

Surface Modification of PUEs by Poly(vinyl-pyridine) Using Electrophoresis Method

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Surface of polyurethane elastomers(PUEs) was modified by poly(vinyl-pyridine) through an electrophoresis method. PUEs were prepared from the mixture of PEG(Mn=2000) with PTMG(Mn=2000), MDI, and BD/TMP by a prepolymer method. Under the electric field, vinyl-pyridine(VP) was introduced into the surface of PUEs and polymerized. The relationship between voltage and the content of poly(vinyl-pyridine)(PVP) at the surface was studied by FT-IR. The content of PVP increased with increasing the strength of electric field. The morphology and the properties such as hardness, degree of swelling, and water take-up changed with increasing the PVP.

Key word: surface-modification, electrophoresis, morphology, water take-up

1. INTRODUCTION

Polyurethane elastomers (PUEs) have excellent mechanical properties which are widely used in many kinds of fields, such as building materials, sports goods, and biomedical applications. Especially, the properties in the surface of PUEs play significant role in medical, adhesive, and abrasive materials. The surface modification is carried out to improve these properties. Furukawa[1] reported that the molding temperature affected the abrasion of the surface. It was found that abrasion resistance of the surface in contact with the low temperature mold plate evaluated by DIN abrasion test were better than that at high temperature mold plate. Matthew D. Phaneuf[2] and his co-workers reported a novel polyurethane vessel grafted with covalently bound recombinant hirudin. In previous papers[3,4], we proposed a new preparation method to modify the surface of PUEs by an electrophoresis method. Effects of the electrophoresis time on the properties were discussed. In this paper, we modified the surface of the PUEs by the electrophoresis method using poly(vinyl-pyridine), and discussed the changes of morphologies, mechanical properties, and thermal properties with the strength of electric field.

2. EXPERIMENTAL

2.1 Preparation of PUEs

The PUEs were prepared from a mixture of polyethylene glycol (PEG: Mn=2000, Wako Pure Chemical Ind., Ltd., Japan) with poly(oxytetramethylene) glycol (PTMG: Mn=2000 Sanyo Chemical Ind., Ltd., Japan), 4,4-Diphenyl methanediisocyanate (MDI: Nippon Polyurethane Ind. Co. Ltd., Japan), and a mixture of 1,4-butanediol (BD, Wako Pure Chemical Ind., Ltd., Japan.) with trimethylol propane(TMP, Wako Pure Chemical Ind., Ltd., Japan) as a chain extender by a prepolymer method. Prepolymer was prepared by reaction of PEG/PTMG (75/25 wt.%) and MDI ([NCO]/[OH]=3.3) at 70°C for 3h under nitrogen

atmosphere. The pre-polymer and chain extender (BD/TMP, 75/25 wt%) ([NCO]/[OH]=1.05) were well mixed for 90s and the viscous product was cured for 1.5h at 130°C. Then, a sheet of 2 mm thickness was demoulded, and the sheet was post-cured at 110°C for 24h under air atmosphere.

2.2 Surface modification of PUEs

The sheet of PUEs was swollen in THF/H₂O (30/70 v/v) solvent at an ambient temperature for 24h. The solvent included ammonium peroxydisulfate and N,N'-methylene-bis-acrylamide which were 2 wt% and 4 wt% of the monomer, respectively. The electrophoresis apparatus was set up with the swollen sheet as shown in Fig.1. The cells were filled with the solvent. Hydrochloric vinyl-pyridine salt was added into the anode cell, and the electric field of 5V or 15V was impressed for 1h, then the monomer was polymerized at 60°C for 24h. Finally, the modified PUEs were dried at 70°C under reduced pressure. On the other hand, surface modification was also carried out by the swelling method. The monomer is diffused into the surface of PUE for 1h without impressing electric voltage.

