$BaTiO_3$-P(VDF-TrFE) Composite Ink Properties for Printed Decoupling Capacitors

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KEYWORDS: A. Polymer-matrix composites (PMCs); B. Electrical properties; D. Electron microscopy; E. Cure; E. Screen-Printing

Abstract

In this research a composite for printable capacitors using screen printed structures and low temperature curing ferroelectric ink was investigated. The realized ink consisted of 40 vol-% barium titanate in a poly(vinylidenefluoride-trifluoroethylene) matrix. DuPont silver ink 5064H was used for the conductive lines in the design and the maximum process temperature was 130 °C. The thickness of the composite and the area of the printed capacitor were 43 μm and area 25 mm^2, respectively. The obtained relative permittivity of the composite was 46 and the tan δ was 0.15 at 1 MHz. Additionally, the microstructure of the composite was investigated and the temperature dependence of the dielectric properties measured. The capacitance of the parallel plate structure was approximately 200 pF at 1 MHz. This is easily adjustable by changing the printing pattern, number of layers or the filler loading. The freedom of choice in integration and capacitance value selection makes the ink highly usable in, for example, decoupling capacitors that are compatible with inorganic, organic and even flexible, substrates.

1 Introduction

In modern electronics, active components play an important role. However, this also has had the effect that the number of passive components needed in applications has greatly increased. Today passive components may cover more than 80 % of the printed area of electric circuit boards; in mobile phones, for example, the ratio of passive to active components is greater than 20:1. This, especially in the case of capacitors, has created a need for smaller, inexpensive and more freely integrated components. **[1-2]** Decoupling capacitors are one of the most used capacitor applications. They are responsible for filtering the power source voltages and reducing problems of signal integrity and electromagnetic compatibility in the electronic devices. The number of decoupling capacitors increases directly with the number of digital circuits in a design. For example, one simple and widely used guideline is to include a local decoupling capacitor next to every supply voltage pin of an active component. This gives some indication of the ratio of decoupling capacitors to the active components in electronic applications. Depending on the complexity of the application, the capacitance values of decoupling capacitors vary roughly between 0.01 to 100 μF and the required operation frequency between 1 kHz to 100 MHz. **[3-6]**

Selection of decoupling capacitors is based on finding the value and right type of capacitor, together with the best location for maximum effect. The capacitance value with discrete components cannot be selected freely in that only the nominal values of the available components can be used. Additionally, inductance caused by the structure of the component and its implementation plays a large role in selecting the type of capacitor and the design of the layout. The inductance of the implemented decoupling capacitor depends on its type and on the area of the loop that forms between the ground and supply voltage lines. This generally includes the leads and pads of the component, the location of the power planes or traces and the active components. **[3-6]** Printable capacitors based on polymer matrix composite inks provide several advantages in the case of decoupling components. The capacitance value can be selected within a certain range by the loading level of the filler and the layout of the capacitor (especially its shape) and its optimal location can be more freely designed. Also, composites based on a polymer matrix are more compatible with printed circuit board integrations, especially if the substrate is flexible. **[1-2, 7]**

Ceramic-polymer composites enable the combination of the best dielectric properties; the high relative permittivity and low dielectric loss of ceramics and the low processing temperature and flexibility of polymers. [**1-2, 7-15]** Such types of composites, i.e. ceramic-polymer, are easy to process and their electrical properties are not particularly sensitive for small variations of filler loading rates even at near the percolation threshold in contrast to composites having conductive fillers. **[1,2,7]** However, it should be kept in mind that the effects of the agglomeration of particles and percolation must be taken into account, since both may weaken the mechanical properties of these composites by increasing the porosity and making the distribution of the polymer irregular within the microstructure and by so affect also to the electrical properties **[1,7 10-14]**.

The combination of polyvinylidenefluoride (P(VDF)) and its copolymer with trifluoroethylene: poly(vinylidenefluoride-trifluoroethylene) (P(VDF-TrFE)) as a matrix material with $BaTiO_3$ (BT) as ceramic filler have been previously suggested for use as composites with moderate permittivity (around 35 - 45 at 1 MHz) [**8-15**]. These polymers are ferroelectric because of their semi-crystalline ferroelectric β-phase. The ferroelectric phase is built into the copolymer when the TrFE content becomes more than 10 to 15 mol.%. **[16-18]** Although crystallinity increases the permittivity of the polymers, they suffer from quite a high dielectric loss, which is a characteristic for this composite group. However, some applications such as embedded capacitors, which can be used for decoupling, do not suffer from higher losses, but instead have too low a relative permittivity. **[8-15]**

In this paper P(VDF-TrFE) – $BaTiO_3$ composite ink for a fully printed low temperature cured capacitor is researched. Instead of conventional extrusion or moulding and hot pressing methods, here the screen printable ink was fabricated through a relatively straight-forward chemical solution process using a specific surfactant. Parallel plate capacitors were printed and measured in order to investigate the microstructure and dielectric properties of the cured composite ink.

