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Doctoral Dissertation

Material design of high-performance elastomers
with gradient structure

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Abstract

Material design of high-performance elastomers with gradient structure

With the increasing demand for new materials, there is a need for advanced material design methods that can meet various performance requirements. This thesis presents a novel approach to material design by creating graded structures using a simple thermal treatment technique. Typically, crosslinked rubber is assumed to have a homogeneous distribution of crosslinking points. However, in most conventional rubbers, especially those produced by compression molding, a crosslink density gradient exists due to variations in thermal history, depending on the distance from the mold. This phenomenon is reasonable because polymeric materials generally have low thermal diffusivity, meaning it takes longer to reach an equilibrium temperature profile during heating processes, including vulcanization. As a result, the core region in rubber is exposed to high temperatures for a shorter duration than the skin layer, leading to a difference in crosslink density. Following this concept, a temperature gradient was applied during vulcanization to fabricate rubber with a graded crosslink density.

In this thesis, graded rubber with a crosslink density gradient in the thickness direction was prepared using conventional Styrene-Butadiene Rubber (SBR). The mechanical properties of the graded rubber were systematically studied and compared with those of homogeneous rubbers. The graded rubber exhibited significant strain recovery and high energy absorption. Moreover, it demonstrated interesting swelling behavior. These phenomena correspond to the presence of a gradient structure, where the mutual interaction between high-crosslink and low-crosslink regions is the origin of the peculiar properties. Finally, the segregation behavior, which is known to lead to a concentration gradient, was investigated in the SBR/tackifier blend to clarify the mechanism of segregation. By using this technique, the properties of the graded material could be easily tailored.

It is hoped that this thesis will contribute to a profound understanding of the unique properties of graded rubber and other materials with gradient structures. The findings of this research are also intended to inspire the design of novel smart materials in material science.

Key words: material design; temperature gradient; graded rubber; strain recovery; swelling; segregation.

Do Quoc Viet

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Achievement

Acknowledgement

Chapter 1

General Introduction

1.1. Introduction

1.1.1. Polymeric materials & material design

The formal study of polymer science began only around 100 years ago by Herman Staudinger since 1919 when he introduced a novel definition of polymers ¹. Today, polymeric materials are widely used in many areas as common products like packaging and sports gear to high-tech fields like cars, airplanes, electronics, and sensors ². In order to fulfill the increasingly complex demands of final products and expand the range of applications, polymer blends and polymer composites have become cutting-edge developments in polymer science. Blending method represents one of the most efficient and cost-effective processing techniques for fabricating multiphase polymeric materials. This is a simple method combining two or more existing polymers ³. Furthermore, the future of polymer science and technology is closely related to the development of more sustainable, adaptive, and high-performance materials. Nowadays, material design is important for advanced products that require the ability to tailor structures for specific properties ⁴⁻⁹.

1.1.2. Polymer graded materials

Since the original idea of Functionally Graded Materials (FGM) was suggested in 1972, this material has been widely developed in various fields of material science ^{10,11}. Graded materials exhibit gradual transition properties owing to their spatially variable structures ¹². Because of their unique characteristics, FGMs have attracted the attention of many researchers in the field of both inorganic and organic materials. For polymer material science, various approaches to obtain gradient structures have been developed and applied to different objects. Graded materials have been prepared by introducing gradient covalent bonding, gradient distribution of composition (e.g., filler), and gradient molecular weight. Various methods and techniques have been employed to design and control microstructures of thermosetting polymers. Xuesong et al. ¹³ fabricated a graded composite material based on polyurethane/epoxy resin using layer-by-layer casting method. Zhao et al. ¹⁴ constructed graded polyurethane via curing reaction under gradient temperature. A graded structure was successfully obtained after more than seven hours ¹⁴. Hydrogels, as special materials, are potential candidates for the fabrication of graded materials, owing to their diverse properties. Guvendiren et al. ¹⁵ induced cross-linking concentration of poly(2-hydroxyethyl methacrylate) by solvent mixing method. Liu et al. ¹⁶ choose another approach when they used external magnetic to gradient distributed of magnetic nanoparticles into poly(N-isopropylacrylamide)/clay nanocomposite hydrogels. Recently, UV radiation exposure has also been selected as a common method for producing gradient

gels ¹⁷⁻¹⁹. For thermoplastic polymer, Frederick ²⁰ and Kota ²¹ fabricated a gradient polymer using an extrusion technique. A graded polymer was generated with a gradient distribution of the filler by incorporating a second component through a gravimetric feeder.

1.1.3. Mechanical properties of graded materials

Figure 1.1 shows that the gradient structure can be formed along three dimensions.

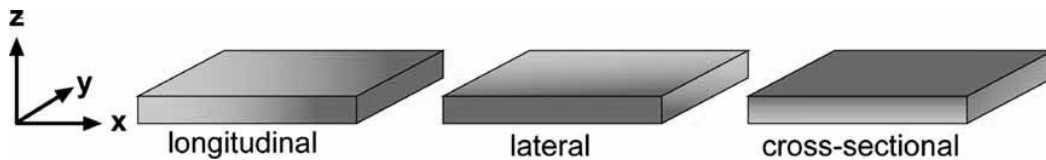


Figure 1.1. Types of graded materials. The gradient structure may extend across three dimensions ²².

Graded materials provide numerous mechanical benefits, including enhanced resistance to contact deformation and damage ²³, anti-crack-tip ^{24,25}, reduced crack-jump distances ²⁶, and reduced concentrations of local stress ²⁷. Furthermore, research has indicated that a material having Young's modulus gradient may potentially prevent crack propagation. The simple method to understand the superiority of graded materials is to compare them with butt joint materials, i.e., bilayer materials ²⁸. Consider two materials, A and B, with stiffness values of E_a and E_b , respectively. Since these materials with different stiffnesses meet at an interface, the interfacial junction often becomes the weak point when subjected to longitudinal stress. The stress at their interface is

known as radial stress. In Figure 1.2, the magnitude of this radial stress depends on the degree of mismatch between material stiffnesses, and proportional ratio of E_b/E_a .

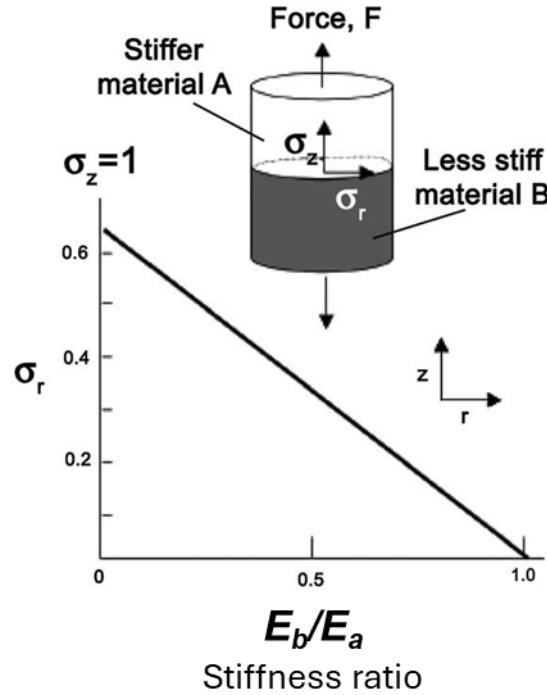


Figure 1.2. A bilayer material is formed when two substances with stiffness A and B are joined at an interface. Upon applying a load along the longitudinal axis z, the radial stress σ_z develops at the point of contact between the two materials. The magnitude of radial stress σ_z is proportional to the ratio E_b/E_a ²².

Graded materials, characterized by a continuously changing composition rather than a sharp interface, are not given to radial stresses ²². Potential applications for polymer-graded materials were already being considered as early as 1972 ²⁹. However, due to limited preparation methods, they were not initially produced until about 15 years later ³⁰. One of the typical graded structures that naturally inspired by the mussel byssus shield is graded

stiffness polymer. Generally, graded stiffness structures were developed by incorporating inorganic fillers or introducing porosity³¹⁻³³. Wen et al. fabricated graded polymer based on polypropylene/talc, with graded structure across the sample thickness. Notably, the graded structure within the sample was found to significantly influence the bending properties³³. In general, researchers often focused on analyzing cut sections of the graded material, with discrete compositions rather than whole graded samples³⁴. However, few studies have reported remarkable results that were analyzed for the entire graded specimens. For example, polymer-graded material based on graded interpenetrating polymer networks (gIPN) composed of poly(2-chloroethyl acrylate) and polymethylmethacrylate demonstrated the improvement of toughness and fracture strain^{35,36}. Various other gIPNs composed of different polymer systems achieved maximum yield stress and high fracture strain, resulting in exceptional toughness³⁷⁻⁴¹. Wang et al. has reported that vulcanization of styrene-butadiene rubber with the diffusion of sulfur can provide better damping properties⁴². Petunova et al. found that the graded material based on polyurethane demonstrated a quasi-elastic behavior, thus, greatly affected relaxation properties⁴³.

1.2. Elastomeric materials

Elastomers are a type of polymer exhibiting both viscous and elastic behaviors. These materials are typically amorphous and feature a cross-linked network structure. When subjected to low stress, elastomers undergo

deformation but return to their original shape after stress removal ⁴⁴. The word “elastomer” combining from “elastic” and “polymer” is often used with the term “rubber”. However, rubber is more frequently applied to elastomers that have undergone vulcanization ⁴⁵.

1.2.1. Rubber elasticity

Before exploring the rubber network, characteristics of an individual chain are briefly explained. In Figure 1.3, a part of polymer chain includes bond angle, bond length, and torsional angle. Typically, the length of bond and torsional angle are constant, unless subjected to extreme forces. The torsional angle switches between three low-energy states: trans, gauche⁺, and gauche[−]. This results in a rod-like zig-zag configuration in the trans state or a disordered shape in the gauche⁺ and gauche[−] states. The frequency of transitions between these states and configurations is affected by the chain's surroundings. For instance, in an appropriate solvent, the configuration changes occur 10^{10} times per second.

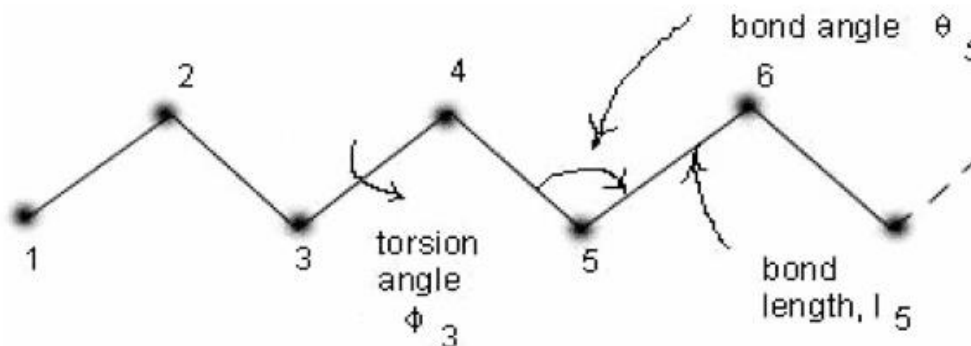


Figure 1.3. A polymer chain with a zig-zag configuration ⁴⁶

Statistical methods can be employed to characterize the attributes of a single chain through the probability P of end-to-end distance r . A random arrangement of a 10-bond chain is depicted in Figure 1.4, with the end-to-end vector. As aforementioned, torsional angle of each bond can be three states, resulting in 3^{10} possible configurations ⁴⁶. Due to the large number of configurations, average mean-square end-to-end distance $\langle r^2 \rangle$ value is typically used. By randomly generated configurations, the average mean-square $\langle r^2 \rangle$ can be calculated (Figure 1.4).

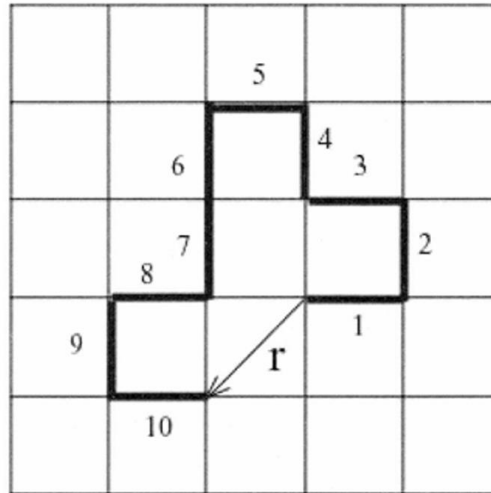


Figure 1.4. A random configuration of a 10-bond chain ⁴⁶.

The Monte Carlo technique is often utilized to produce a substantial number of random configurations. By combining P with the Boltzmann relation and the Helmholtz free energy, the elastic free energy A_{el} of a single chain can be determined as a function of temperature T .

For a single chain with fixed end to end distance, the elastic free energy A_{el} of is given by

$$A_{el} = U - \left(\frac{3kT}{2 \langle r^2 \rangle_0} \right) r^2 \quad (1.1)$$

where U is internal energy, k is Boltzmann's constant, and $\langle r^2 \rangle_0$ is $\langle r^2 \rangle$ of an unperturbed chain.

The tensile force f to stretch the chain is expressed as

$$f = \frac{3kT}{\langle r^2 \rangle_0} r \quad (1.2)$$

This equation indicates that an individual chain exhibits behavior similar to that of a linear spring ⁴⁷.

1.2.2. The vulcanization process

Vulcanization is the process using heat and pressure to induces chemical bonds into rubber material, so called “crosslinking”. Most rubber products cannot be used without vulcanization. This method was invented by Charles Goodyear in 1841 ⁴⁸, when he heated a mixture of natural rubber and sulfur. After vulcanization, the rubber exhibited good mechanical properties, particularly high tensile strength, and a small permanent set.

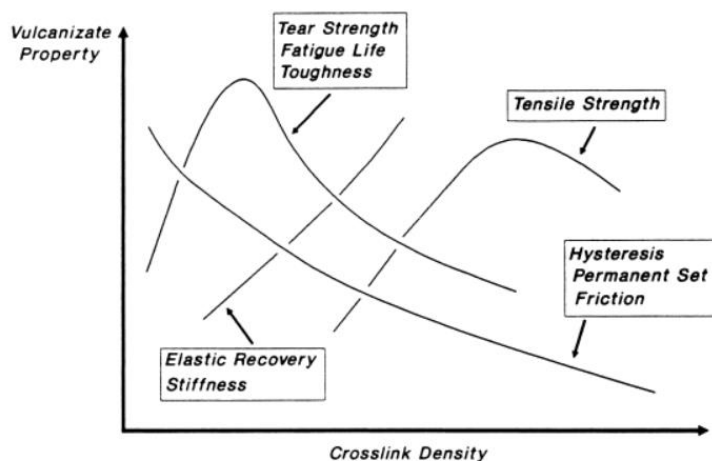


Figure 1.5. Vulcanized rubber properties ⁴⁹.

Figure 1.5 shows the vulcanized rubber properties depending on crosslink density. It should be noted that the vulcanization properties are also affected by the type of crosslink density, e.g., mono-sulfide or polysulfide, and the filler content. In rubber science and technology, cure meter is used to provide the information of vulcanization process. This instrument measures torque changes versus the vulcanization time of the sample under heat and pressure. Figure 1.6 shows the typical cure curves obtained from a cure meter.

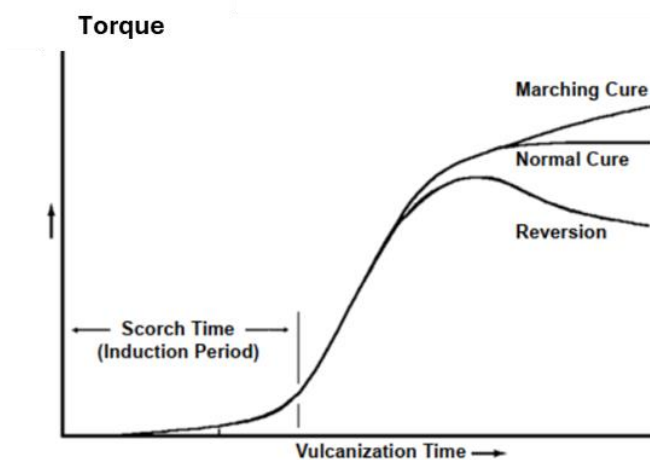


Figure 1.6. Cure curves from a cure meter ⁴⁹.

Vulcanization does not occur during the induction period. Therefore, the torque curves in a steady state and rubber exhibits viscous properties. During vulcanization, the torque proportionally increases with the crosslink density. At the end of the vulcanization process, the rubber is fully crosslinked. Three types of torque curves depend on the material. This is the so-called “post-cure” process. The torque curve sometimes continues to increase to re-construct the new crosslinked points (marching cure), remains in steady state (normal cure), or decreases because of thermal degradation (reversion) ⁴⁹.

1.2.3. Heat transfer during vulcanization

During vulcanization, the temperature not always homogenous. This is because a rubber material, like many polymeric materials, has a low thermal diffusivity, suggesting that it takes a longer time to reach an equilibrium temperature profile during the heating process. When a rubber compound is heated, a temperature gradient forms from the surface to the bulk ⁵⁰. It is widely recognized that the crosslink density depends not only on the vulcanization time but also temperature. Therefore, this temperature lag effect results in heterogeneous structure of a final product (Figure 1.7) ⁵¹.

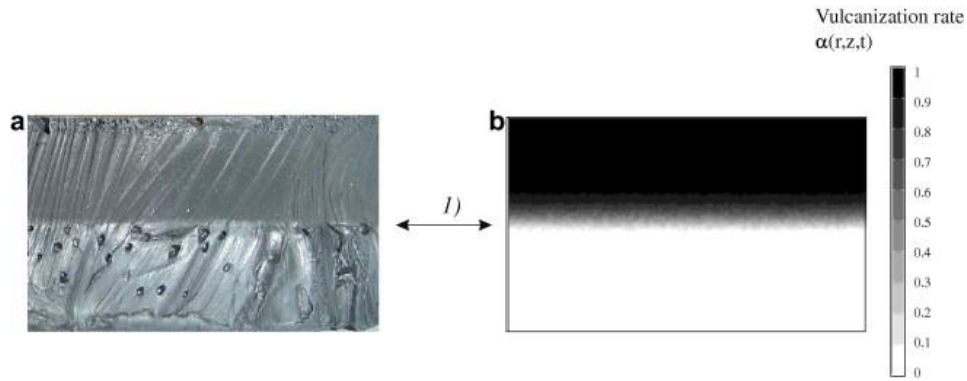


Figure 1.7. Effect of temperature lag on the structure of a final product: (a) cross-section area of real vulcanized rubber and (b) simulated data.

1.2.4. The Mullin effect

The Mullins Effect ^{52,53} is known as permanent change in a material response under cyclic deformation. This phenomenon is obviously seen in filled elastomers. After the first stretch, the stiffness of a material decreased, then gradually stabilizes in subsequent cycles. This is because the material changes its internal structure. During loading process, the breakup of filler network gradually occurs at a low strain (rupture of filler-filler bonding, loss of percolation...). At the bound rubber region, the chain segments near the filler surface tend to orient and untangle in the loading direction. Additionally, as the polymer chains connecting adjacent aggregates near their maximum stretching capacity, some chain segments may partially desorb or completely detach ⁵⁴⁻⁵⁶. As illustrated in Figure 1.8, during loading in subsequent cycles (with increasing maximum strain history), there is a decrease in stress when the applied strain is below the maximum at the previous stretching ⁵⁷.

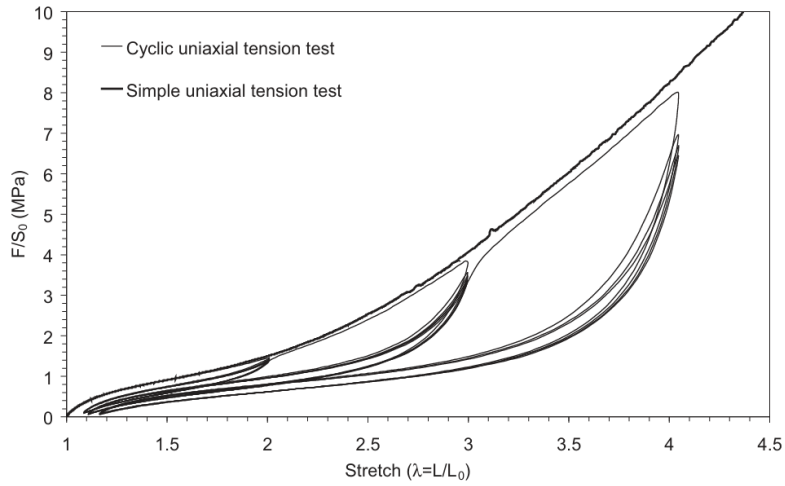


Figure 1.8. Stress-strain curve of carbon-black filled rubber under cyclic deformation ⁵⁷.

