Permittivity of $BaTiO_3$ polymer composite with differing particle size distribution

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ABSTRACT

Polyester reactive resin composite materials with improved dielectric properties have been produced using a commercially available series of barium titanate fillers from one single manufacturer with varying primary particle sizes ranging from 100 nm to 700 nm. The fillers where characterized extensively using SEM, XRD, BET, He-pycnometry and others.

For comparison a number of barium titanate powders from varying manufacturers where used as fillers in composite materials and characterized for their dielectric performance.

It was found that none of the commercially available powders fulfilled optimized dielectric criteria. The smallest tetragonal barium titanate powder available performed best. All available barium titanate powders lie within a very small performance range.

Keywords: polymer, composite, tailored properties, dielectric properties, barium titanate

1 INTRODUCTION

Printed circuit boards (PCBs) play an important role in everyday electronic equipment. Most surface area of the PCB is used – apart from integrated circuits – for passives as resistors, inductors and capacitors [1]. As the number of layers within a PCB is nearly unlimited, the surface area – and therefore the dimensions of the PCB – are limited by the number of passives needed for the electronic circuit. By integrating a number of passives into the layers of the PCB the needed surface area can be reduced significantly. According to the iNemi 2007 roadmap over 40 % of the capacitors contained in portable devices show capacitance values below 0.1 nF. Therefor the replacement of even small capacitance values can save crucial surface area.

For the production of integrated capacitors dielectric materials with special physical properties are necessary. The materials need to be compatible with the existing PCB production process, the production temperatures must stay well below 200°C and the coefficient of thermal expansion must be in the range of the PCBs thermal expansion [2]. Composite materials on the basis of reactive resin polymeric materials fulfill these requirements.

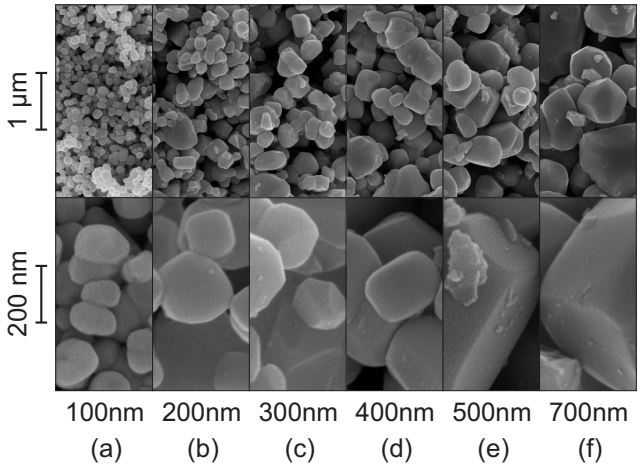

Figure 1: SEM images of Inframat $BaTiO_3$.

Barium titanate is a widely used material for discrete capacitors. The use of commercially available barium titanate reduces the cost and simplifies the production process of the composite material. The downside is the dependence of the dielectric properties on the production process [3]. In bulk material it is known for long that the crystallite size and the phase have great impact on the dielectric properties of the barium titanate [4]. Small tetragonal crystals are the preferred phase. The authors showed in [5] that commercially available barium titanate powders can be optimized in its dielectric properties by annealing. To further reduce production costs, various commercially available barium titanate powders where tested as fillers in composite materials.

2 EXPERIMENTAL

For the main experiments barium titanate powders from Inframat Advanced Materials [1] where used to conduct these experiments. These are available at varying primary particle sizes from 100 nm to 700 nm according to the manufacturers data sheet. For a detailed list of Cat. and Lot # see tab. 1.

As polymeric matrix the polyester reactive resin UP

[1]Inframat Advanced Materials LLC, 74 Batterson Park Road, Farmington, CT 06032, USA, http://www.advancedmaterials.us/

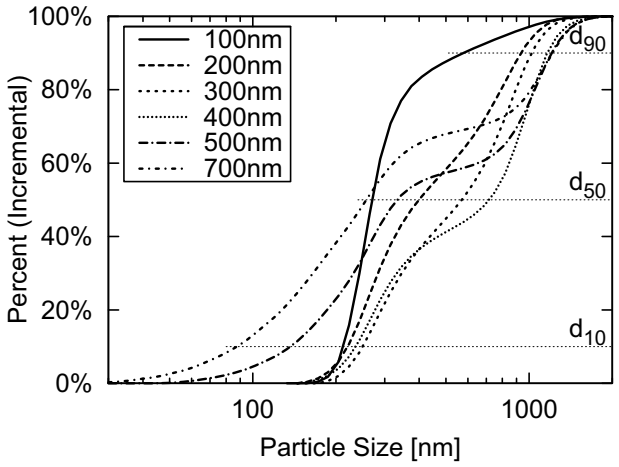

Figure 2: Incremental particle size of Inframat $BaTiO_3$.

