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Electrically Anisotropic Materials: Polyaniline Particles Organized in a Polyurethane Network†

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Abstract: Electrically conducting polyaniline particles were organized by an electric field in a liquid medium, which was subsequently polymerized to produce a polyurethane network. The changes in electrical conductivity during polymerization were recorded. The chains of conducting polyaniline particles oriented in the direction of the electric field became fixed in the polymer network. In this way, electrically anisotropic materials were produced. The conductivity in the direction parallel to the orientation was several times higher than that in the perpendicular one. The conductivity of these composite materials increases with temperature, while the electrical anisotropy decreases. The effect of electrical anisotropy is explained by simple geometric considerations.

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INTRODUCTION

Polyaniline (PANI) is one of the interesting electrically conducting polymers.[1,2] It is easily prepared by the oxidative polymerization of aniline. The product can exist in a variety of oxidation and protonation forms[3,4] that differ in electrical conductivity and other physical and chemical properties. The protonated emeraldine form of PANI has been most extensively studied.[2]

The preparation of electrically anisotropic materials is one of many attractive uses of this polymer. Solvent-cast PANI films protonated with methanesulphonic acid were studied by Adams *et al.*[5] After 600% elongation under uniaxial stress their electrical conductivity in the direction parallel to the elongation was 8·4 times higher than that in the perpendicular one. For PANI–camphorsulphonate this ratio was 3·8 at 60% elongation. Cao *et al.*[6] reported an increase in conductivity by two orders of magnitude after drawing of PANI–dodecylbenzenesulphonate blends with ultrahigh-molecular-weight polyethylene. Optical anisotropy of the stretched blends was also confirmed by absorption spectra.

We have recently observed that electrically conducting PANI particles suspended in a non-conducting organic liquid (1,2,4-trichlorobenzene) become ordered in an electric field.[7] This effect is governed by similar principles as the organization of non-conducting dielectric particles.[8,9] Such suspensions, including those of PANI base or partly protonated PANI,[10,11] behave as electrorheological fluids and their viscosity increases after application of an electric field ($E \approx 10^3\ \mathrm{V\,mm^{-1}}$). The organization of fully protonated PANI particles into conducting chains is observed at much lower field strengths, typically several $\mathrm{V\,mm^{-1}}$. The electrorheological behaviour does not seem to be pronounced, but the electrical properties have features of interest:[7]

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the current passing through the PANI suspension is time-dependent and its limit values depend non-linearly on applied voltage. The current–voltage characteristics resemble those of varistors.[7,12]

It is tempting to order PANI particles in a suitable liquid, which is later converted into a solid and thus the organized structure petrified. Such materials are expected to have an anisotropic electrical behaviour, similar to mechanically oriented PANI films. The conducting particles can be ordered in a liquid, which becomes solid after a decrease in temperature below its melting point. Alternatively, conducting particles can be dispersed in a monomer mixture and oriented in an electric field. The resulting structure can be fixed by polymerization of the medium. The latter approach has been used in the present study and the incorporation and orientation of PANI powder in a polyurethane network have been investigated.

EXPERIMENTAL

Preparation of polyaniline

Aniline sulphate (0·2 M) dissolved in water was oxidized by ammonium peroxydisulphate (0·2 M) at 0–2°C. Next day the precipitate was washed several times with 0·1 M sulphuric acid and then with acetone. The collected powder was dried *in vacuo* at 60°C and sifted through a 200 μm sieve. Individual PANI particles have a typical size of several micrometres. The electrical conductivity of polyaniline sulphate in a compressed pellet was 8 S cm^{-1}.

Polyurethane

Trihydroxypoly(oxypropylene) (LHT 240, Niax Polyol, Union Carbide; molecular weight $\bar{M}_n = 710$; average number of hydroxyl groups per molecule, $f_n = 2{\cdot}97$; moisture $<0{\cdot}04$ wt.%) and a mixture of 2,4′- and 4,4′-diisocyanatodiphenylmethane (Baymidur VP KL 3-5002, Bayer; purity 99·8 wt.%) were used for the preparation of a polyurethane network at an equimolar ratio of functional groups, [OH]/[NCO] = 1·0. The reaction of isocyanate with hydroxyl groups was catalysed by 0·01 wt.% dibutyltin dilaurate.

