SOFT GELS WITH HIGH ELECTRIC, ULTRASOUND CONDUCTIVITY AND STABLE THREE-DIMENSIONAL CONFIGURATION AS ENERGY TRANSMISSIBLE MEDIA

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Abstract: We had synthesized single component permanent gels, segmented polyurethane gels (SPUGs), essentially consisting of gelatinizing component-only, of which almost of segments and dangling chains are liquid state at ambient temperatures. SPUGs transmit energy well such as electricity, light and ultrasound. In this article, SPUGs were improved by adding dispersive media into swollen SPUGs (S-SPUGs), which acquired higher electric conductivity (1.2×10^{-3} S/cm) at room temperature and lower ultrasound attenuation (0.13 dB/ MHz cm) than SPUGs and readily responded to very low mechanical stress (Young modulus 3.7×10^{4} Pa) due to its high flexibility like soft tissues of living body. The S-SPUGs, which have three-dimensionally casting moldability and stable configuration, are potentially applicable to soft biomaterials with energy transmissible, transducing faculty.

1 INTRODUCTION

This research relates to potential application of novel soft gels with stable three-dimensional configuration and high electric, ultrasound conductivity as energy transmissible media for biomaterials.

Gels generally consist of the both components of a material to be gelatinized and dispersion media, and are classified from various viewpoints. In a viewpoint, gels usually form a collection of mobile molecular chains including dispersion media, of which reticular structures are three-dimensionally developing through aggregation, intertwining, molecular orientation, and covalent bonds. The swollen gel that a polymer has absorbed the dispersion medium generally shows molecular aggregation of morphology (A) or (B) in Figure 1. Both of them are two-component systems, and non-ionic gels belonging to (A) are the commonest. The morphology (B) shows polyelectrolyte as hydrogels, which repeatedly shrink and swell in response to external stimulations such as pH, salt concentration, composition of the solvent, ionic composition, temperature, electricity, and light, and the applications as mechanochemical actuators, which directly convert chemical energy into mechanical energy, is being evaluated (Tatara, 1989). Hydrogels categorized in (A) that gelatinizing materials absorbed water as the medium are popularly used as various foods and sanitary goods as well as biomaterials regarded as substitutes for biological gels. However, the medium, water evaporates with time in an open system. Therefore hydrogels are unstable and cannot be used excepting in the closed circumstance where water is always existing. Similarly, organic solvents in organogels, lipid solvents in lipogels and alcohol in alcoogels easily release from the gels with time because of poor interaction between gelatinizing materials and voluminous dispersion media. In view of the disadvantages of these swollen gels, more than 20 years ago, we had synthesized stable single component permanent gels, segmented polyurethane gels (SPUGs) (Shikinami, 1991, Shikinami, 1992) essentially consisting of a single gelatinizing component, of which almost all of segments in a

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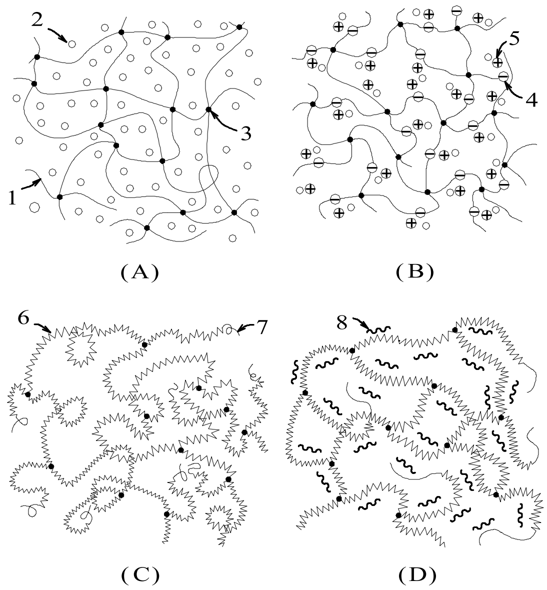

Figure 1: Morphologies of molecular aggregation of swollen gels. SPU consists of PAO (EO/PO) segments (liquid state at ambient temperatures). Swollen SPUG (D) incorporates liquid dispersion media among the PAO network.

1. molecular chain
2. dispersion medium (water, organic solvent, oil)
3. junction 4. ion group 5. pair ion
6. liquid segment 7. dangling chain
8. dispersive media

three-dimensionally cross -linked polymer and its dangling chains are in liquid state at ambient temperatures. Figure 1 (C) shows the molecular aggregation morphology of single component SPUGs, of which segments and dangling chains consist of low weight molecule, oligomers.