1.2.5. Swelling phenomenon

When a crosslinked rubber is immersed into an appropriate solvent, it cannot be dissolved because of three dimensional networks. Instead, the solvent molecules will penetrate the distance between polymer chains, resulting in swollen rubber. The swelling phenomenon was early studied by Flory ⁵⁸ and Gee ⁵⁹ using thermodynamics. Later, by using statistical treatment, Flory ^{60,61} introduced a detail equation that could describe the Gibb free energy of dilution.

The total energy of mixing ΔG_{total} is a sum of mixing energy and elastic energy:

$$\Delta G_{total} = \Delta G_{mix} + \Delta G_{elastic} \quad (1.3)$$

Presumably, the network shows isotropic expand. Therefore, the ΔG_{mix} could be:

$$\Delta G_{mix} = RT \left\{ \ln(1 - v_2) + \left(1 - \frac{V_1}{V_2} \right) v_2 + \chi v_2^2 \right\} \quad (1.4)$$

In equation 1.4, χ is the Flory-Huggin interaction parameter of polymer-solvent, and V_1 and V_2 are the molar volumes of the solvent and polymer, respectively.

The term $\Delta G_{elastic}$ related to the expansion of rubber network ⁶², could be given

$$\Delta G_{elastic} = \frac{RT}{2M_c} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) - \frac{2}{f} \frac{RT \ln(V / V_0)}{M_c} \quad (1.5)$$

with M_c is molecular weight between two adjacent crosslink points, λ_i is the stretching ratio at axis i , V_0 is volume of polymer, and V is total volume of polymer and solvent.

Since ΔG_{total} is zero at the equilibrium state, the chemical potentials of inside and outside the gel are equal. The classical Flory- Rehner is represented by

$$\ln(1 - v_2) + v_2 + \chi v_2^2 = - \frac{\rho_2}{M_c} V_1 \left(v_2^{1/3} \frac{2v_2}{f} \right) \quad (1.6)$$

where ρ_2 is the rubber density.

1.3. Miscibility of polymer blend

The structure of a polymer blend is primarily determined by the miscibility of its components. Thermodynamically, the Gibbs free energy of mixing ΔG_m is expressed by the equation ⁶³:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1.7)$$

where ΔH_m is the mixing enthalpy, and ΔS_m is the mixing entropy determined by the Boltzmann relationship.

In general, entropy consistently favors mixing, as it decreases the order of the system, whereas enthalpy typically disfavors mixing. The Flory-Huggins theory based on lattice chain model^{58,64-66} was originally proposed for polymer solution and was used to derive the entropy of mixing of ideal solutions. However, it can be extended to polymer-polymer mixtures as illustrated in Figure 1.9.

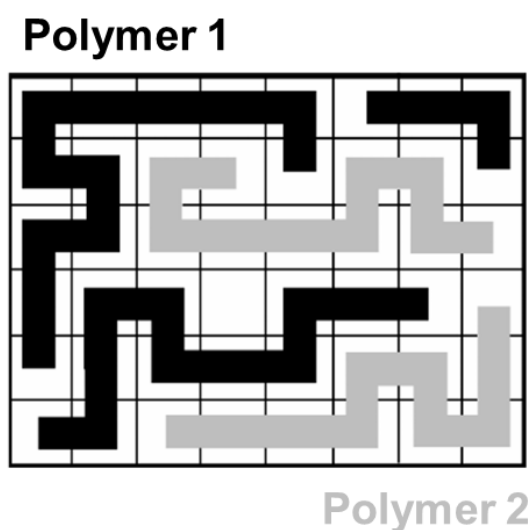


Figure 1.9. Lattice model of a polymer blend⁶⁷.

In this model, the assumption is that the interaction energies between Polymer 1 and Polymer 2 are merely enthalpic and effective only between the nearest neighbors. The two polymer species are arranged on a regular lattice, with structural units of identical size occupying the spaces.

The mixing entropy, ΔS_m , is derived as

$$\Delta S_m = -kV\left(\frac{\Phi_1}{r_1} \ln \Phi_1 + \frac{\Phi_2}{r_2} \ln \Phi_2\right) = -RV\left(\frac{\Phi_1}{r_1} \ln \Phi_1 + \frac{\Phi_2}{r_2} \ln \Phi_2\right) \quad (1.8)$$

where k is the Boltzmann constant, V is the total molar volume, R is the gas constant, and Φ_i and r_i are the volume fraction and the number of segments per chain of polymer i .

The mixing enthalpy, ΔH_m , is given by

$$\Delta H_m = RT\Phi_1\Phi_2\chi \quad (1.9)$$

where χ is Flory-Huggins interaction parameter which is defined as

$$\chi = \frac{zw_{12}}{RT} \quad (1.10)$$

$$w_{12} = \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) - \varepsilon_{12} \quad (1.11)$$

where ε_{ii} is the contact energy between molecules of the same component, ε_{ij} is the contact energy between molecules of different components, and z is the lattice coordination number.

Substitution (1.9) and (1.10) into (1.8), the obtained Flory-Huggins equation expresses free energy of mixing for polymer blends

$$\Delta G_m = RTV\left(\frac{\rho_1\Phi_1}{M_1} \ln \Phi_1 + \frac{\rho_2\Phi_2}{M_2} \ln \Phi_2 + \Phi_1\Phi_2\chi\right) \quad (1.12)$$

where ρ_i and M_i are the density and molecular weight of component i , respectively.

The Flory-Huggins equation provides a basis for a general miscibility of a polymer blend. Because polymers have a high molecular weight, the entropic contribution, i.e., mixing entropy ΔS_m , is negligible. This implies that any small change in mixing enthalpy ΔH_m that is disfavor mixing leads to a positive ΔG_m . It is well known that the temperature strongly affects the mixing energy. As the temperature increases, the molecular motion increases, and the specific interactions between the two polymers become weak. Beyond the critical point, phase separation occurs. Phase separation is a critical factor in many practical applications, making it essential to understand the phase behavior of mixtures. Although many polymer blends exhibit lower critical solution temperature (LCST) behavior, some binary systems such as a blend of Poly(ethylene oxide) (PEO) and Poly(methyl methacrylate) (PMMA) also exhibit upper critical solution temperature (UCST) behavior. The phase diagram for polymer mixtures with LCST and UCST is shown in Figure 1.10.

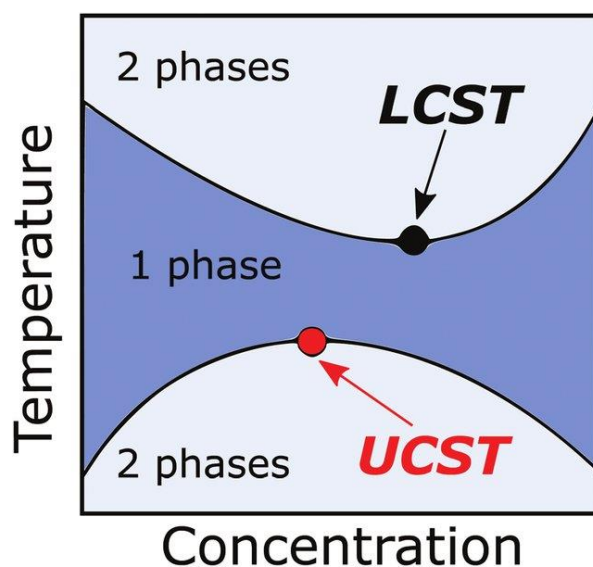


Figure 1.10. Phase diagram of LCST and UCST blends ⁶⁸.

1.4. Segregation under temperature gradient

So far, various researchers have reported segregation phenomena in polymer blends. For instance, surface segregation occurs in solution-cast films of miscible blends due to differences in surface tension. The polymers had high surface tension tending to be exposed on the surface ⁶⁹⁻⁷¹. Additionally, concentration gradients without phase separation have been observed in miscible blends subjected to temperature gradients, in which low-molecular-weight components concentrated in high-temperature areas ^{72,73}. This phenomenon is analogous to the Soret effect in miscible solvents ^{74,75}. Siriprumpoonthum et al. ⁷² found that grading phenomenon may be related with free volume fraction. Low-molecular-weight components, requiring larger free volumes ⁷⁶, accumulate in high-temperature regions. Surface segregation of low-molecular-weight components has also been reported in other polymers ^{70,77}, attributed to the large free volume associated with chain ends and high surface tension.

1.5. Objective of this study

The first objective of this study is to provide a simple fabricating method to design elastomeric materials that could be applicable in industry. In general, the inhomogeneous distribution of crosslink density in vulcanized rubber resulted by temperature lag effect is ignored by most researchers. However, in this research, temperature gradient is a key factor in the fabricating method. By

controlling the temperature gradient, it is a very simple method to prepare graded materials like rubber.

Second, this research also aims to explore the unique properties of graded rubber. In chapter 2, the graded styrene butadiene rubber having graded structure the thickness direction was prepared by vulcanizing under a temperature gradient. The samples showed good strain recovery and high damping properties compared to the homogenous sample. Mechanisms were also discussed in detail. In chapter 3, graded rubber with graded crosslink density also exhibited the anomalous swelling behavior. Upon swelling, graded rubber showed bending toward the low-crosslink side in the early state, and opposite shape in the equilibrium state. The swelling in the equilibrium could be well-explained using the Flory-Rehner theory. However, swelling behavior in the early state has never been reported before. The segregation under temperature gradient of tackifier in the miscible blend based on styrene butadiene rubber was studied in Chapter 4. Although the segregation of low-molar mass in the miscible blends has been previously reported. There have still remained some lacks since the mechanisms are not fully understood due to specific properties of blend systems. Previous researchers reported that low-molecular weight components are found to segregate the high temperature area. Interestingly, the results in Chapter 4 were significantly different from the reports before. After understanding the mechanism of segregation, it is possible to fabricate and control the material that have concentration gradient of tackifier. Eventually, a summary of this research is presented in Chapter 5.

This research provides a new approach to rubber science and contributes to the development of high-performance material, especially graded rubber. Moreover, it also aims to identify any anomalous properties that have not yet been discovered and to clarify the mechanisms behind them. Once these problems are revealed, this modification technique will be used to fabricate graded rubber for specific applications.

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Chapter 2

Graded rubber having gradient crosslink density: Mechanical properties

2.1. Introduction

In general, crosslinked rubber has homogeneously distributed crosslinking points throughout the material. However, the crosslink density of most conventional rubber vulcanized by compression molding is not always homogeneous, particularly when large molds are used in the manufacturing process. This is because rubber, which is similar to many polymers, has low thermal diffusivity. Thus, achieving an equilibrium temperature state at vulcanization process requires a long time ¹. Therefore, the surface region has a longer exposure to a high temperature than the bulk. As a result, it leads to differences in cross-link density. Bellander et al. ² found that a gradient in the crosslink density occurred in a crosslinked styrene–butadiene rubber (SBR). He hypothesized that a temperature gradient may develop as a result of pressure gradient. Because the crosslink density has a proportional relation with the temperature, a gradient crosslink density structure was formed. Prior studies have shown that various techniques can be employed to fabricate a graded polymer material, including the layering of different materials ³ or step-wise photocuring ⁴⁻⁶. For rubber materials, Ikeda fabricated graded rubber by stacking rubber sheets containing varying sulfur concentrations ^{7,8}. Mechanical

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properties, such as tensile strength or hardness, were found to be mostly determined by the high-crosslink part. Additionally, research by Glebova et al.⁹ demonstrated that in the boundary of zinc oxide particles, SBR exhibited a high crosslink density within nanoscale regions (approximately 200 nm). Considering that nanoparticles could be migrated between different rubber interfaces¹⁰, this technique could potentially be applied for developing graded rubbers. By applying temperature gradient, Wang et al.¹¹ fabricated a graded SBR through the diffusion of sulfur across material's thickness from a surface with high concentration to the other. The diffusion constants of curatives have been extensively investigated following the work of van Amerongen¹² and Gardiner¹³, making this technique noteworthy.

In fact, for most rubber products, the effect of gradient structure on the mechanical properties remains largely negligible. However, this phenomenon becomes more noticeable, especially when the vulcanization rate is slow. Some researchers have found that a crosslink gradient structure affected the damping properties¹⁴⁻¹⁶. The damping properties of rubbery materials, associated with their ability to absorb energy, are widely used in industrial applications^{17,18}. In general, a rubber specimen under cyclic deformation losses its energy due to internal friction, resulting in hysteresis^{19,20}. The softening phenomenon, i.e., the Mullins effect, is one of the famous hysteresis loss phenomena observed in a rubber²¹. Hence, understanding hysteresis loss in rubber compounds is crucial for assessing rubbery materials' performance. It is well-known that variables, including strain level²²⁻²⁴, strain history²⁵, and strain rates^{26,27} influence the

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hysteresis of a vulcanized rubber. Previous studies have been conducted mostly based on homogeneous rubber, which consists of a uniform distribution of fillers and crosslink density. In the case of a graded rubber, the material behavior is more complex owing to its heterogenous structure. Considering the structure of a graded rubber as a composite of multiple layers, in which each layer exhibits a distinct mechanical response, these stack layers underwent localized stress-strain fields ²⁸ during deformation. The damping properties, therefore, must be affected. According to previous study ⁷, graded rubber with a sulfur concentration gradient showed a significantly broad peak of $\tan \delta$. Previous researchers ^{11,29} explored hysteresis loss in the nonlinear region of graded rubber with a carbon black (CB) concentration gradient. Their findings indicated that, in the nonlinear region, the graded rubber exhibited low hysteresis loss, whereas in the linear region, it showed a low $\tan \delta$ value. Although several studies have been conducted using graded rubber to provide a method of preparation, only preliminary results have been reported. So far, no comprehensive study has been conducted to reveal the relationship between the mechanical response and the gradient crosslink density, as well as a comparison to a homogeneous one.

In this chapter, graded SBR having gradient crosslink density across the thickness direction was fabricated by vulcanizing under temperature gradient. After stress removal, the strain recovery of the graded rubber was systematically investigated and compared to that of homogeneous rubber. To clarify the behavior of hysteresis, the material's response to cyclic deformation,

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including the effects of strain rate, was thoroughly analyzed in both the linear and nonlinear regions.

2.2. Experimental

2.2.1. Materials

In this study, Styrene-Butadiene Rubber (SBR-1502), provided by Sumitomo Rubber Industries, Ltd. was used. The styrene content is 25%. The Mooney viscosity ML (1+4) was 52 at 100 °C. Zinc oxide (ZnO) was purchased from Fujifilm Wako Pure Chemical Corporation, Japan. Other additives such as carbon black (N220); stearic acid; processing oil; N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylene diamine (Nocrac 6C); 1, 3-diphenylguanidine (DPG); N-cyclohexyl-2-benzothiazolyl (CBS); and sulfur (S), were also used.

2.2.2. Sample preparation

The ingredients for SBR compound is presented in Table 2.1. The mixing process was conducted in three stages. In the initial stage, SBR was mixed with all components excepts curatives such as CBS, DPG and S by a Mixtron BB internal mixer (Kobelco, Japan). The compound was mixed at a rotor speed of 77 rpm for 3 min at 30 °C. The final temperature reached approximately 150 °C. Following the mixing process, temperature was cooled down to room temperature to prevent pre-vulcanization from the mixture. After that, sulfur and accelerators were reintroduced into the mixture and the mixing

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process was continued at 30 °C for 3 min with a rotor speed of 44 rpm. The final temperature attained was approximately 100 °C. In the final stage, the resultant mixture was processed using a two-roll mill (Kansai Roll, Japan) at 60 °C. The nip gap was 2.5 mm.

Table 2.1. Recipe for SBR compound.

Ingredients	Amount (phr)
SBR	100
ZnO	3
N220	50
Stearic acid	2
CBS	2.3
DPG	1.85
Antioxidant (Nocrac 6C)	1
Processing oil (aroma)	5
S	1.45

Vulcanization was performed under 10–20 MPa for 10 min using a conventional compression molding machine. The sample's thickness was approximately 1.3 mm. The vulcanizing temperatures corresponding to the sample codes are presented in Table 2.2 and Table 2.3. In particular, “H” denotes the homogeneously crosslinked samples, in which both surfaces contacted at identical temperatures. On the other hand, graded samples are denoted as "G". At the end of the vulcanization process, the temperatures of both the surfaces were measured again. The unvulcanized sample denoted as

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"UV". Before measurement, all samples were stabilized at room temperature for a minimum of 24 h.

Table 2.2. Sample codes and the temperature settings for the strain recovery experiments.

Sample codes	Set temperature (°C)		Final temperature of vulcanization process (°C)	
	Top plate	Bottom plate	Top plate	Bottom plate
UV	-	-	-	-
H80	80	80	80	80
H110	110	110	110	110
H170	170	170	170	170
G170-80	170	50	170	80
G170-110	170	80	170	110

Table 2.3. Sample codes and the temperature settings for the investigation of hysteresis loss.

Sample code	Set temperature (°C)		Final temperature of vulcanization process (°C)	
	Top plate	Bottom plate	Top plate	Bottom plate
H160	160	160	160	160
H130	130	130	130	130
G170-90	170	60	170	90

2.2.3. Measurements

Time dependence torque was evaluated at 110, 135 and 170 °C by a Curelaster (Eneos Trading Company, Japan) in accordance with ISO 6502 for 600 s.

Dynamic mechanical analysis was performed using a Rheogel-E4000 machine (UBM, Japan). The strain sweep was tested in tensile mode at 30 °C. Dynamic tensile moduli was determined in the temperature between -90 °C and 100 °C and heating rate was 2 °C·min⁻¹. The frequency was set to 10 Hz. The analysis employed rectangular specimens measuring 25 mm in length, 3 mm in width, and approximately 1.8 mm in thickness.

Tensile properties were measured by an Autograph AGS-X testing machine (Shimadzu, Japan). Dumbbell shape die was used to cut the sample sheets according to the No.7 of JIS-K6251 standard. The speed of an increase in the chuck span was 100 mm·min⁻¹, and the initial length was 20 mm.

Stress relaxation was measured using a tensile machine. The stretching speed was mm·min⁻¹. The samples were stretched at a strain of 1.0 and held for 900 s to monitor the force dependence time. Following these measurements, the samples were removed from the tensile machine and stored at 25 °C for an extended period to examine strain recovery. The recovery process of the samples was recorded using an HDR-CX540V digital camera (Sony, Japan).

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To study the hysteresis loss, each specimen was subjected to loading/unloading deformation using the same tensile machine. The details of the test procedure are shown in Figure 2.1.

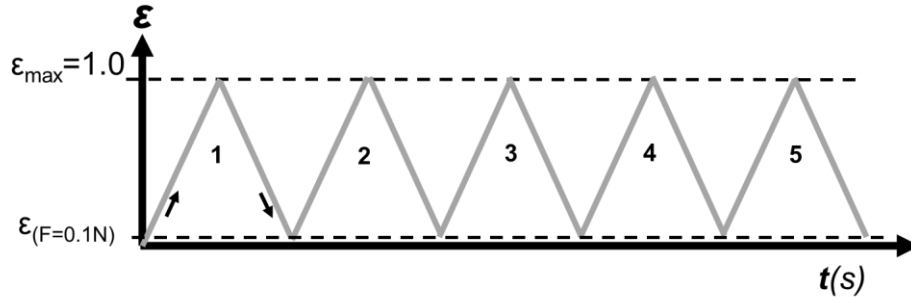


Figure 2.1. Protocol for hysteresis measurement.

Each cycle involved stretching the samples to a maximum strain of 1, followed by relaxation to a strain corresponding to 0.1 N force (approximately 0.028 MPa stress) to prevent buckling. This process was repeated five times for each sample. The loading and unloading were carried out at crosshead speeds of 0.1, 1, and 10 mm.min⁻¹, which corresponded to strain rates of 0.00017, 0.0017, and 0.17 s⁻¹, respectively. Strain was assessed based on the displacement of the crosshead. The hysteresis loss ratio for each sample was calculated using the following formula:

$$\text{Hysteresis loss ratio (H)} = \frac{W_1}{W_1 + W_2} \quad (2.1)$$

where W_1 and W_2 are the areas of a region under the curves shown in Figure 2.2.

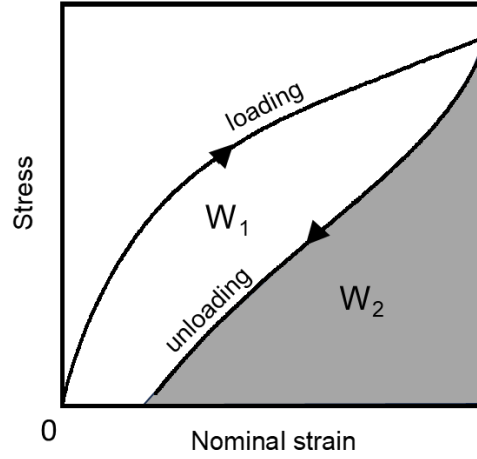


Figure 2.2. Definitions of W_1 and W_2 .