2 Material and methods

The polymer matrix used in the developed composite ink was P(VDF-TrFE) (Solvay-Solexis, Belgium) with a molecular ratio of 56/44 because it produced the highest relative permittivity in this copolymer system **[17]**. BT (Sachtleben, Germany) with an average particle size of 0.2 μm was used as the ceramic filler. The use of particles with 0.2 - 0.3 μm size has been reported to ensure a high permittivity in BT – PVDF composites **[13]**. The BT particles were coated with a surfactant, Malialim® AAB-0851 (NOF Co., Japan). The top and bottom electrodes of the structure were screen printed with a low temperature curable silver ink (5064H, DuPont, USA). The capacitors were printed on alumina (96 % purity, Ceramtec, Germany) to eliminate the mechanical deformation possible in the case of a flexible substrate. Thus the properties of the composite ink could be seen more clearly. For a reference, a pure copolymer sample was fabricated from the P(VDF-TrFE) powder using injection moulding (200°C) and the copper electrodes were laminated (180°C, 4 MPa). The height of the sample and area of the electrodes were 13 μm and 38.5 mm^2, respectively.

2.1 Ink Formulation and Printing

Ceramic particles were milled for 16 hours with surfactant dissolved in acetone and 2-(2-Buthoxyethoxy) ethyl acetate (>99.2%, Sigma-Aldrich, Germany). This was done in order to achieve a single molecular layer of surfactant on top of the particles to prevent agglomerations when suspended in the ink matrix **[1, 7, 10-13]**. The polymer was dissolved with dimethylformamide (>99%, Fluka) and mixed with the ceramic filler solution in a ball mill for 16 hours. The amount of the ceramic content in the cured composite was adjusted to 40 vol-%, which, according to earlier investigations, was the highest loading level to result in high quality printed samples **[19].** After mixing, the excess solvent was evaporated to attain a suitable viscosity for screen printing. Two layers of the composite ink were printed on each sample through a 60 micron mask. All layers (electrodes and composite) were cured separately at 130 °C for 10-50 minutes. The thickness of the cured composite layer (43 μm) was measured with a Veeco Dektak 8 Surface Profiler. The area of the capacitor was 25 mm^2 (Fig. 1.)

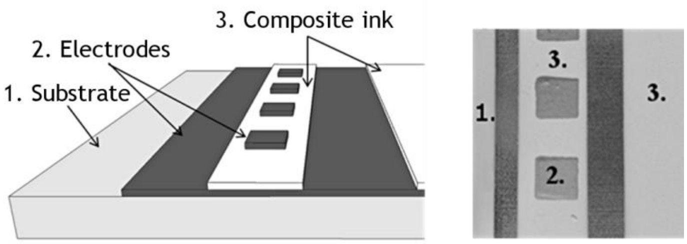

Figure 1. Schematic picture of the sample structure (left) and printed and cured sample (right).

2.2 Experiments

The crystal structure of the samples was observed with XRD (Discover D8, Bruker) between (2θ) angles of 10 - 80°. The BT sample was in powdery form and the composite ink in cured form. The laminated pure copolymer sample was used as a reference. The microstructure of the printed and cured samples was investigated with FESEM (Zigma, Zeiss) on the surface and on the fracture surface. The dielectric properties were measured using an LCR meter (HP 4284A) at room temperature from 100 Hz to 1 MHz and in the temperature range of -30 – 100°C at 100 kHz and 1 MHz frequencies with 1 V_{pp} signal.

3 Results and Discussion

3.1 Microstructure

Figure 2 shows the typical surface (Fig. 2a) and fracture surface (Fig. 2b) of the cured composite showing only very minor agglomeration of the BT particles. The printed composite was clearly 0-3 type because it can be seen there is continuous polymer matrix between the filler particles (light grey areas in Fig. 2). The porosity was very limited which, together with the low agglomeration level, confirmed that the used surfactant was working as expected and the ink layer was well densified. Further improvements could be achieved by more advanced particle treatments and composite mixing, and by printing several thinner layers of composite ink with optimized printing parameters.

