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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 inter-molecular 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.

Keywords: Polydimethylsiloxane; Ionomers; Elastomers

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_{peak}/M_n 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 de-swollen 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