The swelling tests were performed in accordance with ASTM D471-79 standard. Sample with initial weight (m_1) was submerged in toluene at 25 °C for 24 hours until an equilibrium was reached. Upon removal, the swollen specimens were immediately weighed (m_2) and subsequently dried in a vacuum oven at 50 °C until their mass stabilized (m_3). The swelling ratio and the gel fraction were evaluated by:

$$\text{Swelling ratio (\%)} = \frac{m_2 - m_1 / \rho_s}{m_1 / \rho_r} \times 100 \quad (2.2)$$

$$\text{Gel fraction (\%)} = \frac{m_3}{m_1} \times 100 \quad (2.3)$$

where ρ_s and ρ_r are the density of the toluene and specimen, respectively.

For swelling ratio and gel fraction testing, at least three specimens were used to obtain the average values.

2.3. Results and Discussion

2.3.1. Strain recovery of graded rubber and homogenous rubber

Figure 2.3 illustrates the time dependence torque of SBR compound at various temperatures. Torque remained constant for 10 min at temperatures of 110 °C and below, indicating the reaction did not occur at these temperatures. At temperature of 135 °C, the scorch time is 300 s. Beyond this value, the torque exhibited an increase, but did not reach a steady state until the end of measurement. At 170 °C, the optimum cure time, t_{90} , is found to be approximately 140 s. The torque quickly reached a steady state, indicating SBR was fully crosslinked at this temperature.

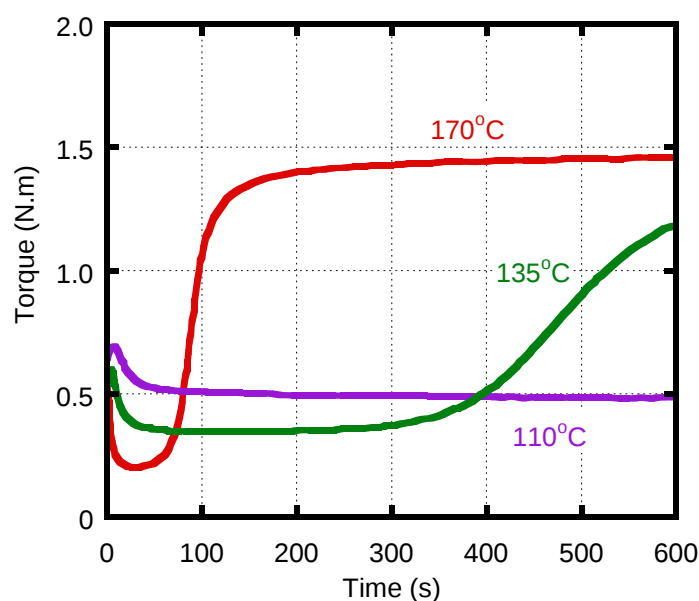


Figure 2.3. Torque curves plotted as a function of curing time at 110, 135 and 170 °C.

Figure 2.4 shows the temperature dependence of the tensile storage modulus (E') and loss tangent ($\tan \delta$) at 10 Hz. Distinct glassy transition and rubbery regions were observed for all the samples.

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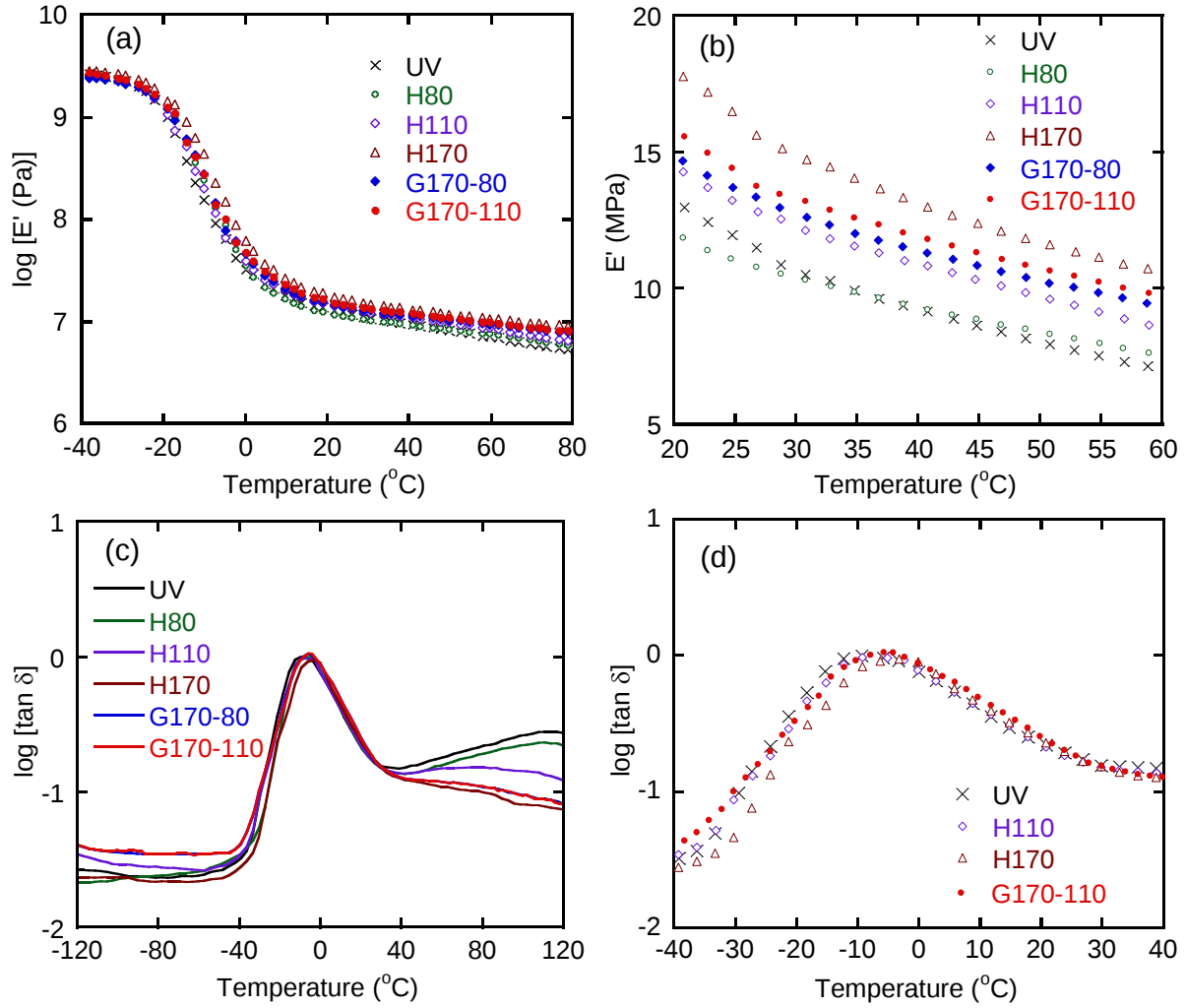


Figure 2.4. Temperature dependence of (a) and (b) tensile storage modulus E' and (c) and (d) loss tangent $\tan \delta$ at 10 Hz.

As shown in Figure 2.4, the E' values in the glassy region are nearly identical, while slight differences are observed in the transition region. In the rubbery region, the modulus is affected by the number of crosslink points. For H170, the highest E' value corresponds to the fully crosslinked sample. In Figure 2.4b, the E' values are presented for the rubbery region. For the homogeneous rubbers, E' increases as the vulcanization temperature rises. In contrast, for the graded rubbers, E' values—such as for G170-80 and G170-

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110—were between those of H110 and H170. This suggests that the region with higher crosslink density contributes to the elasticity of the graded rubber. In the transition region, the graded samples did not show high values of $\tan \delta$, which contrasts with some previous reports^{11,30-32}. However, there is a slight difference in $\tan \delta$ between samples. This might be because the difference in crosslink density between both surfaces is not large enough to observe the large difference. In the temperature range from -40 to -5 °C, the values of $\tan \delta$ for H170 were lower than those for the other samples. As the crosslink density increases, the movement of segments in the rubber chains is further restricted, resulting in a higher T_g ³⁰⁻³³. It is hypothesized that the current samples had fewer dangling chains than those used in previous studies. Thus, at least in the linear viscoelastic region, significant energy absorption is not expected.

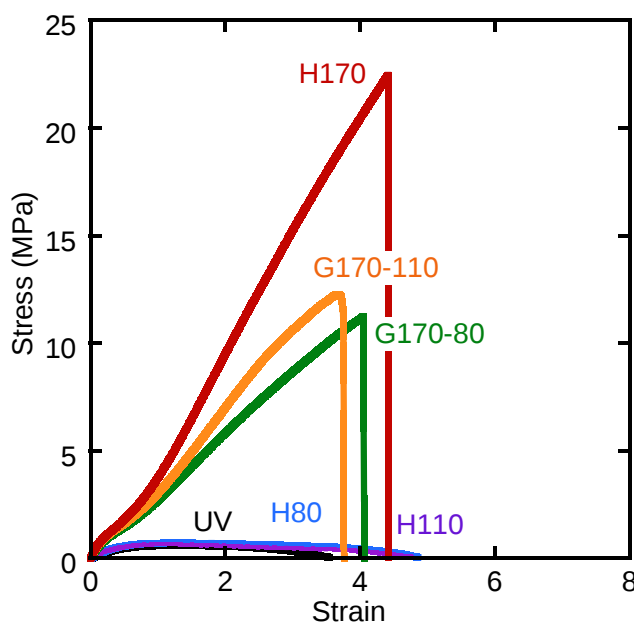


Figure 2.5. Stress versus strain curves

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The stress–strain curves in Figure 2.5 indicate that the tensile strength for the graded samples was between those of H170 and H110. This implies that the surface region with high crosslink density, which exposed to the high temperature during vulcanization, is mainly responsible for the stress generation. These reasonable results are well corresponded with above results and also previous work ⁷.

To evaluate the strain recovery, stress-relaxation measurements were performed. Samples were stretched and held at a strain of 1.0. The normalized stress relaxation curves, where the stress is divided by the strain value at the end of stretching, are depicted in Figure 2.6.

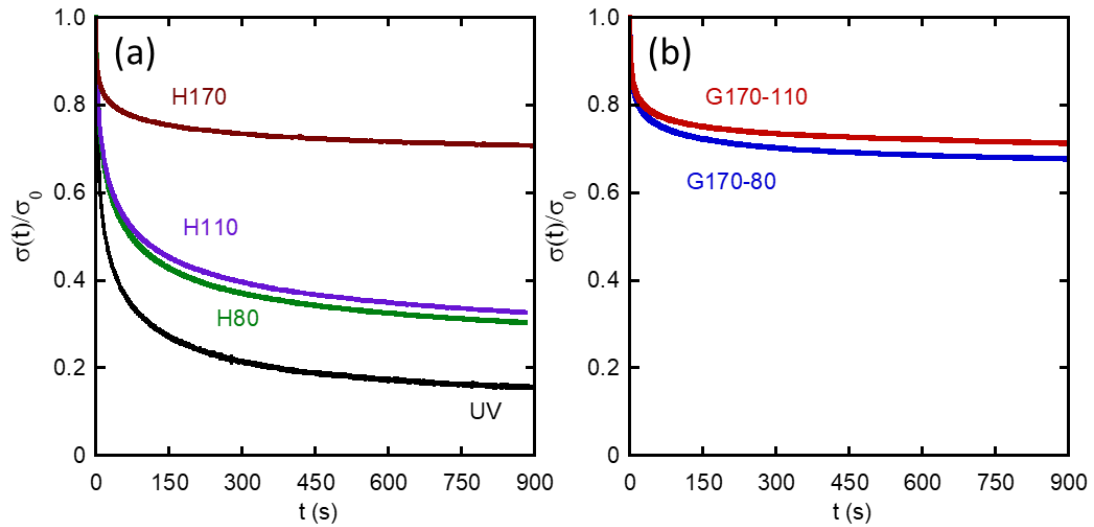


Figure 2.6. Relaxation curves of normalized stress [$\sigma(t)$ divided by the stress at the cessation of stretching] at $\varepsilon = 1$ for (a) homogenous samples and (b) graded samples.

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In the long-time region, the graded samples exhibited high levels of normalized stress. In comparison to homogenous rubber, these values almost similar to those of H170 and significantly higher than those of H110, indicating that the graded samples demonstrated superior rubber elasticity. Analogous to stress generation during stretching, the high-crosslink region primarily contributed to the rubber elasticity. Furthermore, the data revealed that H80 and H110 exhibited higher values than UV, suggesting the presence of a weak network in the sample vulcanized at low temperatures, i.e., below 110 °C.

After the stress-relaxation measurement, which lasted 900 s, the samples were taken out of the tensile machine and placed at room temperature (25 °C) to examine their strain recovery behavior. Images of the samples immediately following stress removal are shown in Figure 2.7. As seen in Figure 2.7a, H170 displayed simple shrinkage with a flat shape, as expected. In contrast, the graded rubber samples showed markable bending (Figure 2.7b), with the inner side corresponding to the high-crosslink region. The bending deformation is attributed to the mismatch in shrinking stresses between the two sides of the graded samples. Upon stress release, the high-crosslink side experienced a strong shrinking stress, which recovered rapidly. On the other hand, the low-crosslink side exhibited weaker shrinking stress, due to the relaxation and reorientation of the chain segments.

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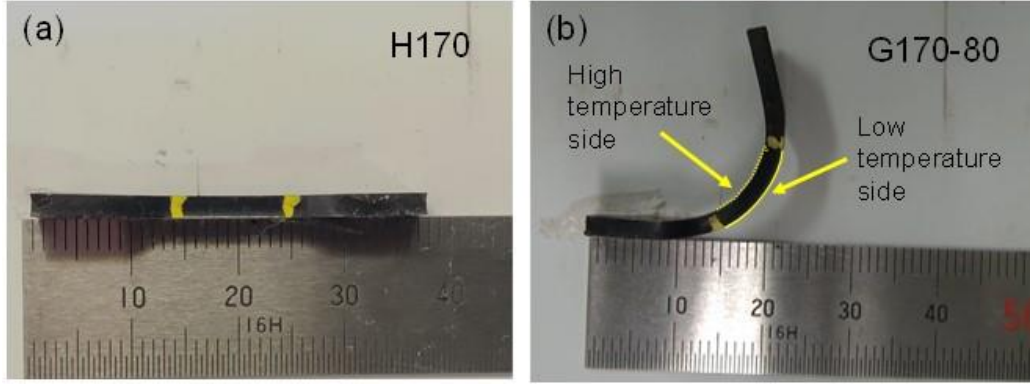


Figure 2.7. Sample's pictures were immediately captured after cessation of stretching for (a) H170 and (b) G170-80. The images were taken from a side view of the samples.

After stress removal, the recovery process of samples was captured by a digital camera. Figure 2.8 shows the recovery process for graded samples.

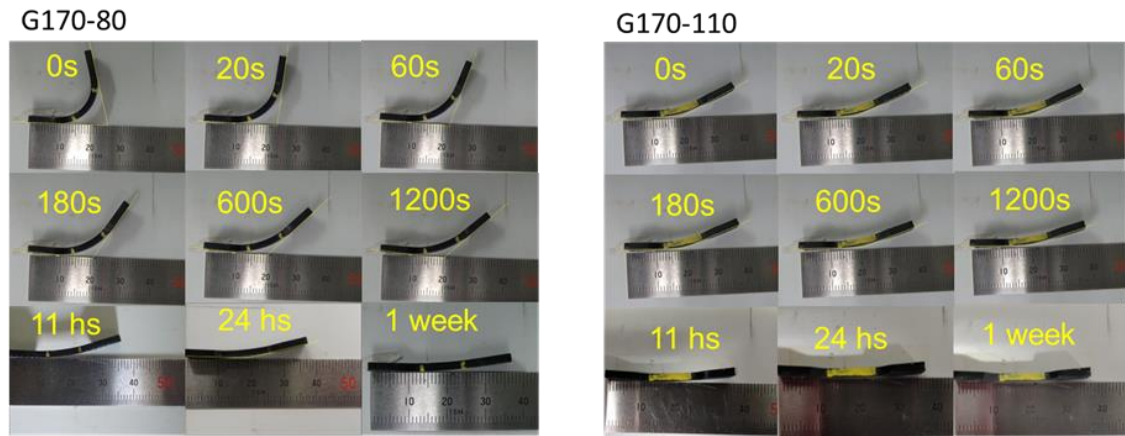


Figure 2.8. Recovery process after stress removal of graded samples.

The recovery ratio $R(t_r)$ as a function of the time t_r was calculated using the following equation:

$$\text{Recovery ratio } R(t_r)(\%) = \left(1 - \frac{\varepsilon(t_r)}{\varepsilon_i}\right) \times 100 \quad (2.4)$$

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where $\varepsilon(t_r)$ is the strain at time t_r and ε_i is the initial strain applied by stretching. In this experiment, ε_i is 1. For graded samples, the outer and inner lengths were evaluated by Image J software using the pictures, and the average values were used as $\varepsilon(t_r)$.

As seen in the Figure 2.9, H170 showed an immediate recovery. This observation was consistent with the fact that the experiments were performed well beyond T_g . The recovery value was $98 \pm 1\%$, indicating that the residual strain, $1-R(\infty)$, was approximately 2%. For homogeneous rubber, the time dependence curves were more pronounced when the crosslink density decreased, i.e., poor rubber elasticity. In other words, samples with a small residual strain exhibited a rapid recovery at room temperature. In contrast, graded rubber exhibited different behaviors. At the equilibrium conditions, graded rubber exhibited remarkable strain recovery. For example, the strain recoveries were $96 \pm 1\%$ and $97 \pm 1\%$ for G170-80 and G170-110, respectively. These values were much better than those for H110 and H80. However, it took a long time to achieve the equilibrium, i.e., the recovery ratio slowly increased with t_r , especially for G170-80 with bending deformation. Because the stress-relaxation curves of graded rubber were not much different from that of H170, it is difficult to predict the strain recovery based on the stress relaxation data (Figure 2.6).

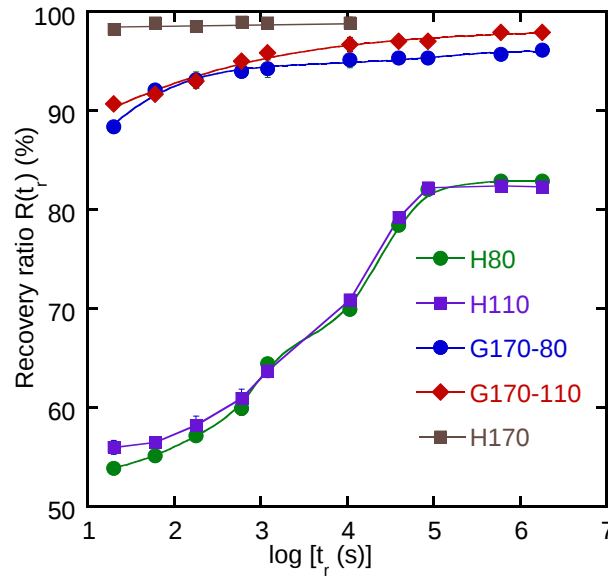


Figure 2.9. Strain recovery ratio $R(t_r)$ after stress removal.

The mechanism of slow recovery after stress removal of graded rubber is shown in Figure 2.10.

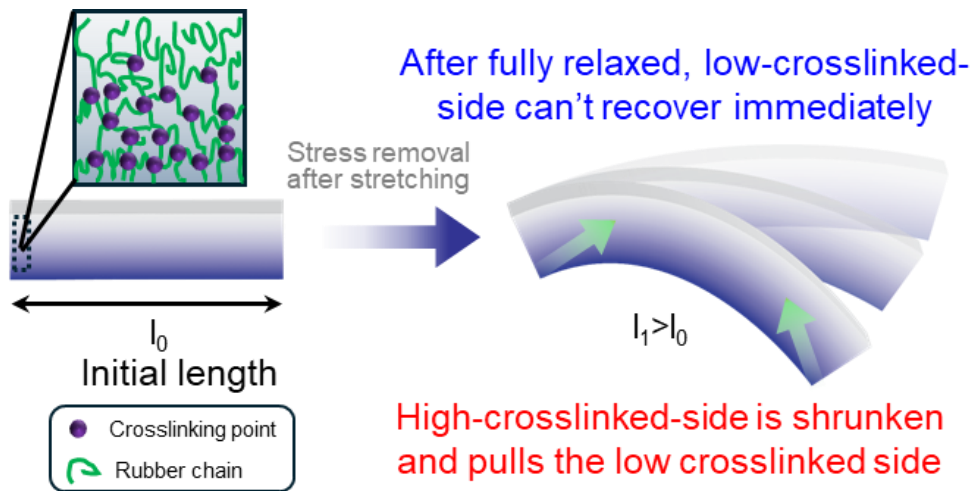


Figure 2.10. Mechanism of slow recovery of graded rubber.

In the low crosslink density region, the segmental orientation was predominantly relaxed upon the removal of stress. After the stress removal, the low-crosslinking side, which had poor elasticity, could not recover immediately.

