NOTE

Functionally Gradient Silicone Sheet Made by Treatment of Swelling and Polymerization with *n*-Butyl Methacrylate

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ABSTRACT: A silicone sheet was dipped into *n*-butyl methacrylate monomer including benzoyl peroxide and was swollen for 0.5 h at 23°C. Then, the sheet was put into a glass tube equipped with a three-way stopcock and was deoxygenated by freezing under dry nitrogen. Polymerization was carried out by heating at 80°C for 2 h under dry nitrogen. The resultant sheet was a component gradient silicone sheet with poly-*n*-butylmethacrylate. The content of poly-*n*-butylmethacrylate increased gradually from either surface to the middle of the sheet. This phenomenon was assumed to occur because of the volatilization of *n*-butyl methacrylate monomer during the polymerization. The properties of the sheet include increased tear strength and decreased gas permeability.
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Key words: functionally gradient; swelling; *n*-butyl methacrylate; tear strength; gas permeability

INTRODUCTION

To date, functionally gradient materials have been investigated extensively mainly in the field of inorganic materials.[1–11] However, in the field of organic materials, reports are relatively limited.[12–16] In fact, such research started in the field of metal or ceramic materials because the procedure to make gradient components of organic macromolecules is difficult. This study describes a procedure to make gradient components of organic macromolecules by a simple method.

EXPERIMENTAL

Materials

Silicone sheet was purchased from Tigers Polymer Corporation (Toyonaka, Japan). *n*-Butyl methacrylate and benzoyl peroxide were purchased from Tokyo Kasei Kogyo Company, Ltd., (Tokyo, Japan).

Swelling and Polymerization Procedures

Procedures for silicone sheet swelling treatment and polymerization with *n*-butyl methacrylate are shown in Scheme 1. Silicone sheet (13.8 g, 90 × 85 × 1.5 mm) was dipped into *n*-butyl methacrylate monomer (130 g) including benzoyl peroxide (222 mg) and was swollen for 0.5 h at 23°C. Then the sheet (26.5 g, 92% swollen) was put into a glass tube equipped with a three-way stopcock and was deoxygenated by freezing under dry nitrogen. Polymerization was carried out by heating at 80°C for 2 h under dry nitrogen.

We tried other methacrylates and acrylates instead of *n*-butyl methacrylate as monomer to swell the silicone sheet and had similar results, but the degrees of swelling were different. Swelling levels with monomers are shown in Table I.

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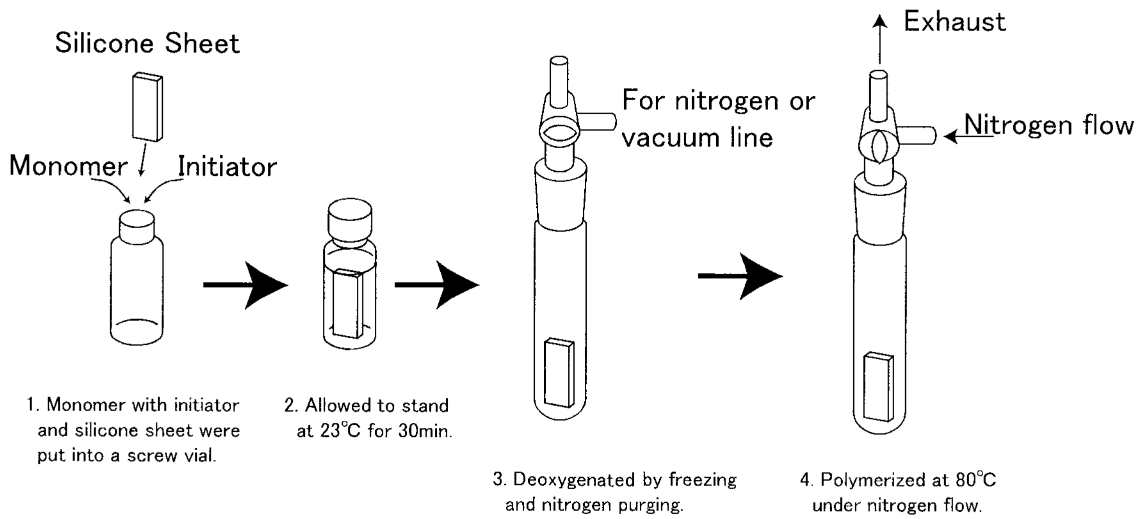

Scheme 1 Procedure to make functionally gradient silicone sheet.

