Macedonian Journal of Chemistry and Chemical Engineering, Vol. **34**, No. 2, pp. 381–388 (2015)

MJCCA9 – 696
ISSN 1857-5552
e-ISSN 1857-5625

Received: November 17, 2014
Accepted: September 23, 2015

UDC: 620.162-039.6:[544.252.24:678.7
Original scientific paper

INORGANIC DOPANTS IN POLYMER CHOLESTERIC LIQUID CRYSTALS

Anka Trajkovska Petkoska

Faculty of Technology and Technical Sciences, Veles,
St. Kliment Ohridski University, Bitola, Republic of Macedonia
anka.trajkovska@uklo.edu.mk

A variety of dopants are used for different types of polymers to change their properties. Inorganic dopants are normally used to change the dielectric properties of the polymers. These compositions find different applications, especially in electronic systems, due to the ease of polymer processing, increased functionality and the low cost of novel materials that are with relatively high dielectric constant compared to the base polymer material.

In this study, polymer cholesteric liquid crystal (PCLC) is used as a host material that is doped by different inorganic dopants, $BaTiO_3$ and TiO_2, all of which affect the dielectric constant of the polymer matrix. This is important from the fact that doped PCLC can be used for a variety of electro-optical applications, e.g. display applications and low energy consuming e-book application. The behavior of inorganic dopants in PCLC is calculated by various existing mixing models; the best fit is observed by the use of logarithmic equation.

Keywords: polymer cholesteric liquid crystals; inorganic dopants; $BaTiO_3$; TiO_2

НЕОРГАНСКИ ДОПАНТИ ВО ПОЛИМЕРНИ ХОЛИСТЕРИЧНИ ТЕЧНИ КРИСТАЛИ

Најразлични допанти се користени за промена на својствата на различни видови полимери. Неорганските допанти обично се користат за промена на диелектричните својства на полимерите. Овие композиции наоѓаат најразлични апликации, посебно во електронските системи, поради лесно процесирање на полимерот, зголемена функционалност и ниската цена на чинење на новите материјали кои се со релативно висока диелектрична константа споредено со основниот полимерен материјал.

Во овој труд полимерни холистерични течни кристали (PCLC) се користени како базен материјал кој е допиран со различни видови неоргански допанти, $BaTiO_3$ и TiO_2, коишто влијаат на диелектричната константа на полимерната матрица. Ова е важно од аспект дека допираниот PCLC може да се користи за најразлични електро-оптички апликации, како на пример, дисплеј апликации и е-книга (електронска книга), апликации кои имаат мала потрошувачка на енергија. Однесувањето на неорганските допанти во PCLC е пресметано со користење различни постојни модели на мешање. Се покажало дека најдобар модел е со користење на логаритамската равенка.

Клучни зборови: полимерни холистерични течни кристали; неоргански допанти; $BaTiO_3$; TiO_2

1. INTRODUCTION

Composite materials obtained by integrating two or more materials can offer the potential to have performance far beyond those of the basic constituents. There are a variety of particulate substances, such as metallic, ceramic, carbon, etc., that can be used as dopants (fillers, inclusions) in materials [1–7]. In particular, polymeric materials are of interest for doping with a variety of dopants and form composites with unique properties. Particle *dopants* can be of different shapes, such as spherical [1, 2, 4], fiber-like [6], or flake-platelets and with dimensions from nano- [2, 6, 8] to micron-sized particles [1, 3, 4]. These heterogeneous mixtures exhibit improvements in their properties compared to those of the neat polymer host in terms of mechanical, electrical, and thermal properties, tailoring them to a variety of applications [1, 3, 6, 9–27].

To raise the dielectric constant of polymer materials, polymer composite materials provide an ideal solution. Ferroelectric ceramics as dopants to polymer hosts usually possess relatively high dielectric constants, but are brittle and have low dielectric strength. On the other hand, polymers are flexible, easy to process with low processing temperature in general, but possess high dielectric breakdown fields. By mixing polymers with ceramic dopants, a unique composite material can be obtained – *high dielectric constant polymeric material*. In general, the most commonly used polymers are epoxy, polyethylene, polypropylene, polyethylene therephtalate, poly-methyl metacrylate, and poly-ethyletherketone, which meet the requirements for the low cost organic substrate process and mechanical flexibility, and can be upgraded with the advantages from the fillers/dopants and obtaining desirable dielectric properties. They find a variety of applications, especially in electronic systems, due to the growing demands of electronic miniaturization or packaging, increased functionality, high performance and low cost for novel material compositions with high dielectric constants [28–45]. The dielectric properties of polymer compositions depend primarily on the content, size, and distribution of dopant particles as well as processing techniques. When very high dopant concentrations are required to increase the dielectric constant of the composite, processing can become more difficult; other properties, optical or physical, may also be disrupted.

Predicting or calculating the dielectric constant of the polymer composites resulting from doping is very important. For this purpose, different dielectric mixing models exist for prediction of the dielectric constant of heterogeneous mixtures [46–48]. The equations for the effective dielectric constant of the composite are generally based on the dielectric permittivity of each constituent and its volume fraction. The following models and equations are described by many other authors [49, 50].

