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Damping Elastomer Based on Model Irregular Networks of End-Linked Poly(Dimethylsiloxane)

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We demonstrate a silicone damping elastomer with a constant high damping performance ($\tan\delta = E''/E' \approx 0.3$ where E' and E'' are the storage and loss Young's moduli, respectively) over a broad temperature range of 180 °C (-30 °C $< T <$ 150 °C) utilizing a slow viscoelastic relaxation of an irregular network structure with many pendant chains. In addition to $\tan\delta$, E' is almost unaltered in the corresponding temperature range. These are in contrast to the markedly temperature-dependent damping and modulus of conventional damping elastomers using the glass transition as the energy dissipation. The temperature- and frequency-insensitive damping and elasticity are of significance to extend the availability in the industrial uses. The irregular networks have been prepared by end-linking a mixture of bi- and monofunctional end-reactive precursor linear poly(dimethylsiloxane) (PDMS) chains with trifunctional cross-linker, or end-linking the bifunctional precursor chains with trifunctional cross-linker at off-stoichiometric ratios. Independently of mechanical testing, the fractions of pendant (W_{pen}) and elastic chains (W_{el}) in the irregular networks have been evaluated using a nonlinear polymerization model. It has been demonstrated that $\tan\delta$ increases with increasing W_{pen}; the pendant chain whose one end is free to move significantly contributes to the dissipation of deformation energy via the viscoelastic relaxation. The temperature- and frequency-insensitive damping originates from a broad relaxation spectrum of the irregular networks comprising the pendant branched chains with various shapes and a wide size distribution.

Introduction

There exists considerable demand for "damping materials" to suppress vibration and noise in industrial fields. Viscoelasticity of polymers has often been utilized as a damping mechanism. In principle, when the time scale of the viscoelastic relaxation is comparable to that of the vibration, most of the vibration energy can be dissipated as heat by the polymer. One can use the loss tangent $\tan\delta$, defined by the ratio E''/E' of the storage (E') and loss moduli (E''), as a measure of the dissipation of deformation (vibration) energy.[1,2] In general, it is desirable for damping material to possess a constant high $\tan\delta$ over broad temperature and frequency ranges. Most of the earlier studies on damping polymeric materials utilized a large $\tan\delta$ around the glass transition temperature (T_g).[3] They also made an effort to broaden the temperature range with large $\tan\delta$, as well as to optimize the T_g to the desired temperatures by blending polymers of low and high T_g,[4] or interpenetrating the polymer networks with different T_g's.[5,6] However, as far as the damping relies on glass transition, the optimized temperature regions are not largely broadened, and in addition, a large change in the magnitudes of $\tan\delta$ and E' between the temperatures below and above T_g are unavoidable due to the drastic transition from the glassy state to the rubbery state of the materials. In particular, the modulus may change over several decades by a small temperature variation around T_g. These characteristics of the conventional methods based on glass transition limit their availability for industrial uses.

Rubbery polymer network with many dangling branched chains is an interesting and promising approach as a temperature-insensitive damping elastomer. As is well-known, a gelling system at the critical gel point becomes viscoelastic ($\tan\delta \approx 1$) over broad frequency range.[7] This viscoelastic property originates from a tree-like fractal structure of the critical gel comprising many branched chains. However, the elastic modulus

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of the critical gels is too small for practical use as an elastomer due to an extremely low fraction of the elastic network backbone (namely, the elastic part excluding any dangling chains from the network structure). It is a more practical approach to introduce some amount of dangling branched chain into a developed infinite network, or to use a moderately matured infinite network (still possessing a high structural irregularity) slightly above the gelation threshold. The irregular network has a number of relaxation modes with widely different characteristic times due to the tree-like structure. We expect that a high irregularity in network structure will yield not only a pronounced damping but also temperature- and frequency-insensitive damping and elasticity because of a broad distribution of relaxation time.

