oxidized. Dissolved oxygen in the solvent mixture rapidly reacts with alkyl radicals on the PEU chain and forms alkyl peroxide radicals (ROO•). A peroxide radical then abstracts a hydrogen atom from another ether methylene and forms hydroperoxide, following the production of another alkyl radical. Formation of hydroperoxides leads to chain scission and various decomposition products according to the proposed radical mechanism. The alcoxy radical, produced by homolysis of the hydroperoxides, can form an ester by hydrogen fragmentation. Also, the hydrolysis of the ester bonds may lead to the formation of alcohol and carboxylic acid groups. It should be emphasized that traces of resulting products accelerate the oxidative degradation of PEU. For instance, the hydroxyl radical increases with time and forces the oxidation reaction to undergo an autocatalytic process because hydroxyl radicals are also included in the initiation of oxidation.[25] Anderson et al.[7] and Payet et al.[26] reported that oxidative degradation of polyether in water under oxygen led to products with aldehyde, alcohol, and carboxylic acid moieties. However, our results from NMR spectroscopy reveal that esters were mainly formed instead of aldehyde, alcohols, and carboxylic acid moieties. This result implies that alcoxy radials, produced on the chains from hydroperoxide during degradation, were converted to esters or that resulting products may have been formed by the esterification
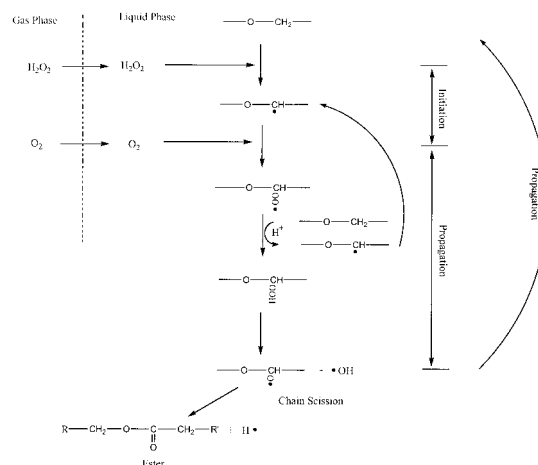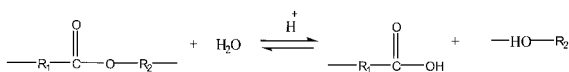

Figure 7 Hypothesized oxidative degradation mechanism of polyetherurethane in water and ethanol binary mixture with air conditioning.

Scheme 1

reaction presented in Scheme 1. The ester formation may be due to the presence of ethanol, which reacts with carboxylic acid. Although esters can be converted to carboxylic acids with water through hydrolytic reaction in the presence of an acid catalyst, esters seem relatively stable in this ethanol–water condition.[27, 28] Therefore, the ester groups created on the polymer chain or low molecular weight esters can be considered as the main products of the degradation of PEU in an ethanol–water (80/20 v/v %) environment.

Stabilization of PEU

Stabilization of PEU was attempted by two approaches based on the oxidation mechanism presented in Figure 7: (i) elimination of hydrogen peroxide and oxygen participating in initiation and propagation by replacing air with nitrogen environment and (ii) reducing various radical concentrations in the liquid phase by employing a radical trapping antioxidant (vitamin E or BHT). The changes in M_n with aging for 2 weeks at 20, 40, 60, and 80°C in the ethanol–water (80/20 v/v %) mixture are shown in Figure 8. At 20°C, the reduction in M_n was not significant in all samples, but it gradually increased with increasing temperature. At 80°C, the extent of reduction was apparently different from that of samples kept under different conditions. The M_n of PEU in nitrogen with vitamin E remained at 91% of the initial M_n, whereas the M_n of the PEU sample stored in nitrogen with BHT showed only 87% of the initial M_n. Under other conditions, there was significant loss of M_n. The M_n values of PEU
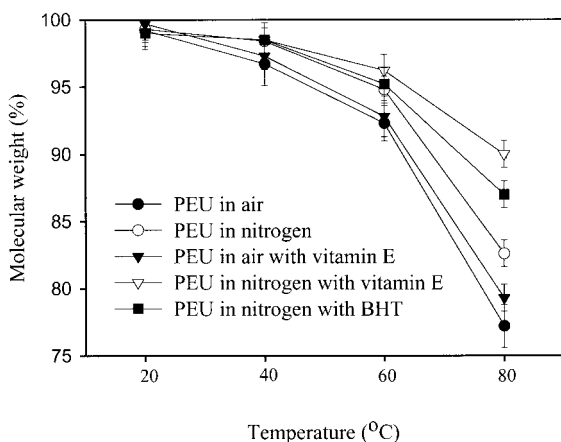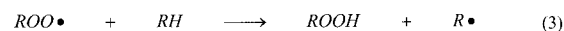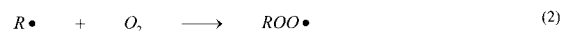

Figure 8 Molecular weight change with time for 2 weeks at 20, 40, 60, and 80°C in ethanol–water (80/20 v/v %) solvent mixture in various conditions ($n = 3$): molecular weight (%) = [M_n (after 2 weeks)/M_n (at initial condition)] · 100.

