

Functionally Graded Polyurethane Elastomers Prepared By Electrophoresis

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ABSTRACT: Functionally graded polyurethane elastomers PUEs/grad. Poly(dimethylammonium ethylacrylate bromide)(PDMAEA) were prepared by the method of electrophoresis. Results of elemental analysis showed that concentration of PDMAEA had gradient across the thickness(2mm) of the base PUEs. The modified PUEs(PUEs/grad. PDMAEA) containing high concentration of PDMAEA displayed low degree of swelling in benzene which was poor solvent for PDMAEA, and high degree of swelling in water which was good solvent. For the each layer of modified PUEs, glass transition temperature, dynamic storage modulus were studied by DSC, Rheovibron DDV-IIC dynamic viscoelastomer. The chemomechanical properties of modified PUEs was explored by the electric-stimulus.

Keywords: functionally gradient, PUEs, electrophoresis, degree of swelling, T_g, modulus

I. Introduction

Among the wide variety of polymeric composite materials that have been developed recently, compositions with a gradient of physical or chemical properties have become of interest. These materials include the gradient interpenetrating polymer networks (GIPNs), which were investigated since 1970s.^{1,2}

If a gradient in composition is achieved through a sample, a continuous change in properties would be expected.^{3,4} In addition, if a spatial gradient improves phase intercon-

nection, a further increase in performance may be reached.^{4,5} Such gradient in structure opens up the possibility of making polymer systems with tailor-made properties.

Gradient polymer are usually formed as a result of the swelling of a preformed host network(base material). The base material are swollen in the solution containing monomer, initiator, and crosslinking agent, the swelling is terminated at a certain stage before equilibrium is established, and then polymerization is carried out to produce the guest network. In this case, the concentration of the guest network in the host network has a gradient. As a result, the properties of the system differ from those of both individual

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networks and traditional IPNs.

In this paper, we proposed another way to prepare the functionally graded interpenetrating networks. Functionally graded interpenetrating networks were prepared by the electrophoretic method of ionic monomers. The ionic vinyl monomer (dimethylammonium ethylacrylate bromide)(DMAEA) was introduced to host networks (PUEs) by the electrophoretic method, then radical polymerization was carried out to produce the guest network(PDMAEA). The concentration of PDMAEA through the thickness of modified PUEs was determined by elemental analysis. Water and benzene were used to determine the degree of swelling. Variation of the glass transitions temperature, storage modulus throughout the modified PUEs were studied by DSC, dynamic viscoelastomer. Chemomechanical properties were explored by the electric-stimulus.

II. Experimental

1. Preparation of PUEs

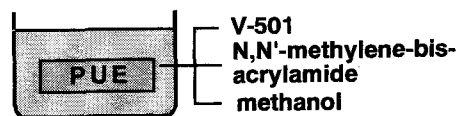
PUEs were prepared from a mixture of ploy(oxytetramethylene)glycol (PTMG:Mn=2000, Wako pure Chemical Industries, Ltd., Japan), 4,4'-diphenyl- methane diisocyanate(MDI: Nippon Polyurethane Industries; Japan), and a mixture of 1,4-butanediol and trimethylol propane(75/25 wt. %) as a chain extender of 1,4-butane diol and trimethylol propane(75/25 wt.%) as a chain extender by prepolymer method. Prepolymer was prepared from PTMG/PEG(50/50wt.%) and MDI[NCO]/(OH)=

3.3] at 70°C for about 3h under a nitrogen atmosphere. The prepolymer and chain extender[(NCO)/(OH)=1.05] were well-mixed for 90s and the viscous reaction product was poured into a mold heated at 130°C and cured for 1.5h at 130°C. Then a sheet of 2mm was demolded, and postcured at 110°C for 24h under an air atmosphere.

2. Preparation of Functionally Gradient(FGIPN)-PUEs

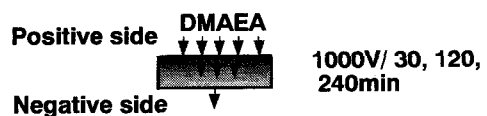
Synthetic scheme of FGIPN-PUEs is shown in Figure 1. PUEs were swollen in methanol

1. Equilibrium swelling of PUE with electrophoretic solution



2. Set up the electrophoretic apparatus, and add DMAEA to the side of positive electrode

3. Electrophoresis



4. Polymerization of DMAEA



5. Dry

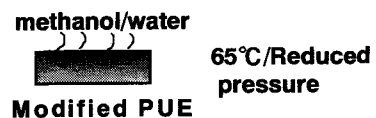


Fig. 1. Modification scheme of PUE sheets by electrophoresis.