In the present study, we prepare the elastomeric irregular networks by end-linking the end-reactive linear poly(dimethylsiloxane) (PDMS) chains with trifunctional cross-linker. Compared to conventional random cross-linking, the end-linking method has the great advantage that one can evaluate the structural parameters such as the numbers of elastic chains, cross-links, and dangling chains in the resulting networks on the basis of a nonlinear polymerization theory[8] with the data of the amounts of each reactant and the extractable materials. The end-linking method enables us to make a "model irregular network" with topological parameters that can be estimated.[9] Using this merit, we elucidate the correlation between the amount of dangling chain and the damping property, as well as that between the amount of elastic chain and the network modulus.

Some earlier studies[10−12] reported the dynamic mechanical properties of some irregular rubbery networks of PDMS[10,11] and polyurethane.[12] However, none of them removed the extractable materials (namely, the material which is not incorporated into the infinite network) from the networks after the cross-linking reaction. The cross-linking reactions for the irregular networks yield a large amount of extractable material, and it often exceeds several tens of wt %. It should be noted that the extractable materials in the networks act as plasticizer; they also behave as additional relaxation components when the molecular size is sufficiently large.[13,14] Thus, the presence of extractable materials in the irregular networks disturbs the accurate evaluation of the damping performance originating purely from the irregular (infinite) network structure. In the present study, we fully wash out the extractable materials from the networks after the reaction, and use the networks without extractable materials for dynamic mechanical measurements. To the authors' knowledge, this is the first investigation of the dynamic mechanical properties for "pure" irregular polymer networks.

Experimental Section

Preparation of Model Irregular Networks. The commercial vinyl-terminated bi- and monofunctional PDMS (Gelest Inc.) were employed as end-reactive precursor chains after the fractionations with a mixture of methanol and 2-butanone to narrow the molecular size distributions. The bi- and monofunctional PDMS were designated as B-PDMS and M-PDMS, respectively. The number-average molecular masses (M_n) for B-PDMS and M-PDMS are 29 600 and 25 700 mol/g, respectively. Triskis(dimethylsiloxy)silane and a platina chloric acid ($H_2PtCl_6\cdot 6H_2O$) dissolved in 2-propanol were used as trifunctional cross-linker and catalyst for hydrosilylation reaction between vinyl group and silane hydrogen, respectively. The molar ratio of [catalyst]/[Si−H] was 0.01.

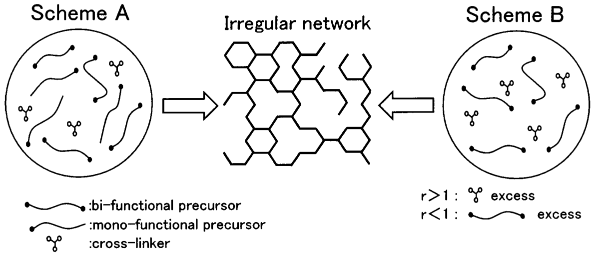

Figure 1. Schematics for Scheme A and B.

Two different schemes were employed to prepare the irregular networks of PDMS. The schemes are shown in Figure 1. In Scheme A, a mixture of B-PDMS and M-PDMS was end-linked with trifunctional cross-linker. In this case, M-PDMS is incorporated into the network as a dangling chain which is an origin of irregularity in the network structure. The content of M-PDMS was varied from 0 to 40 mol %. In the end-linking of the mixtures of bi- and monofunctional precursor chains with trifunctional cross-linker, the critical content of M-PDMS to form an infinite network is 50 mol %. To facilitate complete mixing, the mixtures were dissolved in distilled toluene. After stirring for 1 d, the toluene was completely removed by evaporation under reduced pressure. At this stage, the desired amounts of cross-linker and catalyst were added to the mixtures. The molar ratio of silane hydrogen in the cross-linker to vinyl group in the precursors (r) was 1.3 for all the mixtures.