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The high-crosslink side immediately shrunk; however, it was still constrained owing to the low-crosslink side. Subsequently, the high-crosslink side exerted a pulling force on the other side, that is, a compressive force was applied. This tension serves as the driving mechanism for strain recovery in the low-crosslinking region.

2.3.2. Hysteresis loss of graded rubber and homogenous rubber

In this section, a graded rubber (G170-90) and a homogeneous rubber (H130) were synthesized to ensure that both samples possessed approximately equivalent average crosslink densities. Subsequently, various methodologies were employed to verify the aforementioned assumption. In addition, H160 represented for a fully crosslinked rubber was also evaluated for a comparison.

Figure 2.11a shows a picture of the swollen graded rubber, i.e., G170-90, after immersing in toluene at 25 °C for 24 h. G170-90 showed bending deformation, at which the high-crosslink side was inner. This observation similar with the previous work⁸ and can be attributed to the presence of gradient network along the thickness direction, wherein the high-crosslink side demonstrated a lower swelling ratio compared to the low-crosslink side.

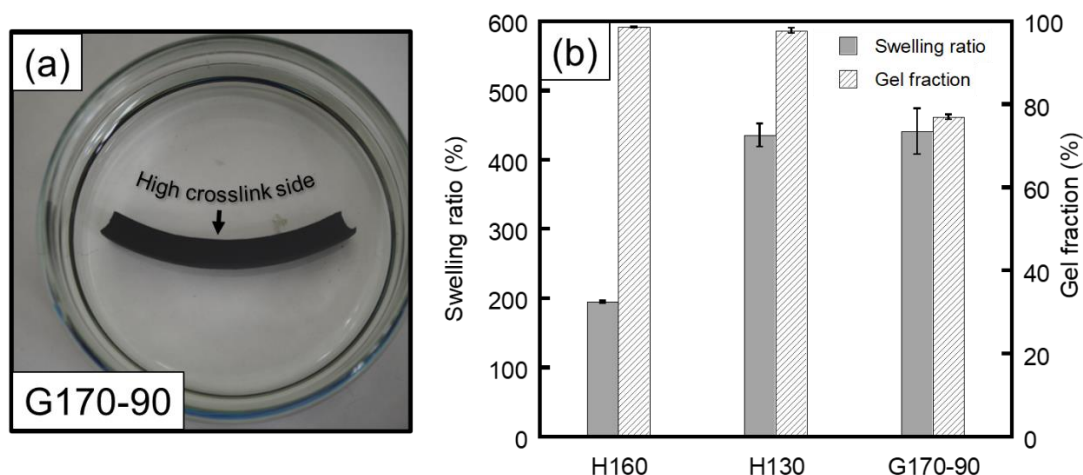


Figure 2.11. (a) Swollen graded rubber (G170-90) after 24 h in toluene at 25 °C; and (b) swelling ratios and gel fractions of the graded rubber and homogenous rubbers.

As demonstrated in Figure 2.11b, H160 had the lowest swelling ratio (approximately 200%), whereas G170-90 and H130 had swelling ratios were comparable (approximately 430%). This observation suggests that G170-90 and H130 possess similar average crosslink densities. Conversely, the gel fraction exhibited a distinct trend. The gel fraction values of H160 and H130 were approximately 100%, while the value of G170-90 was approximately 77%. As indicated in the curing curves (Figure 2.3), the torque increased after 10 min at 130 °C. In contrast, it is found at 110 °C, vulcanization did not occur. Therefore, the side exposed to a 90 °C in the graded rubber, of course, contained soluble portions. As a result, the gel fraction decreased.

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The viscoelastic response was characterized by strain sweep at 30 °C. In accordance with Onogi et al.³⁴ and Matsumoto et al.,³⁵ the stress σ generated by a large strain amplitude γ_0 with angular frequency ω was expressed by:

$$\sigma = E_1' \gamma_0 \sin \omega t + E_2'' \gamma_0 \cos \omega t - E_3' \gamma_0 \sin 3\omega t - E_3'' \gamma_0^3 \cos 3\omega t + E_5' \sin 5\omega t + \dots \quad (2.5)$$

Figure 2.12 shows the primary component of the tensile storage moduli (E_1') as a function of strain. For strain below $< 0.1\%$, the E_1' values remained constant regardless of strain, indicating the linear region. The modulus of the G170-90 was approximately 6.38 MPa in the linear region, which was similar to that of H130 (6.50 MPa). This similarity was anticipated due to the similar swelling ratios exhibited by both samples.

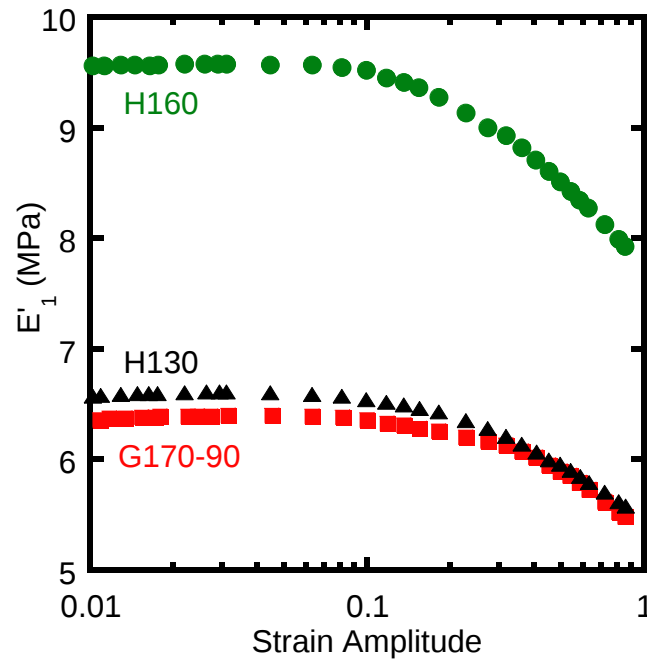


Figure 2.12. Strain dependence of the primary component of the storage modulus E_1' at 10 Hz and 30 °C.

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All samples exhibited non-linear response when strain exceeded 0.1%. In other words, in the linear region, the linear range was not affected by the magnitude of the storage modulus, i.e., E_1' . Beyond a strain of 0.1 %, the E_1' value of each sample gradually decreased. This phenomenon , commonly referred to as the Payne effect ³⁶, and is attributed to the breakdown of the filler network. The linear region is generally determined by filler-filler interactions, with filler surface area and content being crucial factors. In this study, all samples had identical composition and preparation methods, differing only in vulcanization temperature. Consequently, they shared the same carbon black dispersion state.^{37,38}

Cyclic stress–strain curves

Figure 2.13 shows the cyclic stress–strain curves at different strain rates. The Young's moduli obtained at the first and third loading curves of the samples are summarized in Figure 2.14. The order closely aligned with the E' values in Figure 2.12. The Young's modulus of each sample increased as the strain rate increased. However, G170-90 demonstrated weak strain rate sensitivity, particularly noticeable during the third stretch. These findings suggested that G170-90 exhibited mechanical behavior somewhat similar to that of an ideal rubber.³⁹

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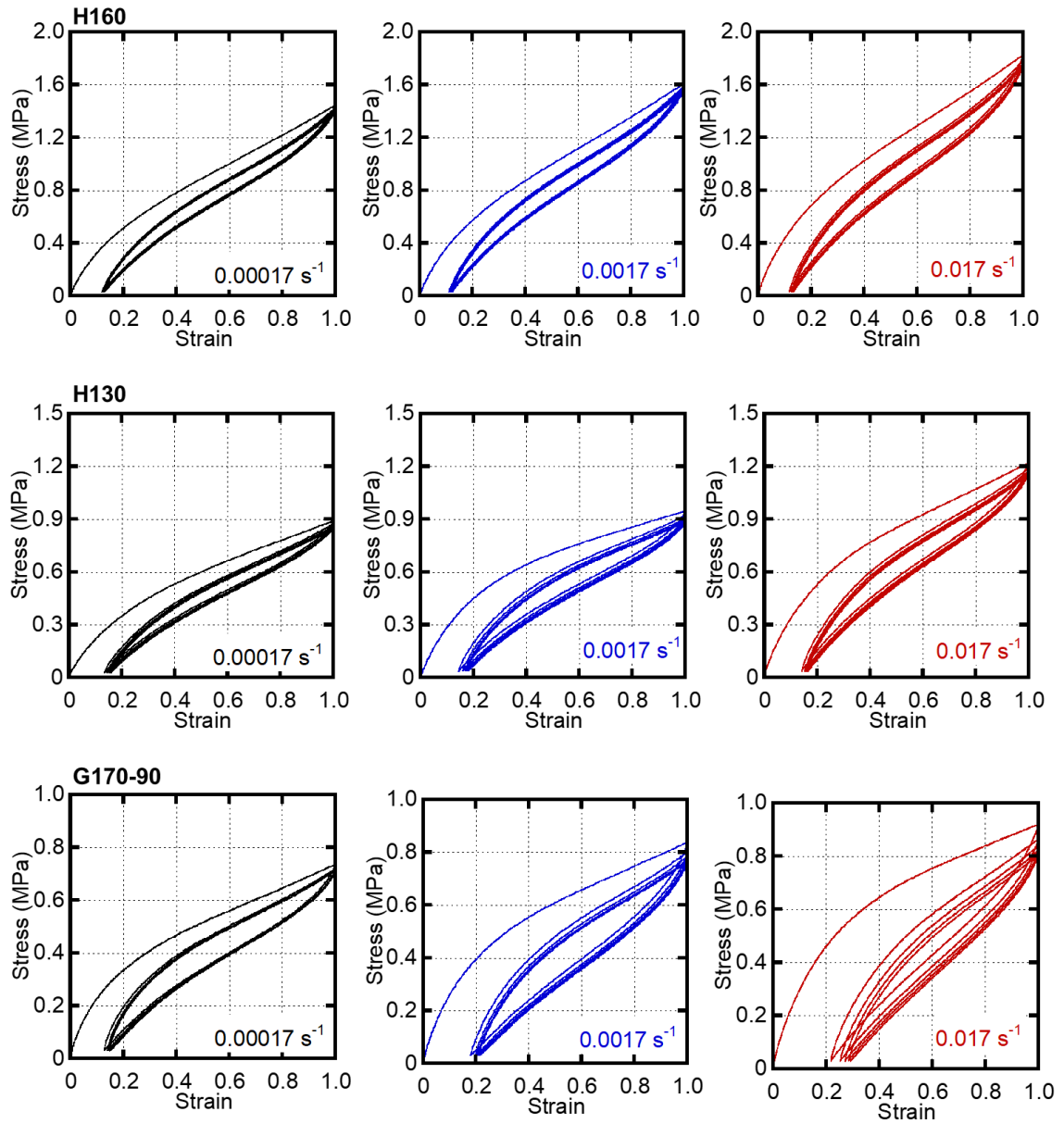


Figure 2.13. Cyclic stress–strain curves of H160, H130, and G170-90 at various strain rates.

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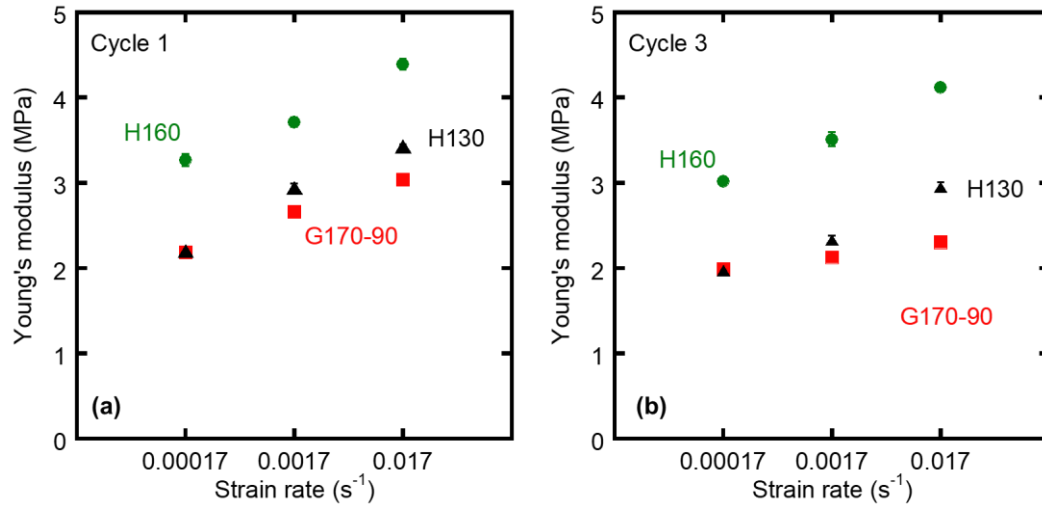


Figure 2.14. Young's modulus of samples at various strain rates in (a) cycle 1 and (b) cycle 3.

Typically, rubbery materials display the Mullins effect when exposed to a cyclic deformation in the non-linear region^{40,41}. The phenomenon described is known as hysteresis loss. The extent of permanent alterations in the microstructure determines the magnitude of hysteresis loss⁴²⁻⁴⁷. Hysteresis loss ratios calculated at various strain rates of both rubbers are shown in Figure 2.15. Hysteresis loss ratios of H130 were higher than those of H160. Moreover, the hysteresis loss ratios of H160 remained constant, irrespective of the strain rate. On the other hand, H130 showed a dependency on strain rate, indicating H130 exhibited a marked viscoelastic response during cyclic deformation⁴⁸. Furthermore, G170-90 demonstrated the highest hysteresis loss ratios at every strain rate, even though its Young's modulus was similar to that of H130. As illustrated in Figure 2.13, following the first loading-unloading cycle, the loading curves for H160 remained consistent in subsequent cycles, regardless of strain rate. For H130, this pattern became apparent after the second cycle.

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On the other hand, the graded rubber demonstrated varying loading curves, particularly at a strain rate of 0.017 s^{-1} . Figure 2.16 presents the relationship between residual strain and hysteresis loss ratio at different strain rates. It is evident that G170-90 displayed significant instantaneous and irreversible strain, or residual strain, even after the second cycle at a strain rate of 0.017 s^{-1} . This suggests that hysteresis behavior was influenced by the loading duration.

In section 2.3.1, graded rubber showed good strain recovery although it required a prolonged recovery time once the stress was removed. Once the stress was released, the region with higher crosslink density shrank immediately, leading to bending deformation. Following that, the side with lower crosslinks also shrank. This required a change in the conformation of the chain segments, which took a considerable amount of time. Based on this mechanism, the large residual strains observed were not in equilibrium, at least not at a strain rate of 0.017 s^{-1} .

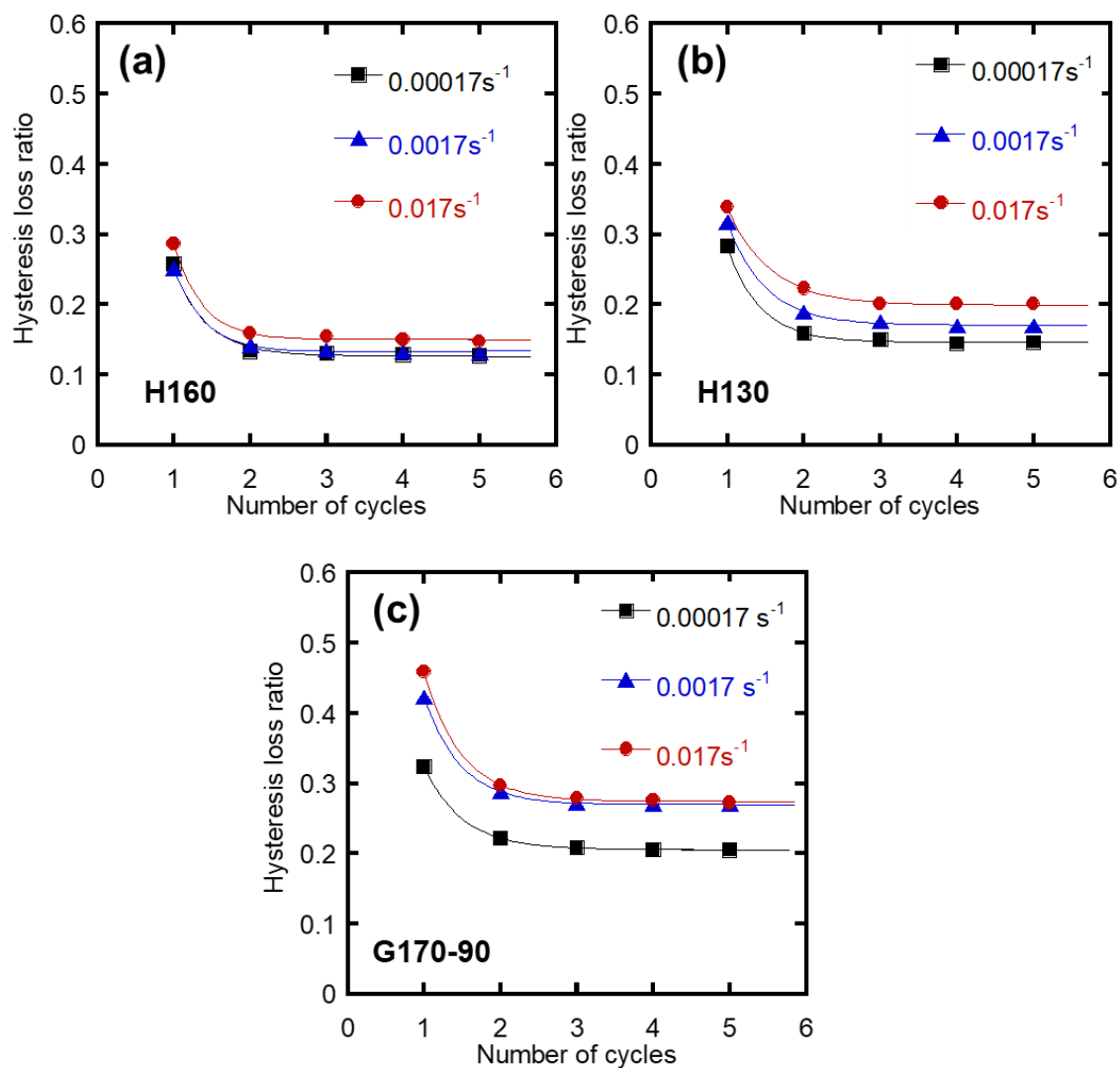


Figure 2.15. Hysteresis loss ratio calculated from the cyclic stress–strain curves at various strain rates.

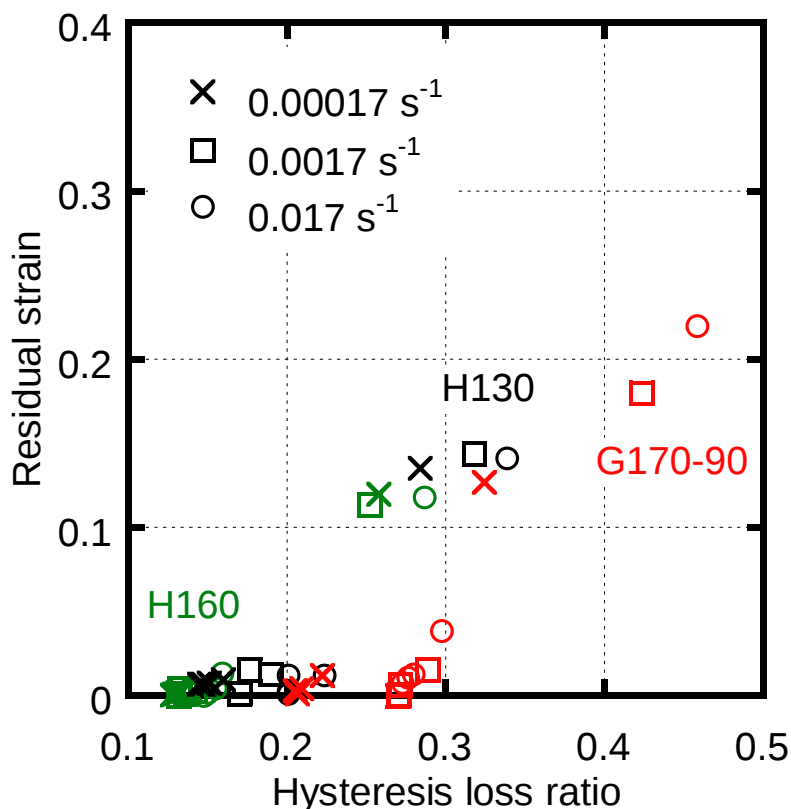


Figure 2.16. Relationship between residual strain and hysteresis loss ratio for samples at different strain rates.

To verify statement made above, the actual residual strain after each stretching cycle at a strain rate of $0.017 s^{-1}$. Following each loading/unloading cycle, the samples were removed from the machine and stored at $25^{\circ}C$. After stress removal, the graded rubber exhibited immediate bending and slow recovery. The actual residual strain was recorded once the graded rubber had flattened, which took around one day. The same procedure was followed for the homogeneous rubber samples. The results can be found in Table 2.4.

