Synthesis and Properties of Polyurethane-Urea-Based Liquid Bandage Materials

Soo-Jeong Choi,[1] Jung-Hee Lee,[1] Young-Hee Lee,[1] Dae-Youn Hwang,[2] Han-Do Kim[1]

[1]*Department of Organic Material Science and Engineering, Pusan National University, Busan 609-735, Korea*
[2]*Department of Biomaterials Science, Pusan National University/PNU-Laboratory Animal Resources Center, Miryang 627-706, Korea*

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ABSTRACT: To obtain ideal liquid bandage polymer materials, a series of polyurethane-urea dispersions were synthesized from 4,4′-diisocyanato dicyclohexylmethane (H_{12}MDI) and ethylene diamine with different molar ratio of polyol blend [polyethylene glycol (PEG, M_n = 2000 g/mol)/hydroxy terminated poly(dimethylsiloxane) (PDMS, M_n = ~ 550 g/mol)] and acetone/ethanol as a solvent. The effect of PDMS content in PEG/PDMS on the viscosity, mechanical properties, water contact angle/surface energy, insolubility in water (%), water absorption (%), equilibrium water content (%), and water vapor transmission rate (g m^{-2} day^{-1}) of polyurethane-urea films was investigated. As PDMS content increased, the water contact angle, insolubility in water, and tensile strength/elastic recovery of film sample increased; however, the surface energy, water absorption (%), equilibrium water content (%), and water vapor transmission rate (g m^{-2} day^{-1}) of film sample decreased. By a wound-healing evaluation using a full-thickness rat model experiment, it was found that a wound covered with a typical polyurethane-urea liquid bandage film (PD2 sample) was filled with new epithelium without any significant adverse reactions. These results suggest that the polyurethane-urea-based liquid bandages (samples: PD2 and PD3) prepared in this study may have high potential as new wound dressing materials, which provide and maintain the adequate wet environment required to prevent scab formation and dehydration of the wound bed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3516–3524, 2011

Key words: polyurethane-urea; polydimethylsiloxane; liquid bandage; wound healing

INTRODUCTION

Generally, a dressing is used to protect and help heal wounds. The most common wound dressings have been gauze, but they can stick to wounds causing wound damage during dressing changes, increasing the probability of infection, and lengthening healing time. Subsequently, multilayered systems, which are an improvement over gauze dressings, have been designed with a film backing. However, they can be stiff and bulky and can also be susceptible to foreign material and bacteria to enter wounds.[1–3] There are several types of dressings on the market, such as hydrocolloid, hydrogel, medicated dressings, adhesive moist bands, and liquid bandages.

The principal function of a wound dressing is to provide a moist environment to encourage the establishment of the best milieu for natural healing. When wound is directly exposed to air, it dehydrates and forms scab or eschar. It has been reported that healing with a wet environment is faster than that with a dry environment. This is because a wet environment facilitates formation of renewed skin, instead of eschar.[4–6] Meanwhile, it has been recommended that the water vapor transmission rate (WVTR) in the range of 2000–2500 g m^{-2} day^{-1} would provide adequate level of moisture without risking wound dehydration.[7] Hydrogel dressings, which provide a wet environment to the wound bed, are an insoluble three-dimensional network of hydrophilic polymers with water content (%) between 90–95%. Various hydrogels can be found and their differences consist in varying abilities to donate water and absorb fluid from the wounds.[8–10] Because hydrogels are soothing and absorptive, they are especially valuable for partial-thickness wounds, such as superficial thermal burns, friction blisters, chemical peels, dermabrasion, facial laser resurfacing, and ulcers.[11–14] Adhesive moist bands can also provide a wet environment to the wound bed, but they have very low WVTR.

Liquid bandage is usually a polymer dissolved in water or organic solvent, sometimes with an added antiseptic, although the alcohol in some brands may serve the same purpose. The liquid bandages protect

Correspondence to: H.-D. Kim (kimhd@pusan.ac.kr).
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the wound by forming a thin film of polymer.[15] A liquid bandage is a semitransparent adherent material that can be sprayed or painted directly on wounds, permitting some visual observation of the wound without removing the dressing. It reduces pain by covering nerve endings and helps wounds heal by maintaining a proper moisture balance and keeping bacteria and debris out. The bandages work by sealing the wound until the damaged area heals and the surrounding skin and bandage slough off. Liquid bandage does not easily fall off while taking a shower. They stick better than plastic or fabric adhesive bandages to hard-to-bandage area, such as knuckles and between fingers. Therefore, liquid bandages can be the most convenient and effective dressing for various slight wounds, such as minor cuts and scrapes.

The liquid bandage is applied directly to the wound, the solvent is evaporated and/or precipitated, or the solution is coagulated *in situ* leaving a polymer film covering over the wound. Polymers used may include polyvinylpyrrolidone (water based), pyroxylin/nitrocellulose or poly(methylacrylate-isobutene-monoisopropylmaleate) (alcohol based), and acrylate or siloxane polymers (hexamethyldisiloxane or isooctane solvent based). Other types of liquid bandages (more suited for use when the wound is actively bleeding) are based on cyanoacrylates.[16] Other polymeric film coverings such as polyvinylidene chloride and polyvinyl alcohol may be used as well. Since these polymers are not elastomers, they do not provide elasticity and recovery to the formed film. Because of their high softening temperatures, they do not permit the film to flow as a result of the skin and body heat. None of the above wound coverings provide all of the desired combination of properties needed for enhanced wound healing, such as elastic recovery and low glass transition temperatures for improved conformity to the site. Several studies[8–10,17–20] have been proposed to achieve various polymer films for the wound dressings.

