

Reversible modulus reinforcement of end-linked polydimethylsiloxane ionomer networks

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Abstract

We report the mechanical behavior and swelling properties of covalently end-linked networks of polydimethylsiloxane with tailored number of monomers between side carboxyl groups and number of carboxyl groups along the chain. Imperfect carboxyl networks are reinforced by neutralization of the carboxyl groups with gallium ions via conversion of pendent chains into elastically active strands due to formation of intermolecular ionic cross-links. These networks swell in non-polar solvents to a similar degree as unmodified end-linked PDMS networks of comparable moduli. For unannealed samples, the modulus reinforcement is reversed by a polar THF:water solution that breaks the ionic cross-links. Neutralization with transition metal cations such as cobalt causes no initial reinforcement due to weak intra-molecular interactions. Reinforcement in annealed gallium, cobalt or carboxyl networks is not readily reversible.

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1. Introduction

There are various examples of covalently end-linked polymer networks in the literature [1–10]. End-linked polymer networks have been prepared from polydimethylsiloxane [1–6], polyethyleneglycol [7], polystyrene [8], poly(tetrahydrofuran) [9] and polybutadiene [10]. Although occasionally used commercially, end-linked networks serve primarily as ‘model’ polymer networks and have furthered the understanding of structure–property relations of polymer networks. End-linked networks described above as well as most cross-linked networks used in the industry usually have covalently cross-linked structures, but a rich literature also exists on elastomeric ionomers like carboxylated styrene–butadiene, acrylonitrile–butadiene and sulfonated ethylene–propylene–diene terpolymers [11–13] that have ionic cross-linking. Only a few studies [14–18] have been aimed at elastomeric polymers with ionic side groups that are also covalently cross-linked either at their ends or along the chain and that form in addition physical ionic cross-links. Such materials can leverage properties of ionomers and elastic covalently linked networks. The presence of both ionic and

covalent cross-links allows one to tune the properties of polymers especially tensile strength and elongation based on the relative proportions of the covalent cross-links and the ionic cross-links. Presence of ionic cross-links gave rise to greater stress-relaxation and a greater generation of heat in vulcanized carboxylated nitrile rubber elastomers [15]. It has also been observed that ionic cross-links imparted high tensile strength, permanent set, and hardness, while sulfur covalent cross-links introduced high flex crack resistance, elongation at break, and tear strength in the vulcanizates of carboxylated nitrile rubber [17]. The physical nature of the ionic-cross-links can also be used to induce changes as a function of temperature or solvent within a covalently cross-linked matrix that preserves the integrity of the sample.

We examine here covalently end-linked polydimethylsiloxane with carboxyl side groups along the backbone and focus on modulus reinforcement by neutralization of carboxylic groups with various salts. We interpret our results in terms of the diverse flow and mechanical properties of polydimethylsiloxane based ionomer melts as a function of the counter-ion and temperature that have been previously reported [19–21].

2. Experimental

2.1. Synthesis

The synthesis of vinyl terminated polydimethylsiloxane polymers with carboxyl groups (PDMS–COOH) at regular

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Table 1
Molar mass and polydispersity of OH-terminated PDMS precursors used for synthesis

Precursor chains	M_n (kg/mol)	M_{peak} (kg/mol)	PDI
7k	6.4	6.95	1.18
11ka	12.5	11.2	1.32
11kb	10.0	11.6	1.19
21k	19.6	20.7	1.32

intervals along the backbone has been described in detail elsewhere [19]. The intervals between carboxyl groups are determined by the molar mass of the precursor OH–PDMS–OH used in the synthesis. Table 1 shows the molar mass (M_n), the molar mass corresponding to the peak position of the gel permeation chromatograph (M_{peak}) and the polydispersity index (PDI) of the OH–PDMS–OH precursors. The precursor names are rounded-off values of M_{peak} . The average number of COOH groups per chain is calculated as $(M_{\text{peak}}/M_n \text{ of precursor PDMS}) - 1$. As an example of the nomenclature used in the paper 7k-I indicates 7k precursor chains, sample 1. Networks of PDMS–COOH were formed by end-linking with the tetrafunctional cross-linker tetrakis(dimethylsiloxy)silane in the presence of *cis*-dichlorobis(diethyl sulfide)platinum(II) in toluene. Based on a previous study for unmodified PDMS, the molar ratio r of silane hydrogens to vinyl groups was fixed at 1.7 for all networks considered here [1]. The networks were allowed to cure at 75 °C for 1 day.