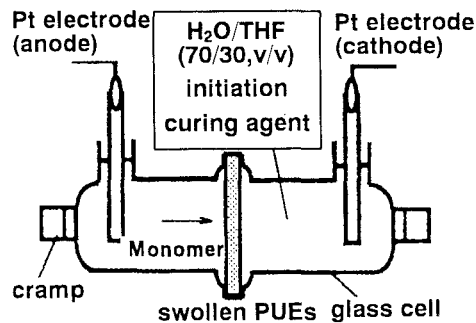


Fig.1 The apparatus of electrophoresis method.

2.3 Properties of the modified PUEs

The surface layers (about 0.4mm) were sliced from the modified PUEs. The layers are designated as E-5, E-15, and ND which were synthesized by impressed for 5V, 15V and the swelling method, respectively. These layers were used to do the following test: Gel fraction was measured by weighing method after equilibrium swelling in water at 60°C. Density was determined by measuring the weight of the sample both in water and air. Micro-hardness was measured with MD-1 micro-hardness tester (Kobunshi Keiki Co. Ltd). Water take-up was measured by weighing method after equilibrium swelling in water at ambient temperature. Degree of swelling was determined by means of a microscope when samples reached in the equilibrium swelling in water or benzene at 60°C. FT-IR spectra were obtained by using a JASCO FT-IR-7000 spectrometer (JASCO Co. Ltd, Tokyo, Japan) equipped with an attenuated total reflection (ATR) instrument at a resolution of 4 cm⁻¹ at ambient temperature. DSC thermogram of the sample was recorded with the aid of a differential scanning calorimetry (DSC) (Rigaku DSC 8230, Rigaku Denki Co, Ltd. Tokyo, Japan) at a heating rate of 10°C/min from -100°C to 250°C under a nitrogen atmosphere. Tensile test was carried out with an Instron type tensile tester (Shimadzu AGS-100A, Japan) at a strain rate of 0.33/min at 25°C. Temperature dependence of dynamic mechanical properties was measured by using a Rehovibron DDV-IIC dynamic viscoelastometer (Orientec Co. Ltd, Japan) at a frequency of 110Hz from -150°C to 200°C at a heating rate of 2°C/min.

3. RESULTS AND DISCUSSIONS

Figure 2 shows IR spectra of the control and three samples obtained by slicing the E-15 across the thickness of sample. FT-IR spectrum of the control has specific peaks of PUEs as follows: 1725 cm⁻¹ ($\nu_{C=O}$ of the urethane), 1531 cm⁻¹ (δ_{N-H} of the urethane), 1601 cm⁻¹, 1460 cm⁻¹ ($\nu_{C=C}$ of the benzene ring). IR spectra of the three samples had new peaks at about 1642 cm⁻¹ which are assigned to the ring stretching of the pyridine. The intensity of the new peak decreased from the modified surface to the reverse surface. It was shown that the poly(vinyl-pyridine) as a binary component distributed and the amount decreased from the modified surface to the reverse surface in the PUEs.

Figure 3 shows the IR spectra of the modified surfaces of ND and E-5. The spectra of ND and E-5 showed the same peaks as that of surface of E-15 described above. The intensity of the peak at about 1642 cm⁻¹ was weaker than that of the E-15. The IR spectrum showed that poly(vinyl-pyridine) as a guest polymer was incorporated into the polyurethane surface by both the electrophoresis method and swelling method. The amount of the guest polymer introduced into PUEs increased with increasing the strength of electric field.

The properties of the modified layers and control are shown in Table I. The gel fraction of control was 97.9%. However, the gel fraction of the modified PUEs decreased. The results suggest that a part of poly(vinyl-pyridine) was not incorporated into the network of PUEs. Density, micro-hardness, and water take-up increased with increasing the strength of electric field respectively.