In the biomedical field, hydrophilic PEG can be used by itself or in combination with other compounds. It can also be incorporated into polymer backbones or immobilized onto polymeric biomaterial surfaces to make them "nonfouling." The nonfouling, or cell and protein resistant, properties of surfaces containing PEG are due to the material's highly hydrated state.[6] Poly(dimethylsiloxane), hydroxyl terminated (PDMS) have found many applications because of their unique properties, which arise mainly from the nature of the siloxane bond (Si—O). PDMS have several advantages, including hydrophobicity, low surface tension, unique flexibility, low glass transition temperature (around −123°C), chemical inactivity, insulating stability, high-temperature stability, UV stability, and so on.[8–11] Polyurethane-ureas based on PEG have been shown to absorb and swell with aqueous media without dissolving.[12] Over the past two decades, considerable attention has been directed at exploiting the properties of PDMS by using it as a soft segment component in segment copolymers, mainly polyurethanes and polyurethane-ureas.

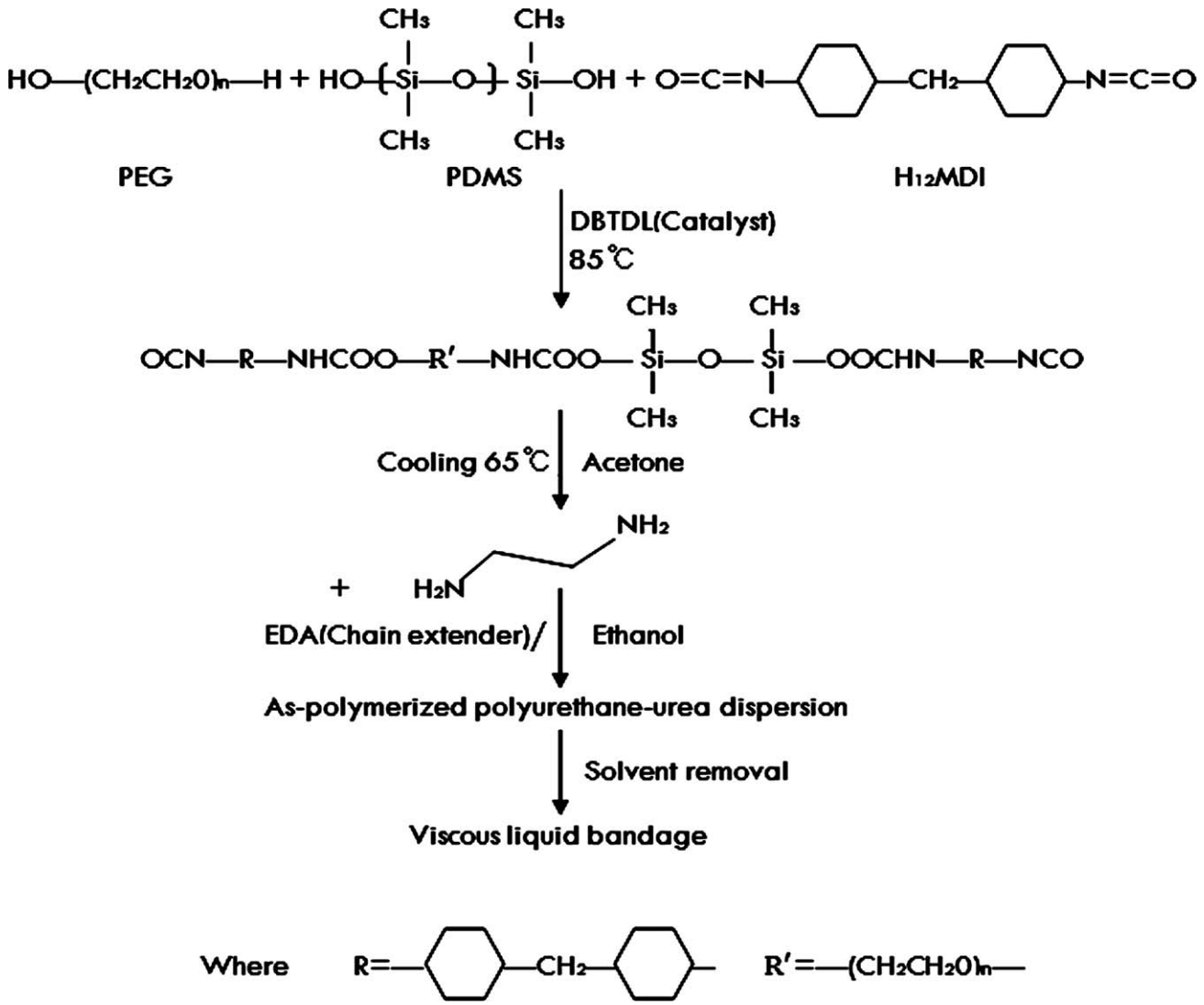
The goal of this study is to investigate the effect of the molar ratio of PEG/PDMS on various properties for polyurethane-urea liquid bandage materials. Polyurethane-ureas containing hydrophilic PEG and flexible hydrophobic PDMS are elastomeric polymers with low glass transition temperatures, providing films with the needed softness/elastic recovery and moist environment. The harmonic combination of both properties of hydrophilic PEG and hydrophobic PDMS in polyurethane-urea may provide an interactive wound care system that solves the problems with other materials. That is, the adequate composition of polyurethane-urea should provide a film covering and interaction with the wound during the healing process, providing the optimum wet environment and elasticity/wound-protecting cushioning for enhancing wound healing, improving patient comfort.