Organization of polyaniline particles and formation of polyurethane network

Polyaniline powder, triol and catalyst were mixed at room temperature and treated in an ultrasonic bath for 30 min to reduce the aggregation of PANI particles. The mixture was stirred for 2 h at 50°C *in vacuo* to remove residual moisture and air. After cooling, diisocyanate was added and the reaction mixture was homogenized for another 5 min. The mixture was placed between aluminium blocks separated by a 5 mm silicone rubber spacer. A DC voltage (255 V) was applied to the electrodes to organize the PANI particles. The whole set was placed in an oven at 90°C and kept there for 24 h. The electric current passing through the reaction mixture was monitored during the subsequent formation of the polyurethane network.

Optical microscopy

Microtome-cut thin sections of polyurethane blocks were mounted for microscopic examination of the composite structure using paraffin oil. A Photomicroscope III (Zeiss-Opton) was used to take micrographs of the samples.

Electrical measurements

The polyurethane block (50 × 5 × 5 mm) obtained after polymerization was cut into two pieces. Gold electrodes were deposited on the sides parallel to the original electric field (first sample) and in the perpendicular direction (second sample). The samples were placed in an oven and gradually heated from room temperature to 90°C. The electric current I passing through the sample at DC voltage $U = 33{\cdot}4$ V was measured with a 610C Electrometer (Keithley Instruments, Inc., USA; input impedance $>10^{14}\,\Omega$). The electrical conductivity was calculated as $\sigma = Id/US$, where d is the thickness of the samples and S is the effective surface of the electrodes. The temperature dependence of the sample dimensions was neglected.

RESULTS AND DISCUSSION

Electrical conductivity during formation of polyurethane network

When PANI powder dispersed in the liquid polymerization mixture was placed between the electrodes and a voltage applied, the PANI particles became polarized. The electrostatic interactions of the induced dipoles organized the particles into chains preferentially oriented parallel to the electric field. The conductivity of the system quickly increased as the particles became ordered (Fig. 1). During the subsequent polymerization the system solidified. The organized particles, which are in electrical contact, are likely to be displaced by the forming network and volume contractions occurring during the polymerization. Consequently, the conductivity decreases (Fig. 1), because the conducting chains of particles are broken. The contact cannot be recovered by transport (movement) of particles by polarization forces, because in the meantime the system became highly viscous or solid.

A similar pattern has also been observed with PANI suspended in 1,2,4-trichlorobenzene (isopycnic medium).

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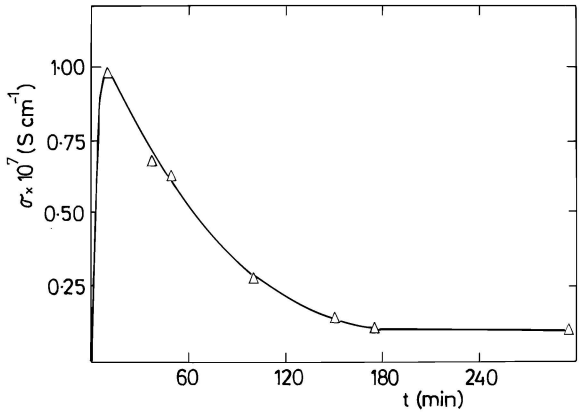


Fig. 1. Changes in electrical conductivity σ after orientation of polyaniline particles (5 wt.%) in reaction mixture and during subsequent formation of polyurethane network at 90°C.

When the PANI particles are organized in an electric field and the temperature is reduced below the melting point of the medium (16°C), the electrical conductivity is reduced by several orders of magnitude. It recovers after the medium has been melted.