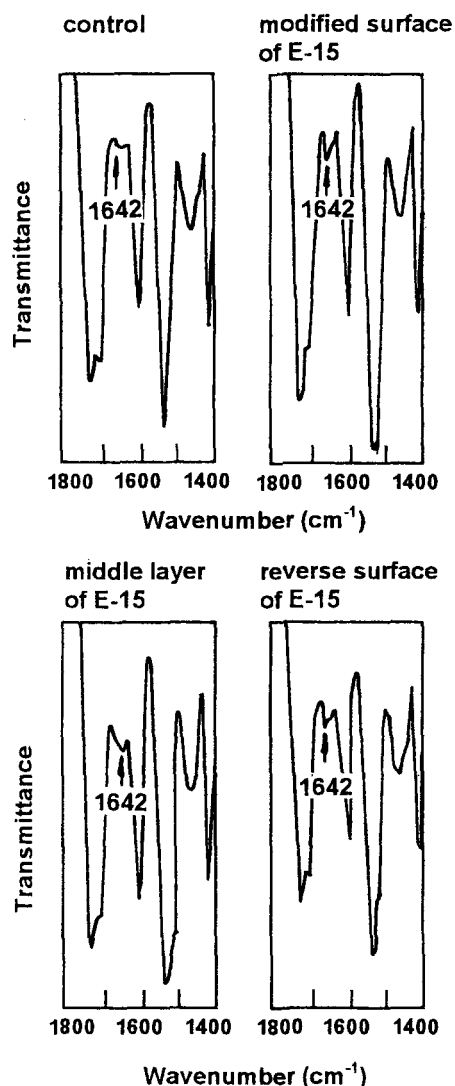


Fig.2 IR spectra of the control and each layer of the E-15 sample.

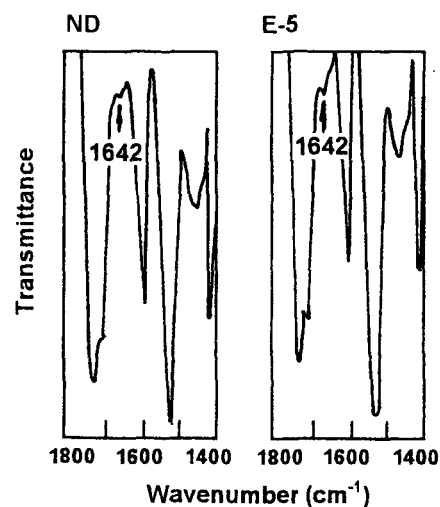


Fig.3 IR spectra of ND and E-5.

Table I The properties of the control and modified PUEs.

Abbreviation	Gel fraction (%)	Density (g/cm ³)	Micro-hardness (IRHS)	water take-up (wt %)
control	97.9	1.08	56.4	50.0
ND	94.3	1.15	57.7	52.8
E-5	94.6	1.24	58.4	53.1
E-15	93.7	1.29	59.0	55.6

DSC thermograms of the control and modified PUEs are shown in Figure 4. The control had the glass transition temperature at about -33.9°C and melting temperature at about 16.7°C . The glass transition temperature is attributed to the micro-Brownian motion of PEG residues. The melting temperature is attributed to melting of the aggregation of domains of polyether chains designated as soft segment. The glass transition temperatures of ND, E-5, and E-15 were -33.7°C , -33.0°C , -29.6°C , respectively. The melting temperatures of micro-crystal were 16.0°C , 15.4°C , and 15.2°C , respectively. The glass transition temperature of the modified surface rose with increasing the strength of electric field. On the other hand, the melting temperature decreased. The guest polymer slightly prevented the micro-Brownian motion of the main chains, and degree of interference increased with increasing the amount of the guest polymer. Since the guest polymer also disordered the aggregation of the soft segment, the melting temperatures of the micro-crystal shifted towards lower side. From the changes of glass transition temperature and melting temperature, it was proved that the surface of PUEs was not covered by the polyvinyl pyridine, and the polymers penetrated in the inside of PUEs.

The relationship between stress with strain is shown in Fig.5. The modified PUEs showed higher tensile strength and lower elongation at break than that of the control. The Young's moduli of the modified PUEs were higher than that of the control. The Young's modulus increased with increasing strength of electric field. Since the aggregation of the soft segment was interfered by the guest polymer to some extent, and the guest polymer provided the additional network, apparent crosslinking density increased with increasing the guest polymer. This was also the reason that the micro-hardness increases with increasing the strength of electric field.