Therefore, to obtain ideal polyurethane-urea liquid bandage materials by controlling hydrophilic component (PEG) and hydrophobic component (PDMS), a series of polyurethane-urea-based liquid bandage materials were synthesized from H_{12}MDI as a diisocyanate and ethylene diamine (EDA) as a chain extender with different molar ratio of polyol blend (PEG/PDMS). The effect of PDMS content on the viscosity, tensile/elastic recovery, water contact angle/surface energy, insolubility in water (%), water absorption (%), equilibrium water content (%),WVTR (g m^{-2} day^{-1}), and wound healing evaluation of samples was investigated.

EXPERIMENTAL

Materials

Polyethylene glycol [PEG, number-average molecular weight (M_n = 2000 g/mol, Aldrich Chemical, Milwaukee, WI)] was degassed at 70°C under vacuum overnight before use. Poly(dimethylsiloxane), hydroxy terminated [PDMS, number-average molecular weight (M_n = 550 g/mol, Aldrich Chemical, Milwaukee, WI)], 4,4′-diisocyanato dicyclohexylmethane (H_{12}MDI, Aldrich Chemical, Milwaukee, WI), ethylene diamine (EDA, Aldrich Chemical, Milwaukee, WI), acetone (Aldrich Chemical, Milwaukee, WI) and ethanol (Aldrich Chemical, Milwaukee, WI), dibutyl tin dilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI) were used without further purification.



Scheme 1 The preparation process for polyurethane-urea/acetone/ethanol dispersions and viscous liquid bandage.

Synthesis of liquid bandage materials (polyurethane-urea containing PEG/PDMS)

Polyurethane-urea-based liquid bandage materials were synthesized using H_{12}MDI/PEG/PDMS/EDA. The PEG/PDMS was placed in a four-necked, round-bottom flask equipped with a thermometer, a stirrer, an inlet of dry nitrogen, a condenser, and a heat jacket, and degassed under vacuum at 90°C for 30 min. Then after cooling to 50°C under moderate stirring, H_{12}MDI and DBTDL were added to the flask and heated to 85°C under moderate stirring. The reaction mixture was allowed to react at 85°C until the theoretical isocyanate (NCO) content was reached. The change in NCO content during reaction was determined using a standard dibuthylamine back-titration method (ASTM-D-1638). Then acetone was added to the reaction mixture for lowering the viscosity of the reaction mixture. The prepolymer was chain-extended by dropping EDA, dissolved in ethanol at 40°C for 2 h, and the reaction was continued until the NCO absorption peak (2270 cm^{-1}) in the infrared spectra had completely disappeared. After evaporation of solvent (acetone: boiling point 55°C/ethanol: boiling point 78°C) at about 55°C, viscous liquid bandage materials of polyurethane-urea were obtained. It was found that almost all ethanol added in the reaction process was remained in the viscous liquid bandage materials; however, the solvent acetone was remained a little. The preparation procedure for polyurethane-urea-based liquid bandages is shown in Scheme 1. The composition of the polyurethane-urea prepared in this study is given in Table I.

Preparation of the polyurethane-urea films

As-polymerized polyurethane-urea solutions were casted onto a Teflon disk under ambient conditions to make films. The films (thickness = 0.1–0.3 mm) were

TABLE I
Sample Designation, Composition, Viscosity of As-Polymerized Polyurethane-Urea/Alcohol/Acetone Dispersions, and Inherent Viscosity ([η]) of Polyurethane-Urea Polymer

	Composition (mole)					
Sample designation	$H_{12}MDI$	PEG ($M_n = 2000$)	PDMS ($M_n = 550$)	EDA	Viscosity (cP)	[η] (dL/g)
PD1	1.1	0.5	0.3	0.2	67	0.92
PD2	1.1	0.4	0.4	0.2	58	0.91
PD3	1.1	0.3	0.5	0.2	52	0.90
PD4	1.1	0.2	0.6	0.2	35	0.89

dried at room temperature for 1 day, and then the remaining solvent was removed at 60°C and 20 mmHg for 1 day and stored in a desiccator at room temperature.

Characterization

A Fourier transform infrared spectrometer (Impact 400D, Nicolet, Madison, WI) was used to identify the polyurethane-urea structure. For each sample, 32 scans at 2 cm^{-1} resolution were collected in transmittance mode.

The inherent viscosity (dL/g) of polyurethane-urea was determined from the ratio of the natural logarithm of the relative viscosity (t/t_o : t = flow time of solution and t_o = flow time of solvent) to the concentration (g/dL) of the polymer in grams per 100 mL of solvent (DMF).

Viscosity of polyurethane-urea/alcohol dispersion was measured at 20°C using a Brookfield digital viscometer (Brookfield LVDVII+, Middleboro, MA). The measurements were performed at 50 rpm using the spindle RV-3 and RV-5.

The mechanical properties of film samples were measured with a sample extension on standard dumbbell-shaped specimens using a tensile tester (United Data System, Instron SSTM-1, Japan) at a crosshead speed of 20 mm/min according to ASTM-D-1822-L. The films have a thickness of 0.3 mm.