Equipment and Measurements

Fourier transform infrared (FT-IR) spectra were measured by the attenuated total reflection (ATR) method with ZnSe on a Shimadzu 8200 PC FT-IR spectrometer. Microscopic FT-IR line analysis spectra were measured with a Bio-Rad Excalibur FTS3000/UMA-500 microscopic FT-IR spectrometer. A Hitachi SEM S-2460N was used to record the scanning electron microscopy (SEM) photograph, and a Horiba EDX EMAX-5770W was used to measure the energy-dispersive X-ray (EDX) spectrum. Tear strength was measured with a Shimadzu AGS-500D autograph.

RESULTS AND DISCUSSION

FT-IR Analyses of the Functionally Gradient Silicone Sheet

FT-IR spectra of the functionally gradient silicone sheet are shown in Figure 1. The spectrum of either surface of the sheet was similar to that of silicone, whereas a sharp signal near 1710 cm^{-1} (assigned to the C=O stretching vibration) was observed in the spectrum of the middle of the sheet. These results show that the sheet was a component gradient silicone sheet with poly-n-butylmethacrylate. The content of poly-n-butylmethacrylate increased gradually from either surface to the middle of the sheet. This phenomenon was assumed to occur because of the volatilization of n-butyl methacrylate monomer during the polymerization.

Table I Monomers and Swelling Degree

Monomer	Swelling Degree (%)
Methyl methacrylate	43
n-Butyl methacrylate	92
2-Ethylhexyl methacrylate	88
Lauryl methacrylate	40
Methyl acrylate	32
Ethyl acrylate	46
n-Butyl acrylate	57
2-Ethylhexyl acrylate	39

Microscopic FT-IR Line Analysis of the Functionally Gradient Silicone Sheet

The microscopic FT-IR line analysis spectra of the functionally gradient silicone sheet are shown in Figure 2.

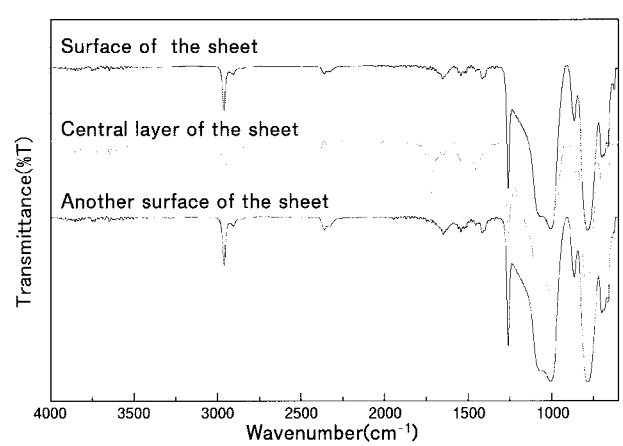

Figure 1 FT-IR spectra of functionally gradient silicone sheet.