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Table 2.4. Actual residual strain after stretching.

	Equilibrium residual strains after stretching		
	Cycle 1	Cycle 2	Cycle 3
G170-90	0.011	0.005	0.003
H130	0.013	0.009	0.002
H160	0.005	0.002	0.002

As shown in Figure 2.16, all samples exhibited relatively small residual strain values compared to those measured after the unloading process. This difference was especially noticeable in G170-90. This behavior is reasonable, as graded rubber materials require a longer time to fully recover. The prolonged recovery time leads to a higher hysteresis loss during cyclic deformation.

2.4. Conclusions

The graded rubber exhibiting a gradient crosslink density in the thickness direction was successfully synthesized through vulcanization under a temperature gradient. The swollen sample demonstrated a bending configuration towards the high-crosslink side in the equilibrium state, providing evidence that the gradient structure was formed subsequent to temperature gradient vulcanization.

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The elongational residual strain of a graded sample was found to depend on the part with a high crosslink density. During the recovery process, graded rubber exhibited good strain recovery although it took a long time to recover. This is because of the mismatch of shrinking force between high-crosslink side and low-crosslink side. After stress removal, the high-crosslink side exhibited immediate shrinkage. However, this side was unable to recover its initial length due to the suppression by the opposing side with a lower crosslink density. Consequently, the high-crosslink side tended to continue recovery, thereby applying the shrinking stress to the low-crosslink side. This led to the need for segment reorganization in the low crosslink region, which is likely the cause of the slow recovery process.

It was found that G170-90 showed a higher hysteresis loss ratio than H130, even though they exhibited almost similar initial moduli. Furthermore, it was found that the residual strains of G170-90 were relatively small. This must correspond to the graded structure. The low-crosslink side shows a large hysteresis loss, whereas the high-crosslink side is responsible for the strain recovery.

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Chapter 3

Graded rubber having gradient crosslink density: Swelling behavior

3.1. Introduction

The swelling behavior of crosslinked elastomers in solvents is a well-known phenomenon that is widely employed to obtain the information about the crosslink density of elastomeric networks. This process involves the diffusion of small mobile molecules into a network of polymer chains, which causes the chains to expand. Eventually, the dimensions of the rubber network increase until the solvent concentration becomes uniform throughout the material, resulting in a state of swelling equilibrium. In the 1940s, Flory ¹ and Gee ² initially applied thermodynamic principles to establish a relationship between conformational entropy and the deformation of an isotropic crosslinked network. The Flory-Rehner equation ³ is written as:

$$\nu = \frac{\ln(1-V_r) + V_r + \chi V_r^2}{V_s \times (V_r^{1/3} - V_r/2)} \quad (3.1)$$

where ν is the crosslink density, V_s is the molar volume of the solvent, V_r is the volume fraction of rubber in the swollen gel, and χ is the interaction parameter between rubber and solvent.

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According to the above equation, a higher crosslink density of the rubber implies a lower swelling ratio (or swelling degree). Therefore, when graded rubber with a crosslink density gradient in the thickness direction undergoes swelling, it is expected to exhibit bending deformation, with a lower crosslink density on the outer side and a higher crosslink density on the inner side. This phenomenon has been confirmed by previous studies ^{4,5}.

When a gel is attached to a rigid substrate and subsequently swells, it leads to inhomogeneous swelling ^{6,7}. Surface instability in a hydrogel attached to a rigid substrate during the swelling process was first observed by Tanaka et al. They developed a model to explain the gel using Euler's buckling theory ⁸. Subsequently, various theoretical and computational investigations on the surface instability of a confined swollen gel have been conducted ⁹⁻¹⁴.

So far, numerous researchers have endeavored to design and control material structures to exhibit actuation performance based on swelling behavior ¹⁵⁻¹⁸. Generally, this concept is predicated based on the phenomenon of anisotropic swelling, wherein the swelling ratios of different components within a material exhibit variation. Consequently, the strategies involve the fabrication of materials with heterogeneous structures, such as bilayers ¹⁹⁻²², layers with gradient structures ²³⁻²⁶, or multi-complex layers ²⁷⁻²⁹. These materials demonstrate asymmetric swelling, wherein the equilibrium swelling ratio of a region with a low crosslink density exceeds that of a region with a high crosslink density.

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In this chapter, the swelling behavior of graded rubber is studied. The swelling phenomenon was observed from the beginning of the swelling process to analyze how a graded rubber with a gradient crosslink density in the thickness direction deforms with swelling time. Graded rubber with varying thicknesses were also prepared to study the correlation between thickness and its performance. The swelling experiments using homogenous rubber were also designed to elucidate the underlying mechanism. Finally, the practical applications of the graded rubber based on its swelling phenomenon were explored, demonstrating its potential use in various fields such as smart materials or soft robotics.

3.2. Experimental

3.2.1. Materials

Ethylene-propylene rubber (EP11, JSR, Japan) with an ethylene content of 52% was utilized. The Mooney viscosity ML(1+4) was 40 at 100 °C. Dicumyl peroxide (DCP) and carbon black (CB) (Nacalai Tesque, Japan) were used in this study.

3.2.2. Sample preparation

The compound was prepared by combining the rubber with 2 phr DCP (crosslinking agent) and 0.5 phr CB in an internal mixer at 90 °C for 5 min. Subsequently, the mixture underwent vulcanization using a compression

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molding machine with a temperature gradient to produce the graded rubber. To fabricate the graded specimens, the upper and lower plates were set at 200 and 150 °C, respectively. This sample code was G200-150. The thickness of the samples varied, measuring 1, 2, and 3 mm. Moreover, for comparison, homogenously crosslinked samples with a thickness of 2 mm were also prepared by vulcanizing at 200 or 150 °C at both plates, denoted as H200 and H150. All samples were vulcanized for 5 min.

3.2.3. Measurements

The swelling behavior of H200 and H150 over time was assessed using a weighing method. Samples measuring $3 \times 3 \times 2$ mm were initially weighed (m_0) and then completely submerged in toluene at 25 °C. To ensure uniform solvent absorption, samples were suspended in toluene using a thin wire. During the first hour, the weight of the swollen samples was recorded every 5 min. Subsequently, measurements were performed at 2, 3, 4, 24, and 48 h. The samples were then dried in an oven at 50 °C until a stable weight (m_d) was obtained. The degree of swelling was determined using the following equation:

$$\text{Swelling degree} = \frac{m_t - m_0}{m_d} \quad (3.2)$$

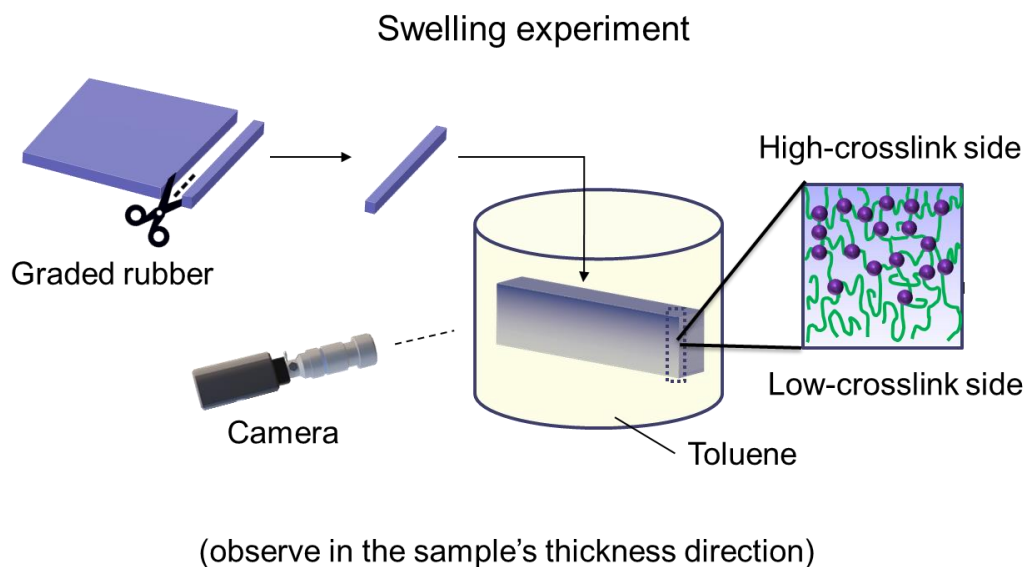
where m_t (g) is the weight of a swollen sample at time t (min).

For the G200-150 (graded sample), a 2 mm thick sheet was cut into a rectangular shape measuring $2 \times 2 \times 30$ mm. A digital microscope camera was

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used to capture the swelling process over time. The resulting images were analyzed using ImageJ software.



Scheme 3.1. Setting experiment for swelling observation of graded rubber.

Furthermore, a rectangular strip measuring $2 \times 0.3 \times 15$ mm was cut from the homogeneous sample sheets and attached to Rayon cloth tape (Askul, Japan). The swelling behavior was then observe using a Jiusion-USB microscope.

3.3. Results and Discussion

3.3.1. Swelling behavior of homogenous rubber

Figure 3.1 compares the swelling characteristics of two homogenous samples, H200 and H150. Both samples achieved equilibrium after a 24h

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(1440-min) immersing. At equilibrium, the swelling degree values were approximately 10 for H200 and 35 for H150. This difference can be attributed to variations in the overall crosslink density between the two samples.

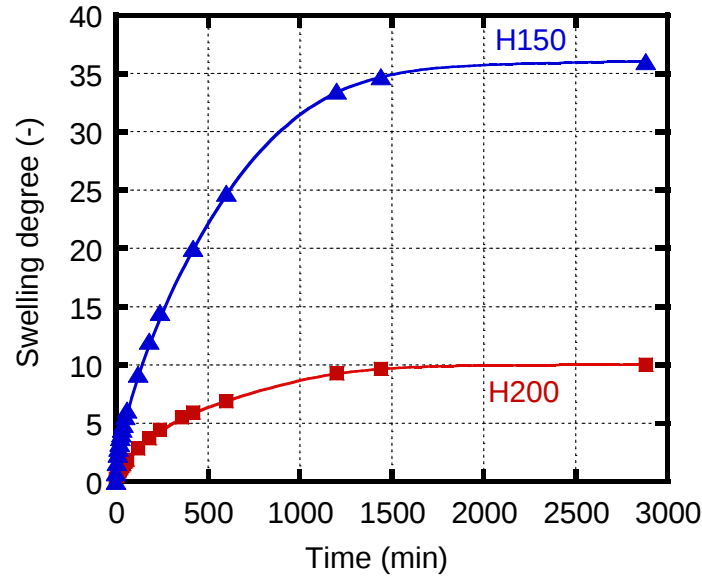


Figure 3.1. Growth curves of swelling degrees for H150 and H200.

From the equilibrium values, the molecular weight between neighboring crosslink points (M_c) and the crosslinking density (ν) of both samples were calculated according to the Flory-Rehner theory in equation (3.1). The interaction parameter χ between rubber and toluene was calculated based on the solubility parameters of both components, which is 0.442. Crosslink densities of H200 and H150 were then calculated to be 3.39×10^{-6} (mol/cm³) and 3.74×10^{-7} (mol/cm³), respectively.

3.3.2. Swelling behavior of graded rubber

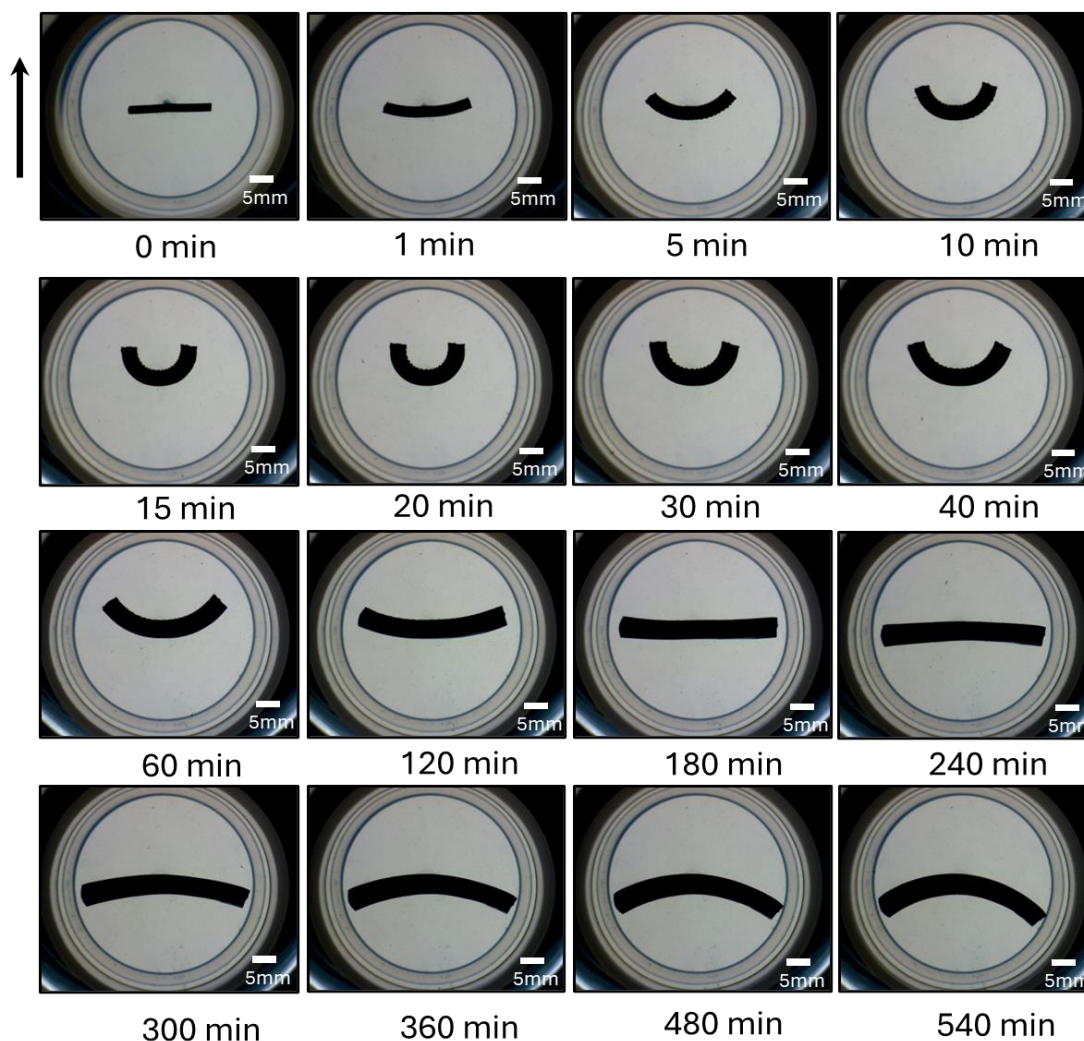


Figure 3.2. Swelling behavior of G200-150 in toluene. The arrow represents the thickness direction. The top view of the sample corresponded to the low-crosslinked side and vice versa. The initial thickness was 2 mm.

The swelling behavior of graded rubber, i.e., G200-150, is shown in Figure 3.2. The vertical axis represents the thickness direction, which corresponds to the gradient in the crosslink density, with the side with the lower crosslink density positioned at the top. Initially, the rubber sheet is flat. Upon swelling, the sample began to curve upward, reaching maximum curvature after

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approximately 20 min. Subsequently, over an extended period of approximately 180 min, the sample gradually flattened before ultimately forming a concave shape.

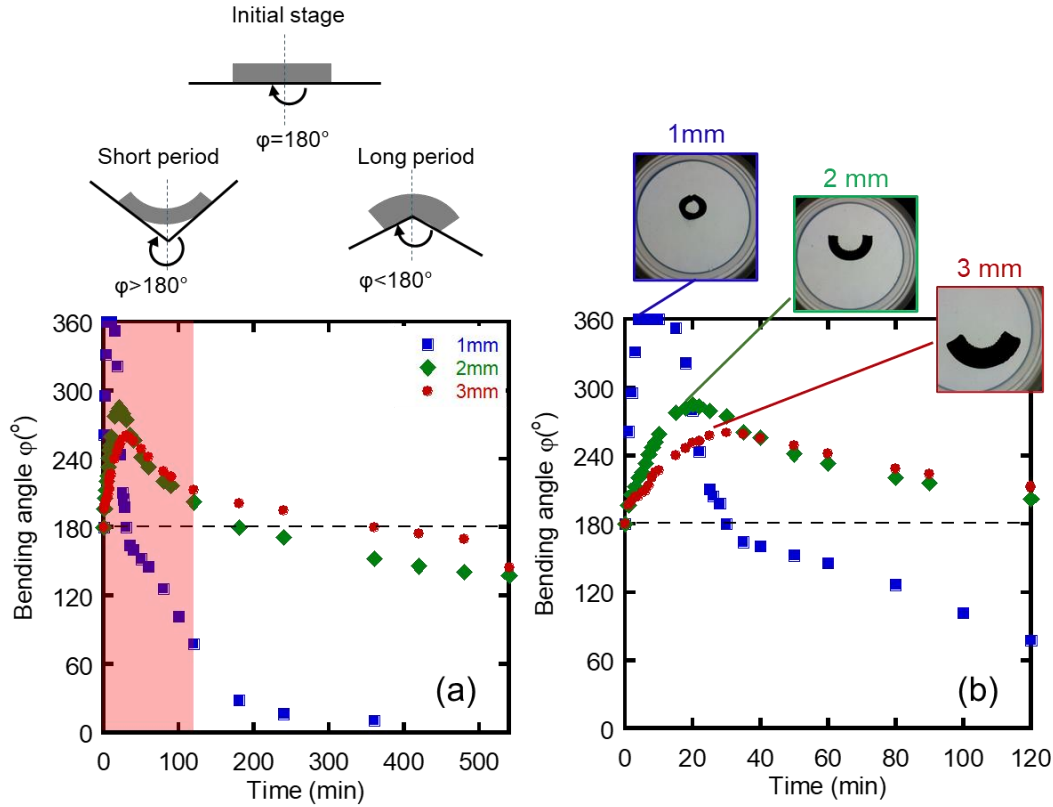


Figure 3.3. Time dependence of the bending angle of G200-150 samples with various initial thicknesses (a) whole swelling process and (b) swelling in the first 120 min.

Figure 3.3 illustrates the time dependence of the bending angle for G200-150 with varying initial thickness. The bending angle in a short period decreased as the sample thickness increased. The sample reached its maximum bending angle after approximately 5 min. With increasing thickness, the time to reach the maximum was delayed, accompanied by a smaller angle. Moreover,

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thicker samples require a longer duration to flatten. This phenomenon likely corresponds to the diffusion time of solvent molecules. Therefore, before reaching the maximum bending angle, the sample must not be completely occupied by solvent molecules. In other words, the core layer remained unswollen during the transient swelling. The main mechanism of swelling in a long period is attributed to the mismatch in swelling degree between both sides as mentioned in Section 3.1. However, this anomalous behavior observed in a short period has not been previously reported in the literature. To elucidate this phenomenon, subsequent experiment was conducted as shown in Figure. 3.4.

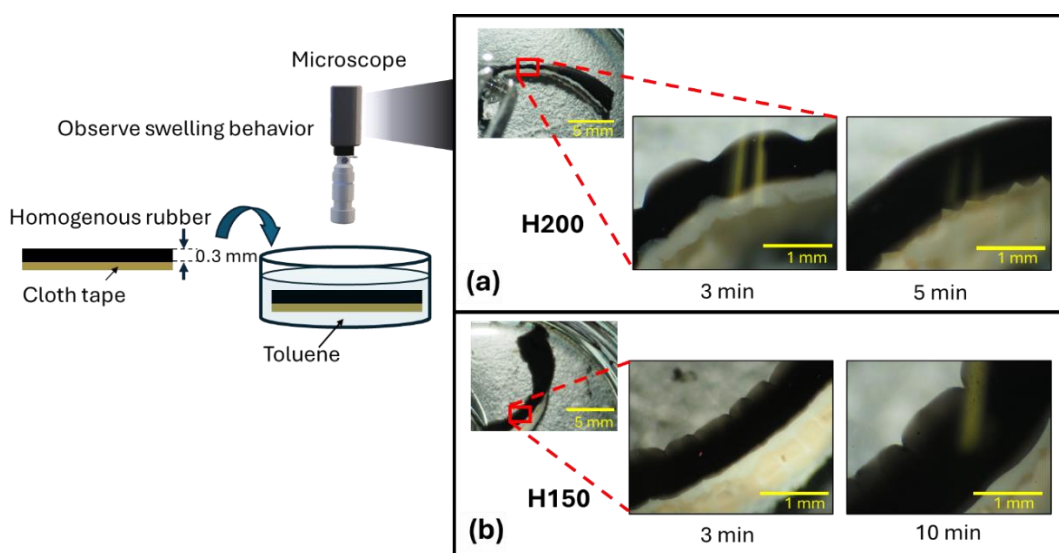


Figure 3.4. Swelling experiment of the homogenous rubbers constrained on a flexible substrate.