The contact angles of water and benzene were measured at 25°C using a contact angle goniometer (Erma Contact Angle Meter, Japan), and the reported results were the mean values of five times. The contact angle, a measure of the surface wettability, was used to determine the hydrophobicity and hydrophilicity. The surface energy of solid film can be calculated by the following equation:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (1)$$

where γ_s represents the surface energy of solid film, γ_s^d represents the dispersion force, and γ_s^p represents the polarity force. γ_s^d and γ_s^p can be calculated by the following equation:

$$\gamma_{11}(1+\cos\theta_1) = 2(\gamma_{11}^d \gamma_s^d)^{1/2} + 2(\gamma_{11}^p \gamma_s^p)^{1/2}\gamma_{12}(1+\cos\theta_2) = 2(\gamma_{12}^d \gamma_s^d)^{1/2} + 2(\gamma_{12}^p \gamma_s^p)^{1/2} \quad (2)$$

where γ_{11} and γ_{12} represent the surface tension of the two testing liquids, including the dispersion item and polar item, there are the following relationships between them: $\gamma_{11} = \gamma_{11}^d + \gamma_{11}^p$; $\gamma_{12} = \gamma_{12}^d + \gamma_{12}^p$. On the conditions that the values of γ_{11}^d, γ_{11}^p, γ_{12}^d, and γ_{12}^p were given, γ_s^d and γ_s^p can be obtained by determining θ_1 and θ_2. Therefore, the surface energy of γ_s can be obtained. The testing liquids used was water (L1) and benzene (L2), and their γ_{11}^d, γ_{11}^p, γ_{12}^d, and γ_{12}^p were 21.8 mN/m, 51.0 mN/m, 28.9 mN/m, and 0 mN/m, respectively.[21]

The insolubility in water (wt %) for the polyurethane-urea films was estimated by measuring its insoluble part after extraction in distilled water at 40°C for 1–5 days. The unsolved part was dried to constant weight at 100°C. Insolubility in water (wt %) was calculated by the following equation:

$$\text{Insolubility in water (wt \%)} = (W_t/W_i) \times 100 \quad (3)$$

where W_i is the dried weight of film sample, and W_t is the dried weight of film sample after extraction.

The water absorption (%) was calculated by the following equation:

$$\text{Water absorption (\%)} = [(W_s - W_d)/W_d] \times 100 \quad (4)$$

where W_s is the weight of swollen film sample, and W_d is the weight of dried film sample. The polyurethane-urea films were immersed in distilled water for regular intervals of time at 37°C. After the excessive surface water was removed with filter paper, the weight of swollen sample was measured until there was no further weight increase.

The equilibrium water content was calculated by the following equation:

$$\text{Equilibrium water content (\%)} = [(W_s - W_d)/W_s] \times 100 \quad (5)$$

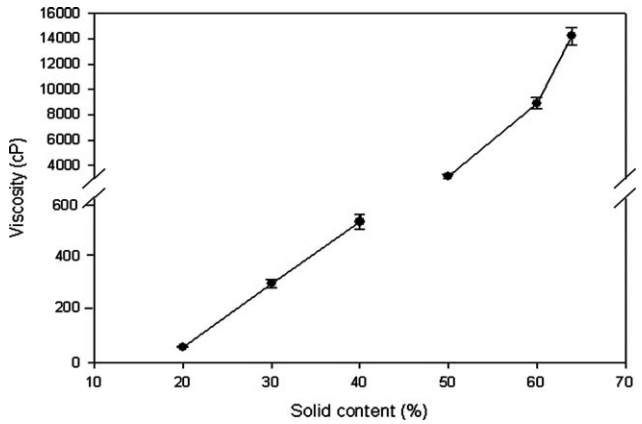


Figure 1 Relationship between viscosity and solid content of a typical liquid bandage material (PD2 sample) obtained by evaporation.

where W_s is the weight of polyurethane-urea film sample at equilibrium swelling, and W_d is the weight of dried sample.

The moisture permeability was determined by measuring the WVTR across the material as stipulated by ASTM E96/E96*M*-05. The polyurethane-urea films were mounted on the mouth of cylindrical aluminum cups (diameter: 60 mm) containing 10 mL of water. The polyurethane-urea films were fastened using Teflon tape across the edges to prevent any water vapor loss through the boundary and kept at 35°C and 35% relative humidity in an incubator. The WVTR was calculated by the following formula:

$$\mathrm{WVTR} = [(W_i - W_t)/A \times 24] \times 10^6 \mathrm{g\ m^{-2}\,day^{-1}} \quad (6)$$

where WVTR is expressed in g m^{-2} day^{-1}, A is the area of the cup mouth (mm^2), and W_i and W_t are the weights of cup containing water before and after permeation of water in an incubator, respectively.