Maxwell-Garnett mixture equation (1) is given as:

$$\frac{\varepsilon_m - 1}{\varepsilon_m + 2} = f_1 \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} + f_2 \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2}, \qquad (1)$$

where ε_m is the dielectric constant of the mixture, ε_1 and ε_2, are the dielectric constants, and f_1 and f_2 are volume fractions of each component (1 refers to the polymer or PCLC matrix, and 2 for dopant). Models for the effective dielectric constant of composites use the same notation.

The *Bruggeman* or the *Bruggeman-Hanai* equation is given as eq. (2). This equation is also known as the *Botcher* equation:

$$f_1 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} + f_2 \frac{\varepsilon_2 - \varepsilon_m}{\varepsilon_2 + 2\varepsilon_m} = 0\,. \qquad (2)$$

The two-phase mixture equation, denote as *MU*, is given in eq. (3):

$$\varepsilon_m = \varepsilon_1 \left[1 + 3\left(\frac{\varepsilon_2 + 2\varepsilon_1}{f_2(\varepsilon_2 - \varepsilon_1)} - 1\right)^{-1} \right]. \qquad (3)$$

The *Logarithmic* or *Lichtenecker-Rother* [42] equation (4) is one of the most commonly used equations for predicting the dielectric constant of statistical/chaotic composites. It is given as:

$$\log \varepsilon_m = f_1 \log \varepsilon_1 + f_2 \log \varepsilon_2\,. \qquad (4)$$

For *insulating fillers* in a polymer, there is a Maxwell-Wagner mixing rule [48] formula that is given as eq. (5):

$$\varepsilon_m = \varepsilon_1 \left\{ \frac{\left[2\varepsilon_1 + \varepsilon_2 + 2 f_2(\varepsilon_2 - \varepsilon_1)\right]}{\left[2\varepsilon_1 + \varepsilon_2 - 2 f_2(\varepsilon_2 - \varepsilon_1)\right]} \right\}. \qquad (5)$$

The above equations give similar results for lower dopant loading in a polymer host. For higher volume fractions of a dopant in a polymer, there are often discrepancies between these models and experimental data. This is possibly due to the following: a) the high volume fraction of the dopant may increase the porosity of the composite material, or b) the high dopant fraction may lead to agglomeration of the powder and a non-uniform distribution through the composite.

In this work, inorganic dopants, like different $BaTiO_3$ and TiO_2, are used and considered *non-conductive (ceramic)* dopants with high inherent dielectric constants. They increase the dielectric constant of polymers when they are added in large concentrations, without affecting conductivity.

Polymer-ceramic materials, polymers doped with ferroelectric $BaTiO_3$ (BT), offer the potential to have both the high dielectric constant due to the ceramic material (BT) and good polymer processing [46, 51]. The dielectric properties mostly depend on: the content, purity, size, distribution of the BT particles and the processing techniques. Usually, very high dopant concentrations (more than 30 vol.% or even higher ~51 vol.% or 67 vol.%) are required to increase the real permittivity of the composite from an undoped value e.g. ~2 (for the polymer host) to ~100 (for the polymer composition) [42, 46, 47, 51]. Sometimes this is not beneficial, because the high dopant loadings in the polymer host can make processing very difficult. Another problem which usually arises for BT is the difficulty in measuring the true value for the dielectric constant of the BT. There is no direct methodology for measuring the dielectric constant of dopants in powder form. Usually, the measured value of the dielectric constant for a bulk sample of BT ceramic is used instead of that for the powder form. The particle (grain) size of BT is very important for determining its dielectric constant. Literature values vary from 100–600 [48] (grain size < 0.7 μm, much smaller than the dielectric constant of bulk BT ceramics), to ~2000 (for grain size of 10 μm, for example), or ~5000 (for grain size between 0.7 and 1 μm) [52]. The dielectric constant of these ceramic-polymer composites increases as the powder size decreases [37, 40–42, 45].

On the other hand, TiO_2/polymer composites are reported to exhibit improved mechanical properties, as well as increased dielectric constants; however, nano-sized TiO_2 has a larger effect compared to micron-sized TiO_2 on mechanical properties in TiO_2/polymer compositions [10, 11, 43, 45, 54]. There are different crystalline forms of TiO_2 powders, such as rutile and anatase. The rutile form of TiO_2 has a higher dielectric constant than the anatase form, usually ranging from 20 to over 200, but this value also depends on the compositeon/purity of TiO_2 material (higher the amount of rutile phase means higher the dielectric constant of composition).

