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ORIGINAL CONTRIBUTION

Modulus-switching viscoelasticity of electrorheological networks

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Abstract To form an electrorheological network (ERN), semiconducting nanoparticles were embedded in a polymer that was cross-linked to restrict particle motion. The microstructure ranged from random to aligned, depending on the degree of field-induced particle alignment during chemical network formation. We investigated in detail the softness effects of the matrix, having a relatively low storage modulus, on the dynamic rheological behavior of the ERN and analyzed its anisotropy. The anisotropy of the microstructure was probed rheologically with the modes of small-amplitude oscillatory shear (loading perpendicular to the field direction) and compression (loading in the field direction). The storage shear modulus was found to be a function of the applied electric field, particle volume fraction, and the pre-alignment electric field strength during the cross-linking reaction of the matrix, which governs the thickness of particle columns and intercolumn distance. Nonlinear behavior at small strain (below 0.1%) was conspicuous; this nonlinear viscoelasticity was accompanied by only a limited deformation of ordered connectivity. Throughout this study, we fabricated the ERN with the highly controllable modulus-switching effect acting in a shear-mode operation. Managing this anisotropy of an ERN by the electrical and chemical process is important in the design of smart materials that will provide improved stability and mechanical strength compared with fluid-type electrorheological materials and faster response time compared with that of conventional charged polymer gel.

Keywords Electrorheological network · Cross-linking · Switching modulus · Polymer gel · Nonlinearity

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Introduction

Electric-field responsive polymer network composites consist of a cross-linked matrix in which semiconducting particles (electrorheological [ER] particles) are embedded and partially aligned to form particle strings or columns. Such electrorheological networks (ERNs), as solid analogs of ER suspensions, have potential as novel materials for applications that require switchable modulus, short switching time, increased strength, and stable structure. The tunable mechanical resistance (modulus) of ERNs makes them attractive materials for damping devices that can adapt to rapidly changing environments (e.g., automotive applications, high-speed damping of sandwich beams for building applications, microrobotics, and compact/hard disk

drives), while the magnetic analogs of such devices are suitable for automotive bushings and engine mounts (Davis 1999). The modulus change of an ERN is reversible for back-and-forth switching. Strength and modulus will be maximized, especially under shear/compressive deformation, along the direction of the electric field. Cross-linking of the matrix suppresses any gravitational settling of ER particles, thereby overcoming the major limitation of instability with elapsed time. Another advantage of ERNs is the relative ease of fabricating specimens of a required shape and in sealing the device effectively, thereby overcoming another major limitation of ER suspensions that has prevented their widespread application.

Only a limited number of experimental studies have considered the rheology of ERNs. A field-sensitive modulus change in ERNs, as first reported in the experiments of Shiga et al. (1993a), results in an increase in storage modulus when the particles are prestructured to form thick columns. The authors also found that the increment of the compression modulus is much larger than that of the shear modulus (Shiga et al. 1993b). When strain is applied to an ERN, displacement of the particles from their original state requires additional energy, as the initial structure represents a minimum in the electrostatic free energy (in cases of pre-aligned structure). The switching modulus as a function of the electric field relies on a stable alignment structure, which is achieved by first aligning the particles with an electric field and then locking them into position by cross-linking of the surrounding matrix. The particle alignment state, including the thickness of particle columns, has a primary effect on the field-dependent shear strength. Martin and Anderson (1998) modeled the field-induced stress of ERNs using the finite element method. The stress in the uniaxially structured composite was predicted to be at least ten times larger than that in a composite with random dispersion of particles. Munoz and Jolly (2000) summarized the rheological characteristics of electric and magnetic field-responsive composites for fluid as well as solid states. Liu and Shaw (2001) compared electrorheological experiments on dielectric particle-filled elastomers with theoretical predictions for Maxwell–Wagner dispersion, showing that particle alignment significantly enhances both the dielectric polarizability and the shear modulus of composites.

As an important design parameter of ERNs, the connectivity of pearl-like particulate chains, as well as that of the polymer matrix network, strongly affects the rheological properties. Pearl-like particulate connectivity patterns have been studied for polymer composites filled with ceramic powder (Randall et al. 1993), which also induces anisotropic material properties such as reflective index, conductivity, and mechanical properties. For ER fluids, the one-dimensional ordering transition of particles in the fluid matrix results in a growth of connectivity that can be treated as a physical gelation process and monitored by rheology (Chin and Winter 2002; Hiamtup et al. 2006). This provides a tool for tailoring the alignment and locking intermediate states of columnar structures into model ERNs. The model ERNs will be developed in the framework of chemical gelation with random three-dimensional connectivity. Accordingly, the network connectivity can be adjusted by controlling the chemical reaction during the cross-linking.

As a primary objective of this paper, we focus on the precise rheological (steady and viscoelastic) probing of an ERN designed for strong electric field-induced switching behavior. A new approach in our report includes an evaluation of the impact of the applied electric field during the chemical cross-linking of a polydimethylsiloxane (PDMS) matrix, yielding a qualitative analysis of the effect of the "softness" of the matrix on the ERN's switching effect, as well as insight into the microstructure of an anisotropic ERN. Moreover, precise rheological probing of the ERN revealed the transition from linear to nonlinear viscoelasticity at very small strain, as is observed for fluids, whereas other reports only refer to linear behavior. The degree of particle ordering is influenced by both the field strength for alignment and elasticity (controlled by cross-linking; off-balancing the stoichiometric ratio of the cross-linker in the end-link reaction of vinyl-terminated PDMS prepolymer), which were found to be critical factors in explaining the results of rheological probing (modulus-switching effect at various modes).

To qualitatively analyze the rheological characteristics of ERNs with various ordering states, we prepared the colloidal particles of semiconducting polyaniline (PANI) dispersed in a model PDMS prepolymer. Upon formation of the three-dimensional network of the matrix (as monitored by time-resolved rheometry; Mours and Winter 1994), the frequency and strain dependence of the ERN samples were characterized to address the fundamental rheological properties in terms of the effects of particle order, elasticity of the matrix, and particle volume fraction, as well as their interplay. Viscoelastic parameters in shear and compression, as well as waveforms of torque, were analyzed and explained in relation to the structural anisotropy probed by the direct observation of an aligned morphology.

Understanding the governing mechanism of field-induced alignment of particles with various shapes and sizes will help to achieve the controlled "locking" of

the configuration for various applications, such as the design of ERN-based fixtures for controllable surface friction and adhesive properties (Kakinuma et al. 2007). Despite the slightly different mechanism of ERN formation with dielectrophoresis, the alignment process for ERNs could also be applied for the fabrication of sorted, organized, and aligned nanowires (when at least one dimension of the object is microscale) that are attractive for memory, chemical sensors, high-frequency mechanical resonator, and photonic components with enhanced performance (Rogers 2008; Jamshidi et al. 2008).

Experimental

Particles for ERNs

Semiconducting PANI particles, an intrinsic polarizing material without any additive such as water, were synthesized using colloidal silica as a steric stabilizer (Stejskal et al. 1996). Aniline hydrochloride and ammonium persulfate (APS, $(NH_4)_2S_2O_8$) were purchased from Aldrich. Aniline hydrochloride was dispersed in water, and colloidal silica (Ludox AS-40, E.I. DuPont, distributed by Aldrich; 40 wt.% SiO_2 aqueous suspension; mean particle diameter, 22 nm) was added. The reaction mixture contained 7.77 g (0.06 mol) of aniline hydrochloride and 57.9 ml of Ludox AS-40 (30 g of silica particles, calculated) in 182 ml water. The solution was cooled (~5°C) and 60 ml aqueous solution of 1 M ammonium persulfate was added dropwise. The molar ratio between the ammonium persulfate and aniline was set to 1.0. The reaction mixture was stirred for 24 h. The polyaniline dispersed in an acidic aqueous medium was washed with water and centrifuged several times to the polyaniline dispersion from the unreacted aniline and silica particles. The mixture was treated with 1 vol.% NH_4OH aqueous solution to set conductivity to within a semiconducting range (Gow and Zukoski 1990), yielding an electrical conductivity in the order of 10^{-9} S/m (two-probe method). Scanning electron microscopy of the prepared PANI particles (Fig. 1) revealed a narrow size distribution, with particle diameters in the range 0.2–0.3 μm, much smaller than the diameters for PANI particles prepared without a steric stabilizer (Chin and Park 2001).

