Research and Reviews in Materials Science and Chemistry
Vol. 8, Issue 1, 2018, Pages 1-20
ISSN 2319-6920
Published Online on June 12, 2018

http://jyotiacademicpress.org

CHAIN FORMATION FOR UNCROSS-LINKED AND CROSS-LINKED POLYURETHANE MAGNETIC ELASTOMERS

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Abstract

Time profiles of the storage modulus at 2Hz were measured for uncross-linked and cross-linked magnetic elastomers and the effect of cross-linking on the alignment time of magnetic particles was discussed. The time profiles of the storage modulus for both uncross-linked and cross-linked elastomers can be fitted by a linear combination of two exponential functions with distinct characteristic times showing the fast and slow processes for particles alignment. The averaged characteristic time for the fast process was determined to be 7.1 ± 0.4s for uncross-linked elastomers and 5.6 ± 0.4s for cross-linked one. The averaged characteristic time for the slow process was

Keywords and phrases: elastomer, magnetic elastomer, magnetorheology, stimuli-responsive gel.

Received April 12, 2018; Revised May 18, 2018; Re-Revised May 28, 2018
Communicated by Ana Rosa Silva.

around 198.3 ± 8.0s for uncross-linked elastomers and 161.9 ± 4.2s for cross-linked one. Using a parallel model, the overall characteristic time at 50mT was determined to be approximately 7.0s for cross-linked elastomers, which was a half of that for uncross-linked elastomers. However, at magnetic fields above 200mT, there was no clear difference in the overall characteristic time for uncross-linked and cross-linked elastomers. A possible mechanism for the fast chain formation observed in the cross-linked magnetic elastomers is discussed.

1. Introduction

Stimuli-responsive soft materials such as temperature, pH, electric fields, have attracted considerable attention as next generation actuators, devices with virtual reality, or soft robots etc. Magnetic elastomer consists of soft polymeric matrices and magnetic particles, and responses to magnetic fields. When a magnetic field is applied to magnetic elastomer, magnetic particles align to the direction of magnetic fields and make a chain structure within the elastomer. The chain structure of magnetic particles contributes to the viscoelasticity increase due to the stress transfer among magnetic particles. Recently, a variety of magnetorheological (MR) soft materials has been widely investigated and reported [1-7]. We have also reported a new class of magnetic hydrogels [8, 9] and elastomers [10-12] exhibiting drastic and reversible changes in dynamic modulus without using strong magnetic fields. Bimodal magnetic elastomers containing nonmagnetic particles endured against high compression load and showed a great possibility as actuators used in heavies [13-16].

To elevate the MR property for magnetic soft materials, the analysis for chain structures, for example, the dynamics of the chain formation should be needed. Because, it leads to the improvement for not only the amplitude but also the response time of the MR effect. An et al. [17, 18] have been fully analyzed the time evolution of dynamic modulus for magnetorheological physical gels cross-linked by self-assembling of triblock copolymers. They cleared that the storage modulus can be expressed by a double-exponential function with two distinct modes; fast

mode by chain formation and slow mode by densification of the chains. One can easily expect that the similar modes of chain formation are also found in a chemically cross-linked magnetic elastomer, although the linear polymers are tightly cross-linked by the covalent bond.

In the present work, we have measured the time development of storage modulus for uncross-linked and cross-linked magnetic elastomers under various magnetic fields. The effect of cross-linking on the chain formation is discussed particularly focusing on the alignment time of magnetic particles.

2. Experimental Procedure

2.1. Synthesis of magnetic elastomers

As shown in Figure 1, polyurethane magnetic elastomers were synthesized by a pre-polymer method. Polypropylene glycols (M_w = 2000, 3000), toluene diisocyanate, carbonyl iron (SM grade, BASF) particles with a diameter of 2.5μm, plasticizer (dioctyl phthalate, DOP), and catalyst were mixed by a mechanical mixer for several minutes. The concentration of DOP was defined by the ratio of DOP to the matrix without magnetic particles and it was fixed at 65wt.%; DOP/(DOP + matrix). The concentration of magnetic particles was kept at 50wt.%, which corresponds to a volume fraction of 0.14. The mixed liquid was poured in a silicon mold and was cured on a hot plate at 100°C for 20 min.