In Scheme B, B-PDMS was end-linked with the trifunctional cross-linker at an off-stoichiometric ratio ($r \neq 1$): the reaction was made under imbalanced conditions in the amounts of precursor and cross-linker. The end-linking at the off-stoichiometric ratios yields an irregular network structure with structural defects such as dangling chain due to the presence of an excess amount of precursor or cross-linker in the reaction. The r values were varied from 0.7 to 1.8. The condition $r > 1$ or $r < 1$ corresponds to the situation where there exists an excess amount of cross-linker or precursor, respectively.

The mixtures for Scheme A or B were poured into a Teflon mold. After the hydrosilylation reaction for 24 h, the resulting rectangular sample was weighed, and then allowed to swell in toluene for 1 week. The toluene was renewed every day to facilitate full removal of unreacted molecules. After the washing procedure, the sample was gradually deswollen in successive mixtures of methanol and toluene, increasing in methanol content. The fully deswollen sample in pure methanol was completely dried in air. The dried sample was weighed to evaluate the weight fraction of soluble molecules (i.e., extractable molecules) $W_{sol} = (W_0 - W_f)/W_0$ where W_0 and W_f are the weights of the dry network samples before and after the washing procedure. The value of W_{sol} for each sample is summarized in Table 1. The dried rectangular samples after the washing procedure, i.e., the network samples from which extractable molecules were sufficiently removed, were employed for dynamic mechanical measurements. The sufficient removal of the extractable materials was confirmed by the fact that the repeated washing did not reduce further the weight of the dry sample. No special care to remove the catalyst residue was taken, but the effect of the catalyst residue on the mechanical properties of the networks, if any, is quite small because of the extremely low catalyst concentration.

Dynamic Mechanical Measurements. The dynamic mechanical measurements of the dry rectangular sample strips

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Table 1. Characteristics of Irregular Networks of End-Linked Poly(dimethylsiloxane)

sample code	r	M-PDMS content (mol %)	tanδ[a]	$E' \times 10^{-5}$ (Pa)[b]	W_{sol} (wt %)	W_{el} (wt %)	W_{pen} (wt %)	p	p_{gel}
A-0	1.30	0	0.090	4.57	0.010	0.815	0.185	0.766	0.620
A-20	1.30	20	0.139	3.89	0.105	0.496	0.504	0.758	0.658
A-30	1.30	30	0.206	2.95	0.183	0.379	0.621	0.765	0.683
A-40	1.30	40	0.217	2.46	0.208	0.335	0.665	0.797	0.716
B-070	0.70	0	0.317	1.95	0.418	0.215	0.785	0.924	0.845
B-085	0.85	0	0.245	2.46	0.201	0.380	0.620	0.881	0.767
B-100	1.00	0	0.082	5.75	0.010	0.812	0.188	0.924	0.707
B-130[c]	1.30	0	0.090	4.57	0.010	0.815	0.185	0.766	0.620
B-180	1.80	0	0.121	4.68	0.065	0.594	0.406	0.598	0.527

[a] At 30 °C and 10 Hz. [b] At 30 °C and 10 Hz. [c] B-130 is identical to A-0.

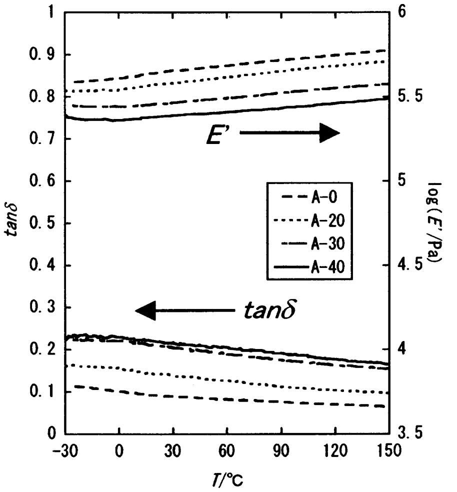

Figure 2. Storage Young's modulus (E') and loss tangent (*tan* δ) at 10 Hz as a function of temperature for the irregular PDMS networks prepared by Scheme A.