ERN preparation: PDMS matrix cross-linking and particle alignment

α,ω-divinylterminated polydimethylsiloxane of $M_w = 10^4$ was used as a polymeric matrix ($\eta = 0.5$ Pa·s).

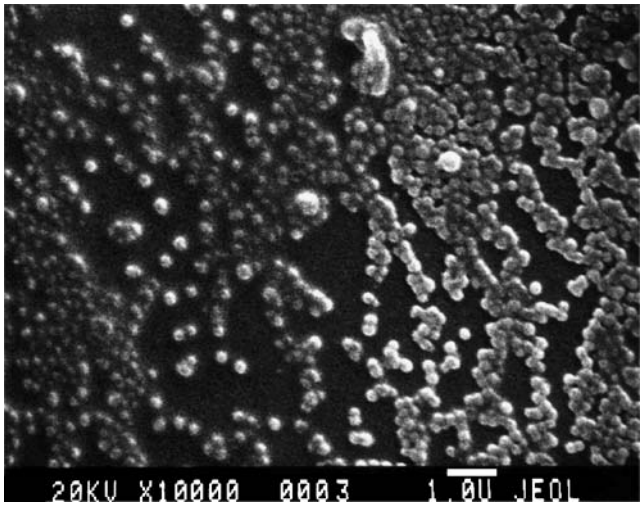

Fig. 1 Scanning electron microscopy image of PANI particles stabilized by nanosilica (Ludox AS-40). Scale is 1.0 μm

PDMS and cross-linker were purchased from United Chemical Technologies Inc. (Bristol, PA, USA). A specified amount of PANI particles (10, 20, or 30 wt.%) was added to PDMS, which was then stirred for at least 48 h to obtain a fine dispersion. The vinyl-terminated PDMS was end-linked with a four-functional cross-linker, tetrakis-(dimethyl-siloxy) silane. The platinum catalyst of the cross-linking reaction, *cis*-dichlorobis (diethylsulfide) platinum (II), was applied in a 1.8×10^{-3} molar solution in toluene. A mixture of PANI and PDMS with specified particle weight fraction was combined with 100 μl of the catalyst solution. The mixture was stirred for 30 min at room temperature and then degassed for 5 min using a vacuum pump. The stoichiometrically required amount of cross-linker was added and the mixture was stirred for another 20 min, including 2 min for degassing under vacuum. The mixture was stored in liquid nitrogen to effectively stop the cross-linking reaction. If a sample is required for an experiment, it is thawed for 5 min at room temperature. To control the elasticity (off-field modulus) of the matrix, the stoichiometric ratio (r) was set to 0.5 for "soft" and 1.0 for "hard". Here, the stoichiometric ratio is defined as the ratio of silane to vinyl group (Chambon and Winter 1987). PDMS networks with imperfections ($r = 0.5$) have a lower number of elastically active strands and show a lower modulus. Direct current (DC) electric fields with various strengths (250, 1,000, and 2,000 V/mm) were applied to pre-align the PANI particles in PDMS precursor before the cross-linking reaction. The field maintained during the entire reaction time was monitored by time-resolved rheometry. ERNs with randomly distributed particles were also prepared without applying the field during the reaction.

Experimental apparatus for pre-alignment and rheometry

Parallel plates of 25 mm diameter in a rotational rheometer (ARES, Rheometric Scientific Inc.) were chosen for both aligning the ERN and rheological measurements. Rigid insulating spacers were placed at the foot of both fixtures, connected to a transducer and actuator. A high-voltage power supply (Model 215, Bertan) provided the DC electric field (see Fig. 2 for the layout). At various electric field strengths, small-amplitude oscillatory shear (for frequency and strain sweep tests) was applied to the ERN samples after the cross-linking reaction had come to completion. A similar set of insulating fixtures was constructed for a squeezing rheometer (RLR, Rheometrics Linear Rheometer) with Labview (National Instruments) for data processing.

Microscopic observations

The morphology of particle strings and columns in aligned *ERN* samples was observed using an optical microscope (Olympus BX-60, magnification ×50). Each specimen was prepared containing 2.0 wt.% PANI particles and PDMS, which was cross-linked at $r = 1.0$ and 0.5. To view the morphology in cross section, the dilute composite was cut by immersion in liquid nitrogen. Top view and cross-section images were taken of specimens prepared at various pre-aligning electric field strengths.

Rheological measurements and data collection

The samples were subjected to small-amplitude oscillations with 0.5% strain. The resulting stress was decomposed into in-phase and out-of-phase contributions related to the storage (G') and loss moduli (G''), respectively. The frequency dependence of dynamic shear moduli, $G'(\omega)$ and $G''(\omega)$, was measured while applying electric fields of varying strength. To confirm the sinusoidal waveform of strain and torque, data from experiments performed at 10 Hz and several stain amplitudes (i.e., 0.5%, 1.0%, 5.0%) were collected through the output channel of the ARES.

Results and discussion

Microstructural evolution: coarsening during the sample preparation

For ERNs with different degrees of particle order, the use of an optical microscope enables direct observations

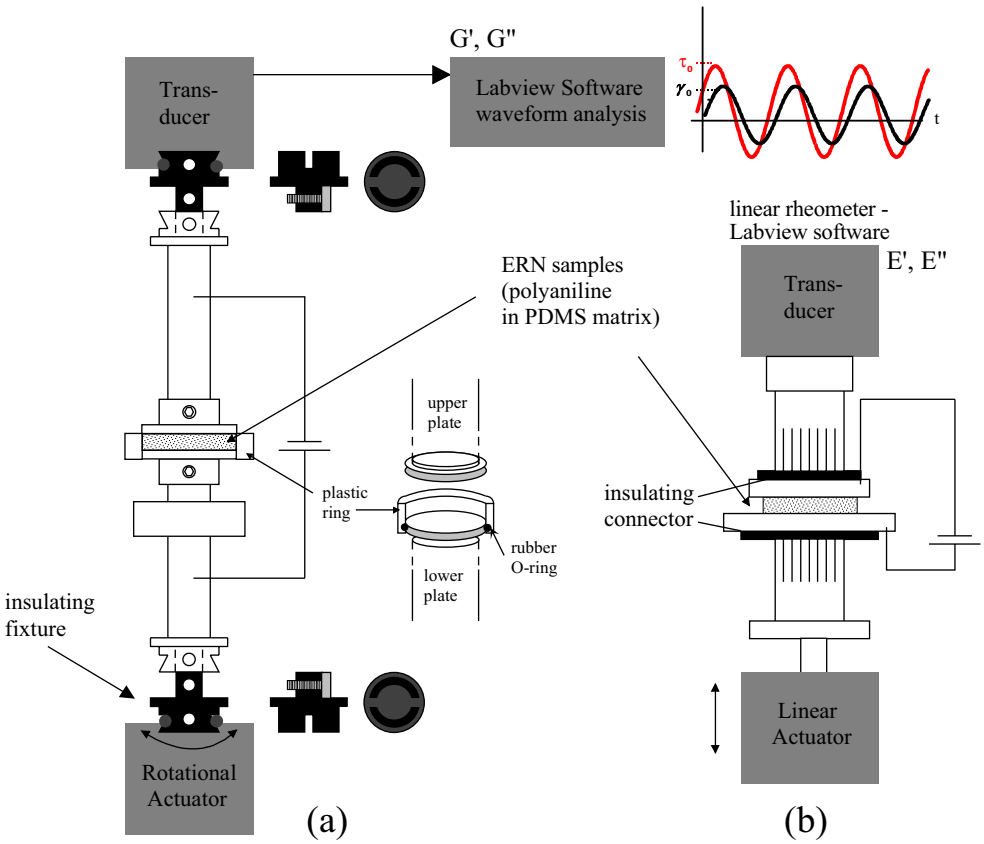

Fig. 2 Schematic diagram of the experimental apparatus **a** used for shear experiments with modified a fixture of 25-mm parallel plates and **b** used for compression experiments

of microstructural patterns both perpendicular and parallel to the field-induced ordering direction. The experiments started with a 2 wt.% PANI/PDMS ERN cross-linked at $r = 1.0$. In Fig. 3, images from the side (cross-section) and along the field direction (top view) show the effect of increased field strength during sample preparation. No field was applied during cross-linking of the sample (Fig. 3a); however, even in the case of random dispersion, the individual nanosized particles tended to aggregate in the PDMS matrix. When a 250 V/mm electric field was applied during the cross-linking reaction, the particles became aggregated into strings (Fig. 3b). The distribution of columns is not uniform at this field strength. As seen in the cross-section view, complete particle chain formation is not possible. As the field strength increased to 1,000 V/mm (Fig. 3c), string-like structures had attracting interaction one another and eventually merged into thick, closely packed columns rather than remaining as a dispersed set of strings (Halsey 1992). The coarsening of individual strings is even more pronounced at higher field strengths (Fig. 3d), generally showing the size distribution of thickness for multiparticle chains (see the top-view images in Fig. 3c, d).