The weight fraction of soluble material, w_{sol} and the equilibrium swelling ratio in toluene Q were determined using standard gravimetric procedures [22]. Network characteristics along with polymer molar masses and polydispersities are reported in Table 2. We note that these networks have large soluble fractions and are therefore quite imperfect. We initially suspected that the cause might be the acidic nature of the side carboxylic groups that affects the efficiency of the catalyst [3] and that some vinyl end groups are clipped off during the *t*-butyl deprotection step of the synthesis. More recent investigations have shown that relative humidity plays a dominant role in the poor cross-linking of these networks. Curing in a dry environment with less than 5% humidity

produced networks with a much higher modulus than reported in Table 2. For example, curing the sample 21k-II between the parallel plates of a rheometer equipped with an oven resulted in a network with a modulus of 0.54 vs. 0.156 MPa for a similar network cured in a normal desktop convection oven. The carboxyl groups along the polymer chain attract water to PDMS–COOH polymers. Water affects the efficiency of the catalyst causing poor cross-linking. However, as we will show later, using imperfect networks was in fact critical to demonstrate the reinforcement of these networks after neutralization via ionic interactions that converted pendent chains into elastic strands.

Networks in which the carboxyl groups are neutralized by either gallium or cobalt ions were prepared by swelling the PDMS–COOH networks in a toluene solution (20 times the mass of the network) of gallium(III) acetylacetonate or cobalt(III) acetylacetonate, respectively, for 3 days on a shaker. Three times excess salt was used. The swollen network is deswollen in a 60:40 toluene:methanol solution overnight. This solution also extracts the excess salt from the network. The low mol% of COOH groups prevents a quantification of the degree of conversion via UV, visible or FTIR spectroscopy. However, use of excess salt should ensure a high degree of conversion. PDMS–COOH networks neutralized with gallium are hereafter referred to as gallium networks and those neutralized with cobalt are referred to as cobalt networks.

2.2. Mechanical measurements

The Young's modulus E for all samples in the annealed or unannealed dry state was measured on a Perkin–Elmer 7e dynamic mechanical analyzer at room temperature in extension mode at small strains between 0.01 and 0.04.

2.3. X-ray scattering

X-ray scattering for gallium and cobalt networks was carried out on a Bruker-AXS general area detector diffraction system (GADDS) at a sample to detector distance of 15 cm.

Table 2
Molar mass and polydispersity of polymers used to prepare PDMS–COOH networks; soluble fraction, equilibrium swelling ratio in toluene and modulus at room temperature for PDMS–COOH networks

Sample	M_n (kg/mol)	M_{peak} (kg/mol)	PDI	w_{sol} (%)	Q	E_{COOH} (10^5 Pa)	Average number of COOH groups per chain
7k-I	61.8	96.1	1.85	22.4 ± 1.8	9.9 ± 0.4	1.17 ± 0.12	13
7k-II	55.3	68.3	1.74	19.5 ± 2.1	9.0 ± 0.5	1.12 ± 0.18	9
7k-III	37.0	46.9	1.85	14.1 ± 0.5	6.8 ± 0.2	1.81 ± 0.08	6
11ka-I	60.0	90.0	1.58	31.0 ± 0.7	14.0 ± 0.4	0.84 ± 0.26	7
11kb-I	52.7	68.3	1.52	34.6 ± 2.9	13.1 ± 0.8	0.70 ± 0.1	5
11kb-II	36.2	48.6	1.51	24.7 ± 0.6	9.65 ± 0.3	1.08 ± 0.18	3
21k-I	63.2	92.9	1.71	19.8 ± 0.7	9.4 ± 0.1	0.96 ± 0.18	4
21k-II	56.3	70.7	1.65	11.2 ± 0.6	7.3 ± 0.2	1.56 ± 0.20	2
21k-III	38.1	46.9	1.49	14.7 ± 0.8	7.7 ± 0.1	1.85 ± 0.09	1

