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PIEZOELECTRIC POLYMERS

by
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April 1980

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this program was the development of improved fluoropolymer resins for transducer applications. The effort involved synthesis, characterization, and processing of new resins with emphasis on those obtained by copolymerizing vinylidene fluoride (VF ₂) with monomers such as tetrafluoroethylene (TFE), vinyl fluoride (VF), trifluoroethylene (VF ₃), and hexafluoropropene (HFP). Variations on the PVF ₂ homopolymer		

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synthesis were also investigated. In a number of cases the piezoelectric activity of the copolymers was found to be as good or better than that of the PVF₂ homopolymer; however, a distinct advantage of the copolymers vs homopolymer is the fact that, in general, the copolymers are considerably easier to fabricate into thick, oriented film configurations, as needed for underwater use.

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PIEZOELECTRIC POLYMERS

I. Description of Project

This program was for the development of improved poly-(vinylidene fluoride) (PVF_2) homopolymers and copolymers for transducer applications of special interest to the Navy. This involved synthesis and characterization of new resin systems based on PVF_2 with potentially superior piezoelectric properties and investigation of new techniques for enhancing those parameters that are particularly relevant to the Navy. Special emphasis has been on copolymers of vinylidene fluoride with other fluorinated monomers, fluoropolymer blends, and the effect of polymerization conditions on the piezoelectric activity of PVF_2 .

II. Summary of Results and Technical Achievements

A. General

As indicated above, the objective of this program was the development of improved fluoropolymer resins for transducer applications. The effort involved synthesis, characterization, and processing of new resins with emphasis on those obtained by copolymerizing vinylidene fluoride (VF_2) with monomers such as tetrafluoroethylene (TFE), vinyl fluoride (VF), trifluoroethylene (VF_3), and hexafluoropropene (HFP). Variations on the PVF_2 homopolymer synthesis were also investigated.

In general, polymerization reactions were carried out at our High Pressure Laboratory using either emulsion or suspension polymerization techniques. The initiators were either peroxides or sodium persulfate. The quantities of resin produced were sufficient for compression molding of

a number of film specimens which were subsequently stretched in an Instron. In several cases sufficient quantities were made for conventional film extrusion and sampling to Navy Laboratories.

B. Piezoelectricity of Various PVF₂ Copolymers and Homopolymers

**1. Vinylidene Fluoride/Tetrafluoroethylene Copolymers
(VF₂/TFE)**

Copolymers VF₂/TFE with monomer ratios corresponding to 95/5 and 70/30 (by wt.) were synthesized in sufficiently large quantities to allow extrusion into thin, continuous film. Piezoelectric activities (d_{33}) in excess of 20 pC/N were measured. The 95/5 copolymer was used to evaluate annealing effects on piezoelectricity. Since it is known that the crystals are of the β morphology in this copolymer, attempts were made to perfect and enlarge these crystals through appropriate annealing conditions. The elevation of the melting point provided indirect evidence that this goal was achieved. Poling of the annealed films, however, indicated that the changes brought about by heat treatment had a deleterious effect on piezoelectricity. Additional information on the VF₂/TFE copolymer systems are included in the Technical Report No. 1, which is summarized later.

**2. Vinylidene Fluoride/Trifluoroethylene Copolymers
(VF₂/VF₃)**

Copolymers of VF₂/VF₃ were prepared with monomer ratios corresponding to 70/30, 85/15, and 95/5. The piezoelectric activities (d_{33}) of compression molded film specimens of these compositions were in the 3-7 pC/N range, which we estimate would correspond to an activity not higher than 15 pC/N if the same film had been extruded and stretch oriented. These values were

obtained at low poling field. The latter was necessitated by the low resistance of these copolymers. High poling fields resulted in dielectric breakdowns.

The 95/5 copolymer was prepared by an alternate synthetic procedure which gave a resin possessing higher resistivity. After poling compression molded films of this resin with 700 KV/cm the d_{33} was about 15 pC/N, indicating that piezo-activities of well over 20 pC/N should be obtained with extruded and oriented film.

3. Copolymers of Vinyl Fluoride (VF) with Tetrafluoroethylene (TFE), Hexafluoropropene (HFP), and Vinylidene Fluoride (VF₂)

Copolymers of VF with TFE, HFP, or VF₂, where VF was the major component, were prepared and evaluated. These copolymers had the advantage of higher melting points; however, processing was difficult and the piezoelectric activities were low. More promising was the system VF/VF₂ when VF₂ was the major component (80-95%).

4. Variations on the PVF₂ Homopolymer Synthesis

PVF₂ homopolymers were synthesized at three different temperatures, 30°, 50°, and 75°C, respectively. An infrared analysis of the resulting resins indicated that the ratio of β to α phase increased with the polymerization temperature. NMR spectra indicated that the percentage of head-to-head polymerization also increased with the temperature. The effects of these changes, however, were not clearly manifested in the piezoelectric activities.

Homopolymer compositions were also synthesized without the use of surfactants. The object was to increase the dielectric strength of the resin by decreasing the amounts of possible impurities. This would allow poling at higher fields. We found that the dielectric strength was not influenced by these changes.

- C. Technical Report No. 1 "The Application of a Dipolar Theory to the Piezoelectricity in Vinylidene Fluoride-co-tetrafluoroethylene Polymers", Harry Stefanou, March, 1978. Published in J. Appl. Phys. 50 (3), 1486 (1979)

The piezoelectric activity of eight vinylidene fluoride-co-tetrafluoroethylene polymers was studied to further our understanding of this phenomenon. Film compliance, density, degree of crystallinity, and piezoelectric activity were measured in this study. It is shown that the piezoelectric d constant is calculable from a molecular dipole theory where the polarization is derived using a cavity reaction field.

- D. Technical Report No. 2 "The Crystallization Thermodynamics of Piezoelectric Copolymers", Harry Stefanou, November, 1979. Manuscript prepared for publication.

The crystallization of piezoelectric vinylidene fluoride-tetrafluoroethylene and vinylidene fluoride-hexafluoropropylene copolymers was investigated. Several compositions of each copolymer were synthesized and the melting point depression was evaluated as a function of composition. Models were examined in which the comonomers were included as defects in the crystal lattice or in which they were excluded. The need to use several approaches before a conclusion can be reached is clearly seen. Our studies indicate that the exclusion model is a less accurate description of the crystallization of these two copolymers. Values for the enthalpy of defect incorporation are evaluated and shown to be reasonable.

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