Pre-aligning occurs when the matrix is still in the liquid state. Much information is available on ordering and coarsening in such a liquid matrix before cross-linking. The field-induced structure (chains of particles and columns for which adjacent particle chains are merged together) is far from perfectly ordered (Fig. 3). The structuring is not driven solely by the electric field (short-range nature of interactions) but by hydrodynamic and Brownian forces. During coarsening, thermally fluctuating columns can either repel or attract one another, depending on the column configuration (Halsey 1992). The timescale of forming the coarsening structure is much longer than that for the original column (chain-like string). In experiments on a system with 0.6 mm diameter columns composed of 20–40 μm sized particles, Chen et al. (1992) observed a coarsening timescale of several minutes. Park and Robertson (1998) confirmed this observation using 10 wt.% glass spheres of diameter 25 μm. For the first 10 s, they found a rapid increase in column diameter up to 300–400 μm, followed by continued increase in column diameter at a much slower rate (coarsening).

For ER particles in a liquid matrix, structure formation induced by the electric field was not observed until λ became larger than unity, where λ is defined as the ratio of the electrostatic (dipolar) force to the Brownian force. A liquid-to-solid transition occurred at a field strength of about 100 V/mm (Chin and Winter 2002) expressed rheologically by the appearance of a gel point (from the slope of tan δ). The transition was attributed to the first appearance of sample-spanning columns of ER particles; however, the column structure was imperfect. Even at higher electric fields ($E_0 = 250$ V/mm), a field-induced column formed rather incompletely. This

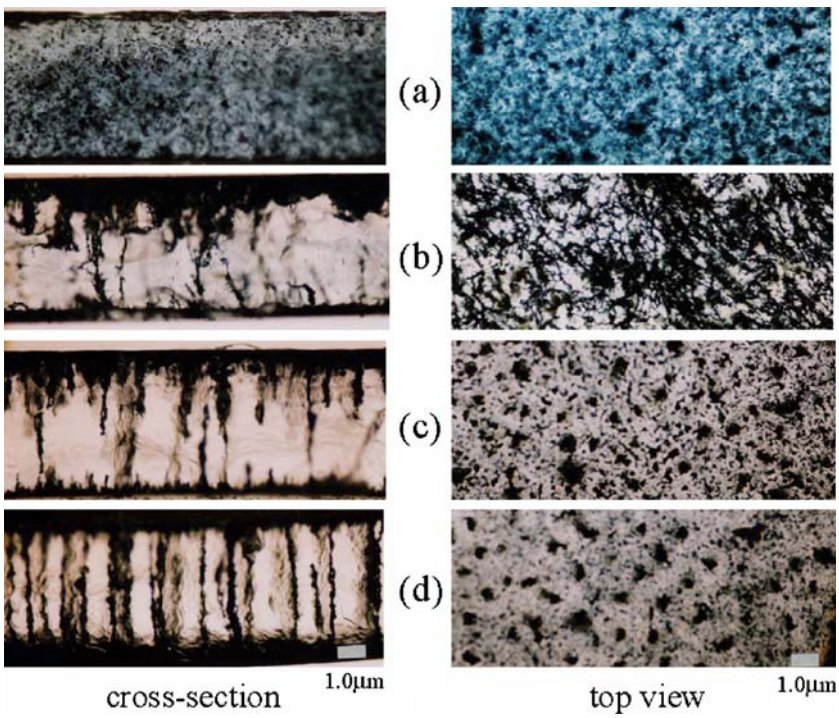

Fig. 3 Microstructures of cross-linked ERN ($r = 1.0$) with 2% PANI particles for **a** random ($E_0 = 0$), **b** $E_0 = 250$ V/mm, **c** $E_0 = 1{,}000$ V/mm, and **d** $E_0 = 2{,}000$ V/mm. Scale is 1.0 μm

finding can be explained by the competition between electrostatic (dipole) interactions and electrophoretic movement. Electrophoretic movement due to the DC electric field, resulting in the deposition of particles on the electrode, was inevitable for the entire range of field strength. Despite the electrophoretic mobility, structural ordering due to particle–particle interactions resulted in sample-spanning columns when a higher electric field strength was applied (see Fig. 3). Figure 3b shows the prevalent deposition of particles on the electrodes, whereas columns are buckled and broken. The top-view morphology shows the complicated bridging structure that is possible between columns. Figure 3c, d describes the coarsening effect of individual more complete columns.

In situ cross-linking of PDMS with field-induced alignment

The formation of the PDMS network was monitored by time-resolved rheometry (Mours and Winter 1994). The addition of PANI filler has a pronounced effect on the cross-linking process. Figure 4a shows the evolution of dynamic moduli at $r = 0.5$ for three different frequencies (PDMS not filled with PANI). The gel point, characterized by frequency-independent tan δ (Chambon and Winter 1987), was found to be around 1,000 s. After 6,500 s, both G' and G'' reach the equilibrium value ($G' \sim 10^4$ Pa at 100 rad/s). With 20 wt.% PANI filler in a reacting PDMS sample, the cross-linking was slowed significantly, with G' and G'' reaching equilibrium after 25,000 s (Fig. 4b). We consider that impurities on the surface of PANI, such as residual moisture, reduce the activity of the Pt catalyst, leading to a reduction in the rate of end-linking of vinyl-terminated PDMS prepolymer. Because the cross-linking process shown in Fig. 4b was probed without an electric field, both storage and loss moduli are not significantly higher than PDMS without PANI particles (Fig. 4a). The application of a field during the reaction would prevent the rheological probing of chemical gelation because of electrically induced connectivity.

Rheological probing: frequency-dependent shear moduli showing switching by the electric field

We measured the dynamic moduli of the ERN as a function of the strain frequency and applied field strength. Figure 5 shows the frequency-dependent storage moduli for concentrations of 10, 20, and 30 wt.% PANI in soft PDMS ($r = 0.5$). The electric field strength for pre-alignment (E_0) was 1,000 V/mm. Be-

