
B. Schumacher* **, H. Geßwein* , T. Hanemann* , J. Haßelt*

* Forschungszentrum Karlsruhe GmbH, Institut für Materialforschung III
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
** corresponding author: benedikt.schumacher@ifm.fzk.de

ABSTRACT

Commercially available barium titanate powder was temperature treated to induce grain growth at temperatures between 500°C and 1200°C. The permittivities of polyester reactive resin composite materials with a filler load of 60m% where examined in dependence of the heat treatment. A permittivity of 25 at 150Hz was achieved using a treatment temperature of about 1000°C while a composite containing the original powder exhibits a permittivity of 11. Temperature treatment of commercial BaTiO$_3$ powder is one crucial step in optimizing high $d_{k}$ composite materials without having direct influence over the powder production process.

Keywords: barium titanate, crystallite size, permittivity

1 INTRODUCTION

The industry needs for highly integrated and compact electronics are steadily increasing. The use of integrated passives technologies is one way to reduce the number of components on top of a printed circuit board (PCB) and therefore reduce precious surface area [1]. To produce embedded capacitors polymeric materials with high dielectric constant, processing temperatures below 250°C and good mechanical stability are necessary [2]. In order to be successful on the market the developed materials need to comply with traditional PCB production processes. To reach high capacities with single layer assemblies the produced high permittivity layers have to be as thin as possible.

This can be achieved through inorganic filler loadings within a polymeric matrix. Barium titanate is a widely used material for high permittivity applications. It’s dielectric properties depend strongly on the crystallite size and lattice [3]. To reduce the layer thickness - and therefore increase the capacitance - small particles are needed. In sintered barium titanate a maximum permittivity has been found at grain sizes around 1µm.

The permittivity of BaTiO$_3$ particles also highly depends on the powder production process [4]. But powder production processes are often not in hand of the composite material manufacturer. Commercially available BaTiO$_3$ powder has been optimized by temperature treatment for high permittivity and low particle size.

2 EXPERIMENTAL

A nano scale barium titanate powder (Nanoamor #1150XW, 99.6%, cubic, 8 - 12 m$^2$/g specific surface area) was used as a basic raw material for all experiments. To initiate crystallite growth 100g samples of the powder where temperature treated (Carbolite, RHF 17/3E) at different temperatures between 500°C and 1200°C with a heating rate of $\frac{2}{K_{min}}$ and a cooling rate of $\frac{5}{K_{min}}$. For temperature treatment the powder was loosely given into a ZrO$_2$ crucible (Friialit-Deggussit, FZY-Material) and covered with a ZrO$_2$ disc. The treated samples where characterized using BET, He-pycnometric, REM and XRD (Siemens, D505).

X-ray diffraction patterns were collected at room temperature from 20° to 80° 2θ with a step size of 0.02 and a fixed counting time of 20s using Cu K$_\alpha$ radiation with a graphite monochromator in reflection geometry. The full-profile-fitting refinements were carried out by the Rietveld method using the FullProf program [5]. To determine the crystallite size, phase contents and the tetragonality ($\frac{c}{a}$) ratio of the powders. A pseudo-Voigt function was used for the peak profile shape. The instrumental contribution to peak broadening was determined with annealed BaF$_2$ powder as a standard material.

Using a spherical model a mean particle radius $r_a$ was calculated using (1); $V$ being the volume of a sphere, $A$ being it’s surface area, $\rho(\frac{2}{V})$ being the density derived from He-pycnometric and $s_0(\frac{2}{g})$ being the specific surface area derived from BET measurements.

$$ r_a = \frac{3 \cdot V}{A} = 3 \cdot (\rho \cdot s_0)^{-1} \tag{1} $$

The temperature treated barium titanate powders where then incorporated into a polyester reactive resin (Carl Roth). To reduce the viscosity 20m% of styrene where added to the reactive resin. As release agent 2m% of INT-54 (Würtz) where added. Three mass percent of MEKP where used as cold hardener. The composite was stirred at 800 rpm (IKA dissolver stirrer 29mm diameter) for 30 minutes before the MEKP was added. Discs
where produced by pouring the composite into cavities made from silicone (Wacker, Elastosil M 4370 A). The composite discs where hardened at 50°C for three hours.