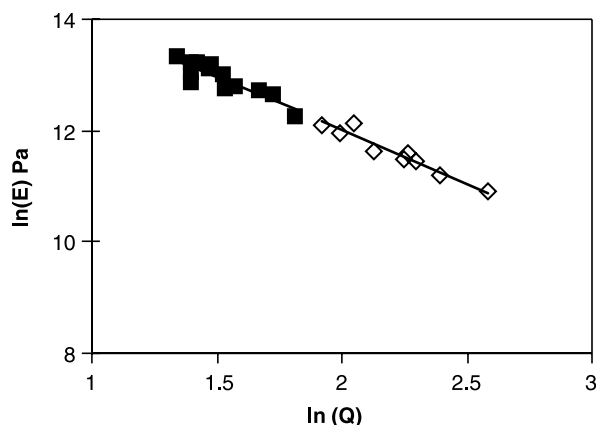


Fig. 1. Modulus vs. swelling ratio in toluene of PDMS–COOH networks; (\diamond) unannealed, (\blacksquare) annealed at 150 °C for 20 days.

3. Results and discussion

3.1. PDMS–COOH networks

We have recently reported that freshly precipitated melts of PDMS–COOH with a low mol% of COOH groups have similar rheological properties at temperatures up to 75 °C as an unmodified reference PDMS of comparable molar mass and PDI [19]. This is attributed to both the weak interactions between COOH groups and the low mol% leading to mostly intra-molecular interactions that convert to intermolecular interactions only very slowly at these temperatures [19]. Therefore, networks prepared by end-linking vinyl terminated PDMS–COOH at 75 °C for 1 day are not expected to show any enhancement in modulus as compared to unmodified PDMS networks. Fig. 1 shows the $\ln(E)$ vs. $\ln(Q)$ plot for these networks swollen in toluene (a non-polar solvent). The scaling law between E and Q is the same as reported for unmodified PDMS [2].

Melts of low mol% PDMS–COOH exposed to high temperatures, such as 150 °C for an extended period of time, form a critical gel and eventually a network [19]. Here, annealing PDMS–COOH networks to 150 °C for 20 days results in reinforcement in modulus that is presented in Table 3. This reinforcement can be attributed to conversion of pendent chains in our imperfect networks into elastically active chains via formation of inter-molecular hydrogen bonds that are

promoted at high temperatures. Fig. 1 also shows $\ln(E)$ vs. $\ln(Q)$ plots for these annealed samples. Linear fit to the data is identical to unannealed samples and indicates that in the presence of a non-polar solvent the physical cross-links are similar to permanent covalent cross-links. An optimal PDMS–COOH network with few defects would have elastic chains with carboxyl groups at regular intervals, but due to the covalent cross-link constraints, physical cross-links would be difficult to form and only a moderate enhancement in modulus may be possible.

3.2. Gallium networks

Fig. 2 shows that gallium networks in the dry state with greater than three COO^- groups per chain have a much higher modulus (2–3.5 times greater) after neutralization than that of the PDMS–COOH networks from which they are prepared. Gallium networks (21k-II, 21k-III) with too few COO^- groups per chain do not show any significant reinforcement in modulus with respect to the PDMS–COOH networks. To interpret these results, we refer to the rheology of melts of gallium ionomers with similar structure reported elsewhere [20,21]. Melts of low mol% gallium ionomers with 5–6 ions per chain freshly precipitated from a good/bad solvent mixture have storage moduli that are greater than the loss moduli and the complex viscosities show a power law behavior in the frequency range (0.01–100 rad/s) indicating the formation of a weak network. This physically cross-linked network forms due to ionic cross-links, which can be single gallium carboxylate quartets consisting of one gallium ion and three carboxylate ions belonging to different polymer chains, or ionic quartets aggregated due to electrostatic interactions. An inhomogeneous distribution of spherical aggregates with an average diameter of 10 nm was observed via scanning transmission electron microscopy (STEM) images [20]. X-ray scattering patterns indicate a low angle scattering upturn but no ionic peaks or shoulders.