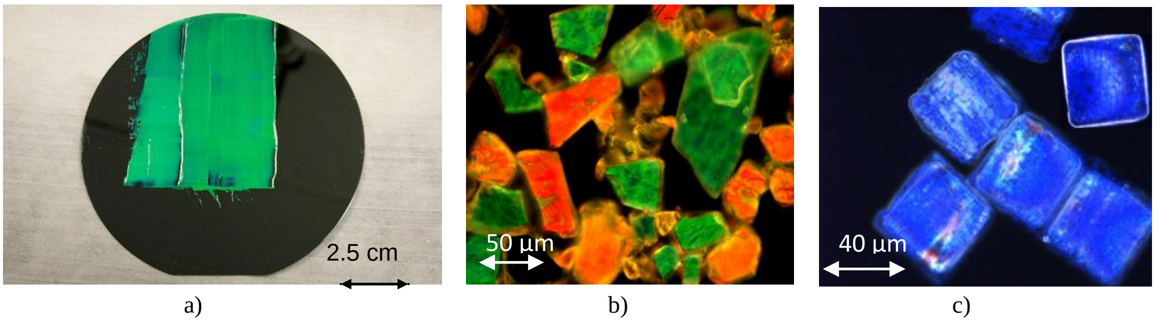
The PCLC material in this study was of the particular interest for the author, it possesses unique optical properties: selective reflection and circular polarization of the reflected light due to the helical structure [45, 55, 56]. As a result of its doping, the use of PCLC extends to novel optical, photonic and electronic applications. The most important are electro-optical applications, such as display and sensor applications, color filters, and electronic labels, besides the known passive applications such as use in the military as decals, decorative/cosmetic inks and paints, document security, retarders, waveplates, filters, polarizers, etc. [45, 56–60].

2. EXPERIMENTAL

2.1. *Materials*

The polymer cholesteric liquid crystal (PCLC) material used as a polymer matrix in this work is a non-cross-linkable cyclic polysiloxane material. It is left-handed cholesteric liquid crystal that belongs to the class of side-chain liquid crystalline polymers (product of Wacker–Chemie GmbH, Munich, Germany) with a glass transition temperature ~50 °C and a clearing point (T_c) of ~200 °C (as measured by the manufacturer and other researchers) [45]. PCLC exhibits unique optical properties, such as selective reflection and circular polarization due to its helical structure, and has the potential in many optical, photonic and electronic applications [45, 55–58]. Figure 1 shows PCLC material made into thin film (Fig. 1a) and into the form of tiny particles (flakes), irregular or regularly-shaped, presented in Figure 1b and Figure 1c.

Dopants considered in this work are listed in Table 1. They are $BaTiO_3$ (BT) and TiO_2 materials.



a) b) c)

Fig. 1. a) Thin PCLC film prepared on a silicon wafer substrate, b) irregularly shaped PCLC microparticles prepared by freeze-fracturing of the film with liquid nitrogen, c) tailored shaped blue PCLC microparticles prepared by soft-lithography technique [45].

Table 1

Dopants for PCLC used in this work

Dopant	Particle size*	Particle shape
Neat PCLC (no dopant)	–	
Inorganic		
$BaTiO_3$-1 (BT-1)	70 nm	spherical
$BaTiO_3$-2 (BT-2)	1 to 1.1 μm	spherical
$BaTiO_3$-3 (BT-3)	1.3 to 1.8 μm	spherical
TiO_2-1	30 nm	spherical
TiO_2-2	10 nm × 40 nm	needle-like

[a] Primary average particle dimensions

Namely, three different types of BT dopants and two of TiO_2 with different particle sizes and shapes are used [45, 59, 60]. Nano- and micro-sized $BaTiO_3$ powders were selected knowing that the dielectric constant of this type of dopant varies substantially with particle size. Two types of rutile type of TiO_2 are investigated: one of them, TiO_2-1, consists of particles with a spherical shape (30 nm in diameter, product of Marketech International, Inc., Port Townsend, WA), while the other type, TiO_2-2, are particles with needle-like shapes (dimension of 10 nm x 40 nm, Nanostructured & Amorphous Materials, Inc., Los Alamos, NM). [Note: these are primary particle dimensions. By SEM, it is determined that both of these powders are highly aggregated] [45]. The dielectric constant values of TiO_2 dopants were not provided by the vendors; for theoretical calculations for ε_2 (TiO_2) in this work, a value that varies from 20 to 200 was used.

2.2. *Measurement on PCLC/dopant composites*

Doped disks (pellets) made from PCLCs (product of Wacker–Chemie GmbH, Munich, Germany) and a particular dopant were prepared in order to determine the dielectric properties of the compositions. Pellets made from pure dopant powder are not easily prepared because of their high melting temperatures or their inability to be compressed into pellets. For each system (PCLC/dopant), ~10 or more samples with different dopant concentrations are prepared with a diameter of ~2 cm and a thickness of ~0.5 mm by using a “thin film-maker tool” with controlled heating and pressure (constant-thickness filmmaker and thin-film–making kits are products of International Crystal Laboratories, Garfield, NJ) [45].