Organization of polyaniline in polyurethane network

The organization of PANI particles fixed in the polyurethane network can be seen by optical microscopy (Fig. 2).

When the vector connecting the centres of two particles (having an induced dipole) is parallel to the electric field, there is an attractive force between these particles. If the line connecting the particles is perpendicular to the direction of the electric field, the interaction is repulsive.[13] At all other angles there is a torque on the particle pair acting to order the particles along the electric field lines. The particles are thus organized into chains or strands aligned in the direction of the electric field.

The force is exerted on particles until they become part of a chain. Within a chain the particles are short-circuited and the force is then applied on the chain as a whole. The chains associate until conducting paths covering the distance between the electrodes are produced (primary chains). Secondary chains then crosslink the primary chains or become connected to them as loops.

At low concentrations of PANI, when the number of particles is small, only a few primary chains are formed. Secondary chains are forced by the electric field to be in their vicinity. As a consequence, only a few robust strands are produced (Fig. 2(a)). When the number of particles is higher, many chains between the electrodes are easily produced, these being crosslinked by numerous secondary chains (Fig. 2(b)). At still higher PANI content the network structure dominates. It is much more subtle and more homogeneous (Fig. 2(c)) compared with the previous cases.

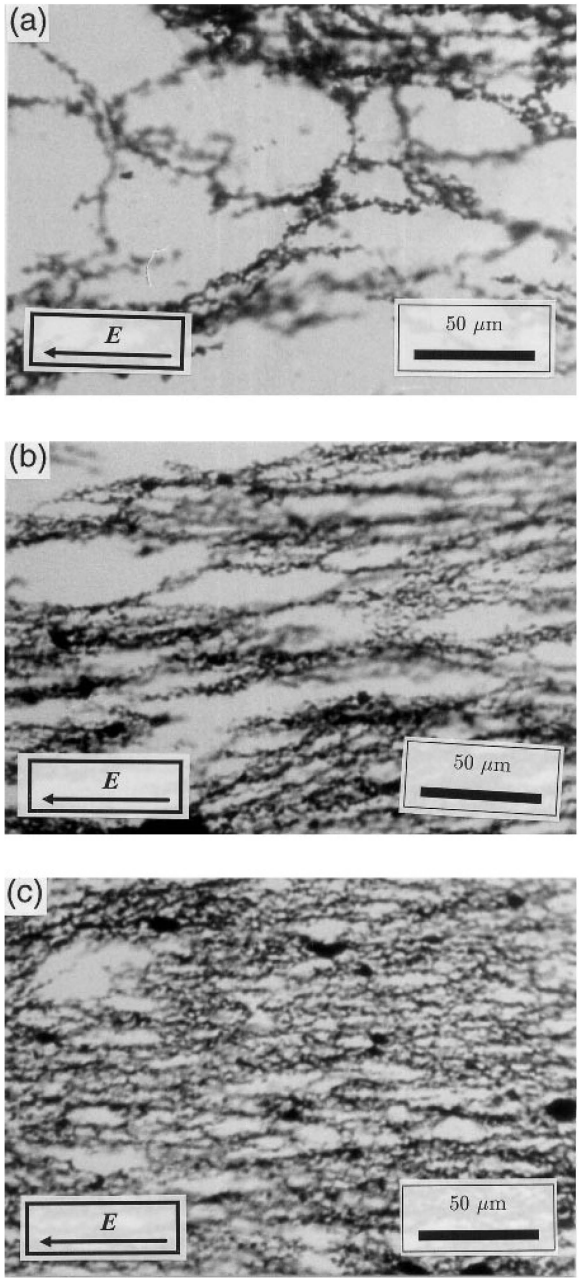


Fig. 2. Micrographs of polyaniline particles oriented in polyurethane network at electric field strength $E = 51\ \mathrm{V\,mm^{-1}}$ for polyaniline contents (a) 1, (b) 5 and (c) 10 wt.%.

