Appendix 1

Proposal to NASA Langley Research Center
G. E. Wnek, G. L. Bowlin and T. W Haas, VCU School of Engineering

"Electric Field-Mediated Processing of Polymers"

Summary
Significant opportunities exist for the processing of polymers (homopolymers and blends) using electric fields. We suggest that a broad range of properties can be achieved using a relatively small number of polymers, with electric fields providing the ability to tailor properties via the control of shape, morphology, and orientation. Specific attention is given to electrospinning, but we note that electroaerosol formation and field-modulated film casting represent additional processing options.

Brief Overview
Work in our laboratories has focused on the use of applied electric fields which can act on polymer solutions or melts to allow the production of fibrous webs (electrospinning) for tissue engineering (Stitzel et al., in press), homopolymer blends with pearl-chain or column-like phases (Serpico et al., 1991, Ye et al., 1996), block copolymer-homopolymer blends with non-equilibrium nanophase morphologies (Serpico et al., 1992), and aligned biopolymer films with non-linear optical activity (Mogul et al., 1998). Here we give specific attention to electrospinning, but we note that electroaerosol formation and field-modulated film casting represent additional processing options.

The technique of electrospinning, outlined in Figure 1 (Reneker and Chun, 1996), is remarkable in its simplicity. The basic elements are a high voltage supply, collector (ground) electrode, source electrode, and a solution or melt to be spun. The sample is usually confined in a narrow glass tube (a disposable pipette tip will suffice) with a very thin source electrode immersed in it. Fundamentally, a large enough voltage will polarize ions in the liquid or melt at the electrode tip, leading to deformation and eventually creating a 'jet' that spans the gap between the source and collector. Extensive splaying of the initial jet leads to the formation of very thin fibers (down to 0.05 microns). The collector can be a flat plate or wire mesh, or in more sophisticated modifications can be a rotating metal drum on which the polymer fibers are wound. While both solutions and melts can be electrospun, we will confine our attention to polymer solutions to obviate the need to heat the materials during spinning. Importantly, the process is rapid, with mats ca. 1 mm thick and several square centimeters in area being deposited in just a few minutes.

Electrospinning is very forgiving with respect to polymers and solvents that can be electrospun. Examples of electrospinning systems include poly(hydroxybutyrate-co-valerate) in chloroform, aqueous solutions of poly(ethyleneoxide) or DNA (Reneker and Chun, 1996), and poly(lactic-co-glycolic acid) or poly(ethylene-co-vinyl acetate), EVA, in methylene chloride and chloroform (Fig. 2; Wnek and Bowlin, in preparation). Mats can be spun in batch or
continuous (wound) mode, and shapes such as tubes are easily obtained with a rotating mandrel. We also believe that it will be possible to fabricate mats and tubes from monomers that polymerize quickly during the electrospinning process (‘reactive electrospinning’).

**Proposed Work**

We propose to explore, over about 6 months, the prospects for electrospinning of several polymer materials systems of potential interest to NASA Langley, including piezoelectrics, electromechanically active hydrogels, and scaffolds for tissue repair. The program of course has great flexibility, and all polymers systems suggested by NASA will be explored.

**Electromechanically and magnetomechanically active polymers.** Electrospinning will be utilized to prepare thin (sub-micron) fibers of electroactive polymers initially including polyaniline and polypyrrole (Baughman et al., 1991), sulfonated triblock polymer hydrogels (Ye et al., 1996), and polyacrylamide gels (Kurauchi et al., 1991). Electromechanical response from polyaniline is the result of doping-induced volume changes, whereas ion gradients leading osmotic pressure gradients are responsible for field-induced deformation in the gels. As noted earlier, ion transport kinetics dominates the response, and facile transport and hence mechanical deformation is expected with the very small electrospun fibers. Electromechanical response times of fiber bundles of less than 0.1s, in the regime of typical muscle, will be targeted. It is also proposed to ‘dope’ spinning solutions with polymer-stabilized ferrofluids and/or microbeads (polystyrene-encapsulated ferromagnetic particles) to prepare magneto-active fibers. The feasibility of mats of fibers to exhibit facile deformation in modest magnetic fields will be explored provided that the modulus of the polymer matrix is low. Ethylene-vinylacetate copolymer (40 wt% VA) is an appropriate choice as its $T_g$ is near room temperature and the polymer is biocompatible.

**Piezoelectric Polymer Mats and Tubes.** Electrospinning offers the opportunity to simultaneously process and pole piezoelectric polymers. It is conceivable that electrospun polymers can have significant chain and dipole orientation. We propose to spin poly(vinylidene fluoride) from DMF as a model system, and then extend this work to new piezoelectric polyimides and related materials being developed at NASA Langley.

**Tissue engineering scaffolds.** We will investigate the use of electrospun mats to serve as scaffolds for tissue growth and repair. Poly(lactic-co-glycolic acid) will be used for this purpose, and variables will include fiber size and orientation. Also, magnetically active tubes of compliant EVA copolymers will be used as scaffolds for muscle cell growth in collaboration with Dr. David Simpson, Dept. of Anatomy, VCU, where the influence of steady mechanical deformation (magnetically actuated) on the structure of muscle and its rate of growth will be investigated.

**Minimum Deliverables**

Mats of electrospun polymers, 100 cm$^2$; tubes of various diameters; scanning electron micrographs, correlations between morphology and processing variables (voltage, field strength, polymer solution concentration, effect of ionic additives); final report and prospects/directions for continuation. Our proximity ensures close interaction with NASA Langley personnel.

**Proposed Budget** (June 1, 2000 - December 31, 2000)

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Literature Cited