The discs where abraded to get plane surfaces and its dimensions (thickness and diameter) where determined. For dielectric measurement electrodes where attached to both sides of each disc using conductive silver paint (RS Components, Silver Conductive Paint). The complex capacity of the discs was measured between 150Hz and 10MHz using an impedance analyzer (Agilent, HP4194A) and the permittivity was calculated using (2) with measured capacity of the disc C, average thickness of the disc t and radius of the disc r.

\[
\varepsilon_r = \frac{C \cdot t}{\pi \cdot r^2 \cdot \varepsilon_0} \quad (2)
\]

Unless specified otherwise measurements where conducted at room temperature.

3 RESULTS AND DISCUSSION

The optical morphology of the temperature treated powders starts to change at about 1000°C. This can be observed from the REM images shown in figure 1. At this point grain growth across particle boundaries starts to take place and is visually recognizable.

![REM images of heat treated BaTiO₃ nanopowder (maximum Temperature given).](image)

Figure 1: REM images of heat treated BaTiO₃ nanopowder (maximum Temperature given).

The density of the powder samples increases steadily from 5.53 g/cm³ to 5.94 g/cm³ (see. fig. 2), coming close to the literature value of 6.08 g/cm³ [6]. The BET surface area slightly increases from 58.0 m²/cm³ to 71.5 m²/cm³ at 650°C treatment temperature. Above 650°C treatment temperature the BET surface area decreases steadily to 6.5 m²/cm³ due to grain and particle growth of the powder.

The average particle radius derived from BET and He-pycnometric measurements increases slowly up to a temperature treatment of 1100°C. Above that temperature the particles start to grow rapidly as can be observed from figure 3. This is in good agreement with the REM images (see fig. 1).

![Average particle radius derived from BET and density using a spherical particle model (see (1)).](image)

Figure 3: Average particle radius derived from BET and density using a spherical particle model (see (1)).

The original BaTiO₃ powder consists of two different phases. A tetragonal fraction t and a cubic fraction c in equal parts (see tab. 1, compare [7]). With growing crystallites the tetragonal fraction increases and at a treatment temperature above 1000°C the cubic fraction vanishes. The lattice parameter of the cubic phase \(a_c\) changes rapidly when heating the powder to 500°C (see tab. 1 and fig. 4 top two plots peak shift) and stays constant for any higher heat treatment. The \(\frac{a_t}{a_c}\) ratio of the tetragonal phase undergoes similar changes than the cubic phase, but only stays constant up to 800°C and rises with higher temperatures. This is in good agreement with the particle diameter (see fig. 3) as larger crystallites show a higher \(\frac{a_t}{a_c}\) ratio [7].

The x-ray density \(\rho_{x\, r\, d}\) undergoes less rapid changes
Figure 4: XRD patterns of temperature treated BaTiO$_3$ powders with varying treatment temperature.

Table 1: Physical properties of temperature treated BaTiO$_3$ powders.

<table>
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<tr>
<th>$T$[°C]</th>
<th>$t$[%]</th>
<th>$c$[%]</th>
<th>$\frac{a}{a_0}$</th>
<th>$\frac{c}{c_0}$</th>
<th>$\rho_{he}$</th>
<th>$\rho_{xrd}$</th>
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An X-ray diffraction (XRD) study was conducted to determine the effect of temperature treatment on the crystal structure of BaTiO$_3$ powders. The intensity of the peaks varied with treatment temperature, indicating changes in the crystallinity of the material.

Figure 5 shows the composite viscosity at three different temperatures, fixed shear rate of 100 s$^{-1}$ and constant solid load of 60 m% as function of the BaTiO$_3$ heat treatment conditions. With increasing heat aging temperature up to 800°C a slight viscosity increase can be observed (section I). Between 800°C and 1100°C filler heat treatment temperature the viscosity remains almost constant (section II), followed by a pronounced drop at larger temperatures (section III).