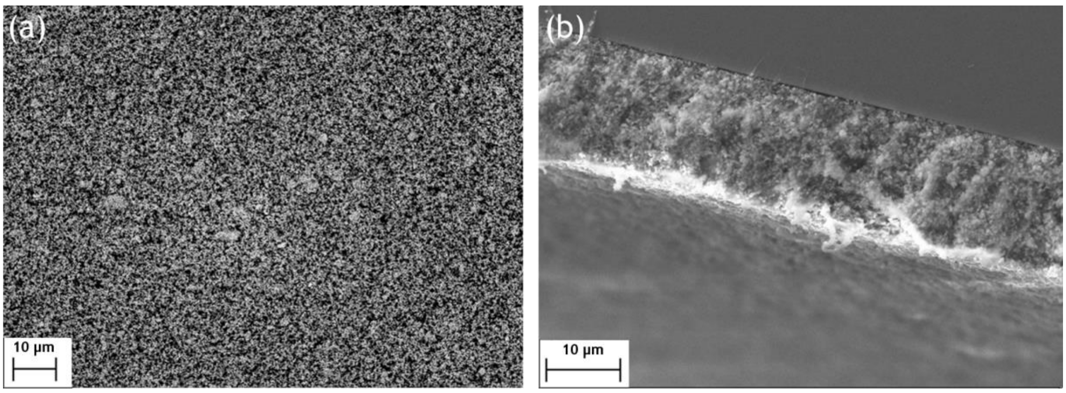

Figure 2. FESEM backscattering pictures of surface (a) and fracture surface (b) of a cured composite layer.

The results of XRD measurement are shown in the Figure 3. The peaks between 18 - 20° are characteristic for the piezoelectric β-phase in the copolymer **[16 - 18]**. These results clearly show that the reference sample and the polymer matrix of the composite had the required phase structure without any extra amorphous phases. The diffraction peaks of the pure BT (Figure 3c) match very well with the tetragonal barium titanate also clearly visible in diffraction plot of the composite.