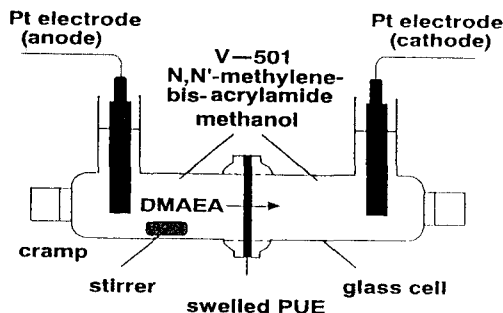


Fig. 2. Apparatus of electrophoresis.

including radical initiator (4,4'-Azobis(4-cyanovaleric acid) and crosslinking agent (N, N'-methylene-bis-acrylamide) (2wt.%, 4wt.% of monomer respectively) at an ambient temperature for 24h, then set up the electrophoretic apparatus as shown in Figure 2. Electrophoretic cell was filled by the swelling solvent. Monomer(10wt.% of the swelling solvent) was added into the anode side cell, and introduced into PUEs by impressing 1KV for 30, 120, and 240min. Monomer was polymerized at 70°C for 24h. Finally, the FGIPN-PUEs were dried at 65°C under reduced pressure.

Compared with the electrophoretic method, FGIPN-PUEs were also prepared by the swelling method. PUEs were swollen in the swelling solvent containing monomer(DMAEA) (10wt.% of the swelling solvent), radical initiator (4,4'-Azobis(4-cyanovaleric acid) and cross-linking agent (N,N'-methylene-bis-acrylamide) (2wt.%, 4wt.% of monomer, respectively) for 240min at an ambient temperature, then polymerization was carried out to produce the guest networks.

3. Determination of the Electric Current

The value of electric current flowing within the electrophoretic cell was measured by a digital multimeter (VOAC 81, Iwatsu Electric Co.Ltd.,Japan).

4. Slicing of FGIPN-PUEs

Perpendicular to the direction of monomer flowing in the electrophoretic cell, the FGIPN-PUEs (2mm thickness) were sliced up to five layers (approximately 0.4mm thickness) by splitting machine (Fortuna Werke Maschonen fabrik AG, Model NAF-470-D, Germany). Each layers from anode side to cathode side were designated as follows; AL, AML, ML, CML, CL as shown in Figure 3. The layers of AL, ML and CL were selected to do the following testings.

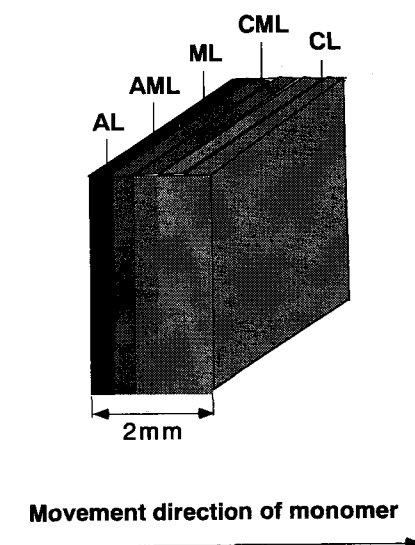


Fig. 3. Designation the name for the sliced sample.

5. Elemental Analysis

In order to determine the gradient profile of the guest networks(PDMAEA), the nitrogen concentration in each layers was determined by elemental analysis.

6. Determination of Degree of Swelling

For the layers of AL, ML, CL, degree of swelling was measured by means of a Measuring Microscope(Pika, Nakamura Works Co.Ltd., Japan). A small cube was cut from the each layer, then the length of one edge(L1) was accurately determined by the measuring microscope. The cube was swollen in the swelling solvent. The length of the same edge(L2) was measured by the same way at the equilibrium swelling. The degree of swelling was defined as $q=(L2)^3/(L1)^3$. Swelling solvents used were water and benzene. Swelling test was carried out at 60°C.

