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CHEMISTRY OF MATERIALS
Communication

Generation of Anisotropic Conductivity in Polymer Films Using Localized Microvoids Formed by Solvent Crazing as Nanoreactors

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Anisotropic conductive films are widely used in flat panel displays,[1−3] chip-on-glass applications,[4] and printed circuit-board interconnections.[5] These films are usually prepared by dispersing electrically conductive particles in a polymer matrix,[6] but films based on arrayed-particle technologies, that is, a regular pattern of metal posts penetrating the polymer film perpendicular to plane, are also known.[7] These patterns are prepared by a combination of photolithography and electroplating and provide an exclusive "through plane" conductivity. However, this elaborate method of preparation cannot be transformed into a continuous process, and the height of the posts is limited by the thickness of the photoresist.

In this communication, we describe a novel approach to the preparation of anisotropically conductive film using the solvent-crazing process[8] and subsequent precipitation of metallic silver nanoparticles in the crazes. Crazing is a universal phenomenon that is observed in all the semicrystalline polymers.[9,10] Plastic deformation of such polymers initially leads to fibrillation, that is, the formation of microvoids bridged by polymer fibrils. In the presence of a medium that wets the polymer surface, the microvoids are filled with the medium and thus stabilized.[8,11,12] If the surrounding medium contains nonvolatile additives, these remain inside the stretched polymer area once the solvent has evaporated.[8,13] Figure 1 schematically illustrates the process. In semicrystalline polymers, craze nucleation (I) starts at the point where the stress−strain curve deviates from linearity[14,15] and the crazes propagate (II) perpendicular to the streching direction. In air, further stretching leads to the formation of a single neck, while in an appropriate solvent multiple necks open (III) and travel toward the ends of the sample (IV), where they finally collapse.

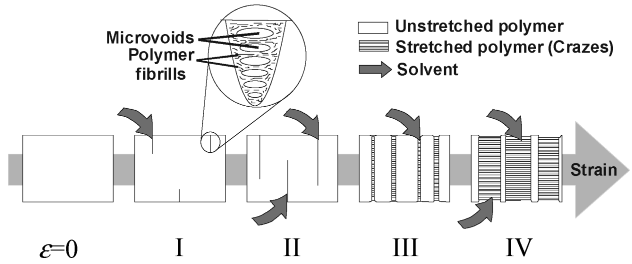

Figure 1. Schematic representation of the solvent-crazing process. Starting at $\varepsilon = 0$, increasing the strain leads to craze nucleation (I), craze propagation (II), neck opening (III), neck propagation (IV), and finally collapse (not shown).

Alternatively to having nonvolatiles being washed into the polymer by the surrounding medium, hybrid materials can be made nanoporous, solvent-crazed polymer films as membranes in counter-diffusion reactors in which the microvoids act as nanosized reactors.[8,13,16] Thus, drawing a partially oriented poly(ethylene terephthalate) film in *n*-propanol leads to the formation of dissimilar crazes, that is, a local network of nanosized voids bridged by polymer fibrils and filled with the

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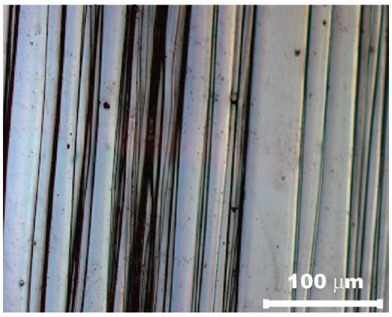

Figure 2. Optical microscopy image of a PET film after uniaxial stretching in *n*-propanol. Dark vertical stripes indicate the crazed areas.

surrounding medium.[8,11,12] PET was chosen as film material because of its good thermal and electrical properties.[17] Previous studies showed that inorganic/organic hybrid structures can easily be prepared by solvent crazing using PET.[13]