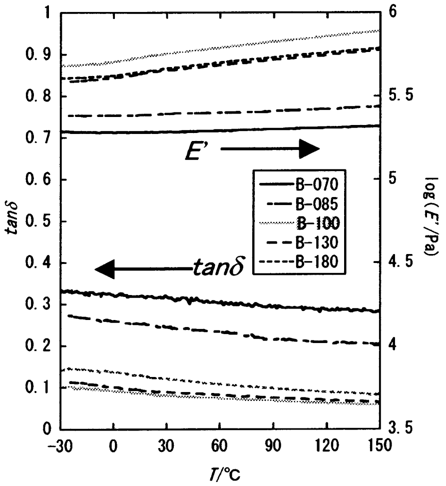

Figure 3. Storage Young's modulus (E') and loss tangent (*tan* δ) at 10 Hz as a function of temperature for the irregular PDMS networks prepared by Scheme B.

were performed with a strain-controlled oscillatory rheometer DVE-V4 (Reoroji). Frequency scans were carried out from 0.1 to 10 Hz, and the temperatures were varied from − 30 to 150 °C. All the samples were in the rubbery state over the whole temperature range examined here because the glass transition temperature and the crystalline melting temperature of cross-linked PDMS are ca. −120 °C and ca. −40 °C, respectively.[9] The oscillatory tensile strain amplitude was within the range of linear viscoelasticity.

After the mechanical measurements, the dry network sample was immersed in a certain amount of oligodimethylsiloxane (solvent) so that the solvent content of the swollen network could be 50 wt %. The dynamic mechanical measurements of the swollen network were performed at room temperature using the oscillatory compressive strain. After the measurement, the swollen network with 50 wt % solvent was immersed again in the solvent to obtain the further swollen network containing 70 wt % solvent. The same procedure was also made for the preparation of the swollen network with 85 wt % solvent.

Results and Discussion

Figure 2 displays the storage Young's modulus (E') and loss tangent (tan $\delta = E''/E'$ where E'' is the loss modulus) at 10 Hz as a function of temperature for the irregular PDMS networks via Scheme A. With an increase in the M-PDMS content, tan δ increases while E' decreases. These results are due to an increase in the amount of dangling chain, because the monofunctional precursor M-PDMS is incorporated into the network structure as dangling chain. Introduction of dangling chain reduces the number of elastically effective chemical cross-links, which lessens network modulus. Sample A-40 with the highest M-PDMS content exhibits tan $\delta \approx 0.2$ at room temperature, which is larger than that for the PDMS network without M-PDMS (A-0) by a factor of ca. 2.5. The value of E' for A-40 at room temperature is about a half of that for A-0, but it is still in the range of E' of conventional elastomers. It should be noted that tan δ, as well as E', is almost independent of temperature, the details of which will be discussed later.

Figure 3 shows E' and tan δ as a function of temperature at 10 Hz for the irregular PDMS networks via Scheme B. B-100 of $r = 1$ shows the maximum in E' as well as the minimum in tan δ among all the networks prepared at various r. This accords with the intuitive expectation that the stoichiometric ratio will yield the most regular structure, namely, the structure with the minimum amount of structural defect. As r deviates from the stoichiometric ratio ($r = 1$), tan δ of the resulting network increases whereas E' decreases, in both the regions $r > 1$ and $r < 1$. This result originates from an increase in the amount of structural defect such as dangling chain in the network structure. The case of the most excessive amount of the precursor ($r = 0.7$) yields the largest value of tan δ (≈ 0.3) among all the networks via Scheme B, and the value is higher than tan δ (≈ 0.09) of the most regular network ($r = 1$) by a factor of ca. 3.2. The modulus of B-070 with the highest tan δ is reduced to ca. 30% of that of the most regular network, but the value of E' is still in the order of 10^5 Pa within the range of typical elastomer. As in the case of the irregular networks via Scheme A, E' as well as