The temperature dependence of $\tan \delta$ for the control, ND, E-5, and E-15 are shown in Fig.6. Dynamic mechanical properties are often used to study the morphology, i.e. the phase continuity and miscibility of polymer blend. In the temperature dependence of $\tan \delta$, one narrow loss factor peak indicates a high degree miscibility, whereas two clearly separated peak at $\tan \delta$ are indicative of gross phase separation. The intermediate situation of one broad is obtained for semi-miscible polymer blend. Compared with the loss factor peak of the control, the peak of the each modified PUEs shifted slightly towards higher temperature side. The E-15 showed a new small peak at about 80°C . These results displayed that the modified PUEs were the

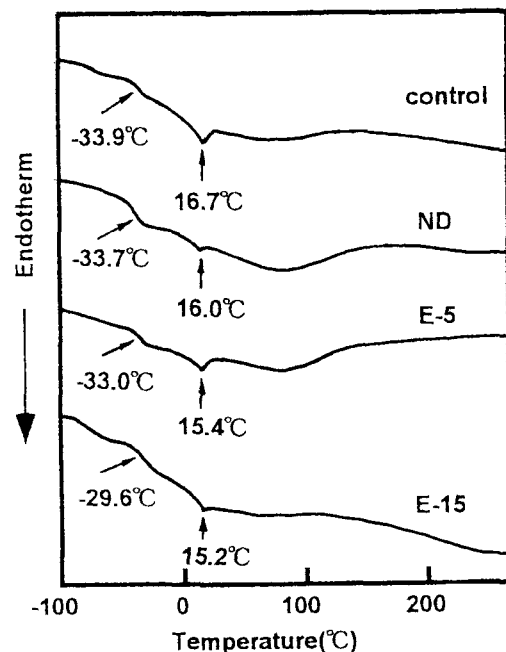


Fig.4 DSC thermograms of each sample.

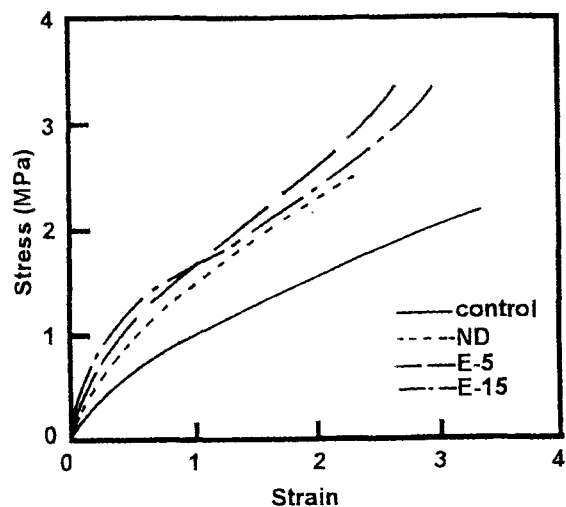


Fig.5 Stress-strain curves of each sample.

semi-miscible described above, with increasing the guest polymer, the phase separation developed to some extent between the PUEs and guest polymer.