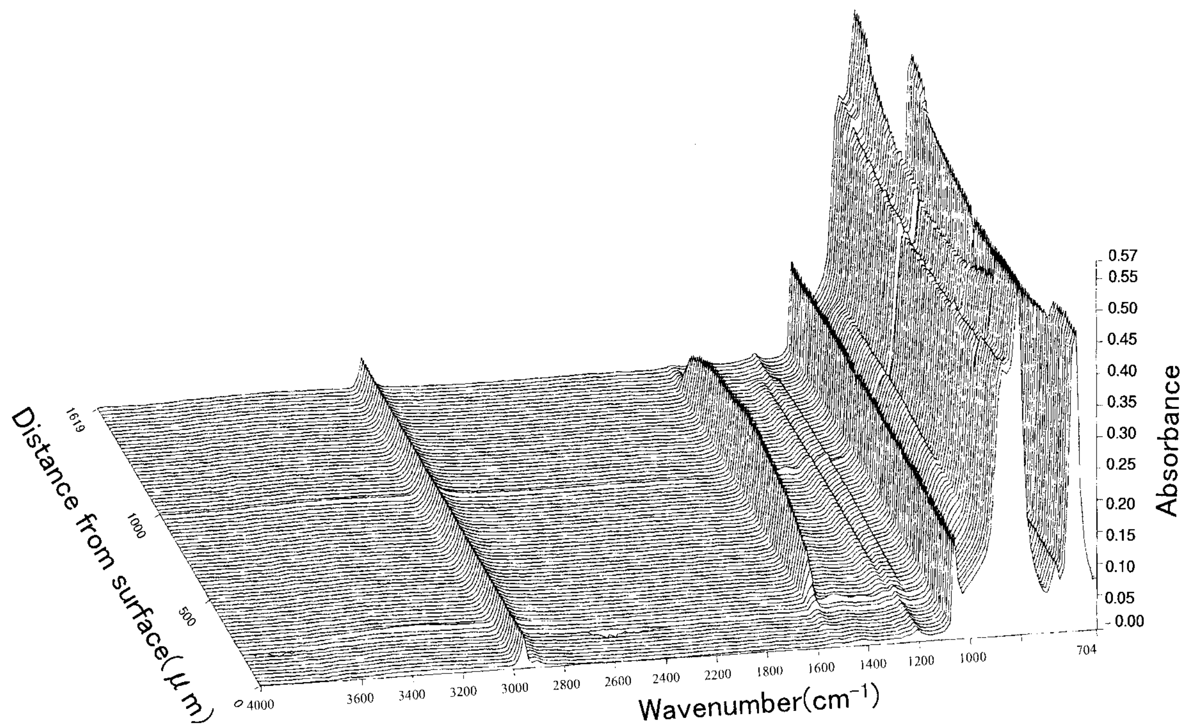

Figure 2 FT-IR line analysis of functionally gradient silicone sheet.

The signal assigned to the C═O stretching vibration (1710 cm^{-1}) of poly-*n*-butylmethacrylate increased gradually from either surface to the middle of the sheet, whereas the signals assigned to silicone structure decreased gradually from either surface to the middle of the sheet. These results show clearly that the sheet was a component gradient silicone sheet with poly-*n*-butylmethacrylate. The content of poly-*n*-butylmethacrylate increased gradually from either surface to the middle of the sheet.

Scanning Electron Microscopy (SEM) Observation and Energy-Dispersive X-ray (EDX) Spectrum of the Functionally Gradient Silicone Sheet

An SEM photograph and an EDX spectrum of the functionally gradient silicone sheet are shown in Figure 3. The EDX spectrum shows that the silicon content of the sheet decreased gradually from either surface to the middle of the sheet. From these results, it was clarified that the sheet was a component gradient silicone sheet with poly-*n*-butylmethacrylate. The content of poly-*n*-butylmethacrylate increased gradually from either surface to the middle of the sheet.

Measurement of Tear Strength

Tear strength of the functionally gradient silicone sheet and the silicone sheet as a control sample were measured in accordance with the procedure described in JIS K 6252-1993. The tear strength of the functionally gradient silicone sheet was 32.7 kgf/cm, whereas that of the control silicone sheet was 23.6 kgf/cm. Generally, one of the disadvantages of silicone is low tear strength, which was assumed to be modified by making a semi-interpenetrating polymer network with poly-*n*-butylmethacrylate in the middle of the sheet. By making a layer with poly-*n*-butylmethacrylate, tear strength would be further modified. There would be, however, other problems such as adhesives selection or interfacial breakage and so on. This paper presents a significant method to improve the performance of the material.