As shown in Figure 3.4, H200 and H150 exhibited opposite bending behaviors. During constrained swelling, H200 bent towards the tape, while

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H150 curved towards the rubber side. Only the rubber layer showed swelling whereas the cloth tape didn't (Figure 3.5). Therefore, the behavior of H200 can be attributed to the discrepancy in the swelling degree. This phenomenon has been consistently reported in previous studies³⁰⁻³⁴ and is similar with the swelling mechanism of graded rubber in the long period.

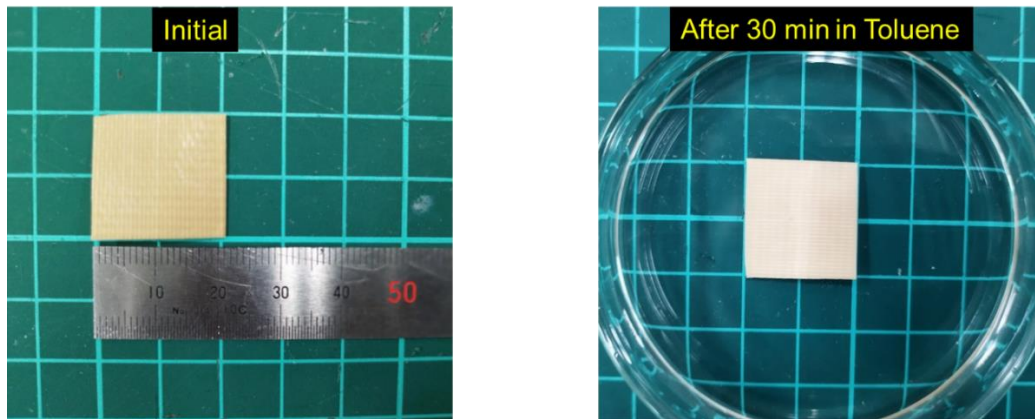


Figure 3.5. Swelling behavior of the cloth tape in toluene at 25 °C.

Interestingly, the swelling behavior of H150 was similar to that swelling of graded rubber in the short period. To explain the mechanism of H150, it is necessary to consider the theory of a swollen gel adhered to a substrate^{10,13,35,36}. Figure 3.6 shows the swelling model of a dried thin gel attached to a rigid substrate. The gel has an initial shear modulus $G_0 = NkT$, where N is the number of polymer chains per unit volume, k is the Boltzmann constant, and T is temperature. The stretch ratios in three directions are λ_x , λ_y , and λ_z .

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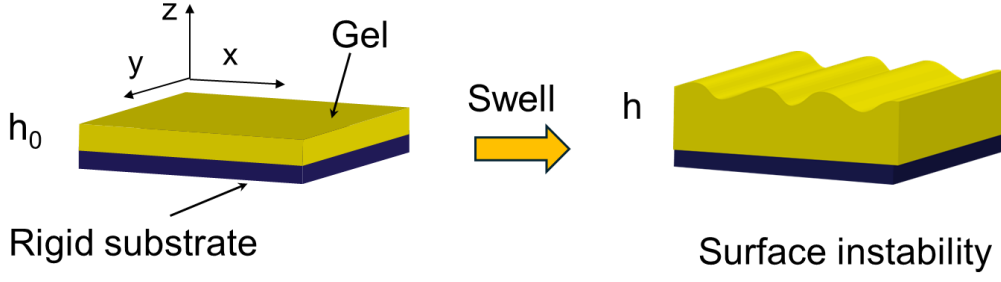


Figure 3.6. Schematic model of swelling-induced surface instabilities.

From the constitutive equation of swelling gel ^{14,37,38}, the relationship between nominal stresses and stretch ratio were expressed in:

$$\frac{\Omega s_x}{kT} = N\Omega \left(\lambda_x - \frac{1}{\lambda_x} \right) + \left[\lambda_x \lambda_y \lambda_z \log \left(1 - \frac{1}{\lambda_x \lambda_y \lambda_z} \right) + 1 + \frac{\zeta}{\lambda_x \lambda_y \lambda_z} - \frac{\mu}{kT} \lambda_x \lambda_y \lambda_z \right] \frac{1}{\lambda_x} \quad (3.3)$$

$$\frac{\Omega s_y}{kT} = N\Omega \left(\lambda_y - \frac{1}{\lambda_y} \right) + \left[\lambda_x \lambda_y \lambda_z \log \left(1 - \frac{1}{\lambda_x \lambda_y \lambda_z} \right) + 1 + \frac{\zeta}{\lambda_x \lambda_y \lambda_z} - \frac{\mu}{kT} \lambda_x \lambda_y \lambda_z \right] \frac{1}{\lambda_y} \quad (3.4)$$

$$\frac{\Omega s_z}{kT} = N\Omega \left(\lambda_z - \frac{1}{\lambda_z} \right) + \left[\lambda_x \lambda_y \lambda_z \log \left(1 - \frac{1}{\lambda_x \lambda_y \lambda_z} \right) + 1 + \frac{\zeta}{\lambda_x \lambda_y \lambda_z} - \frac{\mu}{kT} \lambda_x \lambda_y \lambda_z \right] \frac{1}{\lambda_z} \quad (3.5)$$

where s_x , s_y , and s_z are the nominal stresses at each direction; Ω is the volume of each solvent molecule; μ is the chemical potential of solvent; and ζ is the dimensionless parameter from the enthalpy of mixing.

When a gel swells freely, elastic stresses must equal osmotic pressure. In the case of a gel confined to a rigid substrate, the gel can only swell along

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the thickness direction, the stress ratios are $\lambda_x = \lambda_y = 1$, and $\lambda_z = \lambda > 1$. We also have $s_x = s_y$, therefore the stresses in the in-plane directions thus can be obtained as:

$$\frac{\Omega s_x}{kT} = N\Omega(1 - \lambda^2) \quad (3.6)$$

The equation (4) suggests that the confinement of gel by a substrate induces the in-plane compressive stresses during swelling, i.e., $s_x < 0$. When the compressive force is beyond critical value, surface instability occurs as depicted in Figure 3.6. Because H150 was attached to a rigid (not stretchable) but flexible substrate, i.e., a cloth tape that can be bent with low stress. As a result, the in-plane compressive force caused the H150 strip to curve towards the rubber side. Interestingly, H200 displayed surface instability after 3 min, despite bending towards the tape (Figure 3.4a). This indicates that the compression force was still present but was insufficient to bend the H200 strip towards the rubber side. As the swelling duration increased, the compression force for H200 dissipated, as evidenced by the smooth surface observed after 5 min. In contrast, H150 continued to exhibit surface instability even after 10 min elapsed. In the previous work by Liu et al.³⁷, the critical stress for surface instability was computed as a function of stiffness factor, i.e., NkT/E_s , where E_s represents the modulus of substrate. The authors found that critical stress decreased with increasing stiffness factor. This corresponded with our observation for H200 and H150, whereas both samples show significant differences between crosslink densities and initial shear moduli.

The possible mechanism to explain the swelling behavior observed in the graded rubber during its short period, as illustrated in Figure 3.7.

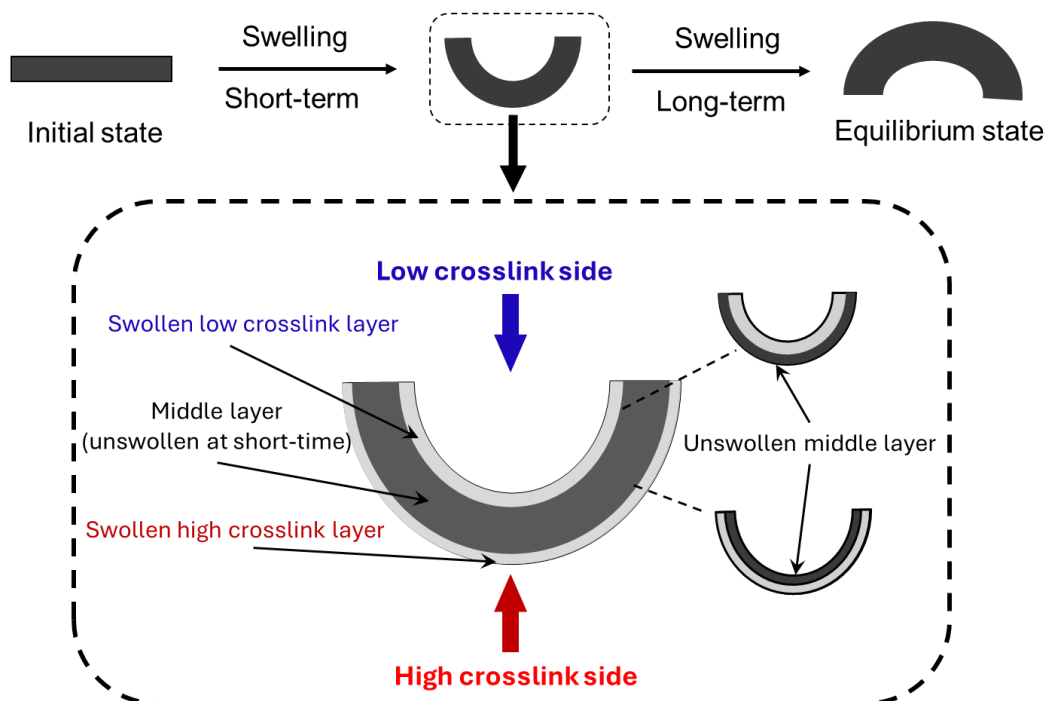


Figure 3.7. Mechanism of swelling behavior in a short period of graded rubber.

At the beginning of the swelling process, both surfaces of the graded rubber surrounded by toluene became swollen, whereas the middle layer remained unswollen. Considering the middle layer as a substrate for a short time, the swelling behavior of the graded rubber in this period is the sum of the swelling of H200 and H150, as shown in Figure 3.4. During the swelling process, both sides showed curves for various reasons. The low-crosslink side bent because of the in-plane compressive stress, which caused surface instability. On the other hand, the high crosslink side bent in the low crosslink direction owing to a higher swelling ratio than the unswollen-core layer. Therefore, the graded rubber bent toward the low-crosslink side in a short

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period. When the solvent molecules diffuse into the core layer, this layer starts to swell, and the bending angle of the sample gradually decreases. In the equilibrium state, that is, after a long period, the shape of the sample flattens out and bends toward the high crosslink side. In this period, the swelling behavior followed the Flory-Rehner theory.

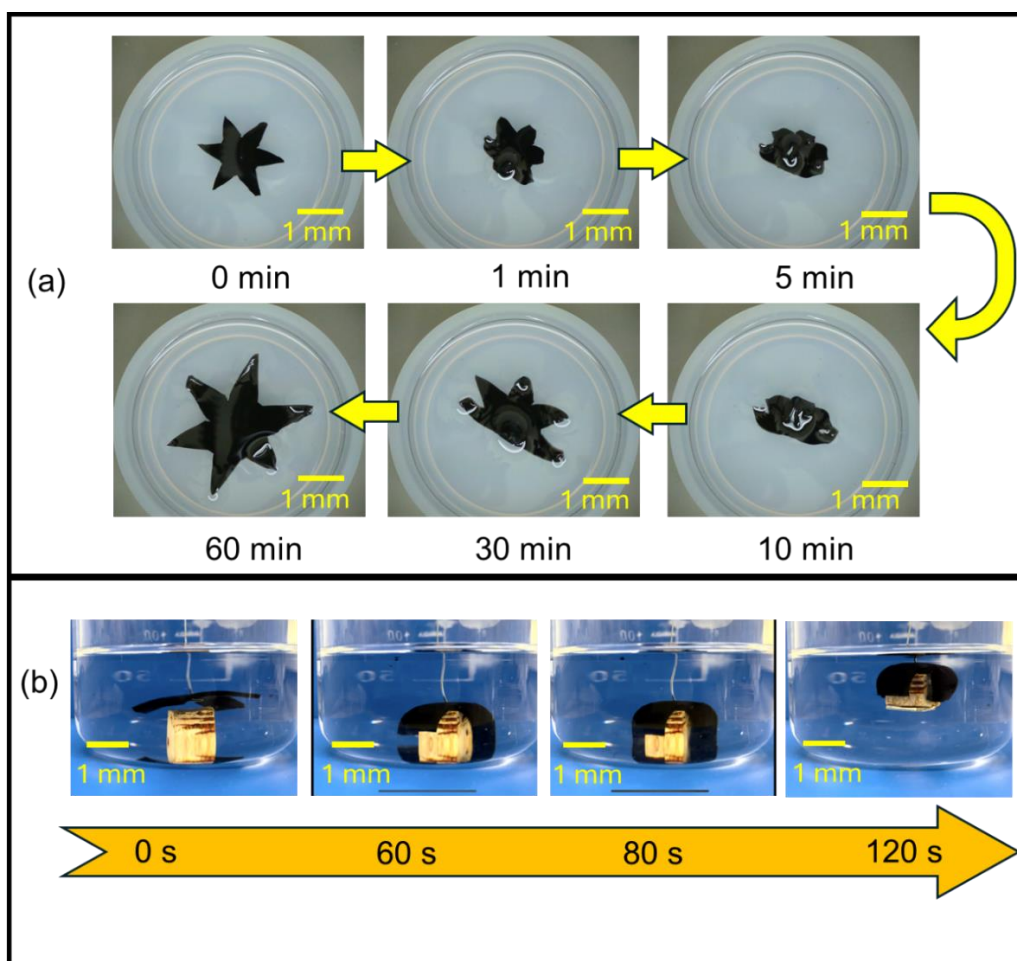


Figure 3.8. (a) Shape transforming of G200-150 in toluene. The high-crosslinked side contacted with the petri dish and vice versa. (b) Gripping processes of G200-150 actuator in toluene. Both experiments were conducted at 25 °C.

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Based on the bending ability of G200-150 toward the low-crosslink side during swelling in the short period, the shape transforming of the graded rubber is investigated. A 1 mm thick star-shaped graded rubber sample was immersed in toluene at 25 °C. Figure 3.8a shows that the sample began folding immediately upon contact with the solvent. At 5 min, the sample exhibited a significant degree of folding, corresponding to the bending angle shown in Figure 3.3. Subsequently, the graded rubber slowly unfolded because the middle layer became swollen. Additionally, G200-150 also demonstrated its application as a gripper in toluene (Figure 3.8b). The cross-shaped G200-150 actuator demonstrated its ability to grasp a cork-cube through shape transformation. The cork-cube was successfully gripped and elevated for 120 s. These findings suggest the possibility of developing materials with controllable deformations. The rates of folding and unfolding are influenced by various factors, including the initial modulus of both sides and the diffusion rate of the solvent. By modifying the thickness of the material or adjusting the swelling temperature, it may be possible to regulate the folding and unfolding speeds of the sample. This swelling behavior is likely to be common among materials exhibiting a gradient crosslink density across their thicknesses.

3.4. Conclusions

This chapter presents an investigation of the swelling behavior observed in graded rubber having a crosslink density gradient in the thickness direction. Typically, a swollen graded rubber exhibits curvature, with outer side bending

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due to lower crosslink density, and vice versa. In this study, it is found that a graded rubber initially bent toward the low-crosslink side over a short period, and then gradually transitioned to the opposite shape at equilibrium. A mechanism was proposed to elucidate this phenomenon based on gel swelling theory under confinement by a rigid substrate. Bending toward the low-crosslink side during transient swelling corresponds to surface instability. The unswollen core layer functioned as a substrate that induced a compressive force. This force governs the swelling behavior of the graded rubber in the short term. Based on this mechanism, graded rubber demonstrates the potential for actuation and shape transformation capabilities, suggesting a promising new approach for soft robotics and smart material applications.

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Chapter 4

Gradient structure in miscible elastomer blend

4.1. Introduction

In any mixture irrespective of polymer or metal, the distribution of one component is not always homogeneous in general ¹⁻³. The surface composition typically differs from that of the bulk. This occurs because components with varying surface energies will naturally arrange themselves to minimize the free energy ⁴. The component with lower surface free energy or tension tends to concentrate at the surface ⁵. Consequently, a gradient concentration of that component is formed from the bulk to the surface ^{6,7}. Segregation of low-molecular-weight components at the surface has been observed in various polymer systems as well ⁸⁻¹⁰. This behavior is commonly attributed to the increased free volume associated with chain ends. The free volume is believed to play a significant role in driving the segregation process. Siriprumpoonthum et al. ¹¹ studied the segregation of mixture of high-density polyethylene (HDPE) containing high and low molecular weights under a temperature gradient. He found that low-molecular-weight HDPE was enriched on the surface exposed to high temperature. Similar results were also obtained by Sako et al. ¹². Although the mechanism has not been clarified yet, the segregation is likely

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related to the concentration of chain ends in the low-molecular-weight component.

Poly(α -methylstyrene), an aromatic C9 hydrocarbon tackifier¹³, is widely utilized in the rubber industry to modify the viscoelastic properties of rubber tires. The incorporation of poly(α -methylstyrene) into styrene-butadiene rubber (SBR) enhances wet traction and reduces rolling resistance¹⁴. Therefore, it is used as an effective additive for tire performance improvement.

In this chapter, the segregation behavior of SBR blends with poly(α -methylstyrene) under a temperature gradient was investigated. Prior to the segregation experiment, the miscibility of the blend was confirmed through dynamic mechanical analysis. The phase diagram was employed to elucidate the temperature dependence of the interaction parameter, providing insight into the mechanism of segregation.

4.2. Experimental

4.2.1. Materials

The materials were used as received without any further treatment. Styrene-Butadiene Rubber (SBR-1502, ENEOS, Japan) [Mooney viscosity $ML_{1+4}(100\text{ }^{\circ}\text{C})=52$] with 25% styrene and poly(α -methylstyrene) (AMS-SA85, TCI, Japan) are commercial products. The composition of the tackifier was as follows; 41.5 % of styrene, 53.2 % of α -methyl styrene, and 5.3 % of 1-methylethylbenzene. The average molecular weight of AMS, determined by a

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gel permeation chromatography as polystyrene standard, were $M_n = 6.8 \times 10^2$ and $M_w = 1.1 \times 10^3$.

4.2.2. Sample preparation

For the blend sample, the compound was prepared by mixing the SBR with 30, 50, and 80 phr (parts per hundred rubber) of AMS using a Laboplastomil internal mixer (Toyoseiky, Japan). The samples were then mixed for 5 min at 100 °C. Subsequently, the sample was taken out, cut into small pieces, compressed under a compression molding machine at 100 °C for 1 min, and quickly cooled to form a sheet. The thickness of each sheet was 1 mm.

The SBR/AMS sheet was exposed under a temperature gradient for 30 mins using the same compression molding machine. The sample code and the temperature of the upper and lower plates are shown in Table 4.1.

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Table 4.1. Sample code and temperature condition for temperature gradient treatment experiments.

Sample code	Set temperature (°C)		Temperature at the end of annealing process (°C)	
	Top plate	Bottom plate	Top plate	Bottom plate
G120-80	120	50	120	80
G140-120	140	90	140	120

4.2.3. Measurements

The dynamic tensile modulus was measured at 30 °C and 10 Hz using a Rheogel-E4000 dynamic mechanical analyzer (UBM, Muko, Japan). The temperature dependence of the dynamic tensile modulus was further evaluated over the range from –100 °C to 100 °C using the same instrument. The heating rate was 2 °C min⁻¹ with a constant frequency of 10 Hz. Rectangular specimens, 25 mm in length, 3 mm in width, and approximately 1 mm in thickness, were used for the analysis.

Fourier-transform infrared spectroscopy (FTIR) measurements of samples were conducted using a Spectrum 100 spectrometer (Perkin Elmer, USA) with wavenumbers ranging from 400 cm⁻¹ to 4000 cm⁻¹, and a resolution of 16 cm⁻¹. The measurement was conducted at ATR mode with the diamond

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ATR crystal. For the sample after treatment under temperature gradient, ATR-IR was conducted within 20 mins after finishing treatment.

For miscibility evaluation, SBR and AMS were dissolved in toluene at blend ratios of 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90 by weight. The solution concentration was 1%. Subsequently, the solutions were stabilized for 48h at room temperature to ensure uniformity. Sample films were prepared by casting on glass Petri dishes. To avoid evaporation-induced phase separation, samples were slowly evaporated at room temperature for 10h, then dried in a vacuum oven at 40 °C for 24h until the solvent was completely removed. The thickness of the obtained films was ca., 160 μm . The samples were maintained at various temperatures for 4h to observe phase separation through visual inspection.

4.3. Results and Discussion

4.3.1. Characteristics of SBR containing AMS before treatment under temperature gradient

Before treatment under temperature gradient, the dynamic mechanical properties of SBR/AMS were studied as shown in Figure 4.1 (a) and (b). The temperature dependence of the dynamic tensile moduli for neat AMS was also measured from 30 °C to 100 °C.