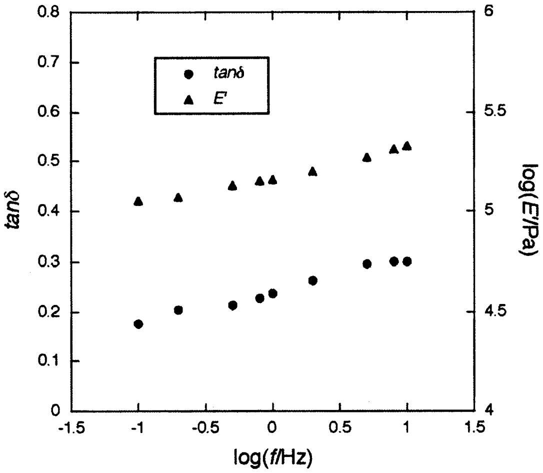

Figure 4. Storage Young's modulus (E') and loss tangent (*tan* δ) at 25 °C as a function of frequency for the irregular PDMS network B-070.

tan δ for the irregular networks via Scheme B exhibits no significant dependence on temperature over the wide temperature range -30 °C $< T <$ 150 °C: The tan δ slightly decreases with increasing T, while E' gradually increases with T due to the entropic elasticity ($E' \sim kT$). Figure 4 illustrates the frequency dependence of E' and tan δ at 25 °C for B-070 exhibiting the highest tan δ among all the networks. The dependence of each of E' and tan δ on frequency is weak. These are in contrast with the significantly temperature- and frequency-dependent damping and elastic properties of conventional damping elastomers utilizing the glass transition. As a measure of the temperature range exhibiting good damping performance, the temperature range for tan $\delta \geq 0.3$ is conventionally employed.[6] In the case of typical damping elastomers, the corresponding temperature range is not as large as 80 °C, and in addition, the elastic modulus changes over at least 1 order of magnitude in the concerning temperature range.[5,6] In the case of B-070, the temperature range for tan $\delta \geq 0.3$ is over 180 °C (-30 °C $< T <$ 150 °C), and the changes in E' and tan δ in the concerning temperature range are less than 10%. It is to be noted that the irregular networks are in the rubbery state over the entire temperature range examined; the damping mechanism does not rely on the energy dissipation originating from drastic structural transition such as glass transition.

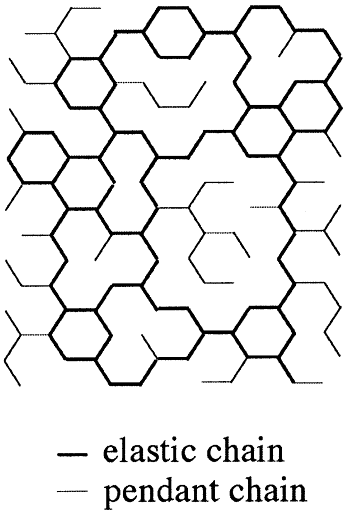

Figure 5. Schematic for "elastic" and "pendant" chains in a trifunctional irregular network. For simplicity, random-coiled network chains are expressed by straight lines.

