*Polypropylene Filled with Barium Titanate: Dielectric and Mechanical Properties**

In a polymeric material, fillers are usually used to reduce cost, improve chemical resistance and/or as a reinforcement to improve mechanical properties. The approach of incorporating fillers in a polymer to modify its electrical properties without impairing its desirable mechanical properties is also attaining some importance.

With the growth of both the electrical and electronic industries, the development of smaller and more efficient capacitors have been receiving increased attention. Dielectrics are being developed that have better characteristics, namely, suitability over a wide range of frequencies and temperatures, with special emphasis on low electrical loss. No single material satisfies all these requirements. Polyethylene and polypropylene have been used increasingly where low electrical loss and high breakdown voltages at moderate temperatures are required.

A capacitor should usually be as small as possible; the problem of reducing the size of a capacitor with a given set of characteristics is twofold: (1) raising the dielectric constant of the material to be used, and (2) reducing the thickness of the material. Different kinds of ceramics have been used to serve different objectives.[1] Difficulty in controlling the purity of material, degree of crystallization, uniformity of density, and size and shape during firing, as well as the lack of ductility causing machining difficulty are some of the serious disadvantages of ceramics. Polymeric materials with reasonably high dielectric constants ($\epsilon' > 5$), low loss ($\tan\delta < 0.005$), and reasonable thermal and mechanical properties would be in great demand in the capacitor industry, if costs were competitive. The present work with polypropylene is an approach towards this objective.

Efforts to incorporate TiO_2 into polymeric materials or to formulate composite substances for similar purposes, have been made by several workers.[2] $BaTiO_3$ is a dielectric that has one of the highest dielectric constants. Work with this material as a filler in an organic polymer such as polycarbonates has been done before.[3] The films with high loading were usually brittle and fragile. However, polypropylene has low dielectric loss ($\sim$0.0002), high dielectric strength, and reasonably good thermal stability. Hence, it has been felt logical to employ $BaTiO_3$ in trying to raise the dielectric constant value of polypropylene, while maintaining the other desirable properties.

EXPERIMENTAL

Preparation of Dispersions

Dispersions of $BaTiO_3$ (about 50% solid by weight) and polypropylene (about 20% solid by weight) were prepared in Deo-Base solvent, using a Dispersol mixer and shaking for 20–30 min. Any particular sample made by mixing the required amounts of the two dispersions were also shaken for 20–30 min in a Red Devil Shaker.

A follow up of this work with conventional Pro-fax™ polypropylene flake of lower molecular weight showed that solution casting and melt compounding followed by compression molding can also be used as fabrication methods to obtain films of comparable electrical and mechanical properties.

Film Preparation

The films were prepared on thoroughly cleaned chrome-plated brass sheets approximately 4 × 6 × 0.1 in. The sheets were placed on flat and horizontal surfaces and the films were drawn by hand with a knife edge caster having a 0.03 in. clearance.

Drying the Films

The films were dried at 400°F for 7 min or at 375°F for 15 min in ovens.

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Measurement of Dielectric Constant and Loss

As the films were in very good contact with the brass plates, the plates were used as one electrode, while a gold electrode was metallized on the other side and a thick brass electrode was used on the gold coating. The measurements were made on a GR-716-C Bridge manufactured by General Radio Co.

RESULTS AND DISCUSSION

The actual value of the dielectric constant of $BaTiO_3$ depends very much on the thermal history of the sample and the particle size of the material.[3] To achieve a high ϵ', the material (TAM) obtained from National Lead Company was annealed at 1950°F for 2½ hr. The dielectric constant obtained by thus making a ceramic sample out of this material was 1700.

We used polypropylene of the particle size average of 0.02–4 μm well dispersed in Deo-Base Solvent, and mixed this dispersion with annealed $BaTiO_3$, also well dispersed in Deo-Base (see Experimental section). Several films have been prepared with different concentrations of $BaTiO_3$. The values of the dielectric constants, dissipation factors, and dielectric strengths are presented in Table I(a). The dielectric constants and dissipation factors for some of the samples measured over a wide frequency range are presented in Figures 1 and 2. These figures show that the dielectric constant values of the samples are almost unaffected by frequency, and that the dissipation factor has a surprisingly low value over the whole frequency range. This seems to be a very striking quality in these films. Further, the films thus prepared are very flexible. The mechanical properties of these films are presented in Table II.