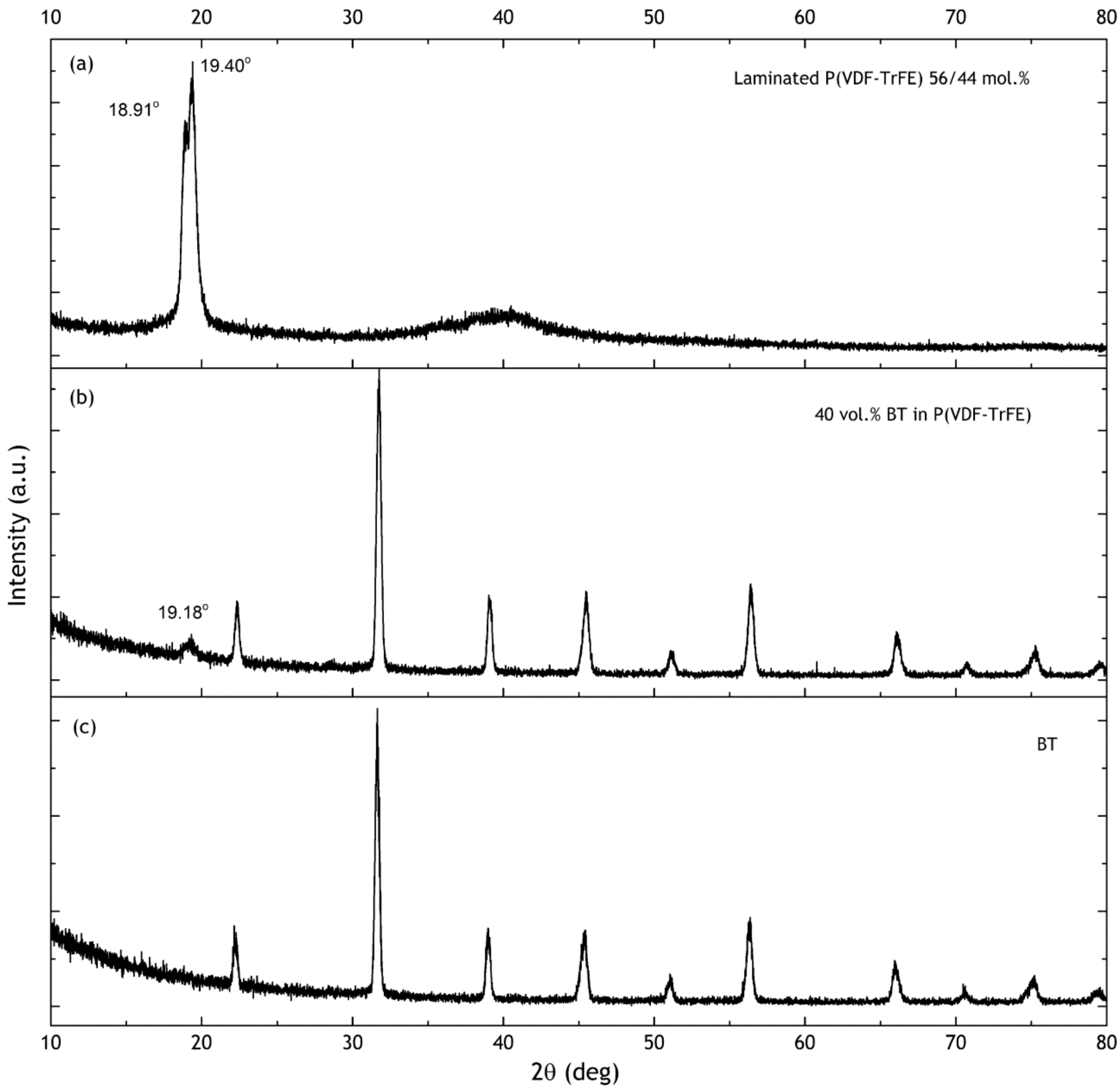

Figure 3. XRD patterns for the reference sample (a), ceramic polymer composite (b) and pure BT (c).

3.2 Dielectric properties

The dielectric measurement results (Figure 4a) show relative permittivity, ε_r, of 15 – 8 at 1 kHz - 1 MHz and loss tangent, tan δ, 0.28 at 1 MHz for laminated PVDF co-polymer. From the composites results it is clearly seen how the BT filler increased the relative permittivity, being 70 - 46 at 1 kHz - 1 MHz, which is more than five times higher than for the laminated copolymer in the measured frequency range. At 1 MHz the loss tangent for the composite was 0.15. An obvious reason for this notable lower dielectric loss is the low tan δ value of pure BT (0.02 at 1 MHz) compared to that of the copolymer. The BT addition decreased the tan δ value, especially in the frequency range 100 kHz – 1 MHz. When the frequency was lower than 4 kHz tan δ was higher in the composite than in the copolymer. A similar observation has been reported by others **[13]**. This might be due to Maxwell-Wagner-Sillars polarization, but the effect is not particularly large with the used loading level and particle size. Figure 4b shows the capacitance value of the device together with its frequency dependence, indicating the potential of this composite for decoupling capacitor applications. It should be kept in mind that only a single layer parallel plate device was realized. However, the dielectric properties of the composite depend on temperature, especially at high temperatures close to the phase transition of the polymer (Figure 5). At lower temperatures, the relative permittivity shows linear regions from -20 to 50°C and from -5 to 45°C at 100 kHz and 1 MHz, respectively, which are about 75 % wider than for the bulk copolymer. The maximum peak of ε_r, which relates to the depolarization of the P(VDF-TrFE), has moved to slightly higher temperatures. This might be due to the BT filler, but is almost certainly also due to the effect of the pressure-free and lower temperature fabrication of the composite on the crystallinity of the matrix **[10, 16]**. The variation of tan δ as a function of temperature is shown in Figure 5b. The dielectric losses of the composite were noticeably lower and more stable at the measured temperatures (solid lines). This is due the properties of the ceramic filler and good densification of the ink in the curing process. The behaviour of tan δ as a function of temperature as well as the high temperature peak of ε_r for the composite follow closely the dielectric characteristics of pure P(VDF-TrFE).

The printed composite showed higher relative permittivity than has been previously reported with the same loading level, while the dielectric losses remain at the same level **[8-15]**. This is almost certainly due to the selection of the matrix material and the particle size, and the new fabrication technique including chemical solution processing with specific surfactant and printing which enabled a low agglomeration level and a more uniform distribution of the filler. In future, the stability of dielectric properties as a function of temperature could probably be improved by increasing the amount of VDF in the copolymer. This would increase the phase transition temperature. However, it is reported that an increase in the amount of PVDF above 55 mol% in PVDF-TrFE blend, will influence to the monomer diad fractions and microstructure of the copolymer, which will notably decrease the permittivity of the matrix polymer and also the overall permittivity of the composite **[17]**. The use of smaller ceramic particles or a mixture of different sized ceramic particles could also improve the stability of the composite against temperature and frequency **[12, 13 and 15]**. Further advanced methods to increase the permittivity would be to use special terpolymers such as P(VDF-TrFE-CTFE) **[1]** or by the addition of small amounts of metal nano particles **[20-21]**. It is also obvious that all these modifications to the processing and material selection would make the composite more complex and may induce some new problems.