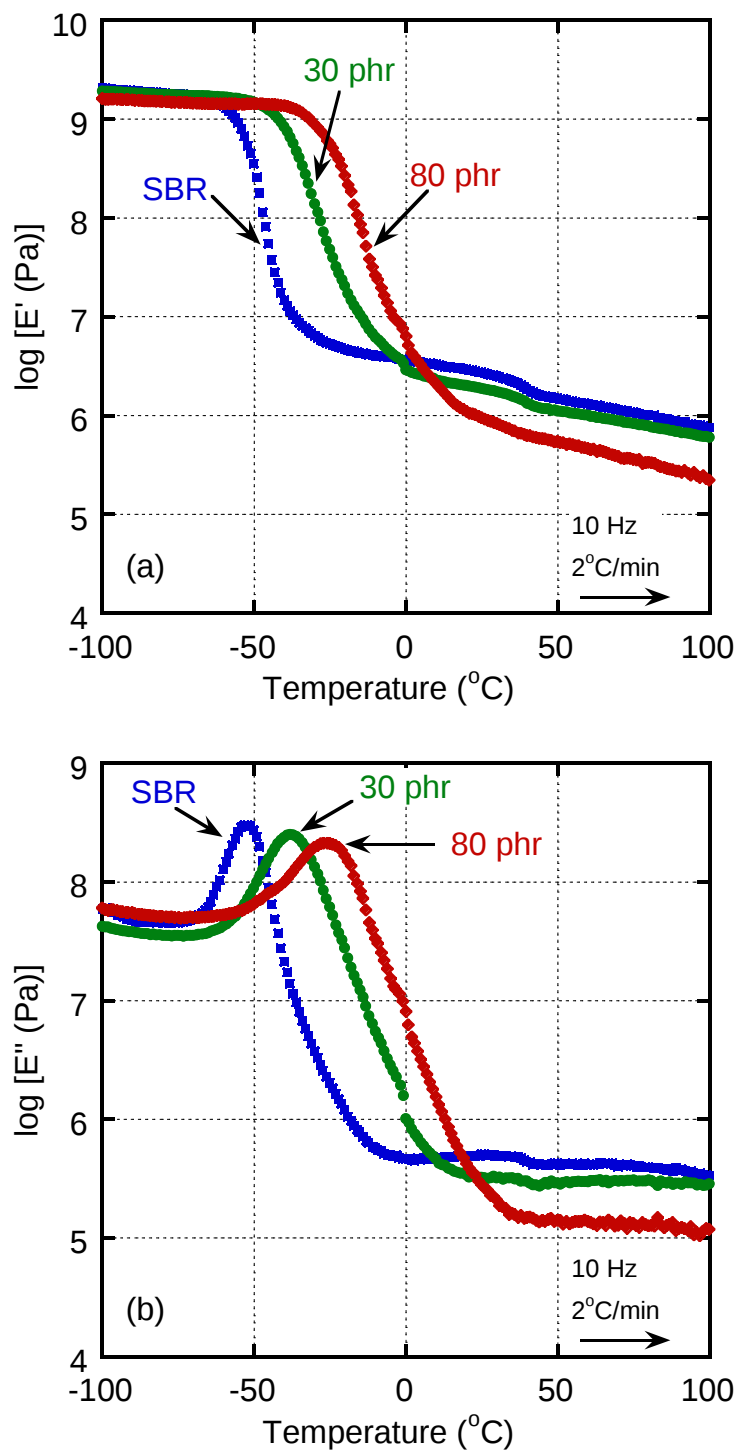


Figure 4.1. Temperature dependence of (a) tensile storage modulus E' and (b) loss modulus E'' for pure SBR and SBR/AMS blends.

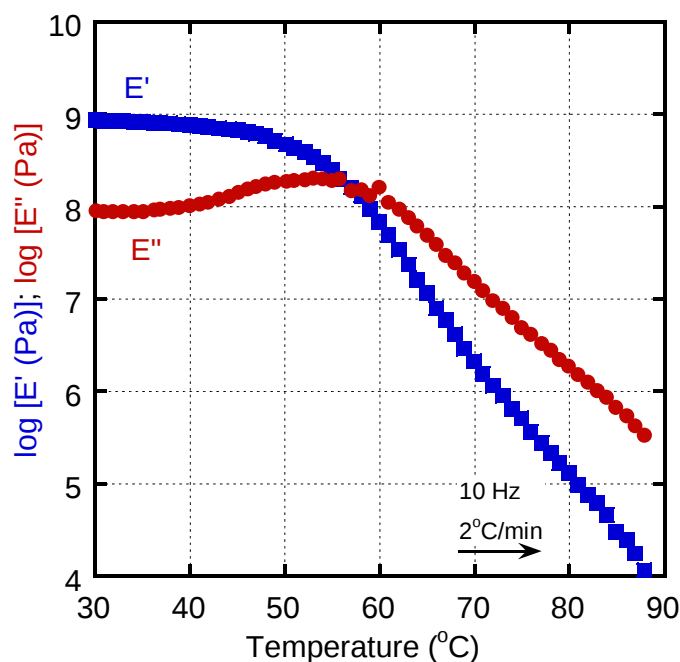


Figure 4.2. Temperature dependence of dynamic tensile moduli E' and E'' of neat AMS.

As shown in Figure 4.1 (a), the storage modulus E' of the compound in the rubbery region decreased with increasing the AMS content. According to previous studies by Class et al.¹⁵⁻¹⁷, the viscoelastic properties of a rubber-resin system could be used to evaluate its compatibility. They determined that miscibility between them is characterized by two key factors. These include a significant shift in the loss modulus peak and a reduction in the storage modulus value in the rubbery plateau region.

The peak temperature of the loss modulus E'' , that is, T_g , of AMS was found to be around 55 °C as shown in Figure 4.2. By introducing AMS into the SBR, T_g of the compound was shifted to a higher temperature. For pure SBR, T_g was –52 °C, while those of the SBR/AMS blends, T_g is –37.3 °C for the

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compound with 30 phr of AMS and -25.5°C with 80 phr of AMS. For a polymer blend system, T_g could be calculated by the Fox equation.¹⁸

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (4.1)$$

where T_g is the glass transition temperature of blend (K), T_{gi} is the glass transition temperature of the i^{th} component (K), and w_i is the weight fraction of the i^{th} component.

Figure 4.3 presents the T_g calculated by the Fox equation and those from DMA results for compounds with various AMS contents.

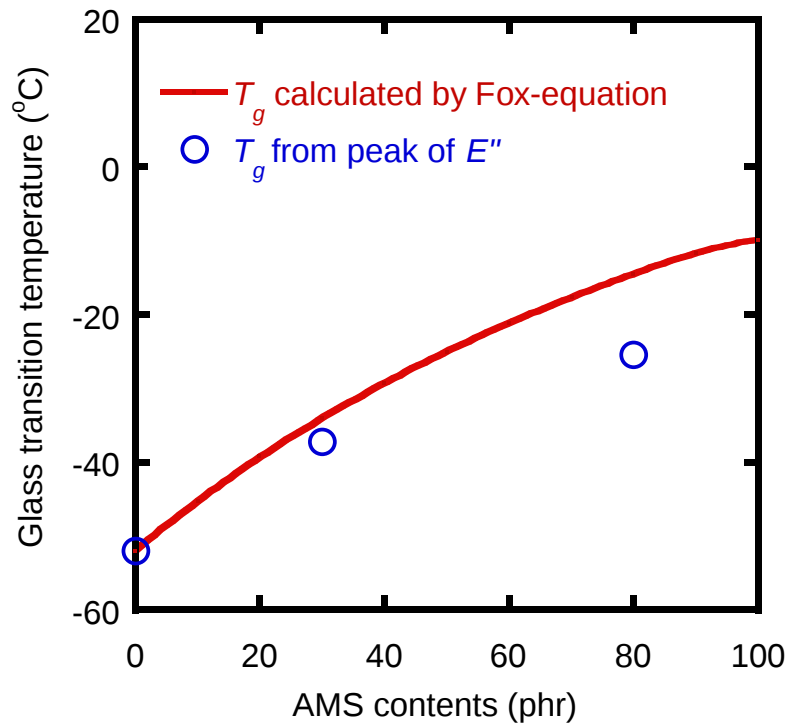


Figure 4.3. Glass transition temperature T_g measured by peak temperature of E'' and calculated ones by the Fox equation for SBR with various amounts of AMS.

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It is seen that the T_g of the sample containing 30 phr AMS was similar with the predicted one from the Fox equation. However, for the sample with 80 phr of AMS, a large deviation was observed. This is attributed to the phase separation^{19,20}. Recently, Wolf et al.²¹ studied the miscibility of SBR and α -methylstyrene/styrene tackifier. They found that phase separation occurred when the concentration of α -methylstyrene/styrene in the SBR was 60–80 phr. Therefore, AMS was fully miscible in SBR only when the concentration was 30 phr or less.

ATR-FTIR measurements were performed to characterize the presence of AMS in the SBR compound. From the chemical structures of SBR and AMS, shown in Figure 4.4 (a) and (b), that both SBR and AMS have aromatic rings, corresponding to styrene units. Figure 4.4 (c) shows the FT-IR spectra of SBR and AMS. For SBR, the peak at 699 cm^{-1} is ascribed to the mono-substituted benenze signal, whereas the peak at 965 cm^{-1} results from polybutadiene unit²². For AMS, therefore, only the peak at 699 cm^{-1} was detected.

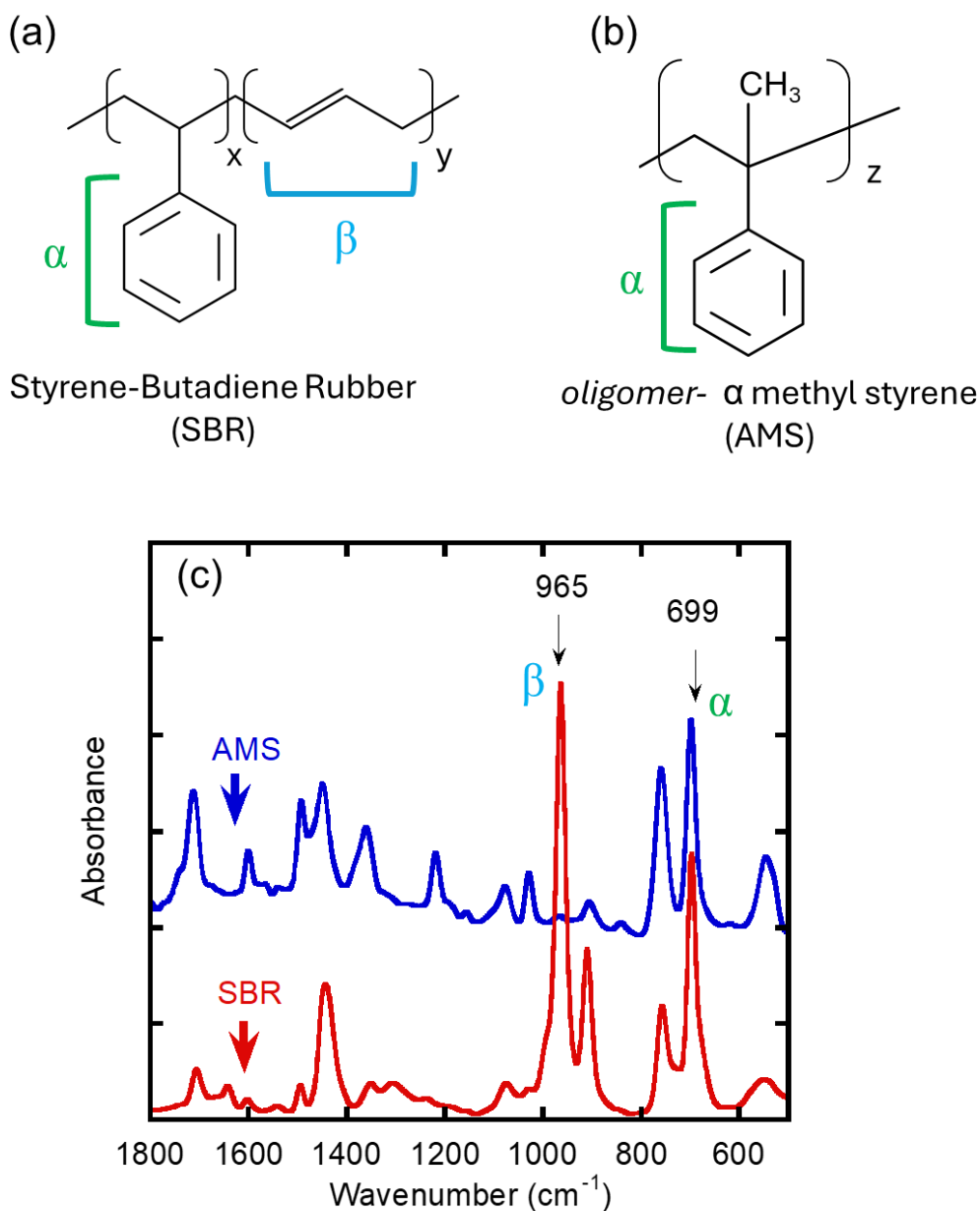


Figure 4.4. Chemical structure of (a) SBR and (b) AMS. (c) ATR-FTIR spectra of AMS and SBR.

When AMS was introduced into SBR, the total styrene content increased, whereas the butadiene signal remained. Therefore, the peak absorbance at 965 cm^{-1} was set to 1 for normalization. The normalized spectra are shown in Figure 4.5.

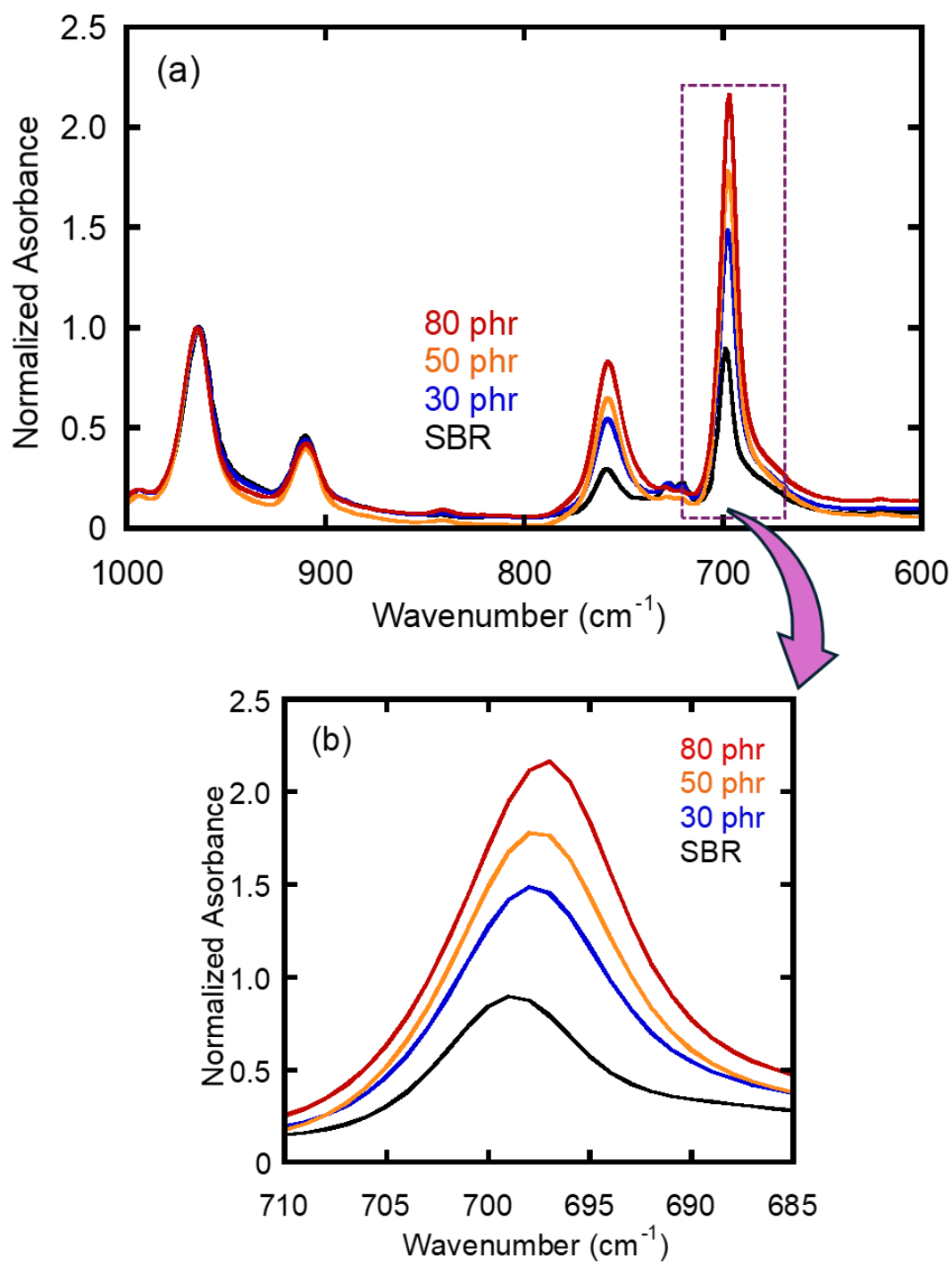


Figure 4.5. ATR-FT-IR spectra of SBR with various amounts of AMS.

In the figure, the peak absorbances at 699 cm^{-1} increased with increasing the AMS content. This indicates that it is possible to estimate the AMS content from total styrene content. To quantitatively analyze the AMS amount on the sample surface after treatment, a calibration curve was constructed by plotting the peak absorbance at 699 cm^{-1} (A_{699}) versus the AMS content, as shown in Figure 4.6. The linear correlation coefficient was 0.997, which indicated the reliability of the calibration curve.

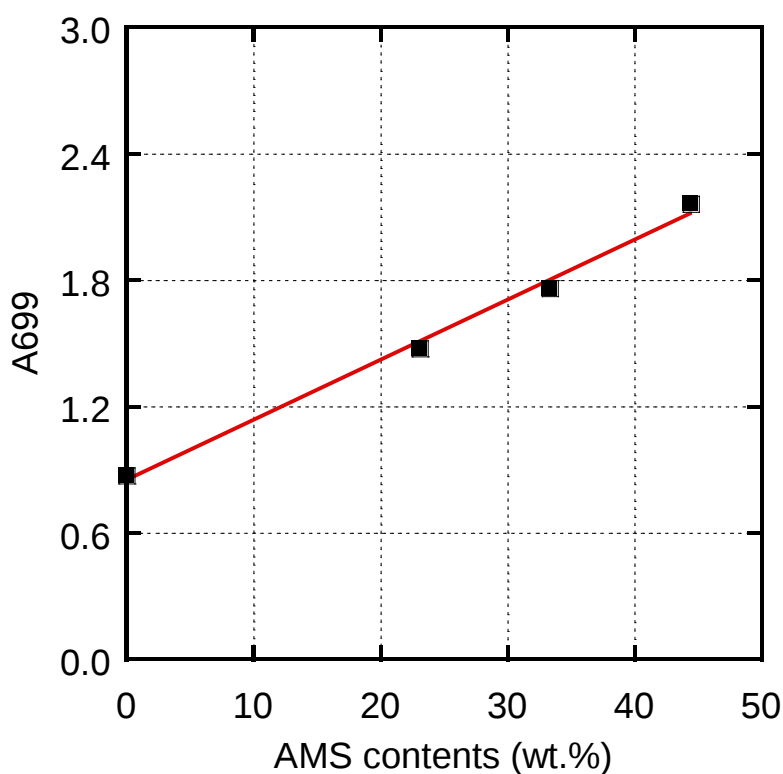


Figure 4.6. Calibration curve for SBR containing various amounts of AMS.

4.3.2. Segregation behavior SBR/AMS under temperature gradient

The SBR sample containing 30 phr of AMS was selected for the temperature gradient treatment, because it showed miscibility. Since the T_g of the SBR/AMS compound is lower than room temperature, both surfaces were measured immediately after the treatment process (within 20 mins) to prevent migration of the tackifier. The results are presented in Figure 4.7.