Initiation:
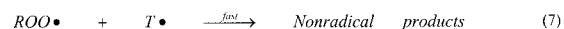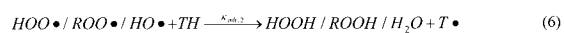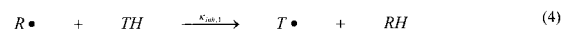
$$RH \xrightarrow{H_2O_2} R\bullet \qquad (1)$$

Propagation:

$$R\bullet \quad + \quad O_2 \quad \longrightarrow \quad ROO\bullet \qquad (2)$$

$$ROO\bullet \quad + \quad RH \quad \longrightarrow \quad ROOH \quad + \quad R\bullet \qquad (3)$$

Termination:

$$R\bullet \quad + \quad TH \quad \xrightarrow{\kappa_{inh,1}} \quad T\bullet \quad + \quad RH \qquad (4)$$

$$ROOH \quad \longrightarrow \quad RO\bullet \quad + \quad HO\bullet \qquad (5)$$

$$HOO\bullet/ROO\bullet/HO\bullet + TH \xrightarrow{\kappa_{inh,2}} HOOH/ROOH/H_2O + T\bullet \qquad (6)$$

$$ROO\bullet \quad + \quad T\bullet \quad \xrightarrow{fast} \quad Nonradical \quad products \qquad (7)$$

Scheme 2

in nitrogen without vitamin E and in air with vitamin E remained at 83 and 79% of initial values, respectively. When PEU was treated in air without antioxidant, M_n decreased to 77%. These results show that the combination of nitrogen environment and vitamin E is superior to other conditions in minimizing oxidative degradation. Thus, nitrogen and vitamin E were synergistic in suppressing oxidative degradation at accelerating test condition. The results suggest that vitamin E in nitrogen can be used as an antioxidant of PEU for long-term storage in the ethanol–water mixture at room temperature.

The chemical reactions associated with the stabilization of PEU are shown in Scheme 2. The oxidation of PEU was initiated by H_2O_2. These reactions can be minimized by replacing air with nitrogen. In the propagation reactions, alkyl (R•) and alkylperoxy (ROO•) radicals lead to oxidative degradation. At termination, the radicals are trapped by vitamin E (α-tocopherol) or BHT. The free radical HOO · can also be removed by the antioxidant. Vitamin E is the primary chain-breaking antioxidant. Radical scavenger activity is dependent on the chain-breaking ability of the antioxidant, which has rate constants of $\kappa_{inh,1}$ and $\kappa_{inh,2}$. From the results shown in Figure 8, the chain-breaking ability of vitamin E must be better than that of BHT. The oxidation of PEU is probably prevented by vitamin E by the process described by eqs. 4 and 6 in Scheme 2. Tocopheroxyl radical (T•) produced during radical scavenge reacts with another peroxyl radical and may produce tocopherones and epoxytocopherones, as shown in eq. 7 of Scheme 2.[15, 29] This phenomenon was observed in the change in color of samples, from clear yellow to brownish solution, with time. Additionally, T · reacts through bimolecular self-reaction with oxygen to form nonradical products.[29] Overall, the nitrogen environment may reduce oxidation of PEU in initiation and propagation, and vitamin E stabilizes the oxidative degradation by trapping peroxide radicals that are produced in propagation.

CONCLUSIONS

A PEU was synthesized via one-step polycondensation using macrodiols of PEO, PTMO, and MDI as an *in situ* film-forming material that can be spread or sprayed on the skin. The polymer was soluble in an ethanol–water mixture, typically at a ethanol–water ratio of 80/20 v/v %. However, degradation of PEU was evidenced by a decrease in molecular weight, viscosity, and tensile properties over time in an ethanol–water (80/20 v/v %) mixture after storage for 4 weeks at 60°C. FTIR peak analysis showed that the height of the ether peak decreased more significantly than that of the urethane peak. The main degradation product was ester, as detected by ^{1}H-NMR and ^{13}C-NMR, indicating that an oxidative reaction mechanism was the major degradation reaction. However, it is necessary to stabilize PEU against degradation for long-term storage in cosmetic applications. This stabilization was achieved by treating PEU with nitrogen and vitamin E. Vitamin E prevented oxidative degradation better than BHT, which is a typical antioxidant for commercial polyurethane. Furthermore, nitrogen and vitamin E had a synergistic effect on stabilizing PEU.

It is concluded that the PEU solution in an ethanol–water mixture can be used as an *in situ* film forming polymeric material for cosmetic application when formulated with vitamin E and stored in a nitrogen environment.

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