In vivo wound healing

Adult Sprague-Dawley (SD) rats were purchased from Samtaco in Korea (Branch distribution point of Taconic). All of the rats were kept in Pusan National University-Laboratory Animal Resources Center (PNU-LAR center) in accordance with the NIH guideline. The rats were given a standard irradiated chow diet (Purina Mills) *ad libitum* and were maintained in a specified pathogen-free state under a strict light cycle (light on at 06 : 00 h and off at 18 : 00 h). Also, the animal protocol used in this study has been reviewed by the Pusan National University-Institutional Animal Care and Use Committee (PNU-IACUC) on their ethical procedures and scientific care, and it has been approved (Approval Number PNU-2010-0006). First, at 10 weeks of age, the SD rats were randomly divided into two groups (n = 6). Twelve rats were anesthetized with intramuscular injection of Zoletil 50 (50 mg/kg) and shaved hair on the back skin. A round wound 8 mm in diameter and 2–4 mm in depth was formed by removing the skin in the shoulder region of back skin using Biopsy Punch (Kasco com). The wound skins of rats in one group were covered with PD2 film while other group covered with sterilized gauze. The PD2 film and gauze were replaced every 2 days for 10 days, and for the next 4 days, the dressings were not replaced. After 2 weeks, all rats were administered euthanasia using carbon dioxide, and the samples of damaged skin were collected from rats to following histological analysis: The wound skins were removed from rats, fixed with 10% formalin, embedded in paraffin wax, routinely processed, and then sectioned into 5-μm thick slices. The skin sections were then stained with hematoxylin and eosin and examined by light microscopy at 100× magnification for the change of skin structure.

RESULTS AND DISCUSSION

Solid content and viscosity of as-polymerized polyurethane-urea dispersions

The molar composition of H12MDI/EDA and solid content (20 wt %) of as-polymerized samples were fixed, while the mole % of lower molecular PDMS in polyol blend [PDMS (M_n : 550 g/mol)/PEG (M_n : 2000 g/mol)] was increased from 37.5 to 75.0%, which gave the increase of hard segment content. The sample designations, compositions, and viscosity of as-polymerized polyurethane-urea dispersions (polyurethane-urea/acetone/ethanol) and the inherent viscosity of polyurethane-urea polymers are shown in Table I. The viscosity of as-polymerized polyurethane-urea/acetone/ethanol materials

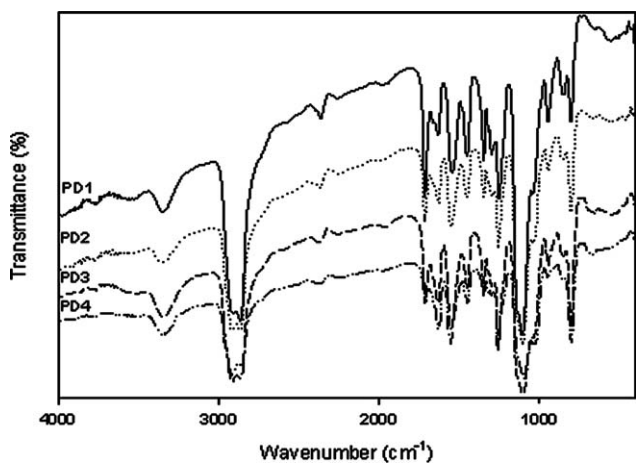


Figure 2 FT-IR spectra of polyurethane-urea film samples.

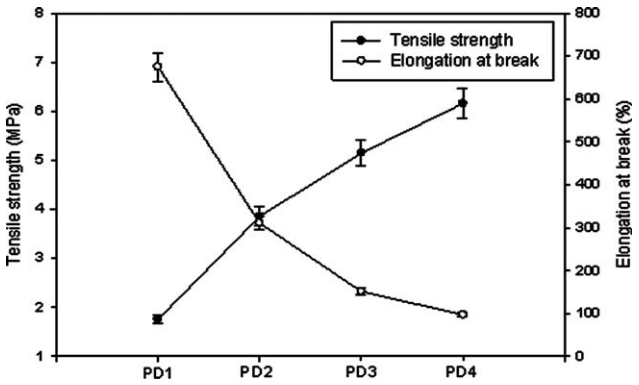


Figure 3 Tensile strength and elongation at break of polyurethane-urea film samples.

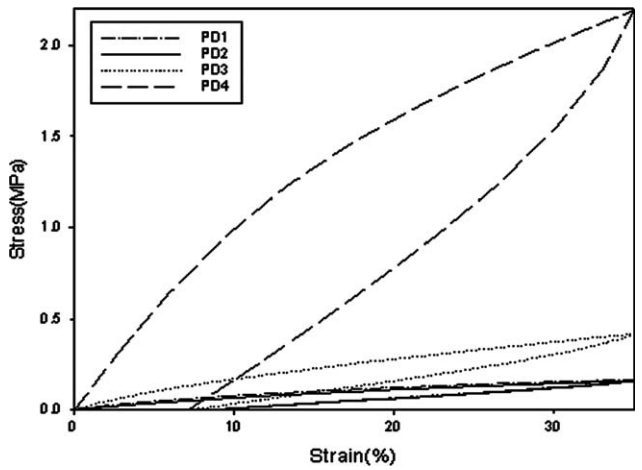


Figure 4 Stress–Strain hysteresis curves of polyurethane-urea film samples.

decreased with increasing PDMS content in polyol PEG/PDMS (see Table I). The decrease of viscosity should be attributed to the hydrophobicity of PDMS component which could not be attracted to polar groups of solvent ethanol/acetone.