Fig. 3(a) shows the X-ray scattering pattern of the gallium networks. A low angle scattering intensity (the inner halo) corresponding to scattering from gallium and a peak (the outer halo) that is also seen in pure PDMS and corresponds to siloxane chain segments are observed. These features are similar to those observed with gallium melts annealed at 150 °C for 5 days (shown in Fig. 3(b)), leading us to believe

Table 3
Moduli of unannealed and annealed carboxyl, cobalt and gallium networks

Sample	E_{COOH} (10^5 Pa)	E_{Cobalt} (10^5 Pa)	E_{Gallium} (10^5 Pa)	$E_{\text{Annealed-COOH}}$ (10^5 Pa)	$E_{\text{Annealed-cobalt}}$ (10^5 Pa)	$E_{\text{Annealed-gallium}}$ (10^5 Pa)
7k-I	1.17 ± 0.12	1.06 ± 0.29	3.39 ± 0.55	3.36 ± 0.83	5.48	6.54
7k-II	1.12 ± 0.18	1.44	4.04	6.76 ± 0.85	7.32	7.82
7k-III	1.81 ± 0.08	1.68 ± 0.11	3.36 ± 0.11	5.42 ± 0.31	5.37	5.72
11ka-I	0.84 ± 0.26	0.51	1.99	3.09	3.26	3.07
11kb-I	0.7 ± 0.1	0.63	2.34	3.55	–	4.17
11kb-II	1.08 ± 0.18	–	2.18	3.34	–	3.96
21k-I	0.96 ± 0.18	1.18	2.67 ± 0.29	4.42 ± 0.24	4.34	3.95
21k-II	1.56 ± 0.20	1.98 ± 0.03	2.07	5.41 ± 0.16	5.21	5.89
21k-III	1.85 ± 0.09	2.03	2.77	5.39 ± 0.39	6.42	6.87

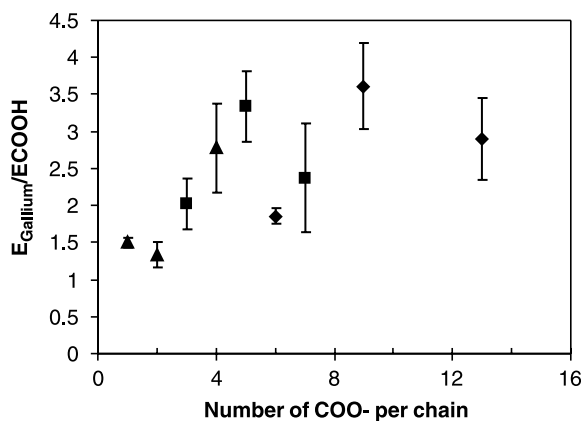


Fig. 2. Moduli of gallium networks relative to moduli of carboxyl networks from which they are prepared. (\blacktriangle) 21k networks, (\blacksquare) 11k networks, (\blacklozenge) 7k networks.

that similar ionic aggregates as observed in melts are being formed in these covalently end-linked networks. Single ionic quartets that act as tri-functional cross-links and ionic aggregates that act as multi-functional cross-links lead to the reinforcement in the modulus. Gallium has a valency of three and if there are fewer than three COO^- groups per chain, it is unlikely that sufficient conversion of carboxyl groups to gallium carboxylate occurs. The small reinforcement in modulus seen in 21k-II and 21k-III gallium networks (Table 3) is likely due to the very few COO^- groups per chain in these networks.