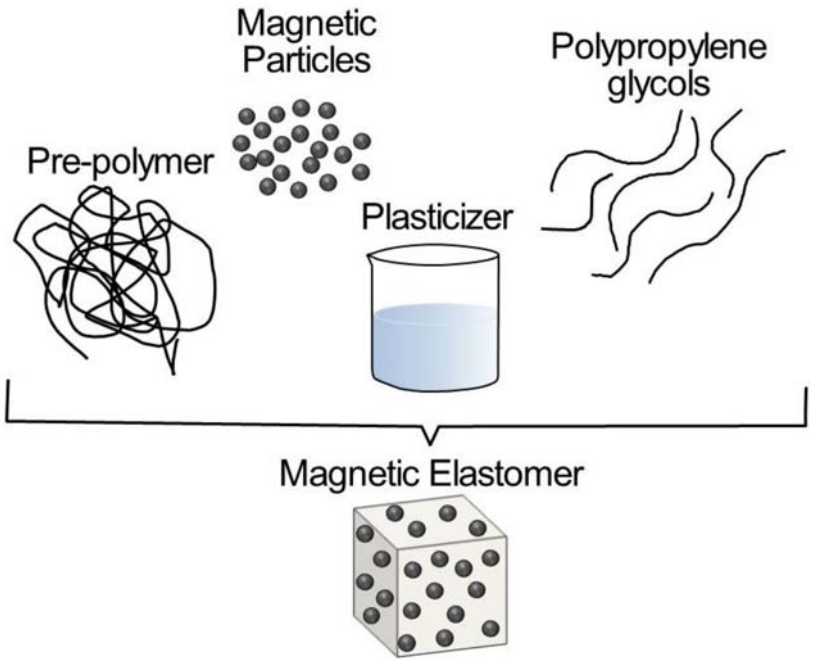


Figure 1. Schematic illustration showing the sample preparation for magnetic elastomers.

2.2. Preparation of magnetic dispersions

Polyurethane magnetic dispersions were prepared without using the catalyst and they were mixed by the similar method for magnetic elastomers. The sample was provided for the rheological measurement immediately after the mixing. The uncross-linked elastomers are in a liquid state and are not cross-linked at an entire sample. On the other hand, the degree of cross-linking for cross-linked elastomers can be characterized by the NCO index. The NCO index calculated from the molar ratio of –NCO to –OH was constant at 0.92 (=[NCO]/[OH]).

2.3. Rheological measurements

Dynamic viscoelastic measurements were also carried out by using a rheometer (MCR301, Anton Paar) with a nonmagnetic parallel plate

(PP20/MRD). The measurement was carried out at 20°C. The strain was constant at 10^{-4}, and the frequency was constant at 2Hz. The sample was a disk 20mm diameter and 1.5mm thick.

2.4. Microscope observations

Microscope observations for uncross-linked and cross-linked elastomers were carried out using an upright microscope (Axio Imager M1m, Carl Zeiss, Inc.) with transmitted light. The film-shaped cross-linked elastomers with a thickness of 0.2mm were synthesized in a cell for microscope observation. The uncross-linked elastomers were poured in the same cell and were provided for observation. The observation for uncross-linked elastomers was performed within approximately 3min. The weight concentration of magnetic particles was kept at 0.7wt.%, which corresponding to a volume fraction of 0.001.

2.5. SEM observations

Scanning electron microscope (SEM) observation was carried out using JCM-6000 Neoscope (JEOL) with an accelerating voltage of 10kV without Au coating. Magnetic elastomers with a volume fraction of 0.15, which were cured under a magnetic field of 50mT, were used.

3. Results and Discussion

Figure 2(a) shows the time profiles of the storage modulus at 2Hz for uncross-linked magnetic elastomers at various magnetic fields. Magnetic fields with 50 ~ 500mT were applied at 30s from the start. The storage modulus at no magnetic fields was scattered and it increased suddenly when magnetic fields were applied. The storage modulus was saturated at around 300s for all samples. This indicates that magnetic particles form a chain with a finite length in uncross-linked elastomers.

Figure 2(b) demonstrates the time profiles of the storage modulus at 2Hz for cross-linked magnetic elastomers at various magnetic fields. Similar to the uncross-linked elastomers, the storage modulus for all magnetic elastomers increased suddenly when magnetic fields were applied and was constant at around 300s.