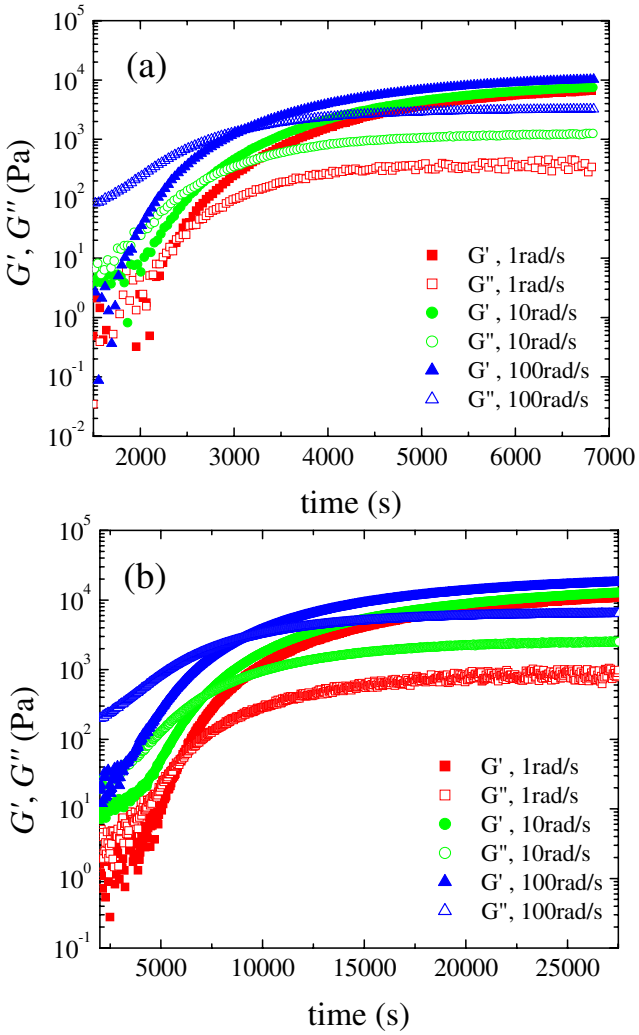

Fig. 4 Evolution of dynamic moduli during cross-linking of ERN without pre-alignment; data are shown at three different frequencies and strain amplitude of 0.5%. **a** PDMS $r = 0.5$ and **b** PDMS $r = 0.5$ with 20 wt.% PANI

cause the particles were locked in an elastic network of PDMS gel, the dynamic moduli exhibited the normal behavior of filled elastomers, which strongly depends on the particle concentration. As the strength of the electric field was increased to 3,000 V/mm, we observed a significant increase in the storage modulus (by up to an order of magnitude) at 30 wt.% particle loading. At $E_0 = 1{,}000$ V/mm, an increase in shear modulus (from 1.2×10^4 to 8.2×10^4 Pa) was observed in an attainable field strength range.

In contrast, the effect of switching is relatively minor in the system with lower particle fraction. Unlike the storage moduli, G'' of an ERN with low fraction (10 wt.%) was found to be almost insensitive to field strength. Moreover, the magnitude of G'' in the electric

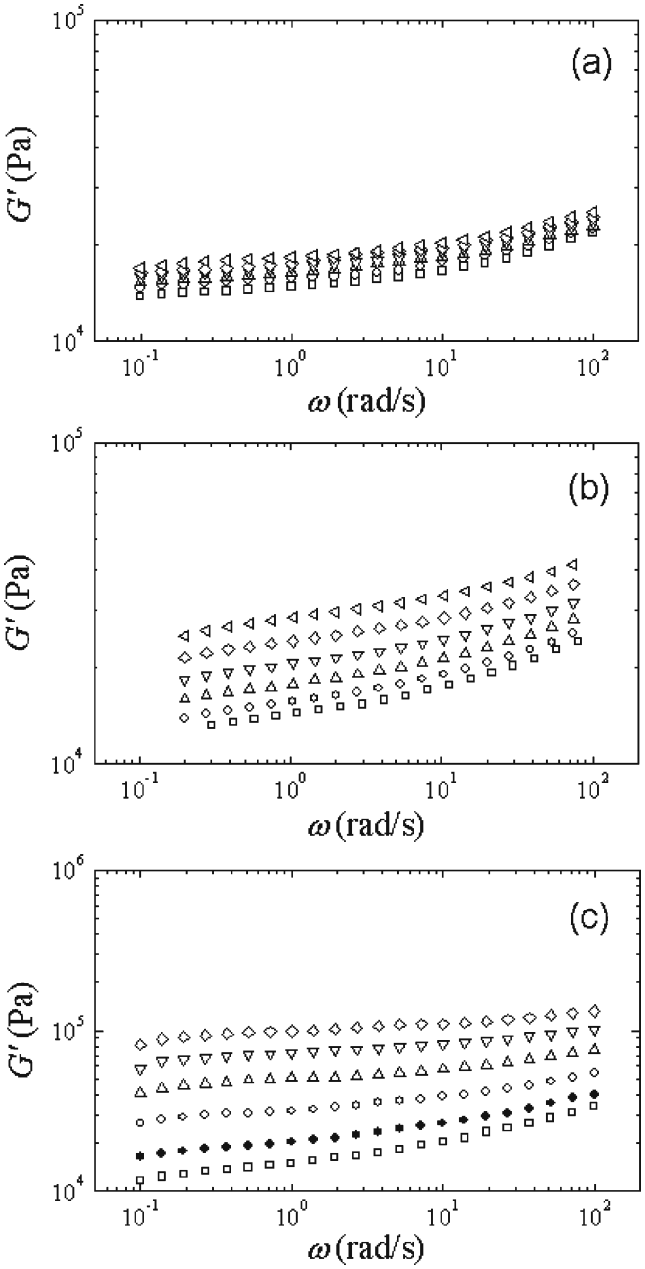

Fig. 5 Frequency dependence of storage modulus, switching as a function of electric field. ERNs are based on a PDMS matrix at $r = 0.5$ for **a** 10 wt.% PANI, **b** 20 wt.%, and **c** 30 wt.%. The strain amplitude is 0.5%. $E = 0$ (*open square*), 500 V/mm (*closed circle*), 1,000 V/mm (*open circle*), 1,500 V/mm (*open triangle*), 2,000 V/mm (*open inverted triangle*), 2,500 V/mm (*open left triangle*), 3,000 V/mm (*open diamond*)

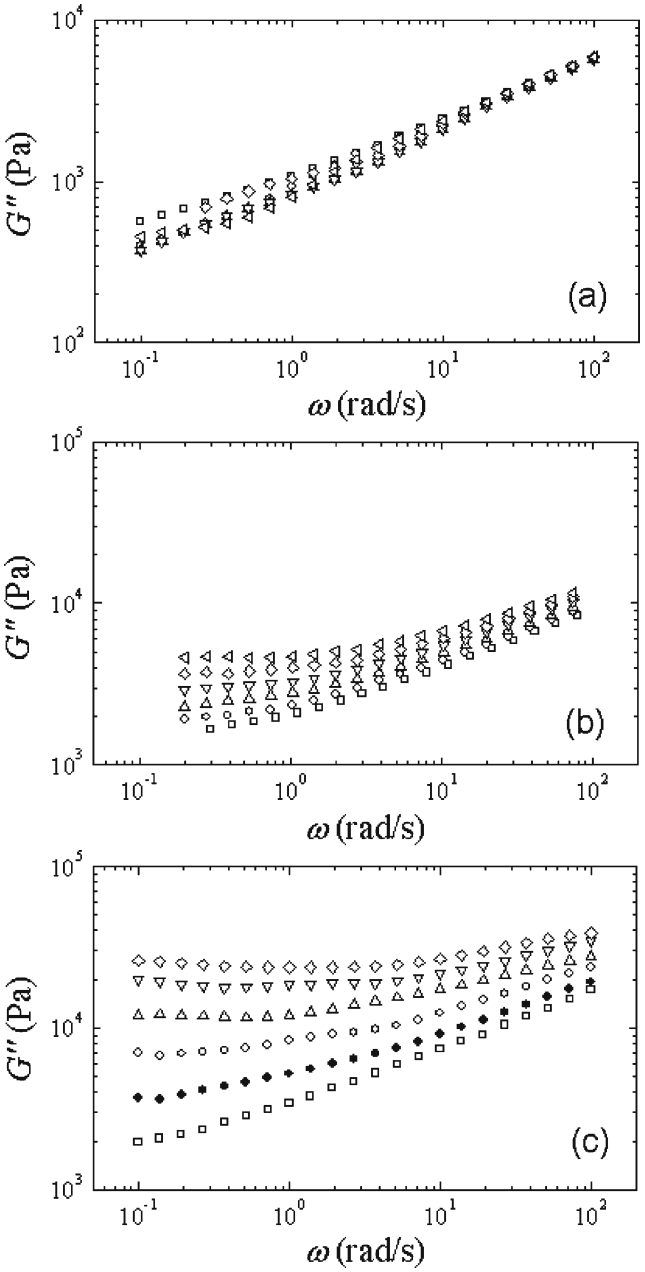

Fig. 6 Frequency dependence of loss modulus, switching as a function of electric field. ERNs are based on a PDMS matrix at $r = 0.5$ for **a** 10 wt.% PANI, **b** 20 wt.%, and **c** 30 wt.%. The strain amplitude is 0.5%. $E = 0$ (*open square*), 500 V/mm (*closed circle*), 1,000 V/mm (*open circle*), 1,500 V/mm (*open triangle*), 2,000 V/mm (*open inverted triangle*), 2,500 V/mm (*open left triangle*), 3,000 V/mm (*open diamond*)

field was even smaller than the off-field loss modulus (Fig. 6a). Such negative effects can be seen in the electrophoretic movement of particles in suspension at low concentrations (Pavlinek et al. 2000); however, this does not apply in the present case because the particles cannot move far enough to accumulate at the surface electrode. G'' also begins to be switched by the application of an electric field for 20 and 30 wt.% samples, although the increment was relatively small compared with the change in the storage modulus.

