J nat Rubb Res, **12(4)**, 237–246

Functionally Graded Polyurethane Elastomers Prepared by Electrophoresis of Monomer[†]

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A novel preparation method of functionally graded interpenetrating network polymer (IPN)-type elastomers, was proposed Functionally graded IPN-type polyurethane elastomers (PUEs) were prepared by electrophoresis of ionic monomers The base PUEs were prepared from poly(oxytetramethylene)glycol (PTMG) and/or poly(oxyethylene)glycol (PEG), 4,4'-diphenylmethane diisocyanate (MDI), and a mixture of 1,4-butane diol with trimethylol propane (TMP) Ionic monomers used were methacrylic acid and quarternary N,N-dimethylamino ethyl acrylate Effects of the electrophoresis time of monomer on morphologies and mechanical properties were studied by DSC, polarising microscopy, etc. *Spherulite sizes of the modified PUEs depended significantly on the electrophoresis time Abrasion resistance of the surface of IPN-type PUEs evaluated by DIN abrasion test was better than that of non-treated PUE*

Polyurethane elastomers (PUEs) have excellent mechanical properties compared with general purpose elastomers. These characteristics are utilised in a wide variety of industrial products, which are industrial parts, building materials, sports goods, daily necessities, and medical equipments. These properties are strongly dependent on chemical structures and super-structures of PUEs[1–5]

In recent years, investigation of graded multicomponent polymers has been conducted. Okinaka *et al*[6,7] studied binary polymer mixtures, poly (2-chlorostyrene)/poly (vinyl methyl ether), undergoing phase separation induced by a temperature gradient. Kano *et al.*[8] designed gradient polymer materials made by acrylate adhesive/fluoro-copolymer blends and analysed gradient structure by depth profiling using PAS-FTIR and TEM observation. Composition exponentially varied in the vicinity of surface, while that of the internal region was nearly constant. In the previous paper[9], we proposed a new preparation method of functionally graded PUEs by temperature gradient casting. These PUEs have gradient morphology with spherulite graded size. Thermal and mechanical properties, and abrasion resistance of these were also graded.

[†] Paper presented at the International Rubber Conference 1997 Malaysia, 6–9 October, Kuala Lumpur

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In this study, we proposed a novel preparation method of the functionally graded interpenetrating network polymer (IPN)-type elastomers. The functionally graded IPN-type polyurethane elastomers were prepared by electrophoresis of ionic monomers; methacrylic acid and quaternary N,N'-dimethyl ethyl acrylate. Effects of the electrophoresis time of monomer on morphologies and mechanical properties were studied by DSC, polarising microscopy, *etc.*

EXPERIMENTAL

Preparation of PUEs

PUEs were prepared from poly (oxytetramethylene) glycol (PTMG: Mn = 2000, Sanyo Chemical Industries; Japan) and/or poly (oxyethylene) glycol (PEG : Mn = 2000, Sanyo Chemical Industries), 4,4'-diphenyl methane diisocyanate (MDI: Nippon Polyurethane Industries, Japan), and a mixture of 1,4-butane diol and trimethylol propane (75/25 wt%) as a chain extender by a prepolymer method. Prepolymers were prepared from PTMG or PTMG/PEG (50/50 wt%) and MDI [(NCO)/(OH)] = 3.30) at 70°C for about 3 h under nitrogen atmosphere. The prepolymer and chain extender [(NCO)/(OH)] = 1.05) were well-mixed for 90 s and the viscous reaction product was poured into a mould heated at 130°C. The viscous product was cured for 1.5 h at 130°C. After this period, a sheet of 2 mm thickness was demoulded, then the sheet was post-cured at 110°C for 24 h under air atmosphere.

Preparation of Functionally Graded IPN-type PUEs

Synthetic scheme of PUEs is shown in *Figure 1*. PUEs were swelled in a mixture of solvent with radical initiator and a curing agent at ambient temperature for 24 h. These swelled PUEs were put in an apparatus for electrophoresis as shown in *Figure 2*. Ionic monomer was added into one of the cells and was moved by impressing voltage during required time. The vinyl monomer included in PUEs was polymerised at 70°C.