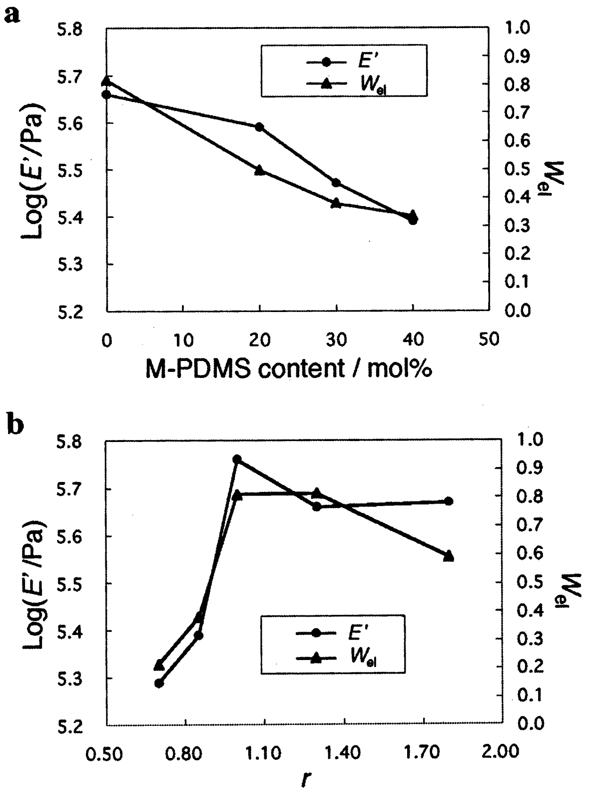

Figure 6. Comparison of the storage Young's modulus (E') at 30 °C with the weight fraction of elastic chains (W_{el}) for (a) the PDMS networks via Scheme A, and (b) the PDMS networks via Scheme B.

In the case of end-linking system, one can evaluate each fraction of "elastic" or "pendant" chains in network structure using a nonlinear polymerization model and the data of the fraction of "soluble" (extractable) chains.[8,10,11] The elastic chain corresponds to the chain which is connected to an infinite network by both ends. The pendant chain is defined as the chain which leads to an infinite network through only one end. The definitions of the elastic and pendant chains are illustrated in Figure 5. Note that this definition counts not only the dangling linear chains but dangling branched chains among pendant chains. The expressions of this model for the present systems are given in the Appendix. In the beginning, the extent of reaction (p) for a functional group in trifunctional cross-linker is determined from eq A1 with the data of the weight fraction of extractable materials (W_{sol}), r, and the relative amounts of the reactants. Equations A5 and A6 with the calculated value of p yield the weight fractions of elastic and pendant chains (W_{el} and W_{pen}, respectively; $W_{el} + W_{pen} = 1$) in the network after removing extractable materials. Table 1 lists the calculated values of p, W_{el}, and W_{pen} for each sample. The critical extent of reaction (p_{gel}) to form an infinite network, evaluated from eq A4, is also tabulated in the table.

Parts a and b of Figure 6 display the comparison of E' at 30 °C with W_{el} for the networks via Schemes A and B, respectively. In both figures, one can recognize a very close relationship between E' and W_{el}: E' decreases with decreasing W_{el}; B-100 exhibits the larg-

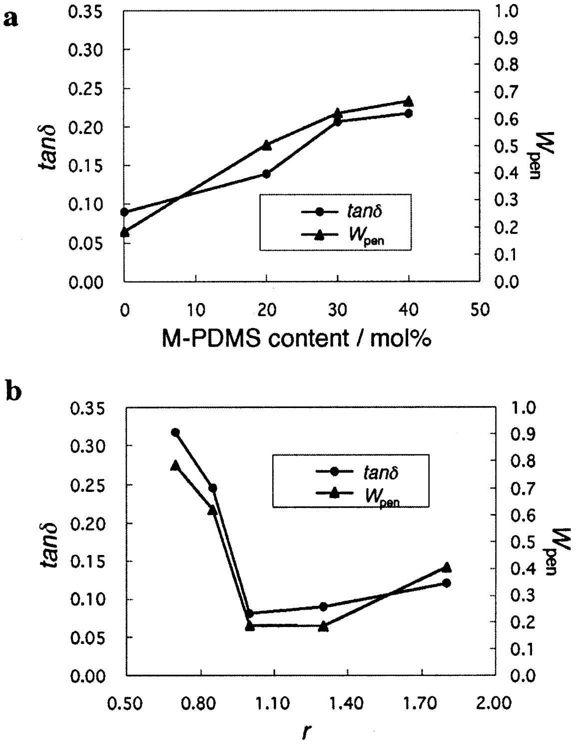

Figure 7. Comparison of the loss tangent (*tan δ*) at 30 °C with the weight fraction of pendant chains (W_{pen}) for (a) the PDMS networks via Scheme A, and (b) the PDMS networks via Scheme B.