Pre-alignment has a significant impact on the modulus of switching (see Fig. 7). The large increase in G' and

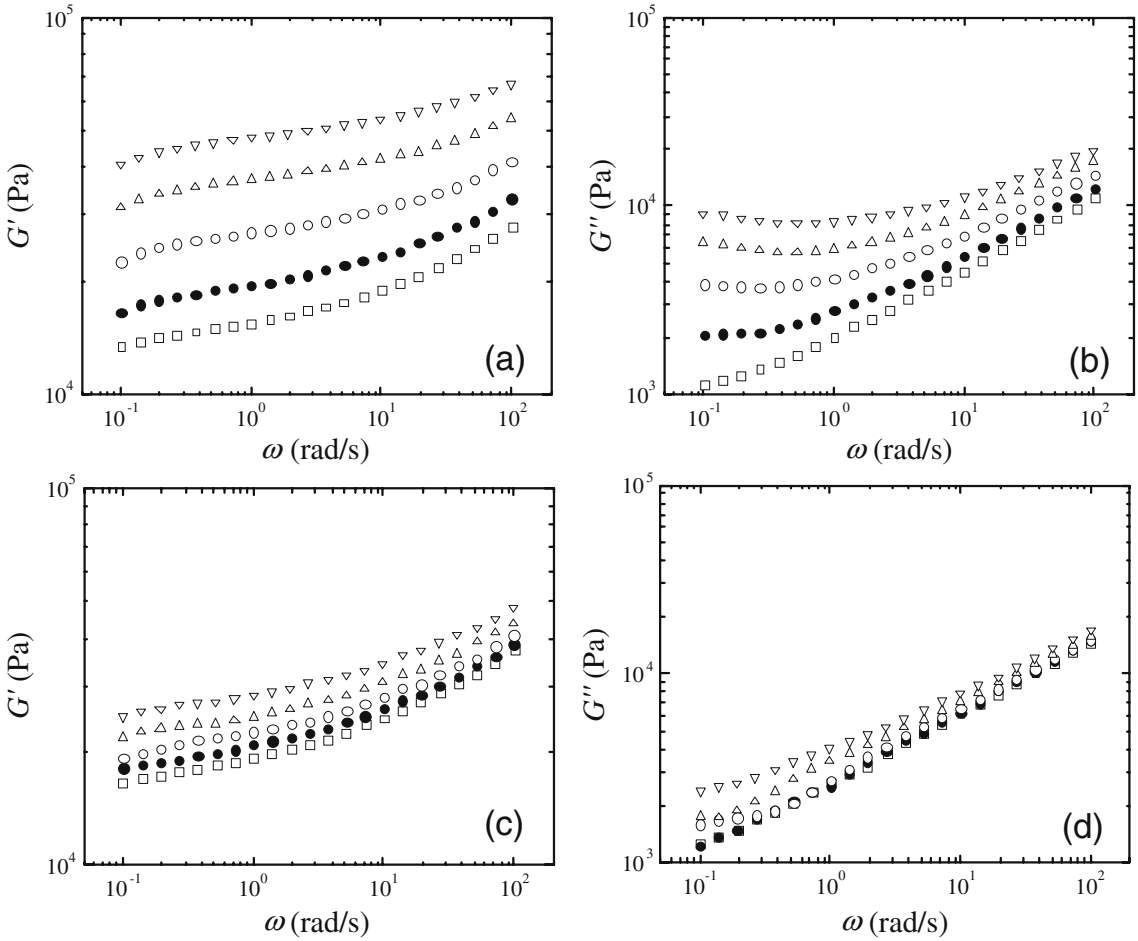

Fig. 7 Effect of pre-alignment on the frequency-dependent dynamic moduli, switching as a function of applied electric field $E =$ 0–2,000 V/mm. PANI of 30 wt.% in PDMS $r = 0.5$ for **a** storage modulus of pre-aligned ERN at $E_0 = 2{,}000$ V/mm, **b** loss modulus of pre-aligned ERN at $E_0 = 2{,}000$ V/mm, **c** storage modulus of random ERN, and **d** loss modulus of random. $E = 0$ (*open square*), 500 kV/mm (*closed circle*), 1,000 V/mm (*open circle*), 1,500 V/mm (*open triangle*), 2,000 V/mm (*open inverted triangle*)

G'', which is the switching effect of pre-aligned ERN (Fig. 7a, b), is not found in random ERNs (Fig. 7c, d). When preparing the samples for our experiments, the timescale of column formation was much shorter than the time required for cross-linking of the PDMS matrix. The cross-linking time was observed as >6,000 s for particle-free PDMS and >20,000 s for 20 wt.% ERN. Column formation and coarsening of PANI particles in PDMS are regarded as being in a steady state when locked in by the PDMS network. It is clear that a soft ERN and a particle fraction of at least 20 wt.% are required for effective shear modulus switching. Although the morphology of coarsening columns at $E_0 = 1{,}000$ V/mm is similar to those at $E_0 = 2{,}000$ V/mm (as shown in Fig. 3c, d), their switching properties showed contrasting electric field dependence.

The relative change during the modulus switching effect, $\Delta G = G - G_{E=0}$, increases with pre-alignment field strength E_0 (Fig. 8). For a soft ERN containing 20 wt.% PANI particles, samples with the highest pre-alignment field E_0 also showed the largest switching effect on storage shear moduli ($\Delta G'$). The use of ΔG* as the abscissa to show the overall slope changes due to the acting field strength (at higher pre-aligning field) represents the change attributed to a microstructural change due to the pre-alignment condition.), The shear modulus $\Delta G'$ increases exponentially with the applied electric field ($\sim E^b$, b = constant shown in Fig. 8). For an ERN with $E_0 = 1{,}000$ V/mm, the exponent for switching effect was 1.82, which is close to the quadratic dependence (E^2). The exponent increases with the ordering of ERN (E_0), but for stronger pre-alignment ($E_0 = 2{,}000$ V/mm), the exponent of shear modulus switching decreased to lower value. The range in field strength of Fig. 8 is generally not a regime of saturation for ordinary ER suspensions up to 30 wt.% particle concentration (Chin and Winter 2002). Therefore, this result will be related to the complicated electrical prop-