7. Thermal Analysis

Thermograms of the AL, ML, and CL were recorded with the aid of DSC(Rigaku Electric Inc. Japan; Thermo Plus,DSC-8230) at heating rate of 10°C/min from -150°C to 250°C under a nitrogen atmosphere.

8. Dynamic Mechanical Thermal Analysis

Dynamic mechanical experiments were performed by using a Rheovibron DDV-IIIC dynamic viscoelastomer (Orientech Co.Ltd., Japan) at operating frequency of 110Hz at

heating rate of 1-2°C/min from -150°C to 250°C.

9. Chemomechanical Properties Exploration by the Electric-Stimulus.

The AL layer which impressed 1KV for 240min. was swollen in the 0.1N KClO₃ aqueous solution. After equilibrium swelling, the layer was hung in the KClO₃ aqueous solution and a transverse electric field about 10V/cm was applied to the AL layer. The behavior of free edge was recorded when the polarity was reversed.

III. Results and Discussion

The value of electric current flowing within the electrophoretic cell was determined. The relationship between the impressed time and the value of electric current was shown in Figure 4. The value of the electric current kept stable during the first 150min, and after 150min, electric current increased rapidly. This phenomenon showed that ionic monomer

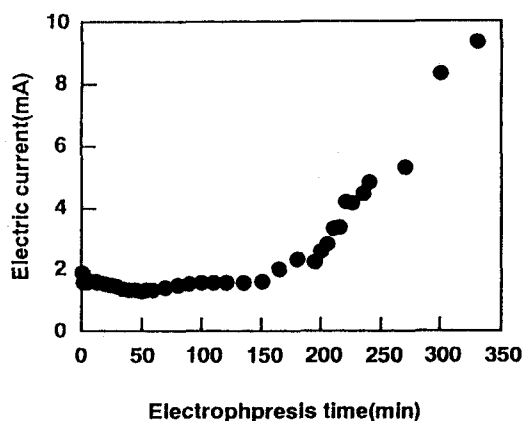


Fig. 4. Relationship between electrophoresis time and electric current.

(DMAEA) moved slowly in host network (PUEs) before 150min, then passed through the PUEs gradually and arrived to the cathode side.

Differences in the properties of the various layers were investigated. The profile of the guest networks (PDMAEA) in base material was determined by measuring the nitrogen content. The PDMAEA contents included in each layer were shown in Table 1. For the sample which was impressed for 30minutes, PDMAEA concentrated at the AL layer, the AL layer contained 5.49wt.% of PDMAEA, ML contained 0.56wt.% and PDMAEA was undetected at CL layer. By increasing the impressed time till 120minutes, the content of PDMAEA in AL layer increased indistinctly (5.63wt.%), but in core layer (ML), the content of PDMAEA(5.35wt.%) improved significantly to approach the value of the surface, and was still undetected in CL layer. For the sample which were impressed for 240minutes, AL, ML and CL contained approximately same amount of PDMAEA, they were 6.20wt.%, 6.06wt.% and 5.07wt.% respectively. These results displayed that the guest networks(PDMAEA) distributed gradually from the anode side to the cathode side of base PUEs. The profile of the guest network

Table 1. Content of PDMAEA(wt%) in modified PUE

Electrophoresis Time(min)	AL	ML	CL
30	5.49	0.56	0
120	5.63	5.35	0
240	6.20	6.06	5.07
240(diffusion)	5.63	0	0

could be controlled by impressed time, and it would be expected that the profile also could be controlled by impressed voltage.

The results of elemental analysis of the swelling method were showed under the broken line. The PDMAEA only concentrated at the surface of the sample. In the core of the sample, the PDMAEA was undetected. So, for the ionic monomer, compared with the swelling method, the electrophoretic method had the advantage that the profile of the guest networks was achieved faster and slope of the concentration of guest network was controlled easily.