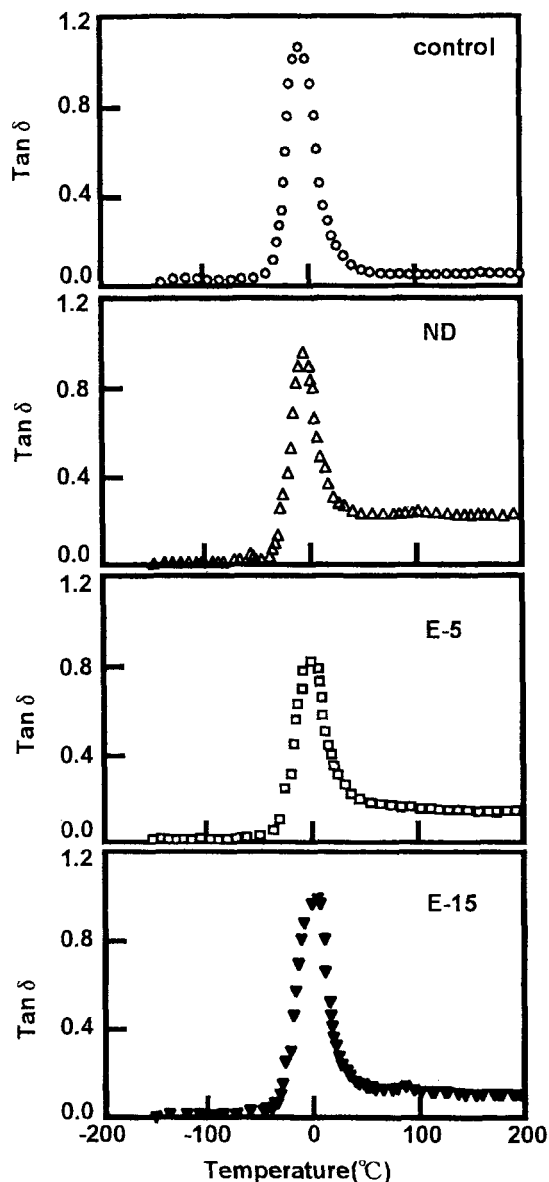


Fig.6 Temperature dependence of $\tan \delta$ of each sample.

Figure 7 shows the degrees of swelling of the control and modified PUEs. When water was used as swelling solvent, degree of swelling of the modified PUEs had higher value than that of the control. The degree of swelling increased with increasing the strength of electric field. On the other hand, degree of swelling of the modified PUEs showed lower value than that of the control in benzene. Degree of swelling decreased with increasing the strength of electric field. These results displayed that poly(vinyl-pyridine) had been formed the interpenetrating networks with the PUEs. These hydrophilic ionic networks swelled in water and shrank in benzene. The result also showed that the polarity of the PUE's surface is able to change by amount of the guest polymer.

It is shown from the result that the properties of surface modified by the electrophoresis method change significantly compared with that of the surface synthesized by the swelling method. It is because that

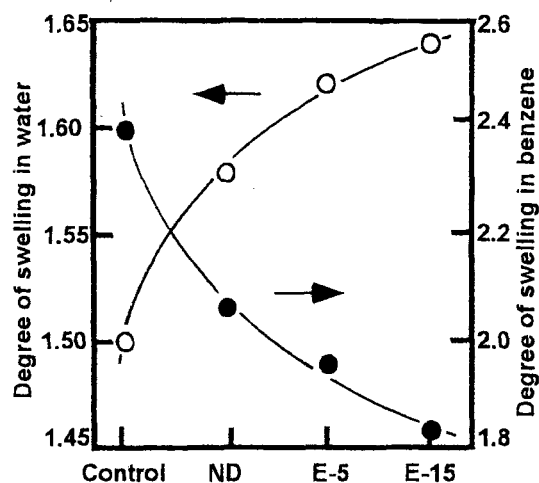


Fig. 7 Degree of swelling of each sample swollen in water and benzene.

the strength of electric field affects chemical potential of the monomer. So, the flux of the monomer transferred from solution to surface by the electrophoresis method is higher than that by the swelling method. The electrophoresis method has advantages for the ionic monomer since the amount of the monomer introduced into PUEs is easily controlled by the strength of electric field, and the modification is achieved at the quick speed.

4. CONCLUSION

The surfaces of the PUEs are modified by the electrophoresis method and swelling method. The ionic monomer is introduced into PUEs. The amount of ionic monomer decreased from the surface to core of the PUEs. The modified surfaces show higher micro-hardness, density, and water take-up. From the thermal properties of the modified surfaces, the aggregation of the soft segment is disordered to some extent. The guest polymer plays the important role in mechanical property as reinforce networks. The phase separation between the guest polymer and PUEs occurs to some extent with increasing the guest polymer. The increment of water take-up and changeable polarity of the modified surface maybe improve the haemocompatibility of the PUEs. The modification of the surface should extend applicable range on the biomedical field.

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(Received December 8, 2000; Accepted February 8, 2001)