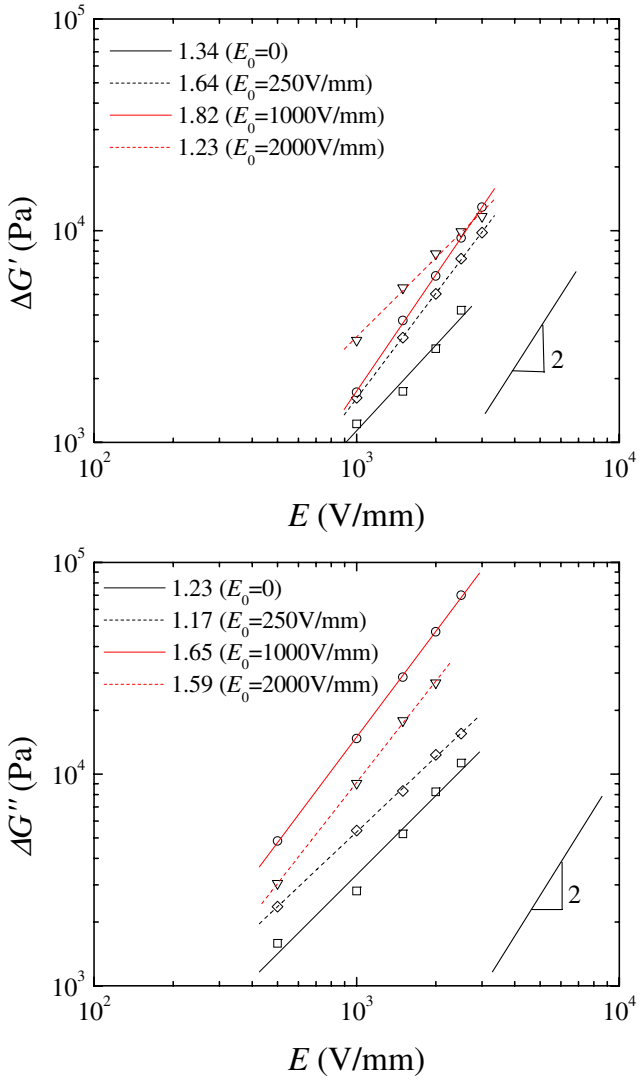

Fig. 8 $\Delta G'$ and $\Delta G''$ as a function of operating electric field strength. The pre-aligning electric field strength was varied as $E_0 = 0$ (*open square*), 250 V/mm (*open diamond*), 1,000 V/mm (*open circle*), and 2,000 V/mm (*open inverted triangle*); data for storage shear moduli (**a**) and loss shear moduli (**b**). Points of G' and G'' were taken at strain amplitude 0.5% and $\omega = 0.1$ rad/s. $r = 0.5$ ERN with 20 wt.% PANI concentration. *Lines* are linear fitting to obtain the slope and exponential value

erties of the ERN, which is an anisotropic composite of polymer filled with semiconducting particles. The slopes less than the quadratic exponent (reported by Shiga et al. 1993a) were qualitatively interpreted at the scaling of yield stress observed in ER fluids (Choi et al. 2001; Sim et al. 2001). The electric field dependence of the loss modulus given in Fig. 8b also indicates exponents lower than E^2-dependence, specifically for $\Delta G''$ at $E_0 = 0$ and 250 V/mm. This finding appears to be attributable to the local drift and relaxation of incomplete columns locked within the PDMS matrix. It is interesting that loss moduli data show a threshold maximum at $E_0 = 1{,}000$ V/mm, which means that lower $\Delta G''$ values were obtained for the ERN with $E_0 = 2{,}000$ V/mm.

Figure 9 shows the strong influence of stoichiometry on the behavior of the ERN. Two representative cases, "soft" PDMS with $r = 0.5$ and "hard" PDMS with $r = 1.0$, were compared. The magnitude of field-induced modulus switching was clearly in the case of the "soft" ERN.

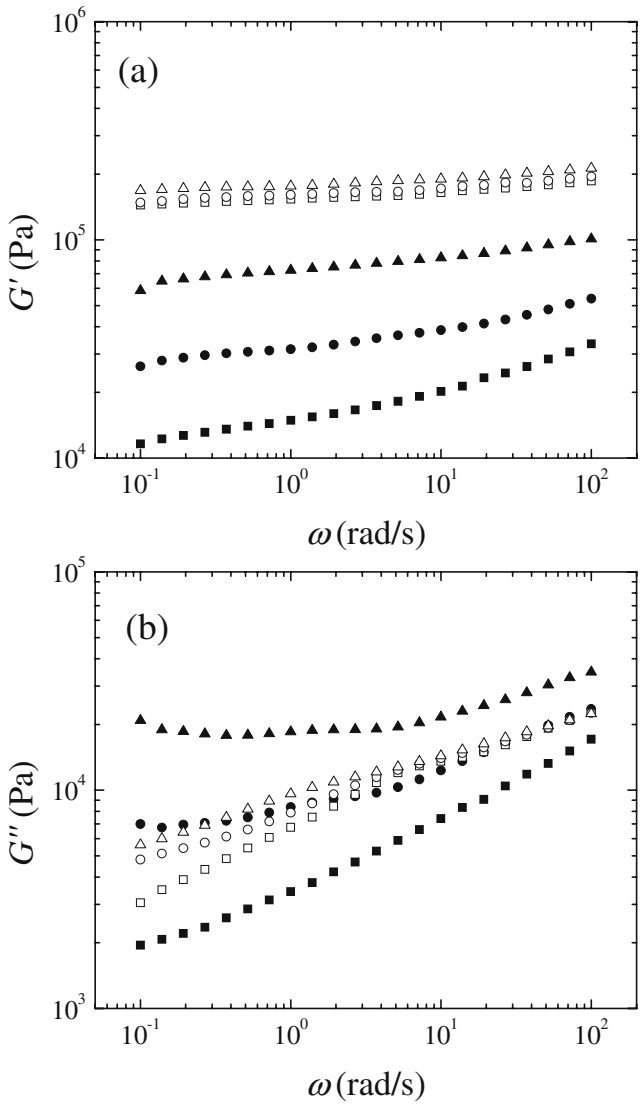

Fig. 9 Effect of matrix elasticity on the dynamic moduli, switching as a function of applied electric field. PANI of 30 wt.% in PDMS with pre-aligned at $E_0 = 1{,}000$ V/mm; *closed symbols*: $r = 0.5$ ERN, for $E = 0$ (*closed square*), $E = 1{,}000$ V/mm (*closed circle*), and $E = 2{,}000$ V/mm (*closed triangle*). *Open symbols*: $r = 1.0$ ERN, for $E = 0$ (*open square*), $E = 1{,}000$ V/mm (*opencircle*), and $E = 2{,}000$ V/mm (*opentriangle*). Data for storage shear moduli (**a**) and loss shear moduli (**b**)

Rheological probing: strain dependence showing the transition to nonlinearity of the ERN

Without an electric field, the pre-aligned PANI/PDMS ERN behaves as a linear viscoelastic material up to a large strain amplitude, as shown in Fig. 10a. The elastic modulus dominates, indicative of a small loss tangent; however, under an electric field of 2,000 V/mm, both G' and G'' decrease when the strain amplitude exceeds 0.1% (Fig. 10b). The linear viscoelastic region is limited to a strain below 0.1% under switching conditions. This critical strain for nonlinearity is even smaller than that of ER fluid materials (Chin and Winter 2002), demonstrating that the infinitesimal deformation of columns

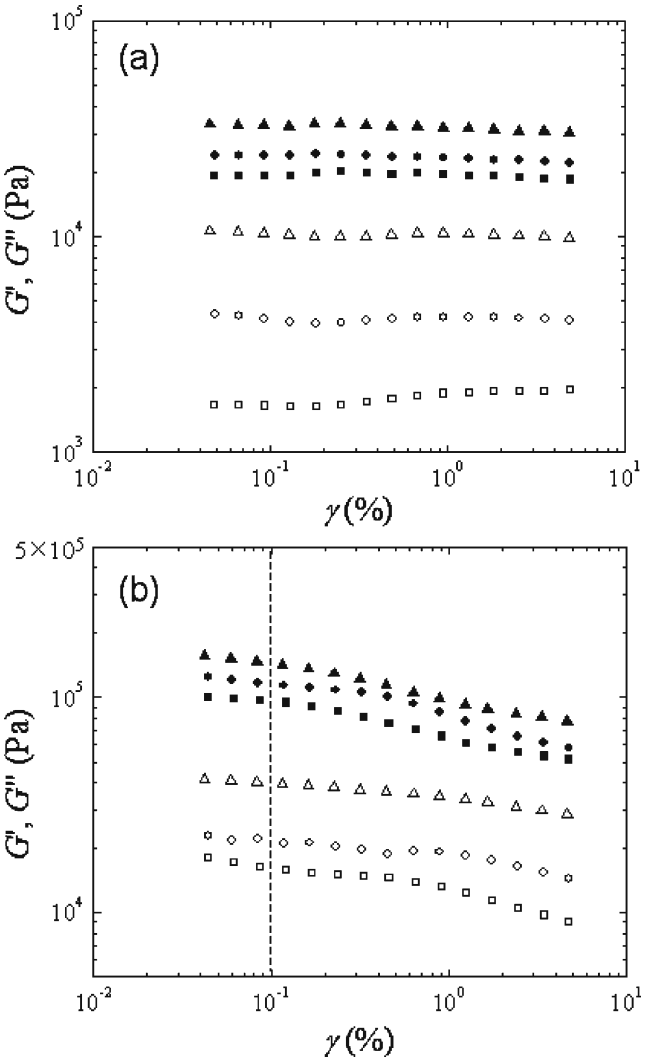

Fig. 10 Strain dependence of G', G'' for ERN of 30 wt.% PANI with $r = 0.5$ PDMS, which is pre-aligned at $E_0 = 1{,}000$ V/mm; **a** no electric field and **b** at $E = 2{,}000$ V/mm. Data at different frequencies are given; G' (*closed square*)/G'' (*open square*) at $\omega = 1$ rad/s, G' (*closed circle*)/G'' (*open circle*) at $\omega = 10$ rad/s, and G'(*closed triangle*)/G'' (*open triangle*) at $\omega = 100$ rad/s