2 PURPOSE OF THIS STUDY

In SPUGs, liquid segments three-dimensionally entangles at junctions move fluidly and dangling chains with free terminals are not involved in the rigidity but increase the viscosity by serving as dispersion media. Therefore, SPUGs with much dangling chains are extremely flexible like highly viscous liquids and have an adhesive surface. A SPUG doped by $LiClO_4$ and a SPUG-alone have been respectively used for functional pressure-sensitive adhesives as skin contact media such as bio-electrodes (disposable electrodes, therapeutic electrodes for low-frequency electric stimulation) and acoustic coupler gels for ultrasonographic examination. In this research, we improved SPUGs into swollen SPUGs (S-SPUGs) without releasing excessive dispersive media in order to enhance the electric conductivity and ultrasound acoustic characteristics, which are flexible and remaining stable three-dimensional (3D) configuration as energy transmissible media for soft biomaterials (Figure 2).

Figure2: S-SPUG as an ultrasonographic coupler gel.

3 METHODS AND RESULTS

Methods, apparatuses and conditions used in this study summarized in Table 1 and each result of S-SPUGs with SPUGs was shown in Table 2.

Table 1: Methods.

	Method, Apparatus and Condition
Density	Density determination device with balance (METTLER TOLEDO Co., Ltd) in hexane at 25°C
Elasticity (Young modulus)	Venustron Biosensor (AXIOM Co., Ltd) at 23°C
Transparency Transmission rate at 600nm [%T]	UV-VIS spectrometry (SHIMADZU Co., Ltd) Wavelength; 600nm Sample thickness; 2mm / 10mm
Ultrasound velocity and attenuation	Sing-around method at 20°C and a reference
Attenuation	Sing-around method by means of UVM-2 (Ultrasonic Industry Co.)
Acoustic impedance	Sound velocity x density
Electric conductivity	Impedance analyzer Li/O = 5 / 100 Frequency(υ); 1kHz at 24°C
Fungus resistance	Test for Fungus Resistance (Japanese Industrial Standards Z-2911)

Table 2: Comparison of S-SPUGs with SPUGs.

Sample		Young modulus [Pa]	Transmission rate at 600nm [%T]	Ultrasound velocity [m/s]	Attenuation [dB/MHz cm]	Electric conductivity (Li/O=5/100) [S/cm]
SPUG	OH/NCO=2.10	4.1×10^{4}	t=2mm 90.0 t=10mm 88.8	1506	1.1	—
S-SPUG-I	OH/NCO=2.10 PC 50wt%	3.7×10^{4}	t=2mm 90.7 t=10mm 89.8	1468 (1450-1550)*	0.13	1.2×10^{-3}
S-SPUG-II	OH/NCO=1.45 TG 50wt%	1.18×10^{4}	t=2mm 90.0 t=10mm 89.3	(1477-1563)*	0.09	3.7×10^{-4}
Human body (Soft tissues)	—	Side abdomen 6.7×10^{4} Stomach 1.06×10^{5} Arm (outside) 1.45×10^{5} (inside) 2.01×10^{5}	—	1540	0.5	—

Density; SPUG=1.03, Swollen SPUG-I=1.13, Swollen SPUG-II=1.02
PC; Propylene carbonate, TG; Tetraglyme
PC 25wt%; E.C. = 5.0×10^{-4}S/cm, PC 60wt%; E.C. = 2.1×10^{-3} S/cm, TG 25wt%; E.C. = 1.1×10^{-4} S/cm
Li/O; ratio of Li ion versus ether oxygen in poly alkylene oxide as segments and dangling chains
OH/NCO; end group of PAO, OH versus end group of Isocyanate, NCO
* Depending upon the concentration of poly acrylic powder contained in the gel

3.1 Molecular Design of SPUGs and Swollen SPUGs

One method to obtain single component gels, of which category has never been found until we had developed (Shikinami, 1998), is to extend low-molecular weight polymers, which are liquid at room temperature, and to loosely crosslink them. SPUGs have liquid segments and dangling chains, which chemically compose of polyalkylene oxides (PAOs) (EO/PO; ethylene oxide and propylene oxide copolymer chains, preferably random copolymers) that function as a medium incorporated into cross-linking segmented polyurethane chains. We have practically used them so far in the field of medical engineering (ME) as skin contact media for energy transmission. Polyethylene glycol (PEG) and its mono methyl ether having molecular weights (Mw) of less than 600 and polypropylene glycol (PPG) having Mw of less than tens of thousands are liquid and flow at room temperature. Also copolymers of ethylene

oxide and propylene oxide (EO/PO) are viscous, fluid liquids at room temperature depending on the ratio of EO in EO/PO and the molecular weight. The aggregation energy of components of these PAOs (Bunn, 1955) and surface tension of the terminal groups and units of repetition are relatively low (0.8~1.77 Kcal/mol). The aggregation energy of the urethane bond (-NHOCO-) obtained as the OH group at the terminal of PAO reacts with the NCO group of poly isocyanate including liquid PAO (these groups are used as multi-functional groups for chain extension or formation of reticulation) is high at 8.74, and makes a highly restrained junction. Therefore, if a segmented polyether urethane (SPEU) consisting of almost all of liquid segments and having many dangling segments of M-PEG can be synthesized, it is expected to be a single component gel-state molecular aggregation. Figure 3 shows the structure of the basic molecule of SPUG. This selection was adequate, and many kinds of SPUGs could be obtained.