est values of W_{el}, as well as E', among all the network samples. This relation accords with the principle of rubber elasticity that the network modulus is proportional to the number of elastically effective network chains.[15]

Parts a and b of Figure 7 show the comparison of tan δ at 30 °C with W_{pen} for the networks via Schemes A and B, respectively. It is clearly found in both figures that the magnitude of tan δ strongly correlates with W_{pen}: tan δ increases with increasing W_{pen}. Evidently, this result indicates that the damping of the networks mainly originates from the pendant chains. Also note that B-070 has the highest value for each of W_{pen} and tan δ among all the networks; the different networks with comparable values of W_{pen} have almost the same magnitudes of tan δ. These results suggest that the amount of pendant chain is the primary determinant for the damping of the network, independently of the methods for introducing pendant chains into the network. The molecular weights of M-PDMS and B-PDMS are comparable, which is a reason the difference in cross-linking method between Schemes A and B yields no significant difference in the topological network structures. The amount of pendant chain in B-070 with the highest tan δ is rather high (ca. 80 wt %), while that of elastic chain is only ca. 20 wt %. This indicates that most of network chains in B-070 belong to pendant chains. Despite the small value of W_{el}, p of B-070 is still higher than p_{gel}, which ensures the formation of an infinite network.

Thus, it has been clearly demonstrated that the introduction of pendant chains into rubbery network structure yields a pronounced increase in tan δ; the magnitudes of tan δ and E' of the irregular networks are almost constant over the wide range of temperature. An important key of the energy dissipation in the irregular networks is the fact that one end of each pendant chain is free to move. This enables the pendant chain to relax to a new equilibrium configuration after a sufficient time when the external strain is applied.[16] The pendant chains dissipate the energy introduced by the external deformation via this relaxation process. In contrast, elastic chains where both ends are fixed to infinite network store most of the deformation energy without dissipating it. The relaxation time of polymer chain strongly depends on the topological shape as well as the molecular size.[1,16] The pendant branched chains in the irregular networks have various shapes and a very broad size distribution, which yields a number of relaxation components with different relaxation times and strengths. The disentanglement processes of the entanglement couplings formed by different dangling chains also contribute to the viscoelastic relaxation of the systems. As a result, the irregular networks have a relatively flat relaxation spectrum over a wide time scale which leads to almost temperature- and frequency-independent tan δ with the considerable magnitudes.

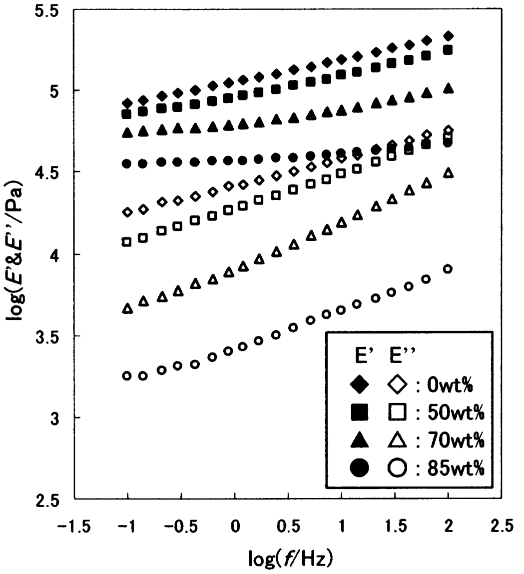

Figure 8. Frequency dependence of the storage and loss Young's moduli (E' and E'', respectively) of the swollen irregular PDMS networks B-070 with different solvent contents.