of aligned ERN particles locked in a cross-linked matrix strongly influences the viscoelastic properties. This is assumed to cause the monotonic decline observed for G' and G''. At higher strain, ER fluids are completely nonlinear in their response because of breaking of the fragile structure; the ordered particle columns break off and freely drift. This fragile behavior has been observed even at the smallest strains (Claracq et al. 2004). The rheology was characterized not purely by elastic properties but also by the dissipation of considerable energy.

The nonlinearity of the viscoelastic properties of the ERN ($r = 0.5$ ERN with 30% PANI, aligned at $E_0 = 1{,}000$ V/mm) increases with applied field strength. This is evident in the stress–strain waveform data shown in Fig. 11. At zero field strength, the hysteresis loops (shear stress vs. shear strain) at 0.5% and 5% were both elliptical, and the Fourier transforms were without higher harmonics. The evolution of nonlinearity occurs as the field strength is increased. The nonlinearity in the ERN can be attributed to a slight rearrangement of induced charge between in-chain particles or adjacent coarsened column structures. At low strain (0.5%; Fig. 11a), increasing the field strength up to 2,000 V/mm caused the elliptical loop to increase in area and rotate its angle between the major axis and abscissa. Both the elastic and viscous components of shear stress were magnified by increasing field strength. A slight deviation from the ideal ellipse had already developed at 2,000 V/mm.

At higher strain (5%), increasing the field strength clearly caused the hysteresis loop to distort, while the area and angle continued to increase (Fig. 11b). Such a nonlinear deviation also expresses itself in the appearance of higher (third) harmonics in the Fourier spectra (especially clear in Fig. 11d). These nonlinear effects in the ERN are still not as significant as those in ER suspensions. Hysteresis loops in ER suspensions are severely truncated, as reported by Garmota et al. (1993), who found distortions to a rhombic shape due to a different damping mechanism.

Compression modulus switching and anisotropic connectivity of ERNs

The compression moduli (E', E'') of pre-aligned PANI/PDMS ERN increase with electric field strength, as shown in Fig. 12. Measurements were performed at small strains for both compression and elongation. Even at a small longitudinal strain of 0.5%, the ERN does not exhibit the linear viscoelastic behavior over the entire frequency range. Even without an electric field, the value of the compression modulus E' (1.55×10^7 Pa) is already three orders of magnitude

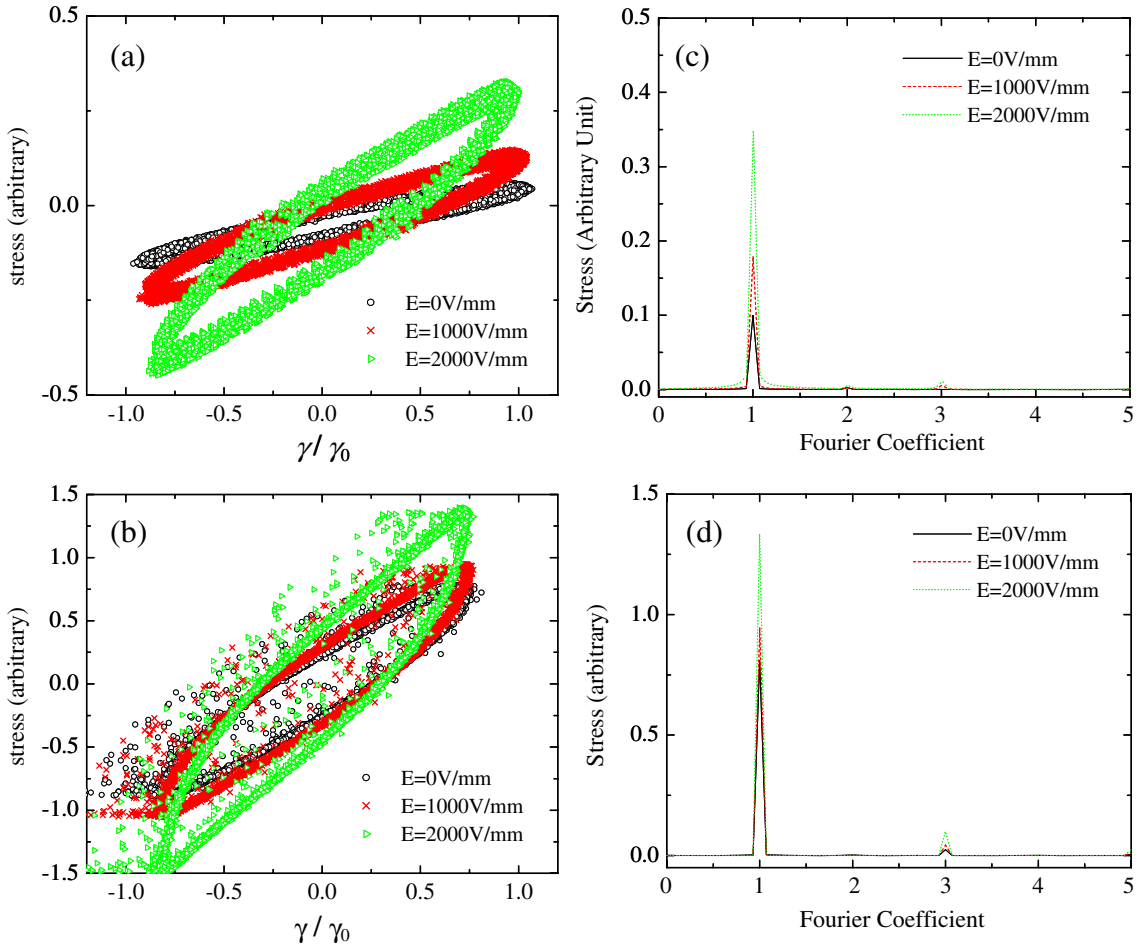

Fig. 11 Hysteresis loops (τ–γ) and Fourier spectra for ERNs generated from strain–stress waveforms. ERNs are 30 wt.% PANI with $r = 0.5$ PDMS, and τ–γ loops at strain amplitude of 0.5% (**a**) and 5% (**b**) are shown. Results of the Fourier spectrum at strain amplitude of 0.5% (**c**) and 5% (**d**) are presented. Data are displayed at three different electric fields ($E = 0$, 1,000, 2,000 V/mm)

higher than the shear modulus G' (2.4×10^4 Pa). The field-induced switching effect on E' and E'' is relatively small, with 30% and 48% increases in E' and E'', respectively. Therefore, the effect of compression-mode switching is not as significant as that for shear-mode switching.