Solid content/viscosity changes of the dispersions by evaporation

The as-polymerized liquid bandage materials (solid content: 20 wt %, ethanol/acetone: 57/43 wt %, and viscosity: 67–35 cP) prepared in this study had too low solid content/viscosity to leave polymer film with the right level of thickness covering over wounds. Therefore, evaporation was needed to leave the least content of acetone and thicken the as-polymerized dispersions to obtain a suitable viscosity for the liquid bandage. The relationship between viscosity and solid content of a typical sample (PD2) obtained by evaporation is shown in Figure 1. The viscosity was sharply increased with increasing solid content. The acetone content in mixed solvent (acetone/ethanol) used in polymerization procedure was markedly decreased by evaporation at about 55°C. This should be due to the lower boiling temperature of pure acetone (about 55°C) than that of pure ethanol (about 78°C). The viscosity and solid content of evaporated PD2 sample were found to be similar with those of commercial salves, at about 8900 cP and 60 wt %, respectively. The composition of remained ethanol/acetone in evaporated PD2 liquid bandage material (solid content: 60 wt %) was found to be 92/8 wt %, and this might serve as potent antiseptic composition.

Curing time and inherent viscosity

In addition, it was also found that the curing time to form the nonsticky film through vaporizing the solvent on skin was dependent on the film thickness. The curing time for films of 0.05-, 0.10-, and 0.15-mm thick was found to be about 3.0, 4.2, and 6.0 min, respectively. It was found that the curing times of PD2 sample was suitable for liquid bandage application. We also found that satisfactory thickness and curing time were 0.15 mm and 6.0 min, respectively. The inherent viscosity values of samples were all quite high at about 0.9 (see Table I). This indicated that the polyurethane-ureas containing PEG/PDMS synthesized in this study were high-molecular weight polymer for high-performance liquid bandage materials. The inherent viscosity of polyurethane-urea decreased a little with increasing PDMS content. This might be due to the lower molecular weight of PDMS compared with PEG.

TABLE II
Contact Angle, Surface Energy, Insolubility in Water at Equilibrium, Water Absorption (%), Equilibrium Water Content, and Water Vapor Transmission Rate of Polyurethane-Urea Film Samples

Sample designation	Contact angle (°)		Surface energy (mN/m)	Insolubility in water at equilibrium (%)	Water absorption (%)	Equilibrium water content (%)	Water vapor transmission rate (g m^{-2} day^{-1})
	Water	Benzene					
PD1	41	19	58	65	956	90	3422
PD2	55	22	48	84	567	85	2524
PD3	67	33	39	89	333	77	2118
PD4	75	35	34	94	149	55	1417

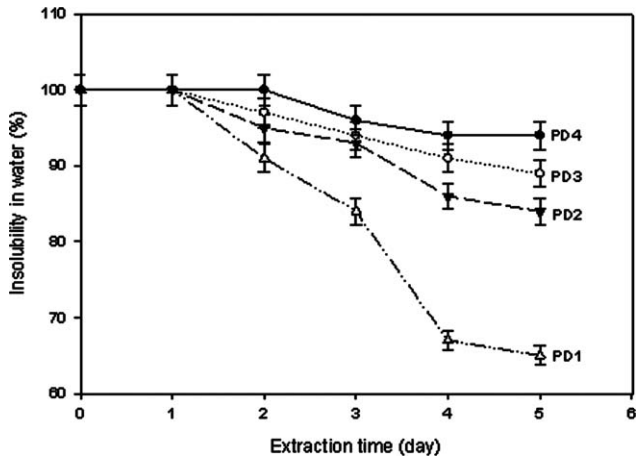


Figure 5 Insolubility in water versus extraction time of polyurethane-urea film samples.

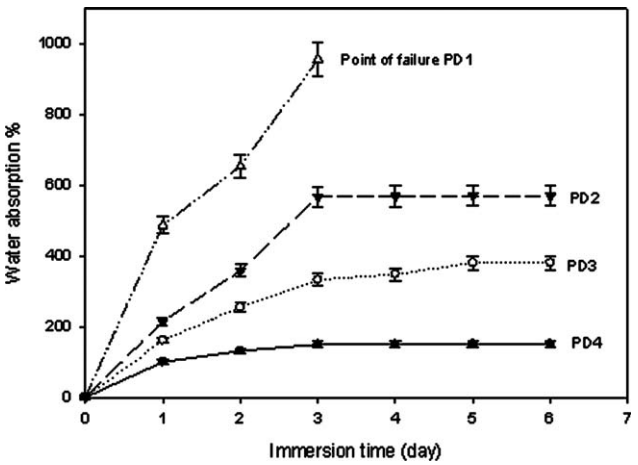


Figure 6 Water absorption percent versus the immersion time of polyurethane-urea film samples.

Identification of chemical structure of polyurethane-urea

The sample designation, composition, and various properties of polyurethane-urea dispersions/films prepared in this study are shown in Table I. The chemical structure of polyurethane-urea films containing PEG and PDMS was identified by characteristic IR peaks (Fig. 2). The urethane/urea groups having H_{12}MDI present the characteristic peaks of N—H stretching band at 3520–3320 cm^{-1}, C=O stretching band at 1740–1700 cm^{-1}, N—H bending and C—N stretching band at 1530–1450 cm^{-1}, CH_2 scissors vibration band at 1475–1450 cm^{-1}, and CH_2 rocking in methylene chains band at 740–720 cm^{-1}. The characteristic peaks of PEG, such as —CH_2— symmetric stretching at 2990–2850 cm^{-1}, in-plane OH bending at 1440–1400 cm^{-1}, C—O stretching at 1200–1015 cm^{-1}, C—C stretching at 965–920 cm^{-1}, and CH out-of-plane deformation at 850–790 cm^{-1}, increased with increasing PEG content. As the PDMS mole ratio increased, the peaks at 2990–2850 cm^{-1}, 1440–1400 cm^{-1}, and 850–810 cm^{-1} due to CH_3 symmetric deformation in siloxanes, Si—O—Si antisymmetric stretching, and Si—CH_3 rocking in PDMS, respectively, are increased. From these results, the chemical structures of four samples were identified.