The impressed time dependence of the degree of swelling were showed in Figure 5 and 6. When benzene which is a poor solvent for PDMAEA was used, the each layers containing the PDMAEA showed lower degree of swelling than the base PUEs. For the sample which impressed for same time, Accompanied with decreasing the content of PDMAEA from the surface to core, the degree of swelling of the each layers increased

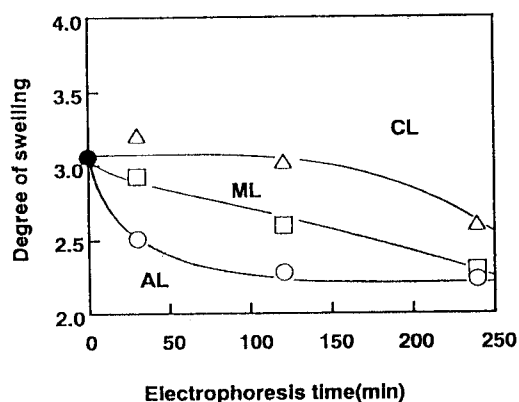


Fig. 5. Relationship between electrophoresis time and degree of swelling(swelled in benzene).

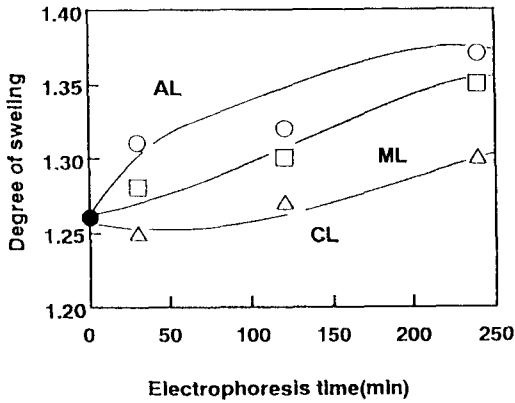


Fig. 6. Relationship between electrophoresis time and degree of swelling (swelled in water).

gradually. On the other hand, water which is a good solvent for PDMAEA was used as swelling solvent. The degree of swelling of the layers containing PDMAEA were higher than the base PUEs. Increasing the content of PDMAEA, the degree of swelling of the layers increased. These changes were contributed to the guest network PDMAEA. PDMAEA shrank in benzene acting as poor solvent, and swelled in water which is good solvent. It was demonstrated that ionic monomer introduced into PUEs had been polymerized into networks interpenetrating the base PUEs. It was also shown that the polarity of modified PUEs changed gradually from the surface to core.

The modified PUEs exhibited two glass transition temperatures, corresponding to the glass transition of the PTMG/PUEs and PEG/PUEs. For the base PUEs, they were -65.5°C and -32.8°C , respectively. In presence of the guest networks interpenetrating the base PUEs, the changes of glass transition temperatures of the PTMG/PUEs were discussed.

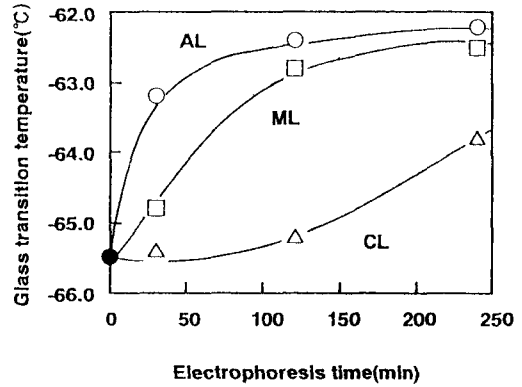


Fig. 7. Relationship between electrophoresis time and glass transition temperature.

The glass transition temperature of the each layers were showed in Figure 7. For the sample which was impressed for 30min, Tg of the AL layer was -63.2°C , ML was -64.8°C , and CL was -65.4°C , respectively. For the AL layer which impressed for 30, 120, 240min., The glass transition temperature were -63.2°C , -62.4°C , -62.2°C . The layer containing the higher concentration of the PDMAEA showed higher glass transition temperature. It was because that the Micro Brownian motion of the main chains of FGIPN-PUEs were interfered by Guest network(PDMAEA) so that the each layers showed temperature between the layers of AL, ML, CL also demonstrated that the ionic polymer(PDMAEA) distributed gradually in the layers of AL, ML, CL also demonstrated that the ionic polymer(PDMAEA) distributed gradually in the base PUEs.