The diphasic connectivity patterns of a particle-filled composite can be referred to as a 3–0 or 3–1 case, which is short-hand notation for a matrix phase of three-dimensional connectivity and an active particle filler of zero- or one-dimensional connectivity, respectively (Randall et al. 1993). Figure 13 schematically illustrates the ERN's alignment configuration with reference to the direction of the field and shear strain. In fact, the size of PANI particles and millimeter-sized coarsened columns are too great to be drawn at this scale. For a 30 wt.% ERN, modulus-switching occurs even in a random ERN (Fig. 13a), as shown in Fig. 7c, d. At this particle concentration, the filled particles tend to come into contact with each other, also forming a three-dimensional network (approximate 3–3 connectivity). Such an isotropic ERN shows only a minor modulus-switching effect with the application of an electric field at lower concentrations. In the pre-aligned ERNs (Fig. 13b), most of the particle alignment was preserved by the cross-linking, meaning that the mechanical properties were anisotropic even in the absence of the field. The field-sensitive moduli presented in Figs. 5 and 6 (particle fractions with 10, 20, and 30 wt.%) were obtained for ERNs with 3–1 connectivity ($E_0 =$ 1,000 V/mm), and showed a noticeable switching effect even at 10 wt.% concentration.

At the highest pre-alignment electric field strength employed in our study ($E_0 =$ 2,000 V/mm), the switching of the field-induced storage modulus is significant. Strong interactions occur between the contacting particles, especially when the structure is coarsened and contains thick columns (formed by high

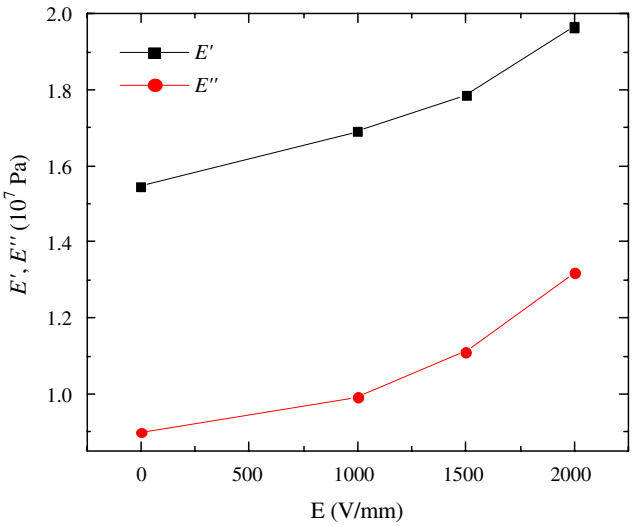

Fig. 12 Compression moduli (E', E'') as a function of applied electric field strength. ERN sample is 30 wt.% PANI with $r = 0.5$ PDMS (pre-aligned at $E_0 = 1{,}000$ V/mm). Points of E' and E'' were taken at 0.5% strain and $\omega = 15$ rad/s

pre-aligned field strength), leading to an increased resistance to deformation, as desired for a higher modulus switching. However, the connected columns also lead to a counter-acting effect, since electric current might pass more easily through the developed sample-spanning columns of particles, which have higher conductivity than matrix PDMS. This opposing effect was reported for ER suspensions when operated in DC electric fields. This optimal value is expected to be different in the case of an ERN due to the difference in dielectric breakdown strength between a liquid and solid matrix polymer.

Numerical simulations performed by Liu et al. (2001) suggest an increase in field-induced modulus, showing a maximum at a particle volume fraction of 0.55, close to the ideal body-centered cubic structure. When applying a shear strain perpendicular to the particle alignment (Fig. 13c), the interparticle spacing within columns increases and the particle–particle interaction shows a significant reduction. The forces on the columns are in tension due to the shear (Fig. 13c) and in compression when a squeezing strain is applied (Fig. 13d).

In this study, nonlinear effects (even at small strain) were conspicuous, unlike the behavior observed by Shiga et al. (1993b) in a study of aligned polyelectrolyte particles in a silicone gel. When the upper plate oscillates, buckling and displacement of particle–particle contacts was introduced and the modulus rapidly became nonlinear. A linear regime could not be identified beyond 0.1% shear strain amplitude, especially in the presence of an electric field. Moreover, buckling of particle columns also induces a nonuniform field distribution and dielectric breakdown at lower field strength, thereby complicating the characterization and application of compression-mode ERN.

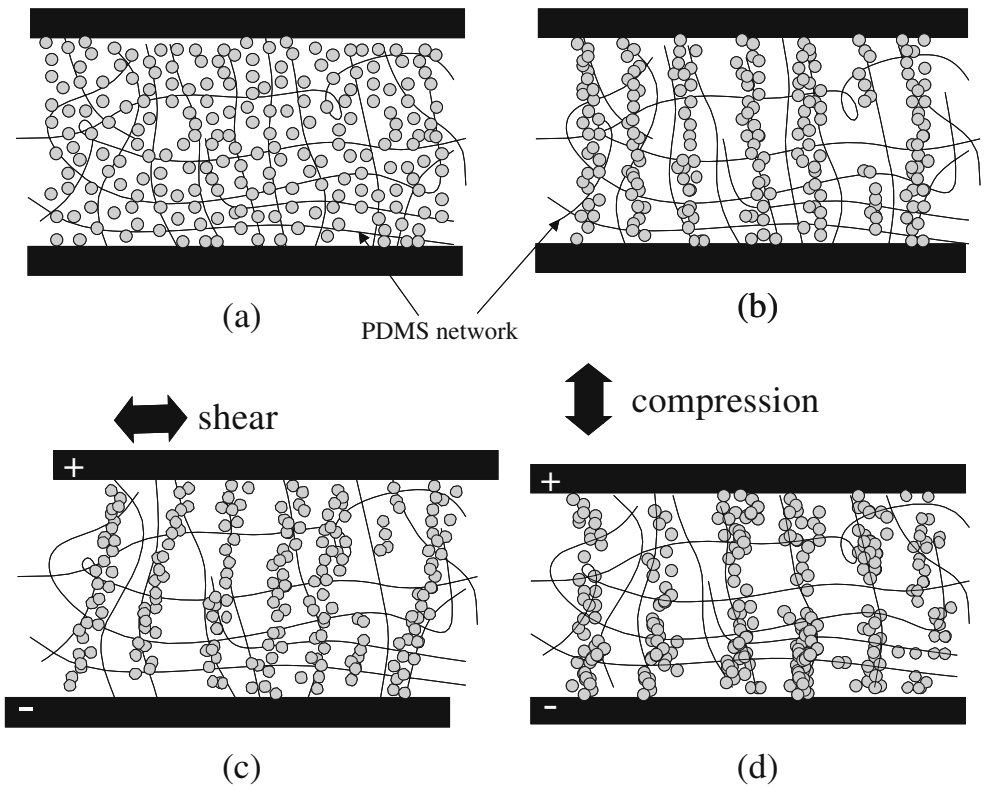

Fig. 13 Schematic of structure evolution during the particle ordering of ERN with a cross-linked PDMS matrix. **a** Random dispersion, **b** pre-aligned ERN, **c** pre-aligned ERN under shear deformation perpendicular to the particle ordering direction, and **d** pre-aligned ERN under compression parallel to the particle ordering direction

Conclusions

We studied the rheology of electrorheological networks composed of dispersed particles aligned by an electric field and blocked in place by an in situ crosslinked matrix polymer. Experimental results based on microscopic observations and rheological characterization revealed that an aligned morphology, which is confined by the three-dimensional polymer network, is dependent on the pre-aligning electric field strength, giving rise to the coarsening effect of particle column distribution. Although the switching effect of the shear modulus ($\Delta G'$, $\Delta G''$) generally depends on E^2, the ERN aligned at a high field (2 kV/mm) showed lower deviation from the quadratic dependence on field strength. An increased magnitude of switching in the dynamic modulus was more strongly observed for a "soft" PDMS network. The ERN's high shear modulus when subjected to a strong electric field was highly sensitive to strain amplitude, showing nonlinear viscoelasticity when strain exceed 0.1%.

The anisotropic pattern formation of an ERN has 3–1 or 3–3 connectivity of dispersed particles and matrix polymer. Connectivity of 3–1 has a highly anisotropic coarsening chain structure, meaning that tension or compression between adjacent particles was generated with the application of a strain parallel or perpendicular to the direction of particle connectivity, respectively. According to the current experimental data, switching of the modulus was more significant in the shear-mode operation of the ERN (perpendicular shear against particle connectivity). New ERN configurations and material selection for more effective compression mode operation will be required for various applications for fast high-load damping devices.

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