Measurement of Gas Permeability

Gas permeability of the functionally gradient silicone sheet and the silicone sheet as a control sample were measured in accordance with the procedure described in JIS K 7126 by the Japan Chemical Innovation Institute. As a result, gas permeability of the functionally gradient silicone sheet was 8.77×10^{-12} mol/m^2·s·Pa for nitrogen and 1.36×10^{-11} mol/m^2·s·Pa for oxygen, whereas that of the control silicone sheet was 2.54×10^{-11} mol/m^2·s·Pa for nitrogen and 4.35×10^{-11} mol/m^2·s·Pa for oxygen. A disadvantage of the silicone sheet is high gas permeability, which was improved somewhat by making a semi-

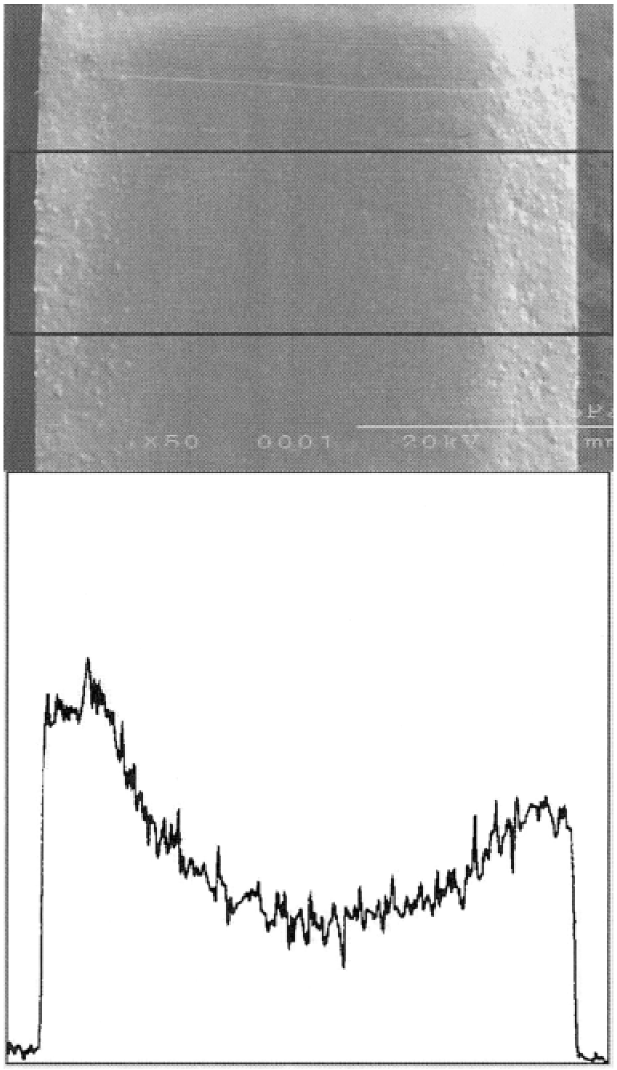

Figure 3 SEM and EDX of silicon of functionally gradient silicone sheet.

interpenetrating polymer network with poly-*n*-butylmethacrylate in the middle of the sheet.

To modify the disadvantageous property of macromolecules, one often uses composite material. Regarding silicone, it is quite difficult to make a composite with other polymer because of its low affinities. In this study, to modify the property of silicone, we tried to make a component gradient silicone sheet by the treatment of swelling and polymerization with *n*-butyl methacrylate. As a result, silicone was assumed to be a semi-interpenetrating polymer network with poly-*n*-butylmethacrylate in the middle of the sheet. A component gradient silicone sheet could be said to be a functionally gradient silicone sheet.

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