Fig. 4 shows the $\ln(E)$ vs. $\ln(Q)$ plot for gallium networks swollen in toluene. The scaling law between E and Q is almost the same as reported for unmodified PDMS (-2.0 for gallium networks vs. -1.9 for unmodified PDMS [2]). This similarity again indicates that in the presence of a non-polar solvent the physical cross-links are similar to permanent covalent cross-links and that the solvent interaction parameter χ of PDMS in toluene is unaffected by the presence of a low mol% of ions along the chain.

3.3. Cobalt networks

Table 3 shows that cobalt networks irrespective of the number of COO^- groups per chain or the number of monomers between ions, do not show any modulus enhancement relative to the PDMS-COOH network from which they were prepared. This stark contrast between cobalt networks and gallium networks can be explained on the basis of the different behavior of cobalt and gallium ionomer melts with similar number of COO^- groups per chain and number of monomers between ions. The cobalt ionomers were found to precipitate as melts that flow and exhibit a zero-shear viscosity [21] due to lack of aggregates (as evidenced via STEM) whereas a gel like behavior due to aggregate formation was observed in gallium ionomers immediately after precipitation [20]. Both the X-ray scattering pattern of cobalt networks and the X-ray scattering pattern of cobalt ionomer melts annealed to 150°C for 5 days (not shown) lack the inner halo and the corresponding upturn observed with the gallium ionomers. The lack of the inner halo

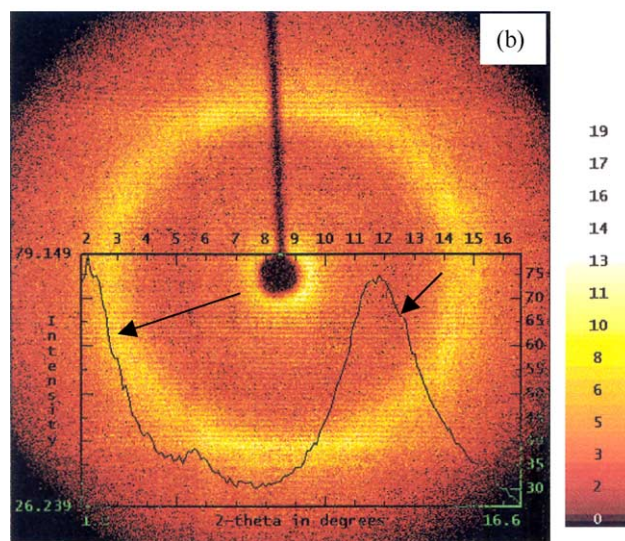
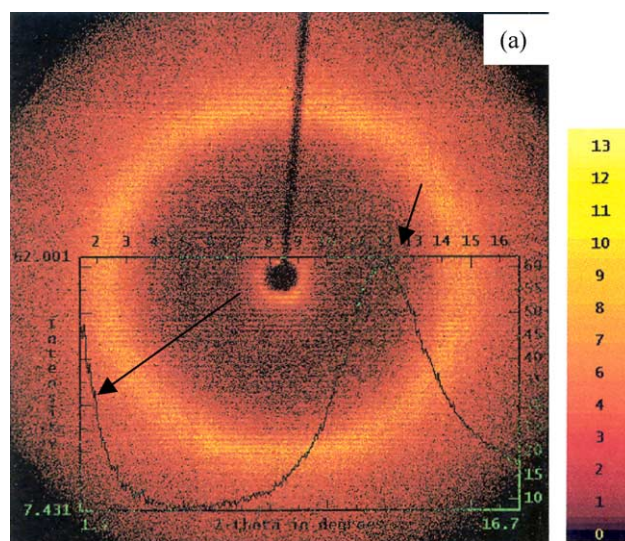


Fig. 3. (a) X-ray scattering pattern of 7k-III gallium network; (b) X-ray scattering pattern of a gallium melt of comparable structure after annealing at 150°C for 5 days.