The presence of the viscoelastic relaxation in the irregular networks is clearly recognizable in the pronounced change in the dynamic viscoelasticity by dilution. Figure 8 displays the frequency dependence of E' and E'' for the swollen irregular networks B-070 with different solvent contents. Both moduli decrease with dilution as a result of a reduction in network concentration. Importantly, the pronounced dilution effect appears in the frequency dependence of E': as the dilution increases, the frequency dependence of E' becomes weaker. In particular, in the highly dilute state (85 wt % solvent), E' becomes almost independent of frequency. This results from the acceleration of the viscoelastic

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relaxation by dilution.[1] Qualitatively, the frequency dependence of the dynamic moduli in the highly swollen network corresponds to that in the dry network at the low-frequency region which is far below the lowest frequency in the experiment. Thus, the finite and positive frequency dependence of E' in the dry network is attributed to the visocoelastic relaxation of the irregular network structure. It is quite difficult to go further than these qualitative considerations, because the relaxation observed is caused by a lot of different relaxation modes in the irregularly branched structures. The relaxation mechanism of a single linear dangling chain provides us a basis to understand the damping mechanism of the irregular networks. The rheological study for the end-linked networks containing a small amount of linear dangling chain with narrow size distribution is now in progress.

The concept of damping based on the irregular network structure is applicable to more rubber systems other than PDMS. For example, if this concept is applied to isobutylene–isoprene rubber (conventionally called butyl rubber) which has originally good damping performance,[17] one may obtain a temperature- and frequency-insensitive damping elastomer with higher magnitude of tan δ relative to the irregular PDMS networks examined here.

Appendix

According to the Macosko-Miller model for nonlinear polymerization,[8,10,11] the weight fraction of extractable materials (W_{sol}) is related to the extent of reaction (p) for a functional group in trifunctional cross-linker (C3) and the relative amount of each reactant by

$$W_{sol} = W_{C3}\,\alpha^3 + W_{B2}\,\beta^2 + W_{B1}\,\beta \tag{A1}$$

where W_{C3}, W_{B2}, and W_{B1} are the weight fractions of cross-linker, bifunctional precursor (B2), and monofunctional precursor (B1), respectively, in the initial reactant mixture. The quantity α represents the probability for the event that no paths from a functional group in C3 leads to an infinite chain, in other words, all paths lead to a finite chain. The quantity β is defined for B molecules in the same way. The probabilities α and β are given by

$$\alpha = \frac{1 - rp^2 b_2}{rp^2 b_2} \tag{A2}$$

$$\beta = rp\left(\frac{1 - rp^2 b_2}{rp^2 b_2}\right) + 1 - rp \tag{A3}$$

where b_2 is the mole fraction of the vinyl groups in B2 among all the vinyl groups in a mixture of B1 and B2. From eq A1 with the W_{sol} data one can determine p for each sample. The critical extent of reaction for forming an infinite network (p_{gel}) is expressed by

$$p_{gel} = [(A_e - 1)(B_e - 1)r]^{-1/2} = (2b_2 r)^{-1/2} \tag{A4}$$

where A_e and B_e are the effective functionality of cross-linker and precursor molecules in the system, respectively, and are given by $A_e = 3$ and $B_e = 1 + b_2$ for our systems.

The weight fractions of elastic and pendant chains (W_{el} and W_{pen}, respectively) in the network after removing extractable materials are calculated by

$$W_{el} = \frac{W_{B2}(1-\beta)^2 + W_{A3}[(1-\alpha)^3 + 3(1-W_A)(1-\alpha)^2\alpha]}{1 - W_{sol}} \tag{A5}$$

$$W_{pen} = \frac{2W_{B2}\beta(1-\beta) + W_{B1}(1-\beta) + W_{A3}[3\alpha^2(1-\alpha) + 3\alpha(1-\alpha)^2 W_A]}{1 - W_{sol}} \tag{A6}$$

where W_A is the weight fraction of one arm part of the cross-linker in one cross-linker molecule.

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