Dielectric measurements of each PCLC/dopant composition as well as on pure PCLC disk are conducted on a frequency response analyzer by using a special holder for solids (Solartron 1260 by Solartron Analytical). These measurements are rapid, accurate and non-destructive, for electrochemical phenomena in materials. The sample holder for solids is designed to allow accurate impedance tests of solids at room temperature. It consists of two parallel electrodes that form a parallel capacitor. The bottom electrode is fixed in position, and the top electrode can be lowered into contact with the sample. After contact with the sample is made, a measurement of the sample thickness can be taken by reading the dial of a micrometer thickness gauge attached to the top electrode. The range of measured impedance values vary from 1 Ω to 100 TΩ and the frequency region for measurement is from 10 µHz to 32 MHz. When a voltage (potential) is applied to the material, a current flows through the test chamber that is determined by the mechanisms characterizing the motion of charge within the material [45, 61, 62]. The output impedance signal after interaction with the sample presented as capacitance, C, and resistance, R, as a function of the frequency is analyzed by frequency response analysis (FRA) [63]. [Calculations of the dielectric properties of the measured samples placed in the parallel plate capacitor are performed by assumption of a circuit where C is in a parallel configuration with R] [45].

Scanning electron microscopy (SEM) micrographs are taken using either an FE SEM LEO 982 (EMSL, Richland, WA) and SEM LEO–EVO 50, while polarized optical microscopy (POM) images are taken on a Leica, DMRX polarizing microscope coupled with a DC300F camera (Leica Microsystems AG, Germany) [45].

3. RESULTS AND DISCUSSION

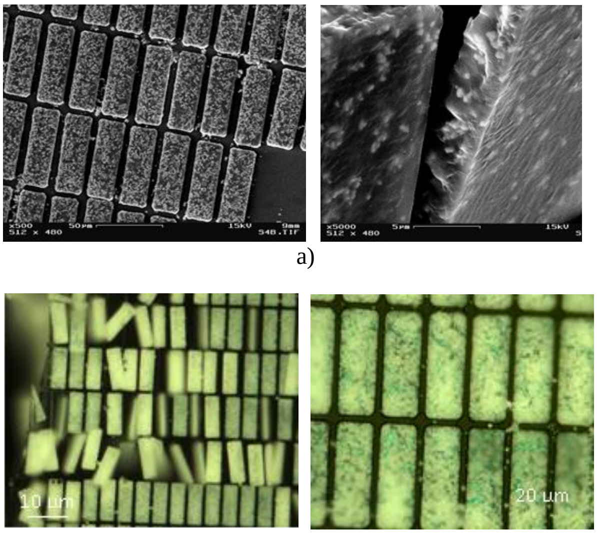
All inorganic dopants used in this work show a similar effect on PCLC dielectric properties. They increase the dielectric constant of the composite at relatively high dopant loadings. The equations given in the Introduction predict that the dielectric constant of PCLC doped with BT and TiO_2 can be increased only by a factor of ~10 or less at relatively high dopant level ~25 vol.% or more. The best fit of experimental data are observed via equations 4 and 5 [45]. Table 2 presents measured dielectric constants of different PCLC/dopant composites.

Table 2

Measured data of different PCLC/dopant composites

Dopant	Dielectric constant of composition PCLC/dopant at 10 kHz (at vol.%)
Neat PCLC (no dopant)	2.1
Inorganic	
$BaTiO_3$-1	7.7 (27.0)
$BaTiO_3$-2	6.1 (32.0)
$BaTiO_3$-3	5.8 (27.0)
TiO_2-1	5.2 (54.4)
TiO_2-2	7.5 (22.0)

Figure 2a shows SEM images of doped PCLC particles with high doping levels of BT-1 (top and side view of the particles made of BT-1/PCLC compositions), while Figure 2b shows polarizing optical microscope (POM) images of BT-1 doped green PCLC particles. [It is noticeable that high BT concentrations in PCLC disrupt the selective reflection as well].

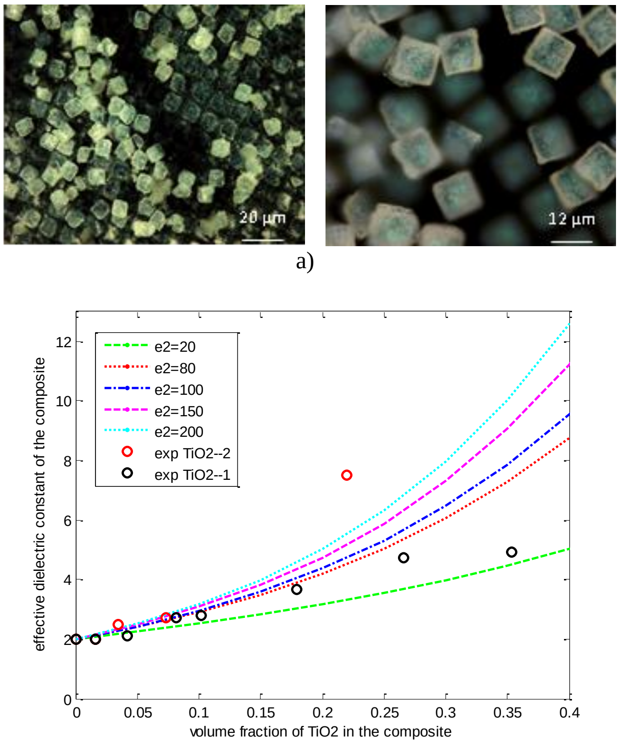


a)

b)

Fig. 2. a) SEM images (top and side view of the particles made of 20 vol.% BT-1 in PCLC), b) POM images of ~20 vol.% BT-1-doped PCLC particles