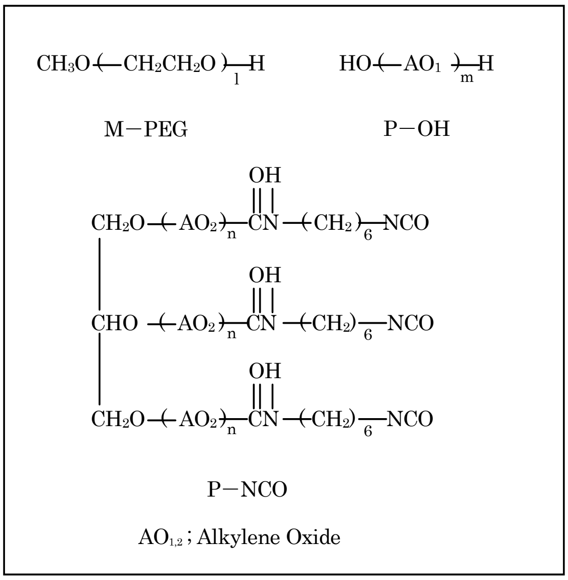

Figure 3: Structures of liquid molecular chains.

3.2 Electric Characteristics of SPUGs (Shikinami, 1991)

The mechanism by which complexes of PAOs, PEG or EO / PO copolymers and $LiClO_4$ enhance electric conductivity due to ionic conduction has already been clarified (Ccallum, 1987). Solid solution of $LiClO_4$ with PAO as a medium is produced by interaction between dipoles (ligands) in PAO and ions. Ionic conduction is originated when Li^+ moves to the other ether oxygen in the physical space with surfboard riding-like motion resulting from molecular movement of PAO (Wright, 1975) segments. As the glass transition temperature (Tg) of the PAO segments is lower, molecular movement becomes greater, and ionic conduction becomes higher, hence a greater specific electric conductivity. From this fact, SPUGs and $LiClO_4$ are also considered to form complexes with large specific electric conductivity because of their low Tg. This specific electric conductivity is obviously dependent on the molecular configuration of segments of PAO. In the ion-conductive SPUGs that we synthesized as skin contact pressure sensitive adhesives, the ionic conduction rate σ (S/cm) becomes highest when the segments of P-OH and P-NCO components are random copolymers of EO/PO (molar ratio: 50/50) was 10^{-4}~10^{-5} at RT~100°C, and 10^{-6} at 0°C when the salt concentration [Li] / [-0-] was 1/100 ~10/100. These values of ionic conductivity are considered to be one of the highest among various ion conductive PAO materials studied to date. This SPUG is presently used as the contact medium of disposable leads for electrocardiography and of stimulation electrodes of various low frequency therapeutic instruments. The SPUG conducts accurately various low-frequency waveforms through the electrode to the skin. However, SPUGs would be utilized in furthermore various ways if electric resistance were lower than these values by one figure, 10^{-3} (S/cm). S-SPUGs were developed for the purpose.

3.3 Ultrasound Acoustic Characteristics of SPUGs

Ultrasound characteristics, conduction velocity, acoustic impedance and absorption coefficient of body tissues have already been examined. Despite slight variations according to the water contents at different sites of the body, i.e. blood, brain, adipose tissue, kidney, liver, muscle, excepting bone, the velocity of ultrasound conduction is around 1,500m/s, and the ultrasound impedance (ρC), which is the product of the density and the sound conduction velocity, is about 1.4 to 1.7(10^6kg/m^2 s), approximately equal with water and the body fluid. Attenuation (α; dB/MHz cm) is about 0.2 to 3.3, while that of water is very low at 0.0022. These values of SPUGs are insufficient for use in the phantom gels for ultrasonograph and improved by S-SPUGs (α; 0.13) as shown in Table 2.

4 CONCLUSIONS

S-SPUGs increased electric conductivity and decreased ultrasound attenuation (impedance) of SPUGs remaining moldability with 3D stable configuration, so that these soft gels serve the potentialities of electroactive polymers for artificial muscles as the electric conductive media and of the stable phantom gel for ultrasound transmission according to the international quality standards that examine ultrasonographic faculty with good fungus resistance unlike unstable hydrogels. The casting moldability into stable 3D configuration and high flexibility give the artificial soft body and muscle for androids with the energy transmissible, transducing faculty (Minato, 2005), in addition to applications as skin contact media of existing SPUGs for disposable electrodes, therapeutic electrodes and ultrasonographic coupler gels.

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