Tensile properties

The tensile strength and elongation at break of the polyurethane-urea films are shown in Figure 3. The values of the tensile strength/elongation at break for PD1, PD2, PD3, and PD4 were found to be 1.8 MPa/674%, 3.9 MPa/311%, 5.1 MPa/151%, and 6.2 MPa/97%, respectively. As the PDMS content increased, the tensile strength of polyurethane-urea film samples increased, but the elongation at break of polyurethane-urea samples decreased. This behavior must be caused by the increase of hard segment content by using lower molecular weight PDMS (MW = $\sim$ 550 g/mol) instead

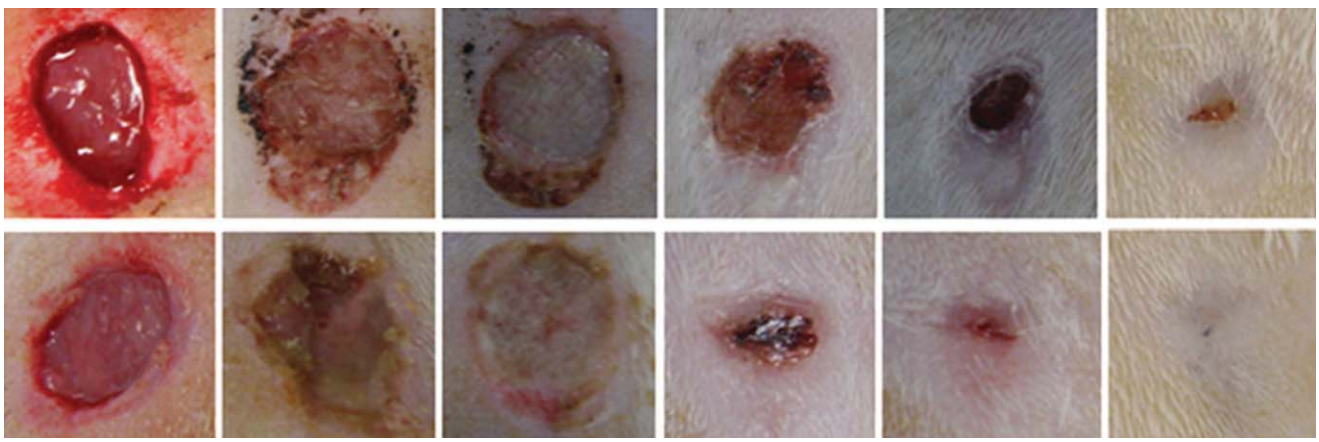


Figure 7 Comparison of wound healing by (a) gauze and (b) liquid bandage (sample PD2) dressings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

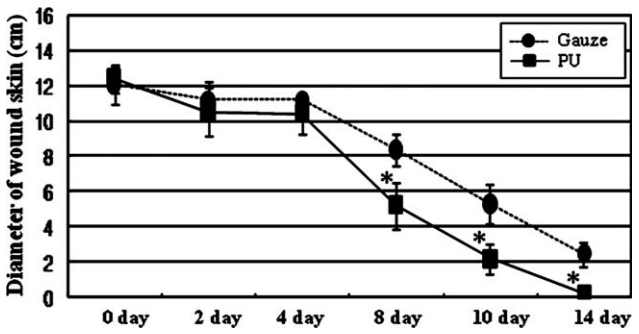


Figure 8 Comparison of diameter of skin wound by gauze and liquid (sample PD2) dressings.

of higher molecular PEG (MW = 2000 g/mol). Ideal liquid bandage material requires softness, elastic recovery, and wound-protecting cushioning properties, which are typical properties of polyurethane-urea. Figure 4 shows the stress–strain hysteresis curves of film samples for a given elongations (35%). The initial modulus (initial slope of stress–strain curve) and elastic recovery (%) of film sample were markedly increased with increasing PDMS content. Especially, the PD4 sample containing the highest PDMS content showed the highest modulus and stress for given strains, indicating that the PD4 sample was the most hard and inflexible material. So, the softness of film samples increased in the order of PD1 > PD2 > PD3 ≫ PD4. This also must be attributed to the increase of hard segment content by using lower molecular weight PDMS. Additionally, it was also found that some soft elastic polyurethane-urea materials (samples PD2 and PD3) having suitable thickness (0.05–0.15 mm) showed wound-protecting cushioning performance.

Water resistance and absorption

Sufficient water resistance and absorption of wound dressings are required not only to prevent excessive solubility but also to make wet environment for the wound. The water contact angle and surface energy of the polyurethane-urea films are shown in Table II. As the PDMS content increased, the water contact angle of films increased, while the surface energy of films decreased. This should be attributed to the hydrophobicity of PDMS component. Additionally, since PDMS had a much lower surface energy than polyurethane, PDMS might migrate to the surface layer during the polyurethane-urea film forming, which resulted in a low surface energy as well as high water contact angle. The insolubility in water (%) of the polyurethane-urea film samples with extraction time is shown Figure 5 and Table II. The insolubility in water (%) of all the samples except PD1 at 3 days of extraction was in the range of 96–100% and then reached to almost constant values in the range of 84–94% after 4 days. They increased markedly with increasing PDMS content. The water absorption versus the immersion time is shown in Figure 6. The water absorption increased with increasing immersion time and then leveled off. The PD1 film sample having the least content of PDMS was dissolved in water after 3 days, indicating that the PD1 sample was much water soluble. This must be due to the high level of hydrophilic PEG content. For this reason, it might be difficult to use the PD1 sample as a liquid bandage material. However, the PD2 and PD3 film samples had high level of water absorption and maintained their dimensional stability after 6 days. The maximum water absorption and equilibrium water content of the film samples were markedly decreased with increasing the PDMS content (see Table II). The sample PD4 had too low water absorption to give good wet environment for wounds. This should be due to the lower hydrophilicity of PDMS component as well as higher hard segment content. From these results, the PD2 and PD3 samples had high potential as new liquid