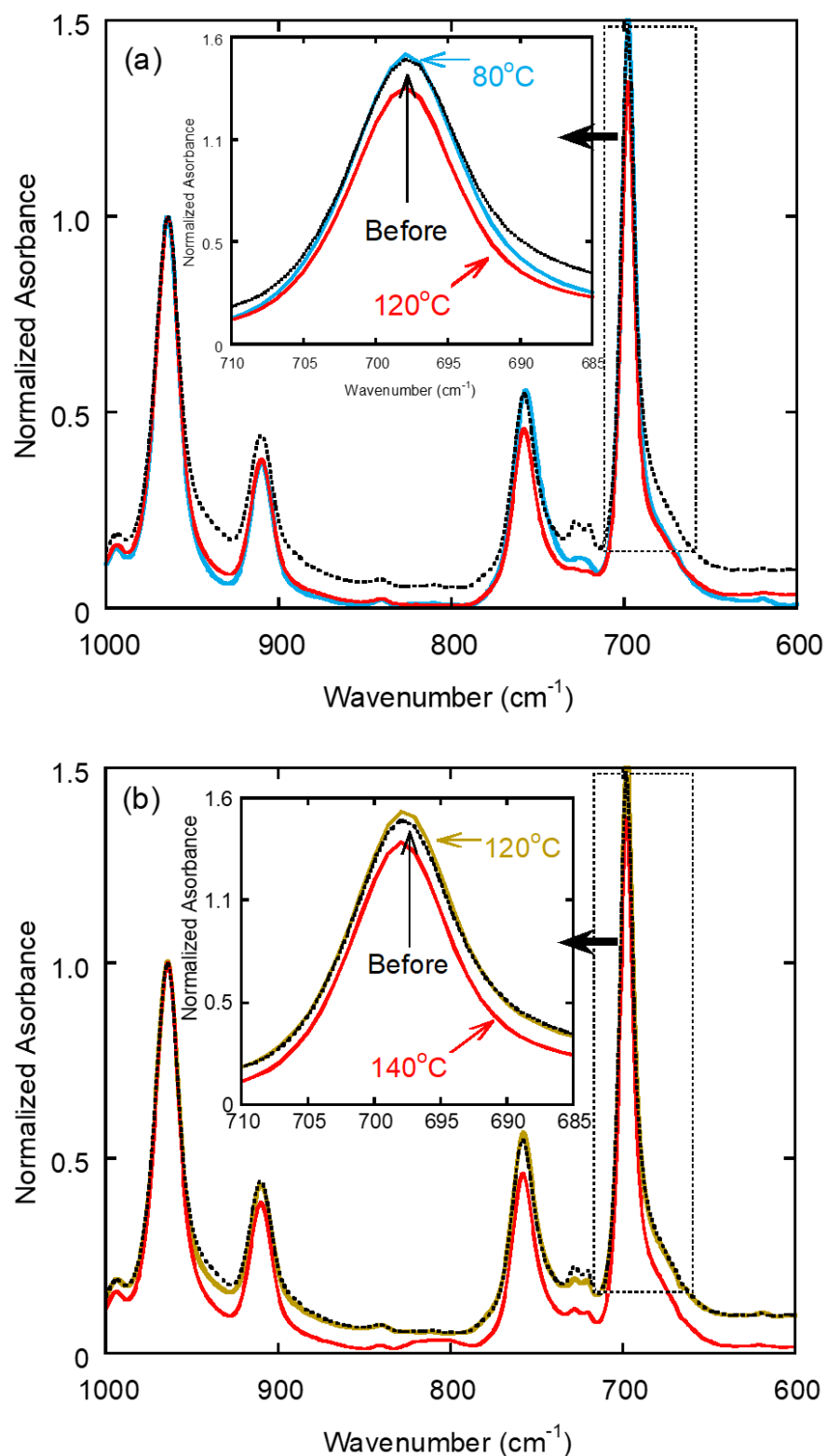


Figure 4.7. ATR-IR spectra of both surfaces of sample SBR with 30 phr AMS before and after treatment under temperature gradient. (a) G120-80 and (b) G140-120.

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The surface on the low-temperature side exhibited a stronger peak intensity at 699 cm^{-1} . In contrast, the surface on the high temperature side showed a weaker intensity. Despite the miscibility of the SBR containing 30 phr of AMS, these results indicate that the AMS content increases at the surface exposed to low temperature, while it decreased at the high temperature side. Using the calibration curve presented in Figure 4.6, the AMS contents on both sides for G120-80 and G140-20 were determine. Figure 4.8 shows the results of AMS content at both sides. The initial concentration of AMS in the untreated compound (30 phr) was converted to weight percentage, yielding a value of 23 wt.%.

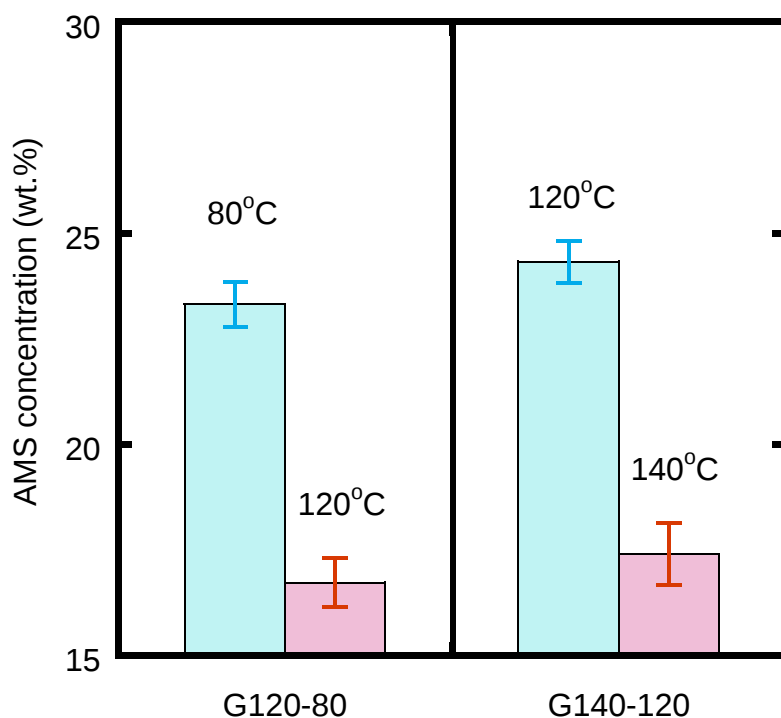


Figure 4.8. AMS content at both surfaces after temperature gradient treatment for G120-80 and G140-120.

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The initial AMS content before treatment, 23.0 wt.%, is indicated by the dashed line for reference. After the treatment, the surface exposed to the low temperature consistently exhibited a high AMS content compared to the surface exposed to the high temperature. For the G140-120 sample, the surface exposed to 140 °C showed an average AMS content of 17.4 wt.%, whereas the surface exposed to 120 °C exhibits a higher AMS concentration of 24.3 wt.%. The results demonstrated that segregation of AMS occurred under the a temperature gradient. Interestingly, it should be noted that the AMS was found to concentrate at the surface exposed to the low temperature. However, according to previous studies ^{11,12}, low-molecular-weight components were found to segregate at the surface exposed to high temperature. Although previous studies did not specify the exact mechanism, the observed segregation was primarily attributed to the concentration of chain ends. The segregation behavior could be driven by both entropic and enthalpic factors ²³. Low-molar-mass components, which possess a higher concentration of chain ends and lower surface tension, tend to localize at the high-temperature region. In this study, the segregation behavior is likely driven by enthalpic factors. To verify this assumption, SBR/AMS blends with various ratios were annealed at different temperatures to observe phase separation. Before annealing, all samples were transparent. Figure 4.9 presents photographs of the SBR/AMS blend (50 wt.%) after annealing at 40 °C and 120 °C. After annealing at 40 °C, the sample still exhibited transparency, suggesting a miscible phase. However, after annealing at 120 °C, the blend became opaque, indicating phase separation.

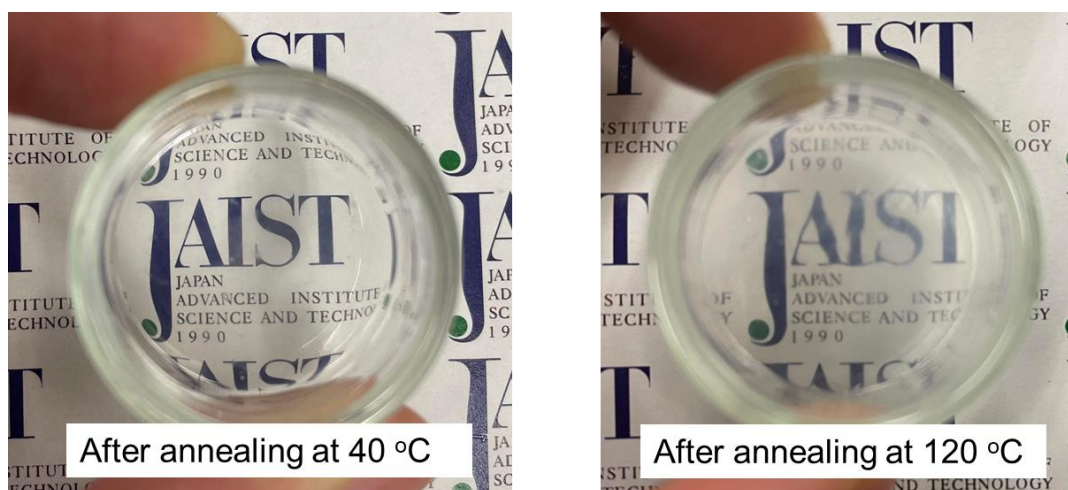


Figure 4.9. Blend SBR/AMS (50/50) after annealing at 40 °C and 120 °C.

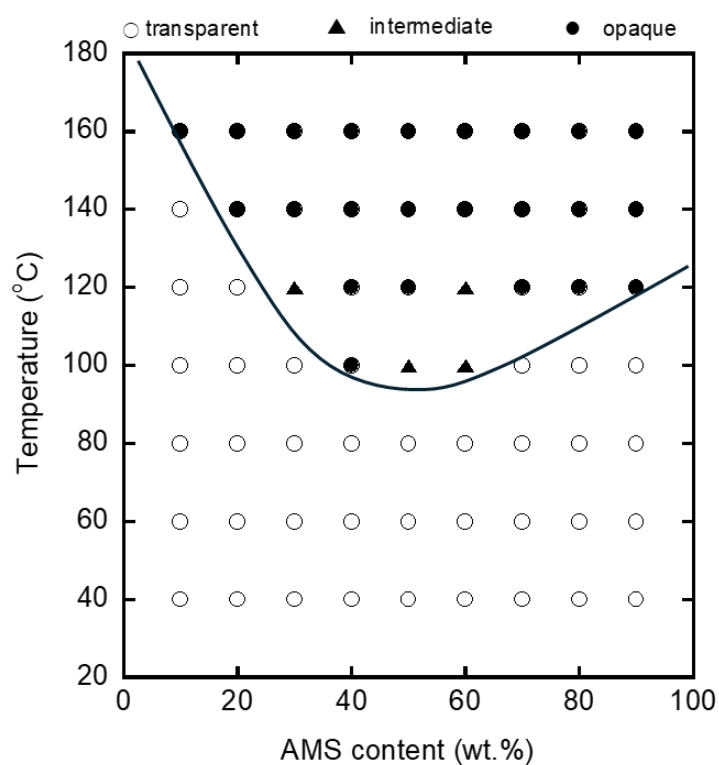


Figure 4.10. Phase diagram of SBR/AMS.

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The phase diagram of SBR/AMS is shown in Figure 4.10. It is seen that SBR/ AMS blend exhibited the Low-Critical-Solution-Temperature (LCST) behavior, where the blends became immiscible at high temperatures. This behavior is typically found in some elastomer/tackifier systems ²⁴⁻²⁶. For the SBR/AMS blend used in the temperature gradient treatment, the AMS content was 30 phr, i.e., 23.0 wt.%. At 120 °C and 140 °C corresponding to the high temperature side in the experiments, the samples were immiscible (opaque) because phase separation occurred. It is widely known that the miscibility of a polymer blend is contributed by the mixing enthalpy. The Flory-Huggin interaction parameter χ could be expressed by the equation ^{27,28}:

$$\chi = \alpha T^{-1} + \beta \quad (4.2)$$

where α and β are experimentally determined coefficients for enthalpy and entropy of compositions.

When the system shows an LCST diagram, the interaction parameter increases monotonically, contributing a positive value to the mixing energy ²⁹. As a result, phase separation occurs, AMS tends to enrich in the low-temperature region. This is the mechanism for segregation in the miscible SBR/AMS blend.

4.4. Conclusions

In this chapter, the segregation behavior of a miscible blend under a temperature gradient was investigated in detail. SBR was blended with 30 phr of AMS, a tackifier. That blend exhibited miscibility, which was confirmed by the dynamic mechanical analysis. After thermal treating under a temperature gradient, the blend showed segregation. The AMS content at the surface exposed to the low temperature is high and vice versa, as confirmed by ATR-IR. Interestingly, this phenomenon did not correspond with the prior study, at which low-molar-mass components were segregated toward the high-temperature surface. The phase diagram of the SBR/AMS system indicated that the blend demonstrated the LCST behavior. Consequently, AMS preferentially migrated to the low-temperature surface, creating a concentration gradient throughout the sample thickness. The temperature dependence of the Flory-Huggins interaction parameter is the driving force of the segregation behavior observed in the SBR/AMS blend under a temperature gradient.

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Chapter 5

General conclusion

Due to the rapidly increasing demand for new materials in recent years, material design now requires the application of advanced knowledge and techniques in creating innovative material products. Technically, there are many methods for gradient structure design, such as diffusion of the concentration gradient or lamination of various layers. This thesis provides a new approach for material design. A graded structure is established using a simple thermal treatment method by applying a temperature gradient. Due to the presence of a graded structure, graded rubber exhibits unique properties. The details of them are briefly summarized in the following chapters.

In Chapter 2, graded styrene-butadiene rubber (SBR) having a gradient crosslink density in the thickness direction was prepared by applying a temperature gradient during vulcanization. According to the dynamic mechanical analysis, $\tan \delta$ of the graded rubber is insignificantly different from that of the homogenous rubber, suggesting that the damping property is not affected in the linear region. Results from stress-relaxation show that the stress curves of the low-crosslink samples decayed considerably, whereas those of the graded rubbers were hardly relaxed. This indicates that the high-crosslink part was responsible for stress generation. After the cessation of stretching, the

graded rubbers showed remarkable strain recovery, although it took a long time. The mechanism of the slow recovery is well explained. This is because of the mismatch in the shrinking between the two sides. After the stress removal, the segmental orientation on the low-crosslink side was mostly relaxed. The high-crosslink side cannot fully recover because it is delayed by the low-crosslink side. Therefore, the high-crosslink side remained in tension and tended to shrink. Consequently, the high-crosslink side exerts a compression force on the low-crosslink side, which acts as a driving force that pulls and recovers the opposite side. This is the common mechanism for the slow recovery of graded rubber with a crosslink density gradient in the thickness direction. Furthermore, graded rubber and homogeneous rubber with a similar average crosslink density were prepared to study their damping properties. It was found that graded rubber exhibits a higher hysteresis loss ratio than homogeneous rubber at all strain rates. Additionally, the residual strain after stress removal is minimal, however it takes a long time.

In Chapter 3, the anomalous swelling phenomenon was observed in the graded rubber. In general, a graded rubber with gradient of crosslink density through the thickness direction is expected to show the bending deformation during swelling, in which a lower crosslink density is on the outer side and vice versa. This is explained by the Flory-Rehner theory. However, in this study, a graded rubber initially bent toward the low-crosslink side over a short period, and then gradually transitioned to the opposite side at the equilibrium state (long period). A possible mechanism is proposed to elucidate this phenomenon

based on gel swelling theory under confinement by a rigid substrate. It is well known that the swelling degree of a gel depends on time and crosslink density. In the short period, the low-crosslink part swells, whereas the core layer remains. The unswollen core layer acts as a substrate that induced a compressive force according to the above mentioned theory. This force bends graded rubber toward the low crosslink side in the short term. In the long period, the swelling behavior of graded rubber follows Flory-Rehner theory. Based on this mechanism, graded rubber demonstrates the potential for actuation and shape transformation capabilities, suggesting a promising new approach for soft robotics and smart material applications.

In Chapter 4, the segregation behavior of a miscible blend under a temperature gradient is studied. SBR was mixed with 30 phr of poly(α -methyl styrene) (AMS), which is known as a tackifier. The blend demonstrates miscibility, as confirmed by dynamic mechanical analysis. After treating SBR/AMS blend under a temperature gradient, segregation occurs. From Attenuated total reflectance-infrared spectroscopy (ATR-IR) results, it is found that AMS is enriched at the surface exposed to the low temperature and vice versa. Interestingly, this phenomenon did not correspond with prior studies, at which low-molar-mass components were segregated toward the high-temperature surface. The phase diagram of the SBR/AMS blend was found to be a LCST type. Therefore, the AMS preferentially migrated to the low-temperature surface, creating a concentration gradient throughout the sample thickness, that is, a graded structure. The temperature dependence of the Flory-

Huggins interaction parameter is the driving force of the segregation behavior observed in the SBR/AMS blend under a temperature gradient.

In general, various treatment conditions result in different graded structures and thus determine the properties of the graded rubber. This research discovered several noteworthy properties, such as remarkable strain recovery after stretching, high hysteresis loss ratio with low residual strain, and anomalous swelling behavior. After these phenomena are revealed and their mechanism is well explained, graded rubber could be suitable for various applications, such as utilizing the swelling behavior of graded rubber for grippers in soft robotics. Moreover, products with specific performance characteristics can be designed by controlling the crosslink density and distribution of the glass transition temperature in the graded rubber. In summary, this research provides basic knowledge regarding the influence of the temperature gradient treatment method on the structure and properties of graded rubber. It is expected that the knowledge and methods obtained in this study will aid in the understanding of the important properties for practical use and will provide useful guidelines for material design.

Achievements

Journal Publications

1. **Q.-V. Do**, T. Kida, M. Yamaguchi*, K. Washizu, T. Nagase, T. Tada
“Anomalous strain recovery after stress removal of graded rubber”
Polymers, 14 (24), 5477 (2022).
<https://doi.org/10.3390/polym14245477>
2. **Q.-V. Do**, M. Yamaguchi*, K. Washizu, T. Mabuchi, T. Tada
“Hysteresis manifestation of graded rubber”
Polymers for Advanced Technologies, 35 (1), e6216 (2024)
<https://doi.org/10.1002/PAT.6216>
3. **Q.-V. Do***, M. Yamaguchi
“Exploring peculiar properties of graded rubber”
Materials Science Forum, (1139), 79 (2024)
<https://doi.org/10.4028/p-lfFf6X>
4. **Q.-V. Do***, M. Yamaguchi, V.A. Doan
“Anomalous swelling behavior of graded rubber”
Journal of Applied Polymer Science, in press.
<https://doi.org/10.1002/app.56782>
5. **Q.-V. Do***, M. Yamaguchi*, T. Tada, V.A. Doan
“Segregation behavior of miscible elastomer blend.”
Submitted to Polymer Journal.

Other publications

1. T.H. Le, **Q.-V.Do***, H. Luu, L.T. Nguyen, L.P.D. Nguyen*, V.A. Doan*
“Mechanical Properties of Ternary Composite from Waste Leather Fibers and Waste Polyamide Fibers with Acrylonitrile-Butadiene Rubber”
Polymers, 15(11), 2452 (2023).
<https://doi.org/10.3390/polym15112453>
2. X. Mei, **Q.-V. Do**, T. Narita, Misaki Yamaguchi, Masayuki Yamaguchi*
“Modification of the rheological properties of a polyamide by adding a copolymer comprising an α -olefin and maleic anhydride”
Molecules, 29 (16), 3730 (2024).
<https://doi.org/10.3390/molecules29163730>
3. N.H. Nguyen, L.D. Nguyen, **Q.-V. Do**, M. Yamaguchi, V. Ho*

Achievements

“A Sustainable Development Framework for Soft Pneumatic Actuators that are: Biodegradable, Self-healable and Re-programmable”

IEEE RoboSoft (2025), accepted.

Presentations

International Conferences:

1. **Q.-V. Do**, T. Kida, M. Yamaguchi, K. Washizu, T. Nagase, T. Tada
“Remarkable strain recovery of styrene-butadiene rubber with gradient crosslink density”
Annual Meeting of Society of Plastic Engineering, ANTEC2023, Denver, Colorado, USA, March 27-31, 2023.
2. **Q.-V. Do**, M. Yamaguchi, K. Washizu, T. Nagase, T. Tada
“Hysteresis loss of the rubber with gradient crosslink density”
Annual Meeting of Society of Plastic Engineering, ANTEC2024, St. Louis, MO, USA, March. 4-7, 2024.
3. **Q. -V. Do**, M. Yamaguchi, T. Tada
“Anomalous properties of rubber having gradient crosslink density”
Polymer Engineering and Science International 2024 (PESI2024), Tokyo, July 21-25, 2024.
4. **Q.-V. Do**, M. Yamaguchi
“Exploring peculiar properties of graded rubber”
The International Conference on Advanced Materials and Technology (ICAMT2024), Hanoi, Vietnam, Oct. 9-12, 2024. (oral presentation)

Domestic Conferences:

1. **Q.-V. Do**, T. Kida, M. Yamaguchi, K. Washizu, T. Nagase, T. Tada
“Strain recovery after stress removal of graded styrene-butadiene rubber”
72nd SPSJ Annual Meeting, Gunma, May 24 -26, 2023
2. **Q.-V. Do**, M. Yamaguchi, K. Washizu, T. Mabuchi, T. Tada
“Energy absorption behavior of graded rubber”
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