Slicing of PUE Sheets

PUEs of 2 mm thickness was sliced up to five pieces (about 0.4 mm thickness) by a splitting machine (Fortuna Werke Maschinen fabrik AG, Model NAF-470-D, Germany). These sheets obtained are used for the following testings.

Measurement of Density

Density was determined by weighing of sample in air and water.

Measurement of Gel Fraction

Gel fraction was measured by weighing method after equilibrium swelling in benzene or *N,N*-dimethyl acetamide (DMA) at 60°C.

Thermal Analysis

Thermograms 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 nitrogen atmosphere.

Observation of Micro-domain Structures

Micro-domain structures were observed by using a polarising microscope (Nikon, OPTIPHOT2-POL, Japan) equipped with a heating stage (LINKAM, TH-600PM). A

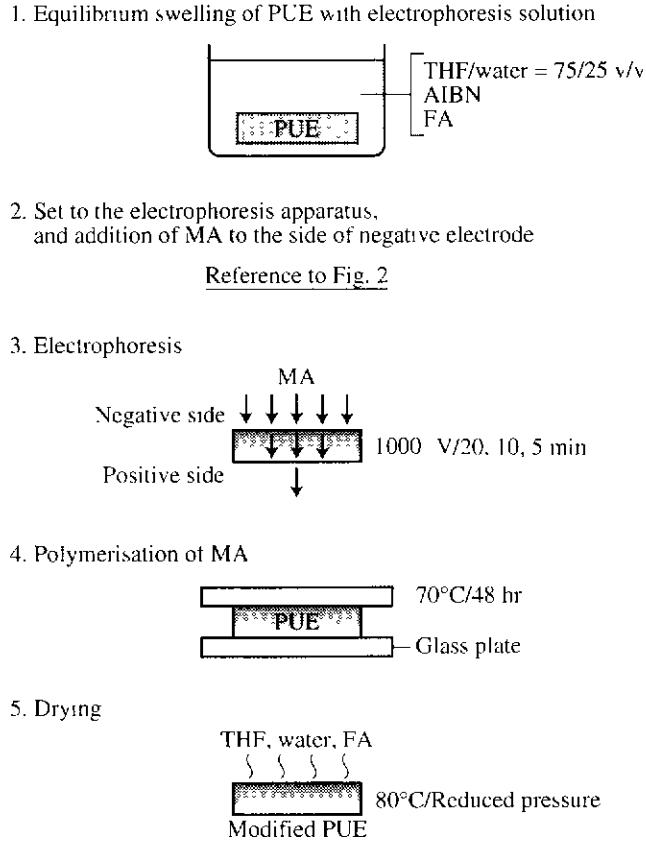

Figure 1. Preparation scheme of functionally graded PUEs by electrophoresis (Example: MA as monomer).

sensitive colour plate (530 mm) was used for birefringence analysis.

RESULTS AND DISCUSSION

Functionally Graded IPN-type PUEs with Polymethacrylic Acid

PMA IPN-type PTMG-PUEs. Methacrylic acid (MA) of 3 wt% to solvent was added into the cell equipped with cathode. A mixed solvent of THF and water (75/25 vol%) was used. When voltge of 1 kV was impressed between both electrodes, initial current value of system was 1 mA. This value was held at 5 min and 10 min of electrophoresis time. However, current value increased to 2 mA at 20 min of electrophoresis time. This result shows that MA monomer ion (CH_2=C(CH_3)-COO) passed through the PUE sheet from the cathode side to the anode side. PTMG-PUE as control was white translucent, while PMA IPN-