The typical size of PANI particles is several micrometres (Fig. 2). The occasional presence of large aggregated PANI particles and their interaction with smaller objects illustrate the forces that are involved (Fig. 3). When the line connecting particle centres is parallel to the applied field, particles attract each other. If there is a large difference in the mass of particles and consequently in their momentum, small particles are

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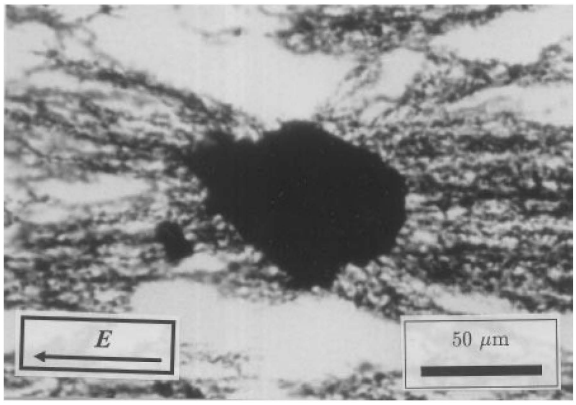


Fig. 3. Organization of polyaniline particles (5 wt.%) in vicinity of large conducting object.

attracted to the large ones and concentrate at their 'poles'. When particles are positioned perpendicularly to the electric field, the pair interaction is repulsive and small particles are forced out of the 'equator' region of the large ones (Fig. 3).

Temperature dependence of electrical conductivity and electrical anisotropy

The electrical conductivity of the composites measured in the direction parallel to the original electric field increases with increasing temperature (Fig. 4). This trend has been observed for composites composed of submicron PANI particles[14,15] embedded in a matrix of poly(vinyl alcohol) or poly(*N*-vinylpyrrolidone). Such composite materials are obtained after drying of PANI dispersions.[16,17] The situation is more complex for pure PANI:[18–20] the positive temperature coefficient of conductivity observed at low temperature often becomes very small or even negative at higher temperature.

The electrical conductivity of the composite materials in the direction of the chains of conducting particles (in the direction of the original electric field) is larger than that in the perpendicular direction. The electrical anisotropy α (defined as the ratio of the conductivity in the direction of orientation to that in the perpendicular direction) decreases with temperature (Fig. 5). Anisotropies are of the same order to magnitude as those reported for mechanically oriented PANI films (where, however, the electrical conductivity in both directions is higher by many orders of magnitude).

Nature of electrical anisotropy

The explanation of the observed anisotropy can be based on simple geometric considerations (Fig. 6). Because of the nature of organization of the particles, virtually all of them become incorporated into a network-like structure which is oriented (distorted) preferentially in the direction of the original electric field (Fig. 2). The distortion, described by the angle $\theta > 90°$

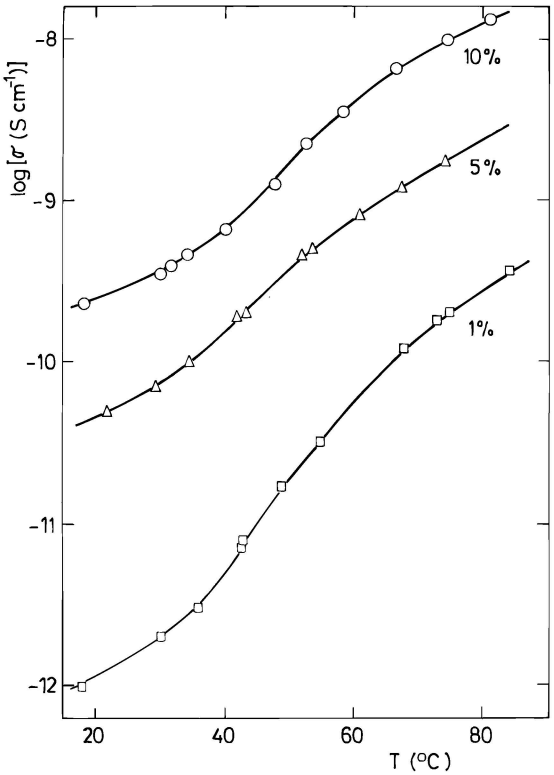


Fig. 4. Temperature dependence of electrical conductivity σ (measured in direction of orientation) of polyurethane networks containing 1 (□), 5 (△) and 10 wt.% (○) polyaniline.