A clear correlation of the viscosity with the filler preprocessing cannot be detected, hence the influence of several filler characteristics on the flow behavior have to be considered. The thermal treatment changes the specific surface area, the average particle size, the particle size distribution as well as the particles morphology resulting in a superimposed impact on the composite viscosity.

The impact of the particle heat treatment on the flow behavior can be depicted from viscosity curves representing the three different sections. Figure 6 presents typical flow curves of composites containing BaTiO$_3$ treated at 500°C, 1150°C and 1200°C measured at a composite temperature of 60°C. While the composite with the filler aged at the lowest temperature show a slight viscosity increase in whole shear rate range, the mixture with the 1150°C treated filler exhibit a pronounced viscosity rise between 10 and 20 s$^{-1}$. Finally the composite with the filler aged at 1200°C possesses an almost Newtonian flow.

The permittivity of polyester reactive resin composite material with a filler load of 60 m% highly depends on the temperature treatment of the filler as can be seen in figure 7. Up to 900°C treatment temperature the permittivity rises steadily from 11 to 25. Between 900°C and 1150°C a plateau can be observed with an absolute maximum of 27 at 1050°C temperature treatment. At temperature treatments of the filler above 1150°C the permittivity of the composite drops rapidly.

The highest permittivity is reached in the same temperature region, where the tetragonal shoulder of the
(200) peak starts to develop visually in the XRD diagram (see fig. 4). Crystal structure and size of the BaTiO$_3$ powder show as expected a large influence on the dielectric properties of the composite material. Barium titanate crystallites with small but mostly tetragonal phases offer the best dielectric behavior (compare tab. 1 cubic fraction c and fig. 7).

![Figure 7: Permittivity at room temperature of BaTiO$_3$ filled polyester resin (60 m%) with varying heat treatment of the BaTiO$_3$ filler.](image1)

The permittivity of such composite materials is - as well as the permittivity of sintered barium titanate - dependent on the temperature of the material. A temperature dependent measurement of reactive resin composite with 60m% of temperature treated BaTiO$_3$ nanopowder filler (treated at 1050°C) is shown in figure 8. The permittivity rises nearly linear from 23.4 at −20°C to 29.9 at 60°C. A peak around room temperature as seen in [3] that results from a crystal phase transition (orthorombic to tetragonal) can not be observed in the composite material.

For minimal grain and particle size in combination with optimal dielectric performance a temperature treatment of 950°C to 1050°C has to be enforced on the filler before incorporating it into the composite material.

Recent publications about the permittivity of epoxy / BaTiO$_3$ composite materials show values of 27 – 35 at 60Vol% filler load [8] and 38 at 50Vol% [9]. Choi et al. published a permittivity of 12 for a PI / BaTiO$_3$ composite at 30Vol% filler load [10]. With the method described in this paper values of 25 – 27 could be reached at much lower filler loads of about 22Vol% permitting improvements concerning the filler load or lower viscosity of the composite material.

Crystal modification by temperature treating commercially available BaTiO$_3$ seems to be a useful and cheap route for the optimization of high $d_k$ composite materials.

![Figure 8: Temperature dependent permittivity of BaTiO$_3$ composite material (60m%). The filler is temperature treated at 1050°C for one hour.](image2)

4 CONCLUSION

The dielectric properties of commercially available barium titanate powder have been optimized by temperature induced grain growth. The permittivity of a polyester reactive resin composite material can double by use of a temperature modified barium titanate filler. The tetragonal phase is the crucial factor for maximizing the permittivity. The transition point where all cubic phases are transformed to tetragonal phases is the point of maximum permittivity.

For further development, the temperature treated barium titanate powder needs to be sieved and conditioned. A dispersing agent is needed to improve the stability of the composite while hardening. To maximize the permittivity the filler load of the composite needs to be increased.

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REFERENCES