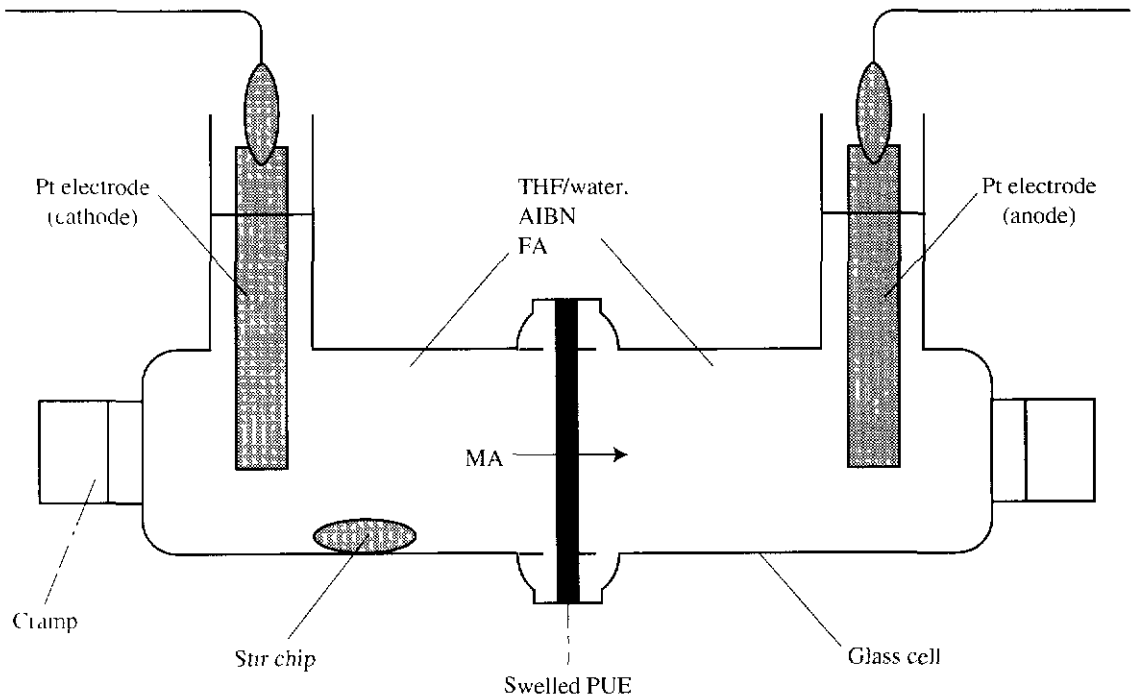

Figure 2. Apparatus for electrophoresis

type PTMG-PUE which was prepared by electrophoresis at 5 min and polymerisation of MA, was light yellowish translucent. The appearance of this IPN-type PUEs changed from light yellowish translucent to deep yellowish translucent with increasing electrophoresis time.

Figure 3 shows polarising micrographs taken at the surfaces of both electrode sides in each PMA IPN-type PTMG-PUEs. *Figure 3* shows also those of the surfaces of PTMG-PUE in which MA was diffused naturally from the negative electrode side to that of the positive electrode side for 20 min. The PTMG-PUE as control had 'negative spherulites' with well-defined Maltese cross, which had a diameter of 25 μm – 35 μm. However, the structure of the spherulites of the IPN-type PTMG-PUE prepared at electrophoresis time of 5 min turned into small spherulites. Though the matrix part in the surface of the positive electrode side