(Fig. 6), is proportional to the applied electric field strength E. Let us consider a volume element of the system composed of conducting PANI particles embedded in insulating polyurethane (Fig. 6). The thickness of this element can be associated with the average diameter of conducting particles, d_c. Its resistivity measured between points A and B can be approximated as $\rho_{AB} =$

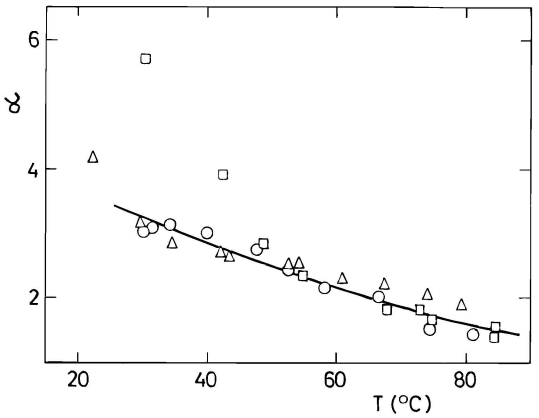


Fig. 5. Temperature dependence of electrical anisotropy α (defined as ratio of electrical conductivities in directions parallel and perpendicular to orientation of particles) of polyurethane networks containing 1 (□), 5 (△) and 10 wt.% (○) polyaniline.

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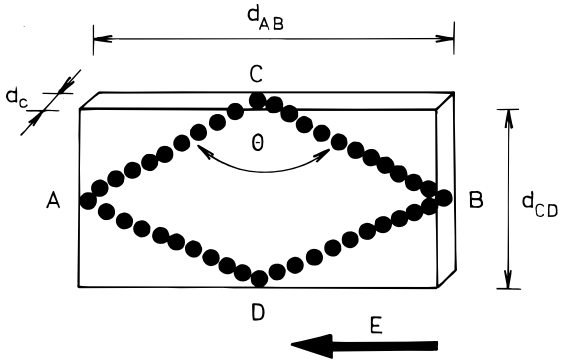


Fig. 6. Sketch of conducting paths in volume element produced by organization of polyaniline particles in electric field E. The angle θ characterizes the distortion of the conducting network.

$R_{AB}(d_{CD}d_c)/d_{AB}$ and, similarly, between points C and D as $\rho_{CD} = R_{CD}(d_{AB}d_c)/d_{CD}$. The resistance of conducting paths connecting points A and B (via C or D) and between C and D (via A or B) is the same, $R_{AB} = R_{CD}$, because they have the same length. Consequently, the anisotropy α in the electrical conductivity σ is

$$\alpha = \sigma_{AB}/\sigma_{CD} = \rho_{CD}/\rho_{AB} = (d_{AB}/d_{CD})^2 = \tan^2(\theta/2) \quad (1)$$

i.e. the anisotropy is expected to increase with increasing orientation of the conducting network. It is not surprising that the observed electrical anisotropy is not dependent on the concentration of PANI particles in polyurethane (Fig. 5) if these composites are prepared at the same electric field strength.

CONCLUSIONS

Electrically conducting PANI particles are organized in a liquid medium by application of an electric field. The resulting structure, composed of chains or networks of particles, can be petrified by polymerization of the medium, e.g. by formation of a polyurethane network. The materials produced in this way have an electrical conductivity several times higher in the direction of the orientation than in the perpendicular one. Absolute values of conductivities are relatively low, $\sigma < 10^{-7}\,S\,cm^{-1}$, lower than those observed in the liquid state.

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