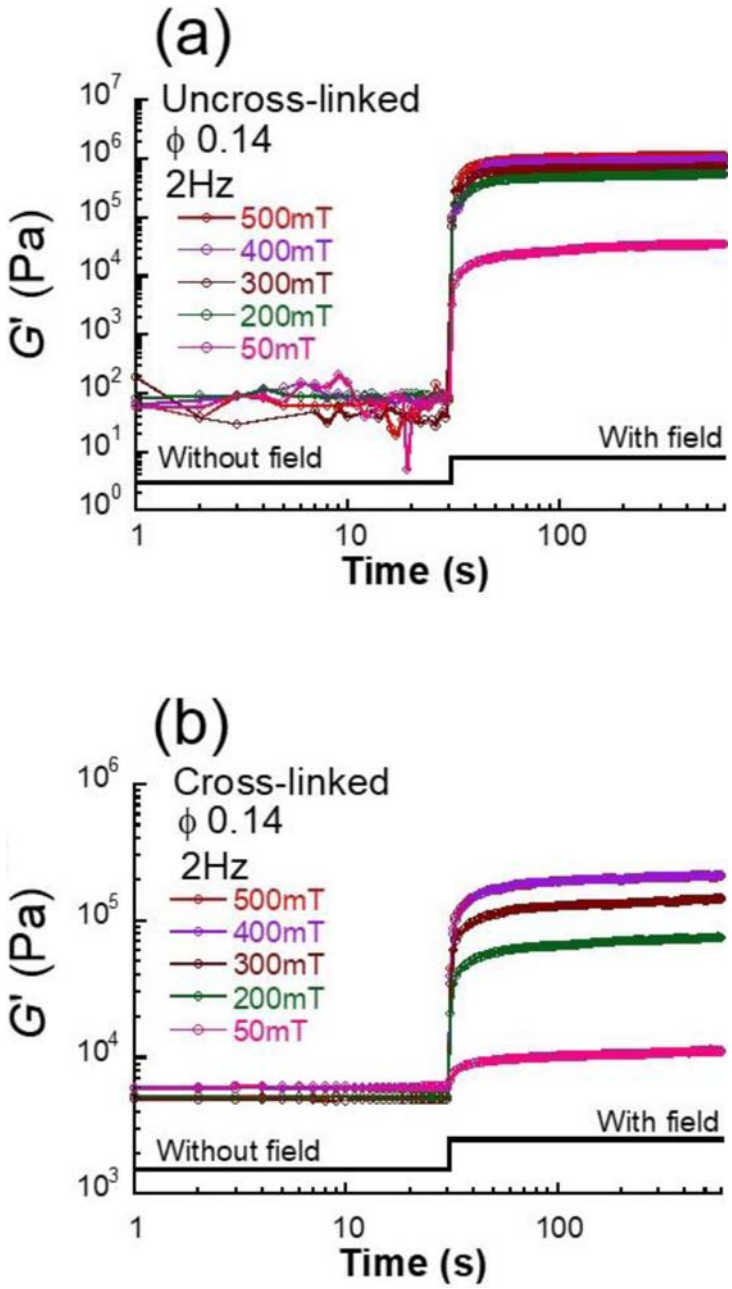


Figure 2. Time profiles of storage modulus at 2Hz for (a) uncross-linked and (b) cross-linked magnetic elastomers at various magnetic fields.

Figure 3(a) indicates the time profiles of $[G'(t) - G'(0)] / \Delta G'$ obtained from Figure 2(a) for uncross-linked magnetic elastomers at various magnetic fields. Here, $G'(t)$ appears the storage modulus at a certain time and the $G'(0)$ stands for the storage modulus at 0s. The $\Delta G'$ is obtained by $G'(\infty) - G'(0)$, where $G'(\infty)$ is the storage modulus at the equilibrium. The value of $[G'(t) - G'(0)] / \Delta G'$ reached an equilibrium in a short time as increasing the strength of magnetic fields.

Figure 3(b) shows the time profiles of $[G'(t) - G'(0)] / \Delta G'$ obtained from Figure 2(b) for cross-linked magnetic elastomers at various magnetic fields. Similar to the uncross-linked elastomers, the value of $[G'(t) - G'(0)] / \Delta G'$ for cross-linked elastomers reached the equilibrium in a short time as increasing the strength of magnetic fields.

The storage modulus at a certain time $G'(t)$ for cross-linked and uncross-linked magnetic elastomers can be fitted by a linear combination of two exponential functions as following:

$$G'(t) = G'_0 + \Delta G_1 \left[1 - \exp\left(-\frac{t}{\tau_1} \right) \right] + \Delta G_2 \left[1 - \exp\left(-\frac{t}{\tau_2} \right) \right], \quad (1)$$

$$\Delta G' = \Delta G'_1 + \Delta G'_2. \quad (2)$$

Here, the $\Delta G'_1$ and $\Delta G'_2$ are the change in the storage modulus for the fast and slow processes, respectively. The τ_1 and τ_2 are the alignment time of magnetic particles for the fast and slow processes, respectively. The values of τ_1, τ_2, and $\Delta G'_1$ were determined by the fitting, and the value of $\Delta G'_2$ was obtained by Equation (2). The time development of G' for cross-linked and uncross-linked elastomers could be well fitted by the above equations, which is in good agreement with previous reports [17-19]. The correlation coefficient for the fitting was 0.988-0.996 for uncross-linked elastomers and 0.985-0.994 for cross-linked elastomers.