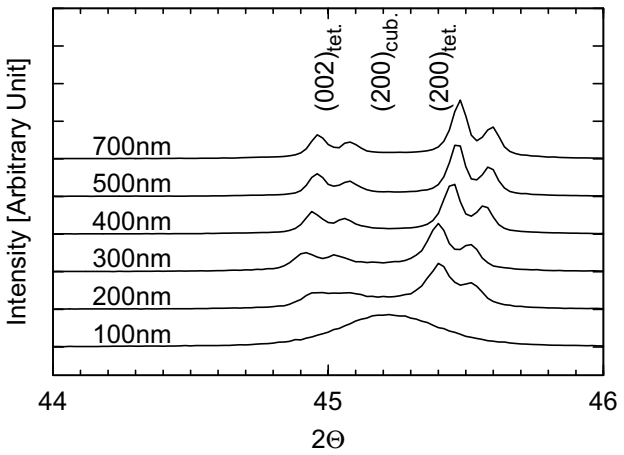

Figure 3: X-ray diffractogram of the (200) peak of Inframat $BaTiO_3$.

from Carl Roth GmbH [2] was diluted with 20 m% styrene to reduce the viscosity of the base material. As release agent 2 m% INT-54 (Würtz) where added. The cold hardener methyl ethyl ketone peroxide (MEKP) from Carl Roth GmbH was used at a concentration of 3 m% to initiate the polymerization reaction.

The fillers where incorporated into the polyester reactive resin - styrene mixture using a IKA [3] dissolver stirrer with a diameter of 29 mm. The composite was stirred for 30 min at 800 $\frac{rev}{min}$ before the hardener was added.

The composite was allowed to harden at 50 °C for at least one hour. For dielectric measurement disks with a diameter of 50 mm and a thickness of ca. 9 mm where cast using silicone models. The disks where smoothed before applying silver conducting paint electrodes. The dielectric properties where characterized using a "HP 4194A" impedance analyzer.

3 RESULTS AND DISCUSSION

3.1 Powder characterization

The six available barium titanate powders have been studied extensively using SEM, laser scattering, He-pycnometry, BET and X-ray diffraction.

SEM analysis reveals that the 100 nm specimen is a very homogeneous powder with spherical particles that show little dents on the surface (comp. fig. 1a). With increasing primary particle size the particles are showing crystalline features with sharply defined edges (comp. fig. 1b to 1f). Further more the particle size distribution becomes inhomogeneous.

The measured particle size distribution using laser scattering is very narrow for the 100 nm specimen with only one powder fraction. For the remaining powders a fraction with larger particle sizes is detected at diameters of about 1 μm (comp. fig. 2). While the 100 nm powder can dispersed using simple ultrasonic methods the agglomeration of the other powders is harder. These results are in very good agreement with the observations of the SEM analysis.

The surface area of the powder specimen decreases from 60 $\frac{m^2}{cm^3}$ (10.4 $\frac{m^2}{g}$) to 10 $\frac{m^2}{cm^3}$ (1.7 $\frac{m^2}{g}$) with increasing primary particle size as expected. The density of the 100 nm specimen is at 5.75 $\frac{g}{cm^3}$ while the other specimen show density values of around 6.0 $\frac{g}{cm^3}$ (comp. tab. 1). These values are in very good agreement with the literature value of 6.08 $\frac{g}{cm^3}$ [6]. The manufacturer found a density of 5.85 $\frac{g}{cm^3}$ for all six specimen.

The particle sizes calculated from BET and density values using a spherical model are given in tab. 1 in comparison to the manufacturers values and the d_{10}, d_{50} and d_{90} values from the laser scattering measurements. While the laser scattering values vary a lot, the values derived from BET and density measurements are in good agreement with the manufacturers values. This suggests, that the individual particles are agglomerated and can not be well dispersed in isopropanol at low concentrations using ultra sonic energy.