Figure 3a) shows POM images of 20 vol.% TiO_2-doped PCLC square-shaped particles. [These composites also exhibit a reduction in the quality of green selective reflection]. Figure 3b compares the theoretical calculations for the effective dielectric constant of the TiO_2/PCLC composite using eq. 4 and the experimental data for both TiO_2 powders (listed in Table 1). The value for ε_2 (TiO_2) varied from 20 to 200 (for the theoretical calculation using eq. 4) and the resulting values for the composite dielectric constant, ε_m, vary from 4 to 12 at dopant level of 35 vol.% TiO_2 in PCLC composite. Experimental data for TiO_2-1 are in better agreement with lower values for ε_2, e.g. 20–80, which suggests that this dopant powder is not purely rutile. TiO_2-2 may be a purer rutile phase, since ε_m data fit better with the higher values of $\varepsilon_2 \geq 200$ (e.g. at ~25 vol.%, a dielectric constant of 8 is found for this composition).



a)

b)

Fig. 3. a) POM images of highly TiO_2-doped PCLC particles, b) comparison of experimental data with theoretical calculations (using eq. 4) for effective dielectric constant for TiO_2/PCLC mixtures for different values for ε_2 (Note: red and black circles in the graph are experimental data for TiO_2-2 and TiO_2-1 types of used dopants, respectively. Different colored lines are theoretical calculations that use different values of dopants' dielectric constant).

Figure 4 compares the effect of all inorganic $BaTiO_3$ and TiO_2 dopants in the PCLC matrix. Generally, all show an increase in composite dielectric constant up to ten at very high dopant levels, e.g., ≥ 20 vol.%. Higher dopant concentrations in PCLC are difficult to achieve. A logarithmic eq. 4 for calculation of the effective dielectric constant of the composite agrees well with the experimental data. The main problem here is choosing an appropriate value of the dopant dielectric constant to use in the model. In this case PCLC/$BaTiO_3$ composites are well fitted with the log equation (4) when $\varepsilon(BaTiO_3)$ is ~150 (vendor supplied value is 150 for $BaTiO_3$-1), while the value used for TiO_2 is $\varepsilon(TiO_2)$ ~80. Deviations between the experimental data and theoretical calculations can be due to: (a) the quality of dopant dispersion in the polymer matrix, (b) agglomeration, and/or (c) incorporation of air voids/pores inside the samples, which can drastically decrease the effective dielectric constant of the mixture, ε_m.

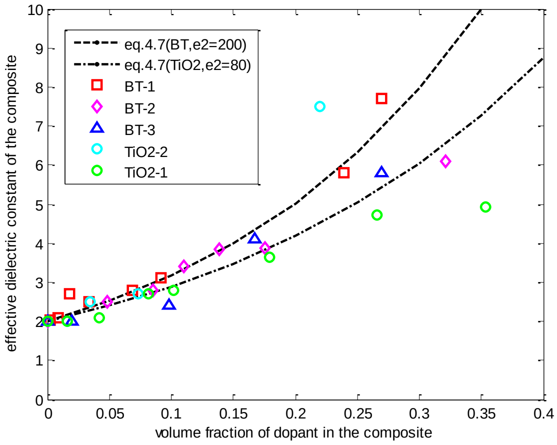


Fig. 4. Comparison of dielectric constant at 10 kHz for PCLC composites using inorganic dopants $BaTiO_3$ and TiO_2, measured (symbols) vs. calculated (lines) values. Calculated values are obtained by use of logarithmic equation (4).

4. CONCLUSION

Ceramic-polymer composites have been investigated for different purposes. These composites have increased dielectric constants compared to the dielectric constant of basic polymer host, with or without increased composite conductivity. Finer inorganic particles (e.g. nano-particles) with a higher ratio of surface area to volume may have better particle-to-particle contact to improve the dielectric constant, dielectric loss, and insulation resistance. As a result, the ceramic-polymer composites have the smallest diameter of inorganic particles, and higher values of dielectric constant.

In this study, dopants like $BaTiO_3$ and TiO_2 in PCLC material were investigated and shown to increase the dielectric constant of PCLC composites. Both dopants showed similar behavior. Namely, all three types of $BaTiO_3$ had almost the same effect on the PCLC composite dielectric constant. TiO_2-2 or a dopant with needle-like particles is more effective than the spherical TiO_2-1 dopant. It is possible that TiO_2-1 consists of mix rutile/anatase phase material that would lower the dielectric constant compared to dielectric constant of TiO_2-2. However, both dopant types used in this work for PCLC compositions fit well with the equations established by various authors. The best fit of these experimental data was observed with logarithmic equation.

Acknowledgments. This work was done at the University of Rochester, Laboratory for Laser Energetics in Rochester, NY, USA. The author thanks Prof. Steve D. Jacobs for his guidance and supervision through this project, and Mr. Kenneth Marshall and Dr. Tanya Kosc for their constructive advice and help. The author also acknowledges the Laboratory for Laser Energetics for Horton Fellowship support.

REFERENCES

[1] A. Maaroufi, K. Haboubi, A. El Amarti, F. Carmona, Electrical resistivity of polymeric matrix loaded with nickel and cobalt powders, *Journal of Materials Science* **39**(1), 265–270 (2004).