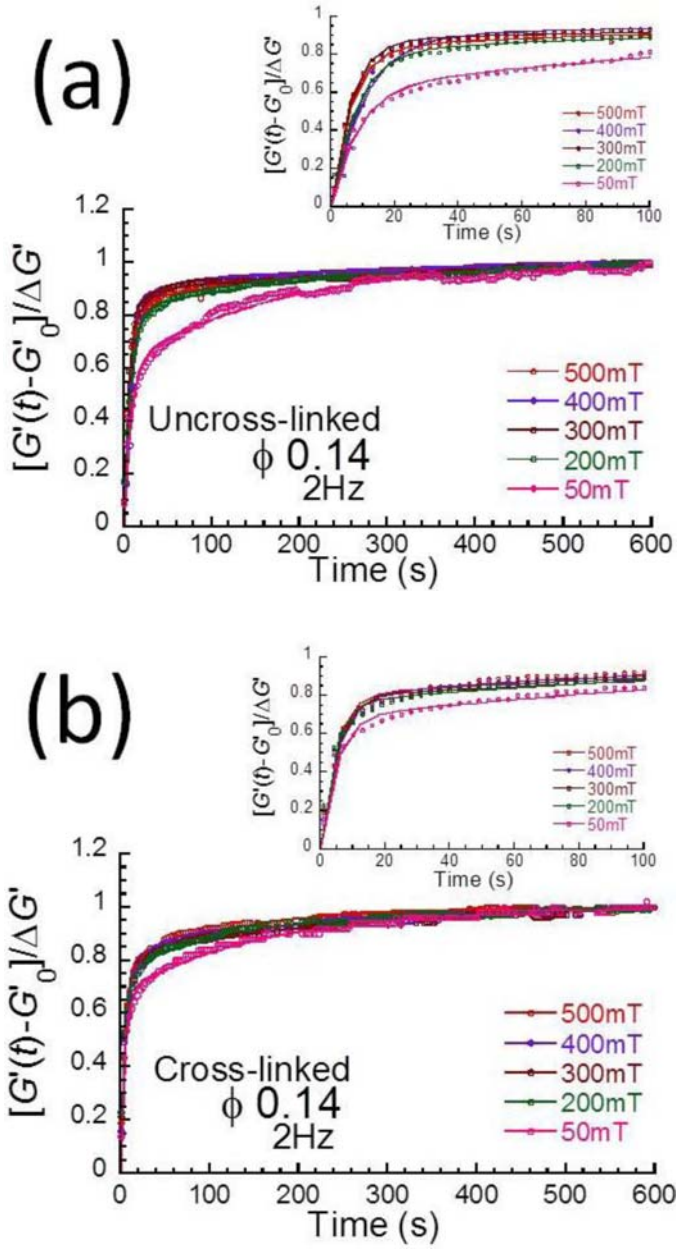


Figure 3. Time profiles of $[G'(t) - G'_0] / \Delta G'$ obtained from Figure 2 for (a) uncross-linked and (b) cross-linked magnetic elastomers at various magnetic fields. Solid lines show the fitting lines by Equation (1).

Figure 4(a) exhibits the magnetic field dependence of the characteristic time for the fast process for uncross-linked and cross-linked magnetic elastomers. The characteristic time for uncross-linked elastomers was independent of the magnetic field, and the magnetic-field averaged characteristic time was 7.1 ± 0.4s. The characteristic time for cross-linked elastomers was also independent of the magnetic field, and the magnetic-field averaged characteristic time was determined to be 5.6 ± 0.4s. Unexpectedly, the averaged characteristic time for cross-linked elastomers was slightly shorter than that for uncross-linked one, indicating that magnetic particles are able to form a chain structure within the cross-linked matrix in a short time. An et al. [18] reported that the fast characteristic time distributes 3.6 – 7.9s and it was independently of the magnetic field strength. Accordingly, this fast process observed here is considered to originate from the similar mechanism of structuring process in magnetic physical gels; that is, the chain formation of magnetic particles.

Figure 4(b) shows the magnetic field dependence of the characteristic time for the slow process for uncross-linked and cross-linked magnetic elastomers. The characteristic time for uncross-linked elastomers showed a trend to increase with the magnetic field, however it took an indistinct and reproducible peak at 300mT. On the other hand, the characteristic time for cross-linked elastomers was independent of the magnetic field. The characteristic time τ_2 observed here is in the same range with that in the literature [18]. Accordingly, this slow process is considered to originate from the similar mechanism of structuring process in magnetic physical gels; that is, the connection or densification of the chain structure. However, the magnetic field dependence of the characteristic time observed here is completely different from that of magnetic physical gels where the characteristic time significantly depends on the matrix viscoelastic property, particle volume fraction, sample's initial particle distribution, and the magnetic flux density [18]. Similar to the fast process, a tendency was found that the characteristic time for cross-linked elastomers was shorter than that for uncross-linked one. The long

characteristic time observed in uncross-linked elastomers might be due to the destruction and reconstitution of chain structures. The chain structure once made under magnetic fields is destructed by the oscillational strain for uncross-linked elastomers.