At the rubbery state, the guest networks (PDMAEA) interpenetrating the PUEs acted as an efficient reinforcing filler. The dynamic storage modulus of the each layers (50°C 110Hz) were showed in Figure 8. The FGIPN-PUEs showed higher storage modulus than

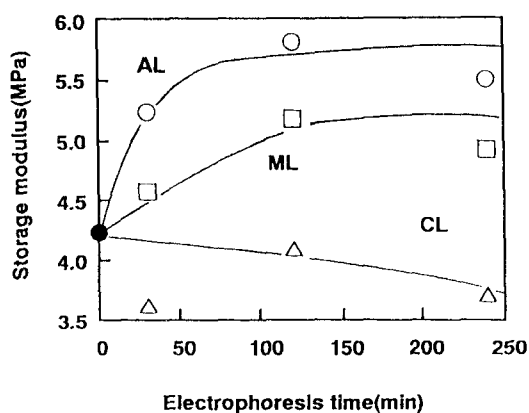


Fig. 8. Relationship between electrophoresis time and storage modulus(at 50°C).

the base PUEs. For the various layers of the same sample impressed for the same minutes, the dynamic storage modulus increased gradually from the AL to CL. For the same layer, accompanied with increasing the impressed time, the storage modulus increased since the concentration of the PDMAEA increased.

The chemomechanical properties of the modified PUEs were explored by the electric-stimulus. The sheet of AL layer (3.6cm × 0.25cm × 0.04cm) which impressed for 240 minutes was equilibrium swollen in the 0.1N KClO₃ aqueous solution, then hung in the solution. When a transverse electric field about 10V/cm was applied to the sheet, the free end of the sheet bent slowly to the cathode side about 1mm. When the polarity of the applied electric potential was reversed, the free end bent back to the vertical position, then to the contrary side. The bending behavior was shown in Figure 9. The reason of the movement under the electric field was described as follows: The counterion (anion) of the PDMAEA in the modified PUEs next to the

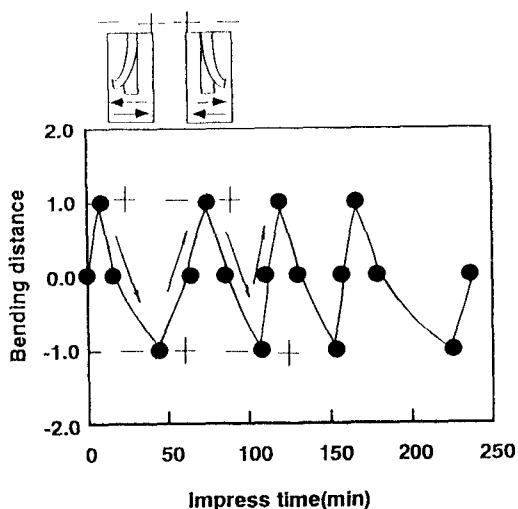


Fig. 9. Bending behavior of AL sheet(0.4mm) prepared by electrophoretic method for 240min. under direct electric field (10V/cm).

anode side was transferred to anode under the electric field, and positive chains (PDMAEA) were stored in the PUEs. In order to maintain the electroneutrality inside the modified PUEs bent to cathode. If the polarity of the applied electric potential was reversed, the counterion was injected into the PDMAEA chains and positive charges were compensated, so the modified PUEs bent to the vertical position. This FGIPN-PUEs were the energy converting polymer turning electric energy into mechanical energy by the electric-stimulus.

IV. Conclusion

In this paper, electrophoretic method was proposed to prepare the GIPN-PUEs. The results of elemental analysis demonstrated that the ionic monomer was introduced gradually

into the PUEs. After polymerization, the ionic monomer formed the guest network interpenetrating the PUEs networks. The guest networks(PDMAEA) distributed gradually in the host network(PUEs). So the degree of swelling, glass transition temperature and dynamic storage modulus were also graded from the surface of the sample to the core. Since the ionic polymers were introduced into PUEs, The modified PUEs showed chemomechanical properties turning electric energy into mechanical energy by electric-stimulus. In comparison with swelling method, the electrophoretic method has the advantages that the gradient profile was achieved faster and controlled easily. This method is possible to synthesis the novel high performance poly-

mer which can be utilized in biomaterial and chemomechanical devices.

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