[2] D. M. Grannan, J. C. Gargland, D. B. Tanner, Critical behavior of the dielectric constant of a random composite near the percolation threshold, *Physical Review Letters* **46**(5), 375–378 (1981).

[3] H. Zois, L. Apekis, Y. P. Mamunya, Structure-electrical properties relationships of polymer composites filled with Fe-powder, *Macromolecular Symposia* **194**, 351–359 (2003).

[4] H. Zois, Y. P. Mamunya, L. Apekis, Structure and dielectric properties of a thermoplastic blend containing dispersed metal, *Macromolecular Symposia* **198**, 461–472 (2003).

[5] F. Carmona, Conducting Filled Polymers, *Physica A* **157**(1), 461–469 (1989).

[6] M. Moniruzzaman, K. I. Winey, Polymer nanocomposites containing carbon nanotubes, *Macromolecules* **39**(16), 5194–5205 (2006).

[7] Y. Xi, H. Ishikawa, Y. Z. Bin, M. Matsuo, Positive temperature coefficient effect of LMWPE-UHMWPE blends filled with short carbon fibers, *Carbon* **42**(8–9), 1699–1706 (2004).

[8] T. W. Ebbesen, Carbon Nanotubes, *Annual Review of Materials Science* **24**, 235–264 (1994).

[9] R. Schueler, J. Petermann, K. Schulte, H. P. Wentzel, Agglomeration and electrical percolation behavior of carbon black dispersed in epoxy resin, *J. App. Poly. Sci.* **63**(13), 1741–1746 (1997).

[10] Y. Lu, W. H. Lee, H. S. Lee, Y. Jang, K. Cho, Low-voltage organic transistors with titanium oxide/polystyrenebilayer dielectrics, *Applied Physics Letters* **94**, 113303 (2009).

[11] S. Chaudhari, T. Shaikh, P. Pandey, A Review on Polymer TiO_2 Nanocomposites, *Int. J. Eng. Res. Appl.* **3**(5), 1386–1391 (2013).

[12] E. Tuncer, G. Polizos, D. R. James, I. Sauers, A. R. Ellis, K. L. More, Dielectric properties of various nanocomposite materials, CP1219 *Advances in Cryogenic Engineering: Transactions of the Cryogenic Engineering Materials Conference-ICMC*

56, U. Balachandran (Ed), American Institute of Physics, 2010.

[13] W. Ling, Q. Xia, L. Yan, C. Wang, M. Cao, L. Liu, Preparation, Morphology and Dielectric Properties of Nano-TiC/Polyimide Composite Films, *Polymers & Polymer Composites,* **22**(2), (2014).

[14] C. Huang, Q. M. Zhang, High-dielectric-constant all-polymer percolative composites, *Applied Physics Letters* **82** (20), (2003).

[15] X. Huang, P. Jiang, L. Xie, Ferroelectric polymer/silver nanocomposites with high dielectric constant and high thermal conductivity, *Applied Physics Letters* **95**, 242901 (2009).

[16] K. Shehzad, A. Ul-Haq, S. Ahmad, M. Mumtaz, T. Hussain, A. Mujahid, A. Tufail Shah, M. Y. Choudhry, I. Khokhar, S. Ul-Hassan, F. Nawaz, F. Rahman, Y. Butt, M. Pervaiz, All-organic PANI–DBSA/PVDF dielectric composites with unique electrical properties, *J. Mater. Sci.* **48**, 3737–3744 (2013).

[17] J. Xu, C. P. Wong, Effect of the Polymer Matrices on the Dielectric Behavior of a Percolative high k-Polymer Composite for Embedded Capacitor Application, *Journal of Electronic Materials* **35**(5), 1087 (2006).

[18] *X. J. Wang,* The effect of the prismatic filler arrangement and cross-sectional shape on the thermal conductivity of polymer composites, *eXPRESS Polymer Letters* **8** (12), 920–931 (2014).

[19] H. T. Oyama, M. Sekikawa, Y. Ikezawa, Influence of the Polymer/Inorganic Filler Interface on the Mechanical, Thermal, and Flame Retardant Properties of Polypropylene/Magnesium Hydroxide Composites, *Journal of Macromolecular Science, Part B: Physics*, **50**, 463–483 (2011).

[20] M. Madani, Conducting carbon black filled NR/IIR blend vulcanizates: Assessment of the dependence of physical and mechanical properties and electromagnetic interference shielding on variation of filler loading, *J. Polym. Res.* **17**, 53–62 (2010).

[21] X. Jin, M. Deng, S. Kaps, X. Zhu, I. Holken, K. Mess, R. Adelung, Y. K. Mishra, Study of Tetrapodal ZnO-PDMS Composites: A Comparison of Fillers Shapes in Stiffness and Hydrophobicity Improvements, *PLOS ONE* **9** (9), e106991 (2014).

[22] A. Ghosh, L. Ma, C. Gao, Zeolite molecular sieve 5A acts as a reinforcing filler, altering the morphological, mechanical, and thermal properties of chitosan, *J. Mater. Sci.*, **48**, 3926–3935 (2013).