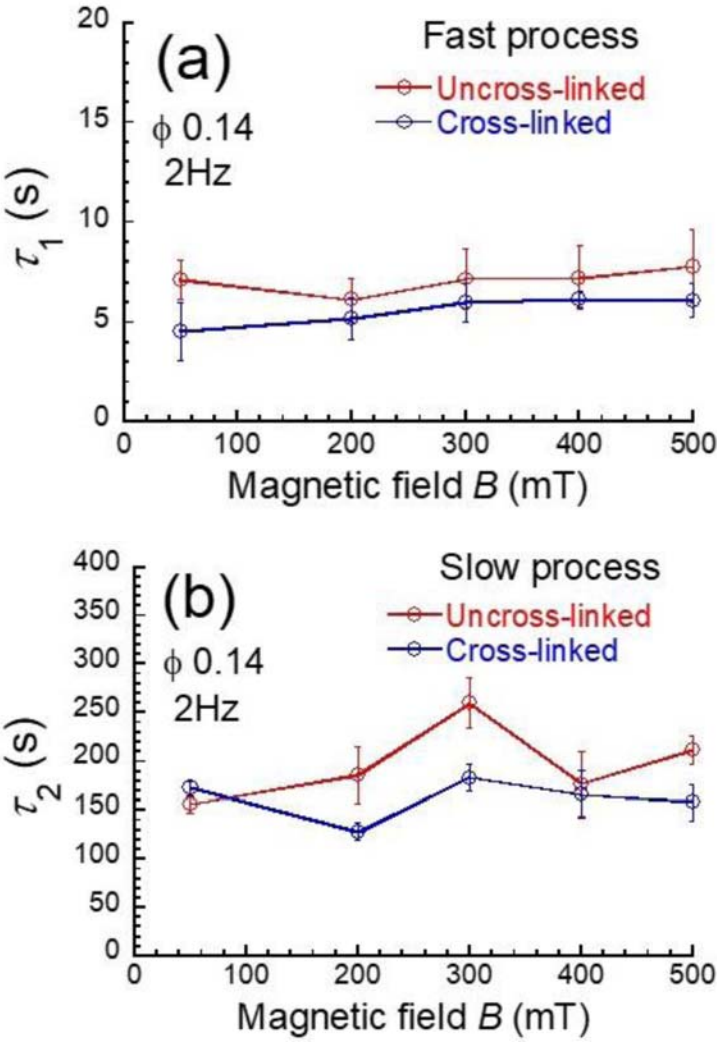


Figure 4. Magnetic field dependence of characteristic time for (a) fast process and (b) slow process for uncross-linked and cross-linked magnetic elastomers.

Figure 5 shows the normalized change in the storage modulus for the fast process $\Delta G'_1/\Delta G'$ and the slow process $\Delta G'_2/\Delta G'$ for uncross-linked and cross-linked magnetic elastomers as a function of magnetic field. For the fast process, the value of $\Delta G'_1/\Delta G'$ for uncross-linked elastomers increased up to 300mT, and it was constant at high magnetic fields. Similar trend was found in the $\Delta G'_1/\Delta G'$ for cross-linked elastomers. This feature seen in the magnetic field dependence of $\Delta G'_1/\Delta G'$ was not seen in magnetic physical gels [18], hence, this might be a characteristic property for chemically cross-linked magnetic elastomers. The value of $\Delta G'_1/\Delta G'$ for uncross-linked elastomers was higher than that for cross-linked one, suggesting that most particles contributes to the fast process of chain formation. For the slow process, the both of $\Delta G'_2/\Delta G'$ for uncross-linked and cross-linked elastomers decreased up to 300mT, and it was constant at high magnetic fields. The value of $\Delta G'_2/\Delta G'$ for cross-linked elastomers was higher than that for cross-linked one, indicating that most particles contributes to the slow process of chain formation.

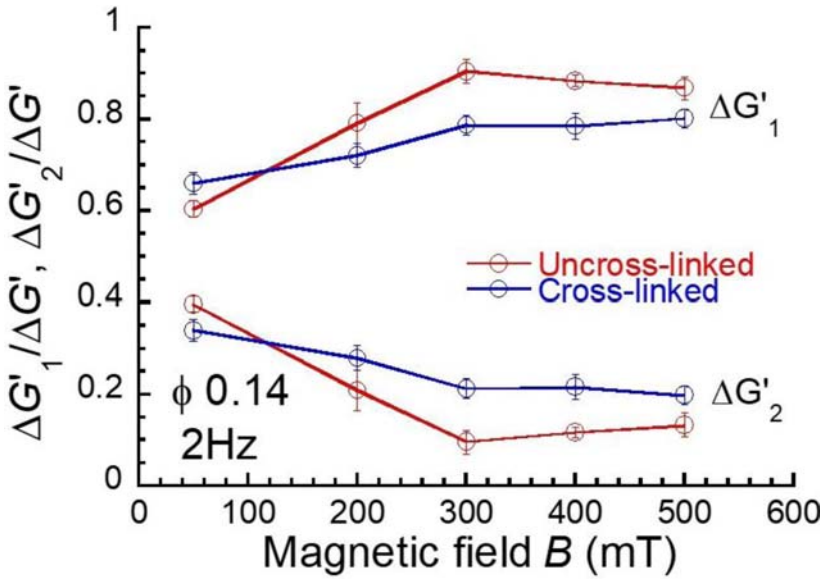


Figure 5. Normalized change in storage modulus for fast process and slow process for uncross-linked and cross-linked magnetic elastomers as a function of magnetic field.