TABLE I

(a) Dielectric Constants and Dissipation Factors at 1 kHz and 75°F for Polypropylene Films with Different Amounts of $BaTiO_3$ Loading

Amount of $BaTiO_3$ percent by weight	Average value of dielectric constant[a]	Average value of dissipation factor[a]
51	4.5	0.0023
65	7.2	0.0032
74	8.8	0.0044

(b) Dielectric Strength of the Films, Measured with a Voltage Increase Rate of 500 V/sec

Amount of $BaTiO_3$ percent by weight	Thickness range in 0.001 in.	Average dielectric strength in KV/0.001 in.[b]
51	3.3–4.02	2.3
65	3.9–6.4	1.6
74	3.0–5.6	1.5
Polypropylene film	4.65–4.72	3.0

[a] Average of results for two samples.
[b] Average of 12–14 readings.

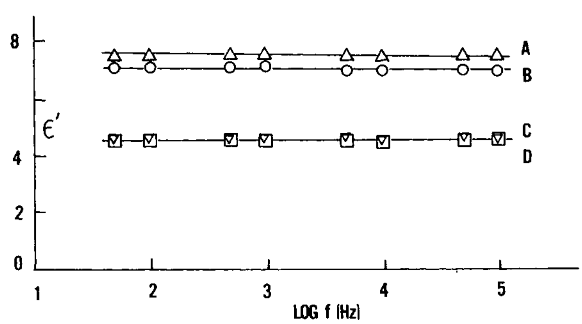

Fig. 1. Dependence of dielectric constant on frequency at room temperature (20.5°C). (a) 65% by weight $BaTiO_3$ loaded PP film, 7 kV across ½/in. (b) 65% by weight $BaTiO_3$ loaded PP film; no field applied during drying. (c) 51% by weight $BaTiO_3$ loaded film.

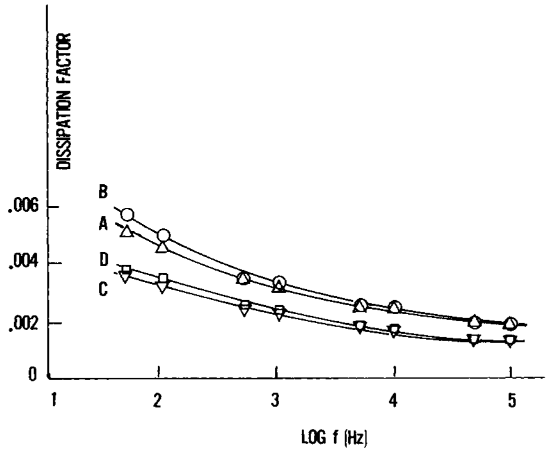

Fig. 2. Dependence of dissipation factor on frequency at room temperature (20.5°C). (a) 65% by weight $BaTiO_3$-loaded PP film; 7 kV across ½ in. separation applied during drying. (b) 65% by weight $BaTiO_3$ loaded PP film; no field applied during drying. (c) and (d) 51% by weight $BaTiO_3$ loaded film.

TABLE II
Tensile Properties of Polypropylene Films with Different Amounts of $BaTiO_3$ Loading

$BaTiO_3$ loading percent by weight	Tensile strength psi	Elongation range percent	Average modulus psi	Average yield stress psi[a]	Average yield strain percent[a]
51	3310	430–520	150,000	3230	8.9
65	3110	40–130	146,000	3110	11
Polypropylene Film (Cast)	7200	700–750	70,000	2323	15

[a] Average of results on five samples.

We have attempted to affect the dielectric constant by orienting the polarization directions of the $BaTiO_3$ crystals by subjecting the films to a high electric field during drying. Samples subjected to dc fields of 2–10 kV. across a ½ in. separation showed no significant change in dielectric constant.

Some of the films thus prepared showed some voids under the microscope. These voids could arise from traces of air trapped in the film or from impurities which volatalize during drying at 400°F. We removed them by pressing the films between chrome plates at 400°F and 1500 psi for 3 min and cooling the films while under pressure. The dielectric strengths of several such films have been measured and the results are presented in Table I(b).

Several authors,[1,2a,4] have attempted to design models and interpret results for such films mainly on the basis of the law of mixtures. The most commonly quoted law of mixtures is

$$\log_{10}\epsilon = \eta_1 \log_{10}\epsilon_1 + \eta_2 \log_{10}\epsilon_2$$

where ϵ_1 and ϵ_2 are the dielectric constants of component 1 and component 2, respectively, and η_1 and η_2 are related to the volumes of the components. Different authors have interpreted η_1 and η_2 in different ways to explain a particular set of results. If we consider them as "volume fractions," the above expression approximately explains the results presented in this work.

SUMMARY

Barium titanate has been incorporated into polypropylene to raise its dielectric constant. Films prepared from mixtures of submicron polypropylene and $BaTiO_3$ dispersions in Deo-Base solvent (Witco Chemical Company Inc.) show substantially raised values of dielectric constants. These values remain fairly constant over a wide range of frequencies (50–10^5 Hz) along with low values of

dissipation factor. The films are very flexible mechanically, and the dielectric strength values compare well with those of unfilled polypropylene films.

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