Figure 2 shows an optical microscopy image of the film stretched in *n*-propanol. The lighter parts represent the unstretched polymer surface and the darker parts the crazed areas containing the microvoids. To use these microvoids as nanoreactors, the stretched film is mounted as a membrane in a dialyzer (Figure S1, Supporting Information) filled with diamminesilver(I) nitrate on one and a reducing agent on the other side. The diffusion of these solutions through the microvoids starts at both sides of the membrane, and the propagating fronts meet inside the membrane to start the reduction. Since the crazes run perpendicular to the streching direction, selective filling of the crazes with metallic silver will consequently lead to a material that resembles an arrangement of parallel wires on the microscale as opposed to the previously reported films.[7] The anisotropic conductivity is, therefore, the result of the preferred orientation of the crazes in the *y*-direction separated by unstretched, nonconductive polymer in the *x*-direction.

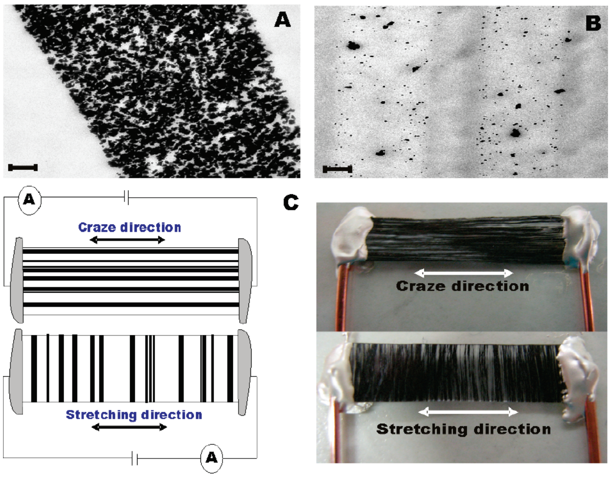

Figure 3. TEM micrographs of the crazed areas (after using hydrazine sulfate as a reducing agent) at the edge facing the side of the silver solution (A) and facing the side of the hydrazine solution (B). Scale bars: 200 nm. C: schematic drawing (left) and image (right) of the devices used to measure the electrical conductivity.

For the initial experiments, aqueous hydrazine hydrate solution was used as reducing agent.[18−23] However, large scale dissolution of the polymer film was observed as a result of the alkaline hydrolysis of the polyester backbone supported by the large surface area of the microvoids. To compensate for this, a stoichiometric amount of dilute sulphuric acid is added to neutralize the pH of the solution. However, using the neutral hydrazine sulfate solution as a reducing agent also leads to film rupture and partial dissolution of the film within 10 min. Although the solution is neutral, hydrazine sulfate is still nucleophilic and can cleave the polymer backbone[24,25] by forming acid hydrazides.[25] Nevertheless, SEM-EDX micrographs (Figure S2, Supporting Information) of the film's cross-section after freeze fracture along the direction of stretching show silver signals but only close to the edge of the side facing the silver nitrate solution. Apparently, diffusion of the hydrazine sulfate solution through the polymer is faster, causing cleavage of the backbone on the way. The films obtained by this treatment are black, very brittle because of incorporated silver particles, and fragile because of potential chain cleavage even in the parts that appear intact.

TEM analysis of these films confirms the differentiation between the two sides. The side facing the silver solution exhibits a dense network of particles (Figure 3A), while the side facing the hydrazine sulfate solution shows very few discrete particles randomly distributed in the crazed areas (Figure 3B). As a result of the application of a strong reducing agent, nucleation and growth is likely to occur simultaneously, and the particles form in an uncontrolled way, that is, with a large size distribution. In the absence of stabilizing agents, which are commonly used in the preparation of stable silver-nanoparticle dispersions,[26] these particles agglomerate giving rise to a percolating network inside the crazes. For conductivity measurements, copper wires were glued to opposite ends of the film, one time in the direction of stretching and a second time in the direction of the crazes using conductive glue (Figure 3C). As expected, conductivity is only observed on the side that exhibit the dense network of particles.