The X-ray diffraction (XRD) pattern shows that the 200 nm to 700 nm specimen are tetragonal in their crystallite structure (comp. fig. 3) and that the single crystals are fairly large (well separated $CuK_{\alpha 1}$ and $CuK_{\alpha 2}$ peaks). With growing primary particle sizes the lattice move to greater $\frac{c}{a}$-ratios which is in very good agreement with [7]. The only specimen showing a cubic crystallite structure is the 100 nm powder. The results from XRD analysis are consistent with the information from the manufacturers material data sheets. According to the

[2] Carl Roth GmbH, Schoemperlenstr. 3-5, 76185 Karlsruhe, Germany, http://www.carlroth.de/

[3] IKA Werke GmbH & Co. KG, Janke & Kunkel-Str. 10, D-79219 Staufen, Germany

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Table 1: Particle sizes from laser scattering and BET / density measurements

Inframat Advanced Materials			Laser scattering			BET / dens.		BET	dens.
Cat.	Lot #	d	d_{10}	d_{50}	d_{90}	d	A_r	A	ρ
		$[nm]$	$[nm]$	$[nm]$	$[nm]$	$[nm]$	$[\frac{m^2}{cm^3}]$	$[\frac{m^2}{g}]$	$[\frac{g}{cm^3}]$
5622ON-01	IAM6287NBTO	100	213	271	578	100	60.0	10.4	5.75
5622-ON2	IAM2197BTO2	200	220	399	934	242	24.8	4.1	5.99
5622-ON3	IAM3287BT3	300	250	571	1021	286	21.0	3.5	5.96
5622-ON4	IAM5206BT4	400	236	717	1162	382	15.7	2.6	6.01
5622-ON5	IAM2024BTO5	500	136	333	1205	475	12.6	2.1	6.07
5622-ON7	IAM7615BTO7	700	88	258	1214	589	10.2	1.7	6.01

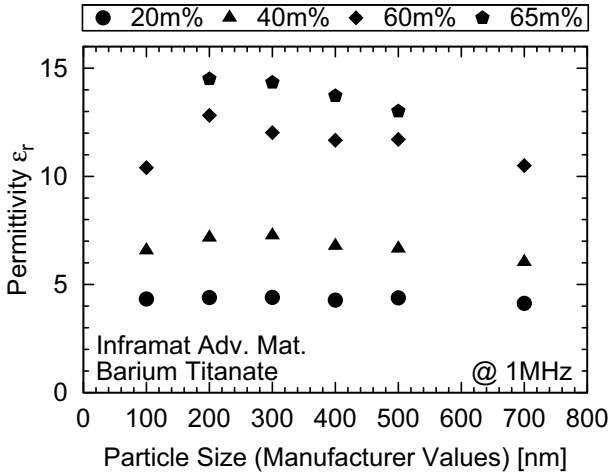

Figure 4: Permittivity of composites with $BaTiO_3$ filler from Inframat Advanced Materials with varying primary particle sizes at room temperature and a frequency of 1MHz.

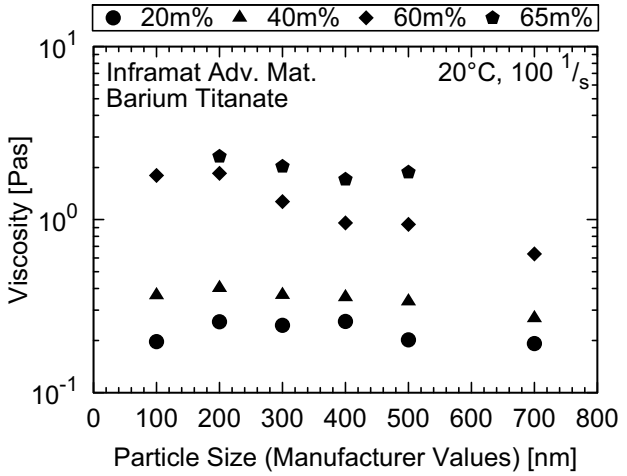

Figure 5: Viscosity of composite materials at 20 °C and 100 $\frac{1}{s}$ at varying particle sizes and loads of the filler

results from the XRD measurements the only powder capable of being enhanced by thermal treatment is the 100 nm specimen – enabling the realization of tetragonal crystallites which are smaller than the commercial ones.

3.2 Influence of the particle size on the viscosity and permittivity of polyester reactive resin composite materials

As expected from the X-ray diffraction pattern results the 200 nm specimen is showing the best dielectric properties as filler in polyester composite materials (comp. fig. 4). The powders crystalline state is fully tetragonal and it is the powder with the lowest primary crystallite size in the series of tested powders. These results are in very good agreement with the results from [5]. The crystallites are already too large to show optimum dielectric performance ($CuK_{\alpha 1}$ and $CuK_{\alpha 2}$ peaks already well separated).

The 100 nm specimen is the only powder that potentially can be optimized using temperature treatment. It is cubic in structure and by applying a well developed thermal treatment program the crystalline structure of best dielectric performance can be preset. The primary crystallites of all other specimen are already too large to perform well as dielectric fillers.