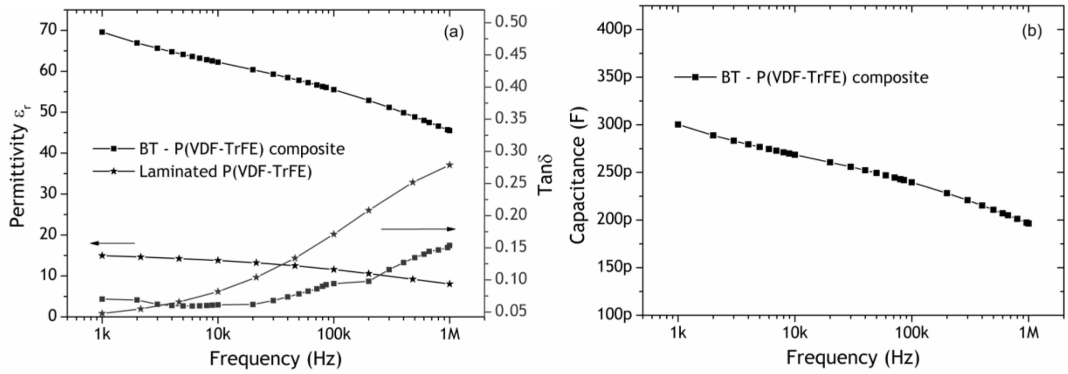

Figure 4. Relative permittivity and dielectric losses (a) and capacitance (b) of the cured printed composite as a function of frequency at room temperature.

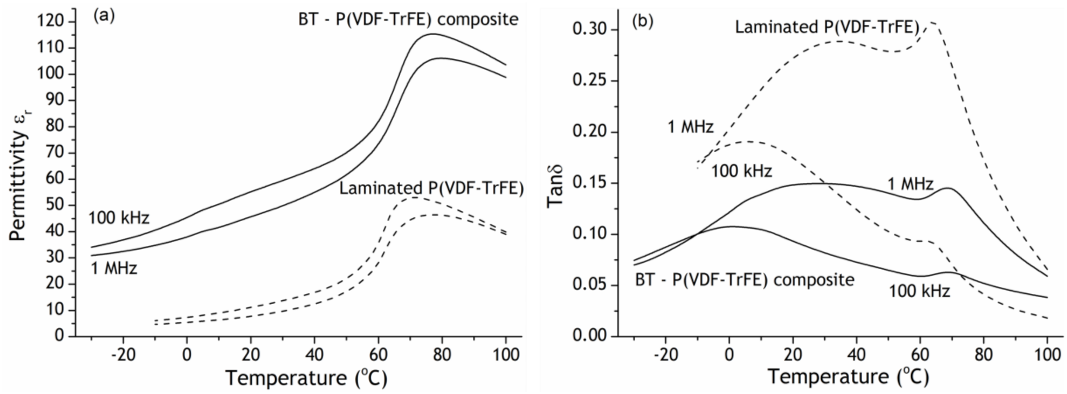

Figure 5. Relative permittivity (a) and dielectric losses (b) of the cured printed composite and laminated copolymer as a function of frequency.

4 Conclusions

A straight-forward low processing temperature method was used to fabricate a fully printable capacitor structure with BT-P(VDF-TrFE) composite ink. The FESEM analyses revealed 0-3 connectivity with a low agglomeration level and uniform distribution of BT particles due to the chemical solution process and special surfactant used. Samples showed high relative permittivity (46) with a linear temperature range of -5 to 45°C at 1 MHz. The temperature dependence of the properties of the polymer matrix was clearly seen in the measurements which showed a much more stable and lower tan δ for the composite than for the pure P(VDF-TrFE). As a conclusion, the BT-P(VDF-TrFE) composite was successfully fabricated in ink form for the first time and the developed fully printable capacitor has a good potential for decoupling applications since it enables a free selection of the capacitance value, shape and location, and it is compatible even with flexible substrates.

5 Acknowledgements

The authors acknowledge Tekes funded project "Innoinks" 906/31/2010 and its co-partners: Jozef Stefan Institute (Slovenia), ITME (Poland), Sachtleben Pigments Oy (Finland), Pulse Finland Oy (Finland) and NOF Corporation (Japan) for supporting this study. Authors T. S. and M. N. appreciatively acknowledge the Riitta ja Jorma J. Takanen foundation and Infotech Oulu Doctoral Program for funding. Author M. N. acknowledges also KAUTE, Tauno Tönning and Wihuri foundations for financial support. Author J. J. gratefully acknowledges Academy of Finland funding (grant agreement No. 267573).

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