The overall mean characteristic time τ_m for uncross-linked and cross-linked magnetic elastomers can be explained by the following equation using a parallel model:

$$\frac{1}{\tau_m} = \frac{(\Delta G'_1/\Delta G')}{\tau_1} + \frac{(\Delta G'_2/\Delta G')}{\tau_2}. \quad (3)$$

Here, the notation in the above equation is the same as symbols in Equations (1) and (2). The overall mean characteristic time is taken in account for the number of magnetic particles contributing to each process.

Figure 6 exhibits the relationship between the overall characteristic time obtained by Equation (3) and magnetic field for uncross-linked and cross-linked magnetic elastomers. At 50mT, the value of τ_m for cross-linked elastomers was approximately 7.0s, which was a half of that for uncross-linked one. The slow formation of chain structures seen in

uncross-linked elastomers is considered to originate from the destruction of chain structures. No clear difference in the values of τ_m for uncross-linked and cross-linked elastomers was observed at magnetic fields above 200mT, which might be due to the decrease in the frequency of chain destruction by strong magnetic fields. The τ_m for uncross-linked and cross-linked elastomers was independent of the magnetic field above 200mT.

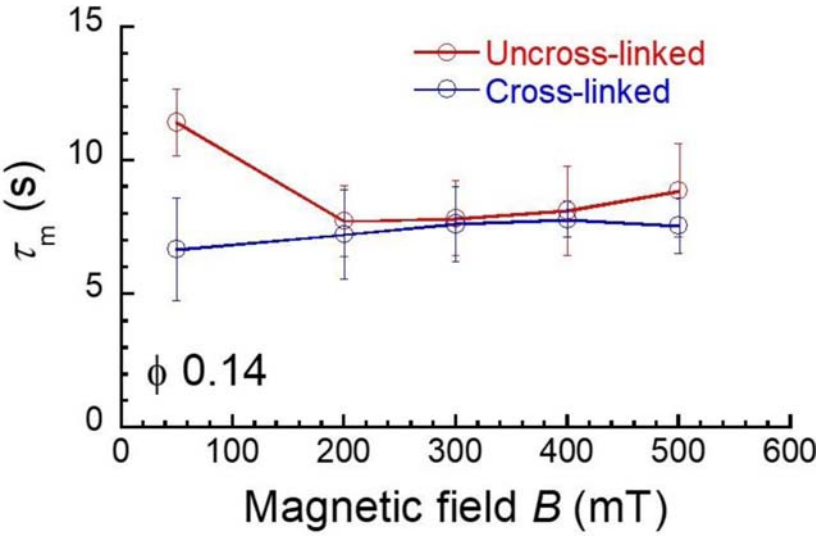


Figure 6. Relationship between overall characteristic time obtained by Equation (3) and magnetic field for uncross-linked and cross-linked magnetic elastomer.

Figures 7(a), 7(c) and Figures 7(b), 7(d) show the microphotographs for uncross-linked and cross-linked magnetic elastomers, respectively. When the samples with high volume fractions of magnetic particles such as the samples used in the rheological measurement, the light transmitted from a microscope was completely blocked by the samples. Magnetic gels with $\phi < 0.01$, were suitable for the observation of particle dispersibility. The thickness of each sample was approximately 100μm.

Magnetic elastomers with extremely low volume fraction of magnetic particles were employed in this experiment in order to observe the particle morphology. Both uncross-linked and cross-linked elastomers exhibited random dispersion of magnetic particles without clear agglomerates.