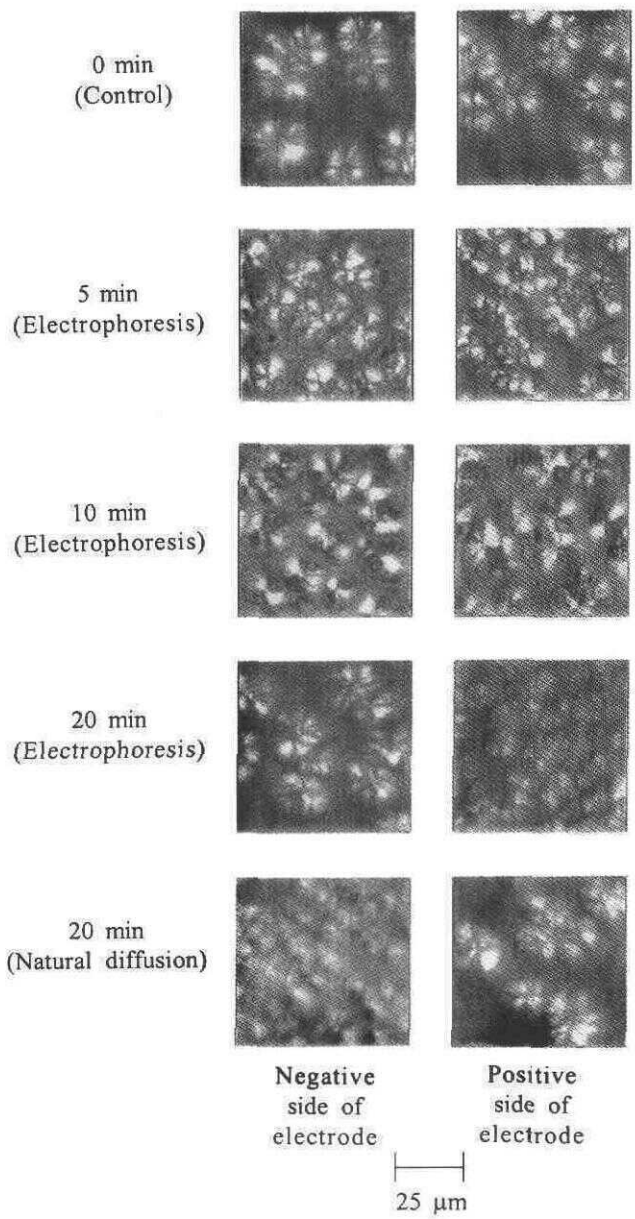

Figure 3. Polarising micrographs of each surface in PMA IPN-PTMG-PUEs prepared by electrophoresis.

was of smooth surface and that of the negative electrode side was slightly of uneven roughness In the IPN-type PTMG-PUE prepared at 10 min, the spherulites observed in both surfaces looked like that of those at 5 min, however, the matrix part of the surface in the negative side of electrode had lost the unevenness and the surface in the positive side of electrode became rough, that is, the surface state of sample obtained at 10 min were reversed While the dimension of spherulites on the surface of the negative side of electrode in the IPN-type PTMG-PUE at 20 min was the same as that in control PUE, and that on the surface of the positive side of electrode was smaller than that in control PUE and spherulites were broken and the surface was rough

As MA was naturally diffused from one side to the other side of PUE sheet for 20 min, the surface contacted with MA was as rough as the surface on the positive side of electrode at 20 min and appearance of another surface did not change These results indicate that the rate of diffusion of MA is significantly faster and that concentration of PMA in each layer is controlled easier in the electrophoresis method than in the natural diffusion method.

Abrasion resistance evaluated by DIN abrasion tester for each surface at electrophoresis time of 5 min and 20 min are shown in *Figure 4*. The specimen obtained by electrophoresis revealed better abrasion resistance than control. In the comparison of surfaces between the negative and positive side of electrodes, the surface of the negative side of electrode obtained at electrophoresis time of 5 min and that of the positive side of electrode at 20 min had better abrasion resistances These results indicate that PMA-rich phase in PMA IPN-type PTMG-PUEs have excellent abrasion resistance because formation of PMA IPN PUEs increase the apparent crosslinked density

PMA IPN-type PTMG/PEA-PUEs PTMG/PEG (weight ration = 1/1)-PUEs were used as base PUEs in place of PTMG-PUEs in order to increase swelling ratio of PUEs in water and decrease the time of electrophoresis.