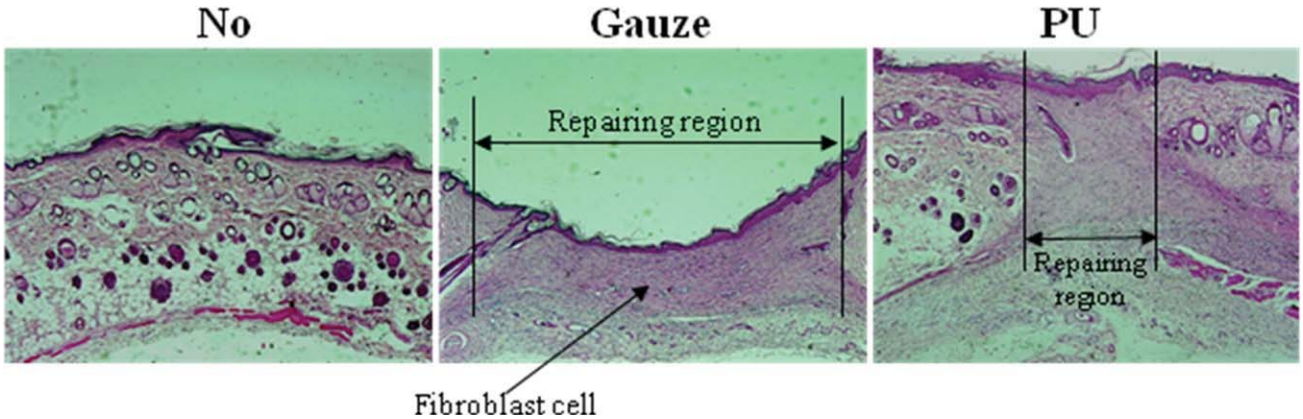


Figure 9 Comparison of histological analysis by gauze and liquid bandage (sample PD2) dressings. The slide sections of skin tissue were stained with hematoxylin and eosin and observed at ×100 magnification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bandage materials, which could provide good wet environment for wounds.

Water vapor transmittance rate

The adequate water vapor transmission of a wound dressing is required to prevent excessive dehydration as well as build up of exudates. It has been recommended that the WVTR in the range of 2000–2500 g m^{-2} day^{-1} would provide adequate level of moisture without risking wound dehydration.[22] The WVTRs of film samples with a fixed thickness (0.2 mm) prepared in this study are shown in Table II. They were in the range of 1417–3422 g m^{-2} day^{-1}. The WVTR decreased with increasing PDMS content. With respect to optimum WVTR, samples PD2 and PD3 (WVTRs of PD2 and PD3: 2524 and 2118 g m^{-2} day^{-1}) were also found to be the most suitable materials for wound dressing without risking wound dehydration.

Comparison of wound healing by gauze and typical liquid bandage (sample PD2)

The wound-healing efficacy of dressing was evaluated with a full-thickness rat wound model. To compare the efficacy at the same condition, wounds in rats were dressed with PD2 film (test material, thickness: 0.1 mm) and gauze (reference material), which were replaced every 2 days for 10 days. For the next 4 days, the dressings were not replaced. The comparisons of the wound-healing efficacy of the typical sample PD2 membrane and gauze dressings are shown in Figures 7, 8, and 9. In the case of the gauze dressing, a scab and scar was present after 14 days. However, by the use of the sample PD2 film dressing prepared here, the size of the smooth subcutaneous tissue was remarkably reduced, and the wound was completely healed after 14 days. The epithelialization with the sample PD2 film dressing was better than that with the gauze dressing. This should be due to the adequate conditions of the PD2 sample, such as good water absorption, and proper WVTR. This result demonstrates the high potential of sample PD2 prepared here for use in new liquid bandage materials.

CONCLUSIONS

In this study, a series of polyurethane-urea based liquid bandage materials were prepared from H_{12}MDI as an aliphatic diisocyanate, hydrophilic PEG/hydrophobic PDMS blend as a soft segment, EDA as a chain extender, and acetone/ethanol as a solvent. In this context, this study focused on the effect of PDMS content in PEG/PDMS on the viscosity, tensile properties, water contact angle/surface energy, insolubility in water (%), water absorption (%), equilibrium water content (%), and WVTR (g m^{-2} day^{-1}) of samples. These properties were found to be noticeably dependent on the content of PDMS. We found that samples PD2 and PD3 prepared in this study proved to be the good liquid bandage materials with the right amount of softness, elastic recovery, moisture absorption, and water vapor permeability. When wound was covered with a typical sample PD2 film, new epithelium filled it completely without any significant adverse reactions. From these results, it was concluded that samples PD2 and PD3 prepared in this study were good candidates for the excellent liquid bandage materials.

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