[23] V. Mittal, Modelling and Prediction of Barrier Properties of Polymer Layered Silicate Nanocomposites, *Polymers & Polymer Composites* **21**(8), (2013).

[24] L. Lee, I.-J. Kim, S. Yang, S. Kim, Electrochemical properties of PEO/PMMA blend-based polymer electrolytes using imidazolium salt-supported silica as a filler, *Res. Chem. Intermed.,* **39**, 3279–3290 (2013).

[25] Aga and Mu, Doping of Polymers with ZnO Nanostructures for Optoelectronic and Sensor Applications, *Nanowires Science and Technology*, Nicoleta Lupu (Ed.), ISBN: 978-953-7619-89-3, InTech, 205–222 (2010).

[26] M. Johlitz, S. Diebels, Effective Mechanical Behavior of Filled Polymers, *Mechanics of Advanced Materials and Structures* **18**, 106–114 (2011).

[27] J. L. Alan kin-tak Lau, *Multifunctional Polymer Nanocomposites*, Taylor and Francis Group, LLC, 2011.

[28] T. Hanemann, J. Boehm, P. Henzi, K. Honnef, K. Litfin, E. Ritzhaupt-Kleissl, J. Hausselt, From micro to nano: properties and potential applications of micro- and nano-filled polymer ceramic composites in microsystem technology, *IEE Proc.-Nanobiotechnol.,* **151**(4), (2004).

[29] J. Lu, C. P. Wong, Recent Advances in High-k Nanocomposite Materials for Embedded Capacitor Applications, *IEEE Transactions on Dielectrics and Electrical Insulation* **15**(5), (2008).

[30] J. Lu, K.-S. Moon, J. Xu, C. P. Wong, Synthesis and dielectric properties of novel high-K polymer composites containing in-situ formed silver nanoparticles for embedded capacitor applications, *J. Mater. Chem*., **16**, 1543–1548, (2006).

[31] J. Xu, L. Wang, G. Liang, L. Wang, X. Shen, A General Quantitative Structure-Property Relationship Treatment for Dielectric Constants of Polymers, *Poly. Eng. Sci.* **51**, 12 (2011).

[32] Q. M. Zhang, H. Li, M, Poh, Feng Xia, Z.-Y. Cheng, H. Xu, C. Huang, An all-organic composite actuator material with a high dielectric constant, *Nature* **419**, (2002).

[33] K. Müller, I. Paloumpa, K. Henkel, D. Schmeisser, A polymer high-*k* dielectric insulator for organic field-effect transistors, *J. Appl. Phys.* **98**, 056104, (2005).

[34] T. Lei, Q. Xue, L. Chu, Z. Han, J. Sun, F. Xia, Z. Zhang, Q. Guo, Excellent dielectric properties of polymer composites based on core-shell structured carbon/silica nanohybrid, *Appl. Phys. Lett.* **103**, 012902 (2013).

[35] Y. Bai, Z.-Y. Cheng, V. Bharti, H. S. Xu, Q. M. Zhang, High-dielectric-constant ceramic-powder polymer composites, *Appl. Phys. Lett.*, **76**(25), (2000).

[36] G. Subodh, V. Deepu, P. Mohanan, M. T. Sebastian, Dielectric response of high permittivity polymer ceramic composite with low loss tangent, *Appl. Phys. Lett.* **95**, 062903 (2009).

[37] J.-R. Yoon, J.-W. Han, K.-M. Lee, Dielectric Properties of Polymer-ceramic Composites for Embedded Capacitors, *Transactions on electrical and electronic materials* **10**(4), (2009).

[38] P. Thomas, S. Satapathy, K. Dwarakanath, K. B. R. Varma, Dielectric properties of poly(vinylidene

fluoride)/$CaCu_3Ti_4O_{12}$ nanocrystal composite thick films, *eXPRESS Polymer Letters* **4**(10), 632–643 (2010).

[39] V. Tomer, C. A. Randall, High field dielectric properties of anisotropic polymer-ceramic composites, *J. Appl. Phys.* **104**, 074106, (2008).

[40] Y. Kobayashi, A. Kurosawa, D. Nagao, M. Konno, Fabrication of Barium Titanate Nanoparticles-Polymethylmethacrylate composite films and their dielectric properties, *Poly. Eng. Sci.* **49**, 6 (2009).

[41] M. Konieczna, E. Markiewicz, J. Jurga, Dielectric Properties of Polyethylene Terephthalate/Polyphenylene sulfide/barium titanate nanocomposite for application in electronic industry, *Poly. Eng. Sci.* **50**, 8 (2010).

[42] R. K. Goyal, V. V. Madav, P. R. Pakankar, S. P. Butee, Fabrication and Properties of Novel Polyetheretherketone/Barium Titanate Composites with Low Dielectric Loss, *J. Electr. Mat.* **40**(11), (2011).

[43] Y. I. Yua, M. H. Yia, T. Ahnb, Synthesis and characterization of a novel polyimide/TiO_2 nanocomposite for solution processable high k dielectric, *J. Ceram. Proc. Res.* **13**(2), 202–205 (2012).