Figure 5 shows polarising micrographs taken at sliced samples of PMA IPN-type PTMG/PEG-PUEs prepared at 1 min and 4 min of electrophoresis. *Figure 5* shows also the surfaces in which MA was diffused naturally from cathode side to anode side for 3 min In the PMA IPN-type PTMG/PEG-PUE prepared at electrophoresis of 1 min, the size of the spherulites was increased to the order of negative side of electrode < middle < positive side of electrode While the globular pattern was observed in the matrix part at the negative side of electrode, these patterns were not observed at middle part and positive side of electrode With increase of electrophoresis time (4 min), the size of the spherulites was increased to the order of the positive side of electrode < middle < negative side of electrode The globular pattern was observed in the matrix part at each specimen In the IPN-type PTMG/PEG PUE prepared by natural diffusion at 3 min, the size of the spherulites was decreased in the negative side of electrode only

Figure 6 shows DSC thermograms of each part of the sliced specimen of these PUEs with PMA and PTMG/PEG PUE *Tg* of PTMG/PEG-PUE was observed at about −70°C and −30°C, assigned to micro-Brownian motion of PTMG and PEG residues, respectively Recrystallisation and melting of soft segment domain were also observed at about −10°C and

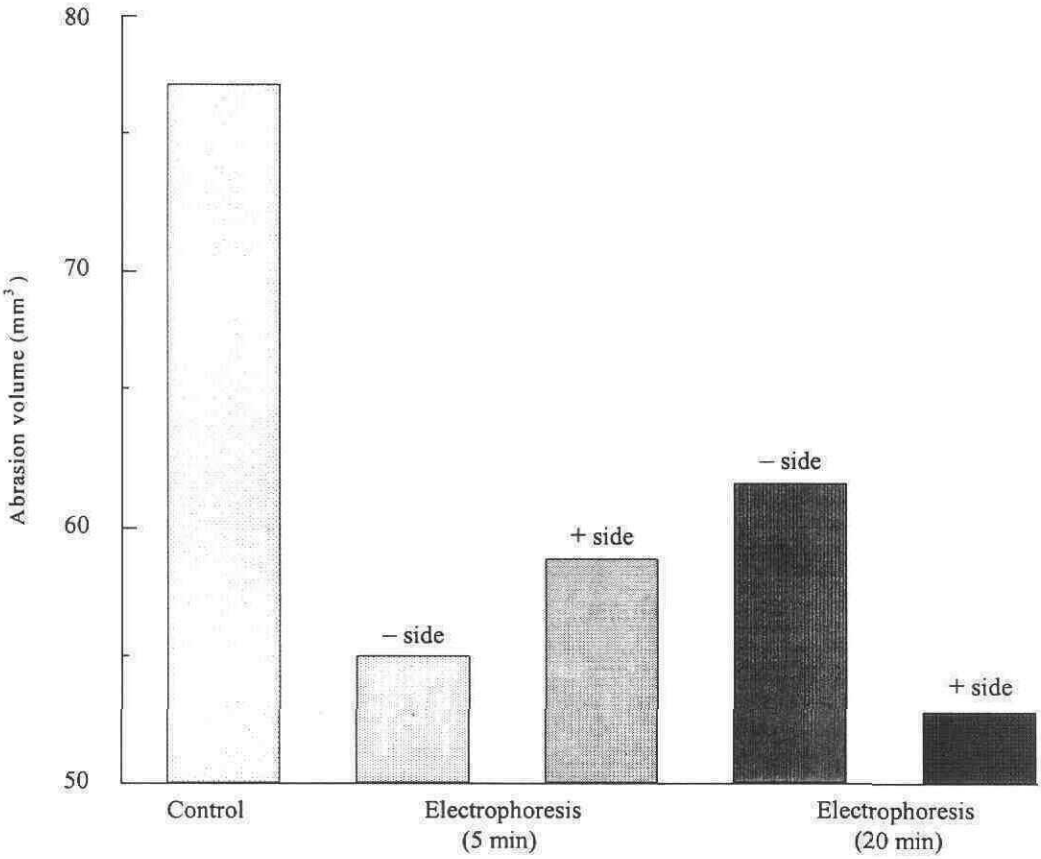

Figure 4. Abrasion volume evaluated by DIN abrasion tests for PMA IPN-type PTMG-PUEs prepared by electrophoresis.