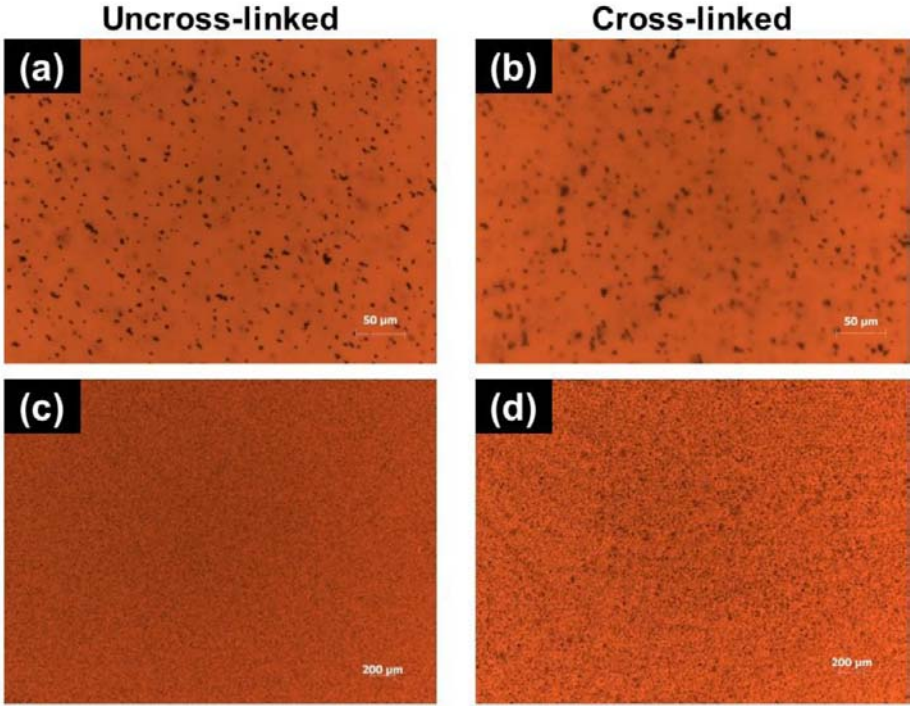
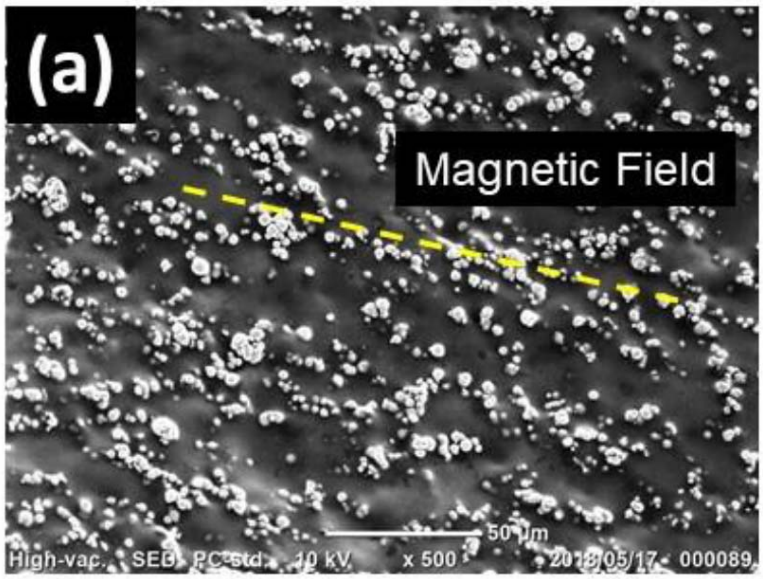


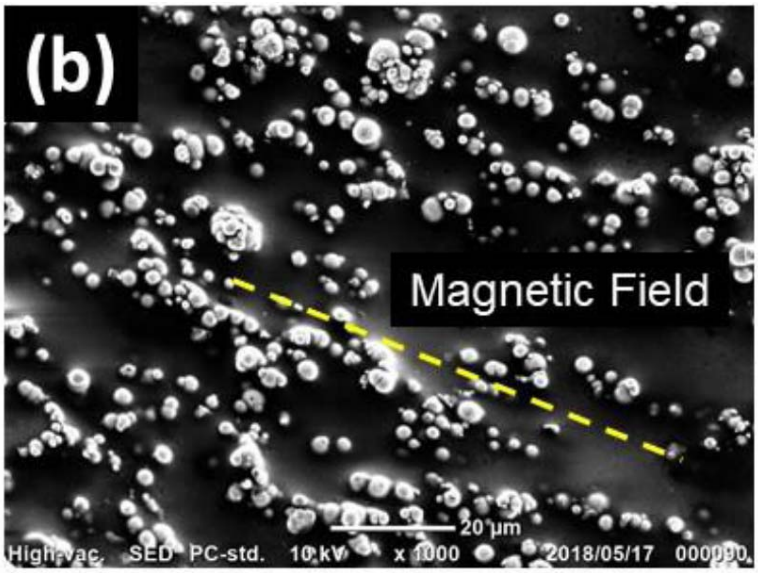
Figure 7. Microphotographs for (a), (c) uncross-linked and (b), (d) cross-linked magnetic elastomers with a volume fraction of magnetic particles 0.001.

As described in the introduction, magnetic particles form a chain-like structure in polyurethane elastomer. An example, SEM photographs for a chain structure consisting of magnetic particles are shown in Figures 8(a) and 8(b). The sample was cured in a magnetic field of 50mT. Note that the chain structure was made in a liquid before the cross-linking and is not made in a cross-linked matrix.