[44] P. Barber, S. Balasubramanian, Y. Anguchamy, S. Gong, A. Wibowo, H. Gao, H. J. Ploehn, H.-C. zur Loye, Polymer Composite and Nanocomposite Dielectric Materials for Pulse Power Energy Storage, *Materials* **2**, 1697–1733 (2009).

[45] A. Trajkovska Petkoska, *Polymer Cholesteric Liquid Crystal Flakes – their Electro Optic-Behaviour for Potential E-Paper Application*, Verlag Dr. Müller, VDM ISBN 978-3-639-06439-1, Germany, 2008.

[46] C. K. Chiang, R. Popielarz, Polymer composites with high dielectric constant, *Ferroelectrics* **275**, 1–9 (2001).

[47] L. Ramajo, M. Reboredo, M. Castro, Dielectric response and relaxation phenomena in composites of epoxy resin with $BaTiO_3$ particles, *Composites: Part A: Appl. Sci. Manu.* **36**(9), 1267–1274 (2005).

[48] S. D. Cho, S. Y. Lee, J. G. Hyun, K. W. Paik, Comparison of theoretical predictions and experimental values of the dielectric constant of epoxy/ $BaTiO_3$ composite embedded capacitor films, *J. Mat. Sci. – Mat. Electr.* **16**(2), 77–84 (2005).

[49] H. M. Musal, H. T. Hahn, G. G. Bush, Validation of Mixture Equations for Dielectric-Magnetic Composites, *J. Appl. Phys.* **63**(8), 3768–3770 (1988).

[50] M. R. Anantharaman, S. Sindhu, S. Jagatheesan, K. A. Malini, P. Kurian, Dielectric properties of rubber ferrite composites containing mixed ferrites, *J. Phys. D - Appl. Phys.* **32**(15), 1801–1810 (1999).

[51] R. Popielarz, C. K. Chiang, R. Nozaki, J. Obrzut, Dielectric properties of polymer/ferroelectric ceramic composites from 100 Hz to 10 GHz, *Macromolecules* **34**(17), 5910–5915 (2001).

[52] M. T. Buscaglia, V. Buscaglia, M. Viviani, J. Petzelt, M. Savinov, L. Mitoseriu, A. Testino, P. Nanni, C. Harnagea, Z. Zhao, M. Nygren, Ferroelectric properties of dense nanocrystalline $BaTiO_3$ ceramics, *Nanotechnology* **15**(9), 1113–1117 (2004).

[53] T. M. Shaw, S. Trolier-McKinstry, P. C. McIntyre, The properties of ferroelectric films at small dimensions, *Ann. Rev. Mat. Sci.* **30**, 263–298 (2000).

[54] C. B. Ng, L. S. Schadler, R. W. Siegel, Synthesis and mechanical properties of TiO_2-epoxy nanocomposites, *Nanostructured Materials* **12**(1-4), 507–510 (1999).

[55] A. Trajkovska-Petkoska, R. Varshneya, T. Z. Kosc, K. L. Marshall, S. D. Jacobs, Enhanced Electro-Optic Behavior for Shaped Polymer Cholesteric Liquid Crystal (PCLC) Flakes Made by Soft Lithography, *Adv. Funct. Mater.*, **15**, 217 (2004).

[56] A. Trajkovska-Petkoska, S. D. Jacobs, The Manufacture, characterization, and manipulation of polymer cholesteric liquid crystal flakes and their possible applications, *J. Mat. Sci. Eng. (A&B), A2* **2**, 137–151 (2012).

[57] A. Trajkovska-Petkoska, Polymer cholesteric liquid crystal flakes as new candidates for display and sensor applications, *NATO Science for Peace and Security Series-B: Physics and Biophysics: Nanotechnological Basis for Advanced Sensors*, Springer, 2011.

[58] T. Z. Kosc, K. L. Marshall, A. Trajkovska-Petkoska, E. Kimball, S. D. Jacobs, Progress in the Development of Polymer Cholesteric Liquid Crystal Flakes for Display Applications, *Displays* **25**, 171–176 (2004).

[59] A. Trajkovska-Petkoska, S. D. Jacobs, Effect of Different Dopants on Polymer Cholesteric Liquid Crystals, *Mol. Cryst. Liq. Cryst.*, **495**, 334 (2008).

[60] A. Trajkovska-Petkoska, S. D. Jacobs, K. L. Marshall, T. Z. Kosc, *Electrically Actuated Doped Polymer Flakes and Electrically Addressable Optical Devices Using Suspensions of Doped Polymer Flakes in a Fluid Host*, U.S. 7,713,436 B1 (2010).

[61] N. D. Cogger, N. J. Evans, An introduction to electrochemical impedance measurement, *Technical report*, No. 6, Solartron Analytical (1999).

[62] Standard test methods for AC loss characteristics and permittivity (dielectric constant) of solid electrical insulation, Designation D 150–95, *ASTM Standard*.

[63] P. E. Wellstead, Frequency response analysis, *Technical report* 10, Solartron Analytical, Control System Principles, Cheshire, UK (2003).