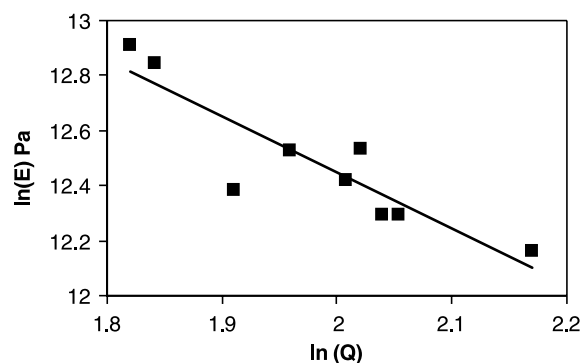


Fig. 4. Modulus vs. swelling ratio in toluene of gallium networks. Slope is -2.0 close to -1.9 for unmodified PDMS networks.

and upturn, coupled with a featureless STEM image was interpreted to indicate the absence of any aggregates in melts, the same may be assumed for the cobalt networks. Weak intra-molecular interactions at room temperature do not form additional cross-links to enhance the modulus of freshly prepared cobalt networks.

3.4. Reversibility of modulus reinforcement of non-annealed networks

Swelling a freshly prepared gallium network in a 60:40 THF:water solution allows water to migrate to the ionic cross-links and break the physical cross-linking. The modulus of the dried network following a THF:water swelling treatment is the same as the modulus of the same network prior to converting it to a gallium network. This demonstrates the reversibility in modulus enhancement that can be achieved with gallium networks. In contrast, swelling in a non-polar solvent like toluene does not affect the physical-cross-links and the modulus remains unaffected. On re-swelling a gallium network whose physical-cross-links have been broken, in a toluene solution of gallium acetylacetonate, and drying the network we recover a modulus that is only slightly less than what was originally obtained. We speculate that the slight decrease in modulus is due to the fact that water cannot be completely expelled from gallium networks swollen in THF:water by drying. Unexpelled water may prevent neutralization of some carboxyl groups with gallium, thereby giving a lower modulus reinforcement than the original reinforcement. Fig. 5 shows the stress–strain curve in the low strain (<0.04) region for 7k-I COOH network, 7k-I PDMS–COOH network converted to gallium, 7k-I gallium network after swelling in THF:water solution and drying and after reconstituting to a gallium network that demonstrates the statements made above.

3.5. Irreversibility of modulus reinforcement of annealed networks

Annealing gallium and cobalt networks at 150 °C for 10 days results in an increase in their moduli (refer to Table 3). This reinforcement can be attributed to conversion of pendent chains into elastic strands via formation of

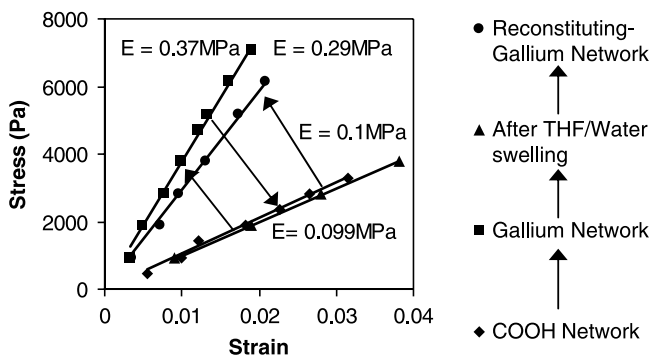


Fig. 5. Stress–strain curves at low strain for 7k-I COOH network, gallium network, gallium network after swelling in 60:40 THF:water and drying, and after reconstituting the gallium network.