15°C. In the IPN-type PTMG/PEG-PUEs prepared at 1 min or 4 min of electrophoresis, *Tg* was slightly differed for each parts. However, behaviour of recrystallisation and melting of soft segment domains significantly differed for each part. In the IPN-type PUE prepared at 1 min of electrophoresis, specimen of the negative side of electrode did not show the recrystallisation behaviour. The middle part specimen had a small peak of recrystallisation. That of the positive side of electrode had significant recrystallisation and the melting behaviour was same as that of control. When MA diffused by 4 min of electrophoresis, the specimen of the positive side of electrode did not show the recrystallisation behaviour. That of the negative side of electrode had significant recrystallisation and melting behaviour same as that of control. On the other hand, each specimen of the PUE prepared by natural diffusion method did not indicate recrystallisation behaviour. These results show

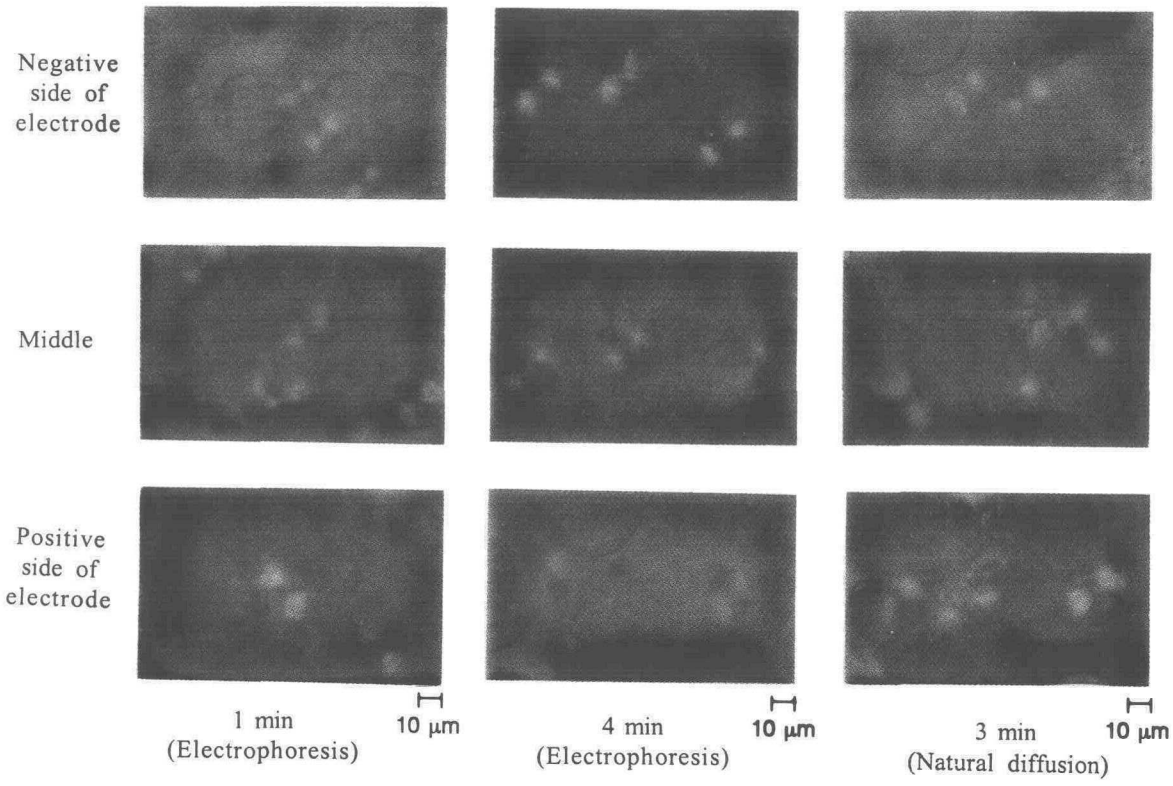

Figure 5. Polarising micrographs of each surface in PMA IPN-type PTMG/PEG-PUEs prepared by electrophoresis.