To circumvent cleavage of the polymer backbone, neutral reducing agents such as Sn^{2+} and β-lactose were used. Both gave rise to the formation of silver nanoparticles

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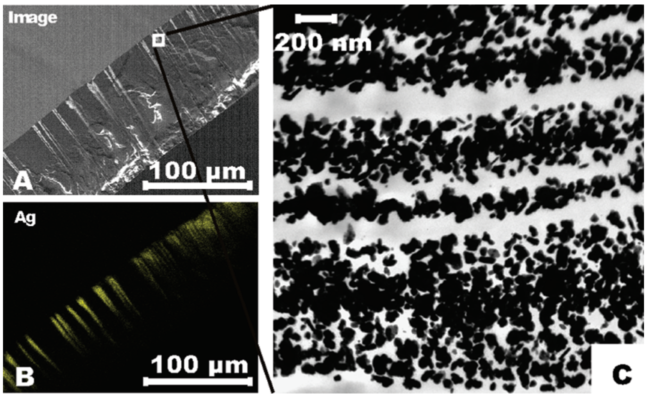

Figure 4. SEM image (A) and EDX Ag-mapping (B) of the film obtained after using aqueous formaldehyde solution as reducing agent. The TEM micrograph (C) is an enlargement of the marked area.

in the crazes, but conductive films were not obtained (cf. Supporting Information).

For a fast reduction under neutral conditions, aqueous formaldehyde solution[27] was chosen as a reducing agent. The obtained films were black and brittle because of the precipitation of Ag particles but not fragile. Film rupture or even dissolution as observed using hydrazine did not occur. To check for potential changes in the polymer as a side effect of the redox reaction, the films were subjected to IR and Raman spectroscopy (Figures S7 and S8, Supporting Information). No changes in the polymer structure or additional signals such as −COOH or −OH groups coming from hydrolyzed chains were observed. However, minute amounts of chain cleavage, especially during streching, cannot be fully ruled out but appears to be below the detection limit.

SEM-EDX images of these films (Figure 4A,B) show the complete penetration of silver veins along the crazes. Microstructural analysis using TEM (Figure 4C) reveals a dense network of silver particles throughout the crazed areas. The particles are 50−100 nm in size and interconnected with each other, thus forming a percolating network from one end of the craze to the other. In the stretching direction, the silver veins are separated by stripes of pure polymer. The width of the silver veins according to TEM analysis is 1.02 ± 0.9 μm, and the space between the veins is 18.6 ± 18.6 μm (determined from SEM images). However, solvent crazing is a random process in such a way that neither the exact position nor the exact width of the crazes or the distance between the crazes can be controlled precisely, and veins from 25 nm to 5 μm as well as spaces between the veins from 1 to 95 μm have been observed. Conductivity measurements on a device analogous to Figure 3C indicate conductivity in the direction of the crazes with a sheet resistance of 6.2 Ω/□ and larger than 20 MΩ/□ (maximum resistance range of the instrument used) in the direction of stretching (film thickness 160 μm).

We have shown that the microvoids formed during the solvent crazing of PET films can be used as nanoreactors to precipitate percolating silver-nanoparticle networks by counter diffusion of diamminesilver(I) nitrate and a reducing agent. Strongly nucleophilic and alkaline reducing agents cleave the polyester backbone very fast. Thus, to generate metallic veins that penetrate the complete cross section of the film, neutral but fast reducing agents such as formaldehyde are required. The resulting structure resembles a parallel arrangement of wires, and anisotropy arises from the repetitive pattern of silver veins and unstretched polymer. By this method, we could generate anisotropically conductive polymer films by means of a simple low-cost process that reduces the use of noxious materials. Since solvent crazing is not limited to PET, similar materials can be prepared using PE, PP, poly(amide)s, and the like. Such materials could be used in electronics, flat panel displays, and interconnection technologies for laptops, monitors, TVs, and cellular phones.

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Supporting Information Available: Detailed experimental procedures and the experimental setup, SEM-EDX micrographs of films prepared using hydrazine sulfate, tin(II) methane sulfonate, and ss-lactose as reducing agents. IR and Raman measurement data. This information is available free of charge via the Internet at http://pubs.acs.org.

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