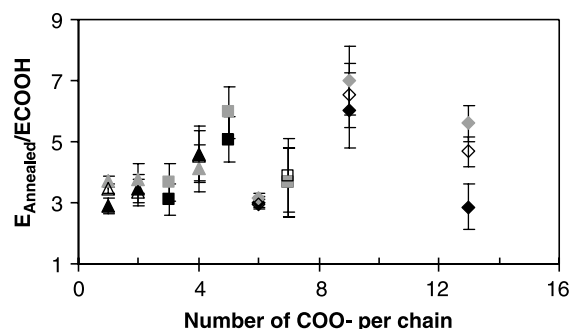


Fig. 6. Moduli of annealed networks relative to moduli of carboxyl networks from which they are prepared. Data of gallium networks are represented by unfilled symbols, those of COOH networks are in black, those of cobalt networks are in grey; (\blacktriangle) 21k networks, (\blacksquare) 11k networks, (\blacklozenge) 7k networks.

inter-molecular ionic quartets bonds that are promoted at high temperatures. Annealing melts of low mol% gallium and cobalt ionomers at 150 °C for 20 days also resulted in strong physically cross-linked networks [19,20]. Fig. 6 shows that within experimental error, the ratio of moduli of annealed networks relative to the PDMS–COOH networks from which they are prepared is the same irrespective of neutralization or the nature of the cation.

Because the PDMS–COOH networks are imperfect networks with a range of soluble fractions, they have different structural defects, and comparisons regarding increase in moduli either as a function of number of ions per chain or the number of monomers between ions cannot be made. Within the error bars, the maximum moduli seen with some networks are similar to the moduli of unmodified covalently end-linked PDMS networks of comparable molar mass of precursors. Since the modulus of the annealed samples represents the maximum modulus possible for a given PDMS–COOH imperfect network, comparisons of moduli as a function of number of ions per chain or number of monomers between ions can be made using the moduli of the corresponding annealed samples as reference points. Therefore, to compare moduli of unannealed gallium networks the ratio $(E_{\text{Gallium}} - E_{\text{COOH}}) / (E_{\text{Annealed-gallium}} - E_{\text{COOH}})$ normalizes the variations of soluble fractions across samples. This ratio represents an increase in modulus of gallium networks at room temperature relative to the increase in modulus in their annealed state. For networks

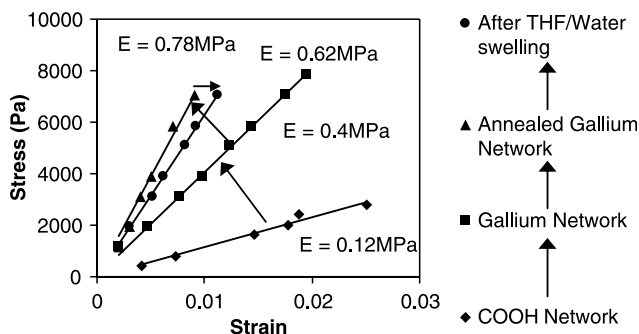


Fig. 7. Stress–strain curves at low strain for 7k-II COOH network, gallium network, gallium network after annealing and annealed gallium network after swelling in 60:40 THF:water and drying.

with greater than three COO^- groups per chain, this ratio is ~ 0.45 , implying 45% of maximum reinforcement possible happens immediately at room temperature irrespective of the number of monomers between ions.

Swelling gallium or cobalt or carboxyl networks that have been annealed at 150 °C for 10–20 days in a 60:40 THF:water solution decreases their moduli by only 20–30%. Thus the moduli-reinforcement in annealed samples is not as readily reversible. This is demonstrated for a gallium network in Fig. 7.

4. Conclusions

We have synthesized covalently end-linked networks of polydimethylsiloxane with tailored number of monomers between carboxyl side groups and number of carboxyl side groups along the chain. Neutralization of the carboxyl groups with gallium ions causes moduli reinforcement of imperfect PDMS networks via conversion of pendent chains into elastically active strands due to formation of inter-molecular ionic cross-links. In the presence of non-polar solvents, these ionic cross-links act as permanent cross-links, swelling the networks to a similar degree as unmodified end-linked PDMS networks of comparable moduli. For unannealed samples, the modulus reinforcement is reversed by a polar THF:water solution that breaks the ionic cross-links. Freshly prepared cobalt networks do not show any reinforcement because of weak intra-molecular interactions compared to gallium networks. Irreversible reinforcement is brought about by annealing gallium, cobalt or carboxyl networks.

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