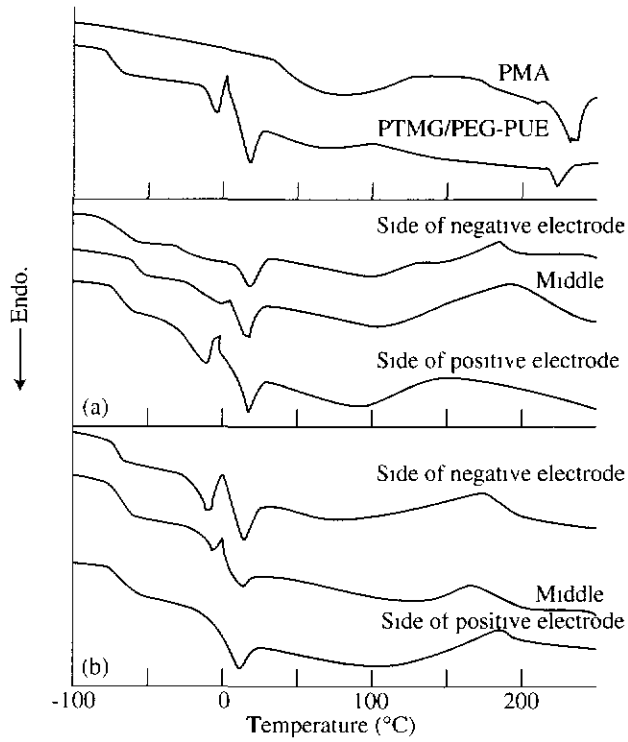

Figure 6 DSC thermograms of PMA IPN-type PTMG/PEG-PUEs prepared by electrophoresis. Time of electrophoresis is 1 min (a) and 4 min (b)

the following: 1) PEG induced to base polyurethane increased the rate of diffusion of MA; 2) PMA in these PUEs has a concentration slope.

Functionally Graded IPN-type PUEs with poly(quaternary N,N'-dimethyl aminoethyl acrylate)

Quaternary dimethylaminoethyl acrylate (DMAEA) is used as a cationic monomer. This monomer was supplied as 80 wt% aqueous solution. In this case, methanol was used as solvent DMAEA, *N,N'*-methylene-bis-acrylamide as a curing agent and PTMG/PEG PUEs as base PUEs. DMAEA (3 wt% to solvent) was diffused from positive side of electrode by electrophoresis (350 V, 1 mA, and 10 min).

In polarising micrographs at each specimen in PDMAEA IPN-type PTMG/PEA-PUE, the sample of positive side of electrode had small 'negative spherulites' with well-defined Maltese

cross and globular part in matrix phase. However, the structures of the spherulites specimen on the middle and negative side of electrode had the same or a little smaller dimension as that of control. These results also indicate that these spherulites of positive side are due to the degradation of aggregation of hard segments by interpenetrating PDMAEA. Nitrogen content determined by elemental analysis was 2.89% for control, 9.78% for PDMAEA, 3.00% for positive side, and 2.95% for negative side. From these results, content of PDMAEA for positive side was 1.6 wt%, while that for negative side was 0.87%, under this condition.

CONCLUSION

In this study, we proposed a novel preparation method that functionally graded IPN type PUEs be prepared by electrophoresis of ionic monomer into the base polymers and polymerisation of monomer. Size and structure of spherulites of the modified PUE have been graded. The thermal properties of the modified PUE were also graded. This method has the advantage of the slope where concentration is controlled easily. Further regulation of voltage and time of electrophoresis is possible in the synthesis of novel high performance polymers which can be utilised in industrial parts, building materials and chemomechanical devices.

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