Figure 8(c) depicts the schematic illustrations representing the chain structure for the fast and slow processes for uncross-linked magnetic elastomers. For uncross-linked elastomers, magnetic particles are randomly distributed in the polyurethane matrix. When magnetic fields are applied, the magnetic particles make discontinuous chains that are 90% of the perfect chain during the time of τ_1. This is the fast process of chain formation. These discontinuous chains connect each other during the time of τ_2, resulting in the perfect formation of discontinuous chains. Since the storage modulus at the equilibrium for uncross-linked elastomers is higher than that for cross-linked one, the magnetic particles for uncross-linked elastomers show well-ordered chain structure. This is the slow process of chain formation.

Figure 8(d) shows the schematic illustrations representing the chain structure for the fast and slow processes for cross-linked magnetic elastomers. When magnetic fields are applied, magnetic particles make discontinuous chains that are 80% of the perfect chain during the time of τ_1, which is 10% lower than that for uncross-linked one. Both τ_1 and τ_2 for cross-linked magnetic elastomers were shorter than those for uncross-linked one. The long characteristic time for uncross-linked elastomers might be due to the time for reaching the equilibrium state by destruction and reconstitution of chain structures.


(a)
Magnetic Field
50 µm
High-vac. SED PC-std. 10 kV x 500 2018/05/17 000089


(b)
Magnetic Field
20 µm
High-vac. SED PC-std. 10 kV x 1000 2018/05/17 000090

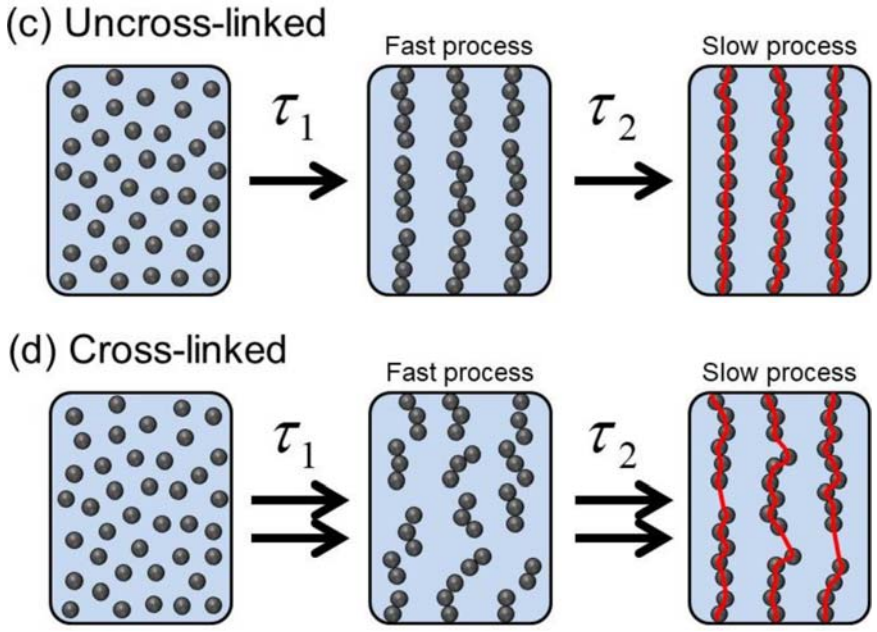


Figure 8. (a), (b) SEM photographs of chain-like structure for magnetic elastomers cured under a magnetic field. Schematic illustrations representing the chain structure on the fast process and slow process for (c) uncross-linked and (d) cross-linked magnetic elastomers.

4. Conclusion

We measured the time profiles of the storage modulus for uncross-linked and cross-linked magnetic elastomers and discussed the effect of cross-linking on the characteristic time for the chain formation of magnetic particles. The time profile of storage modulus can be fitted by a linear combination of two exponential function with two distinct process. The fast process is probably due to the chain formation within a microscopic range, and the slow one is due to the connection (or densification) of chains in a mesoscopic range. For both fast and slow process, the characteristic time for uncross-linked elastomers was longer than that for cross-linked one, which is due to the

destruction/reconstitution of chain structures in uncross-linked elastomers. The overall characteristic time for the chain formation of magnetic particles was determined using a parallel model. The characteristic time for cross-linked elastomers at 50mT was approximately 7.0s, which was a half of that for uncross-linked one. However, at magnetic fields above 200mT, there was no difference in the characteristic time for cross-linked and uncross-linked elastomers.

Acknowledgement

This research was partially supported by a grant from the Cooperative Research Program of "Network Joint Research Center for Materials and Devices" (No. 20171274) and Sasaki Environment Technology Foundation, NAGAI N-S Promotions Foundation for Science of Perception, and UNION TOOL foundation.

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