The viscosity of the composite materials before adding the hardener at 20 °C and 100 $\frac{1}{s}$ for varying filler loads is given in fig. 5. The highest viscosity values have been found for the 200 nm powder. The 100 nm powder – having a larger surface area and therefor a higher expectancy for large viscosity values – is less agglomerated and its particles are nearly spherical (comp. fig. 1 and fig. 2) which can explain the slightly lower viscosity. All specimen with primary particle sizes larger than 100 nm are showing agglomeration and none spherical particles.

3.3 Comparison of commercially available $BaTiO_3$ powders

To conclude the work, thirteen commercially available $BaTiO_3$ powders have been tested for their dielectric properties as fillers in composite materials (see key

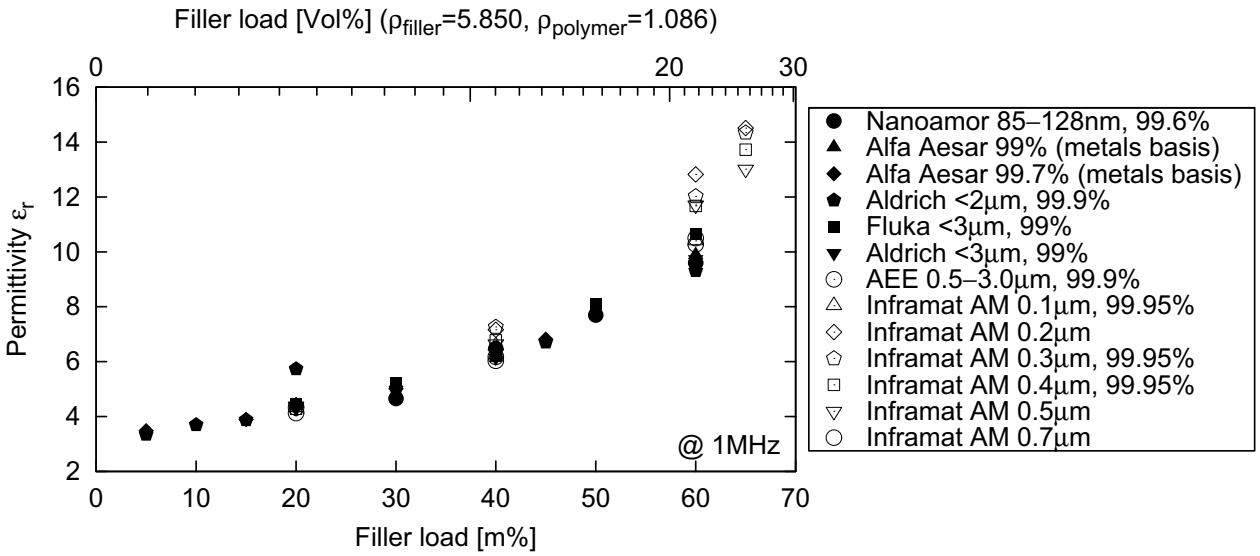

Figure 6: Permittivity of composites with varying filler load and varying commercially available $BaTiO_3$ filler at room temperature and a frequency of 1MHz.

of fig. 6 for manufacturer and powder details). The permittivity reached ranges from about 9 to 15 at a filler load of 60 m% (22 Vol%) when using the $BaTiO_3$ powders without any modification (fig. 6).

Using thermal treatment on the Nanoamor powder the authors where able to reach a permittivity of 25 at 60 m% and room temperature[5]. Recent publications about the permittivity of epoxy/$BaTiO_3$ composite materials show values of 27–35 at 60 Vol% filler load [8], 16 at 40 Vol% [9] and 38 at 50 Vol% [10]. Choi et al. published a permittivity of 12 for a PI/$BaTiO_3$ composite at 30 Vol% filler load [11]. These values are in good agreement with the values found for commercially available powders in this work.

None of the investigated powders is optimized for high-d_k composite applications. The available nano scale powders are in a cubic crystalline state and therefor not applicable. The other powders shows a tetragonal crystal structure with very large primary crystallites. The permittivities of the resulting composite materials lie all within a small range and far off optimized values from thermally treated powders.

4 CONCLUSIONS

Barium titanate powders from Inframat Advanced Materials with primary particle sizes ranging from 100 nm to 700 nm have been investigated intensely for their applicability as fillers in polyester reactive resin composite materials. It has been shown that none of the available powders is optimized for high-d_k composite applications. The 100 nm specimen is cubic, which is not optimal for dielectric applications. The 200 nm to 700 nm specimen are tetragonal in their crystalline structure but the primary crystallites are too large to show optimized dielectric behavior.

Parallel to the Inframat AM powders investigation seven additional powders from five different manufacturers have been tested as fillers in high-d_k composite materials. All tested powders lie within a very small range of permittivity and none of the powders is showing enhanced performances as high-d_k filler.

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