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COMPOSITE MATERIALS ON THE BASIS OF THE RECYCLED CAPACITIVE CERAMICS

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Abstract. *In this paper, the composite materials are convenient for using the recycled raw materials, which mainly are naturally resistive and indestructible, such as the ceramic materials, resin and dissolvers. In the connection with that the composite based on barium titanate and novolac is synthesised from recycled materials. This composition could not be designed as a commonly produced moulding compound of novolac matrix with the ceramic powder as disperse phase because in this case the disperse phase plays an active role. The possibility prognosis of composite dielectric material composed of a barium titanate and novolac (phenolformaldehide) are examined, especially from the standpoint of their application in the electronic components. Here, $BaTiO_3$ phase in the form of particle size less than 100 μm is dispersed in homogenous organic matrix materials. Variation of some composite properties by change in mass ratio ceramic powder, and change of dielectric constant, dissipation factor and microstructure of composite are examined. Microstructure analysis makes possibility to determine the distribution of barium titanate ceramic in the composite matrix and the obtained results allow prognoses in the sense relation composition - microstructure - dielectric properties.*

Key words: *barium titanate, novolac, recycled ceramics, sintering process, hot pressing, electrical properties*

INTRODUCTION

It is common known that phenol [1], is one of the chemicals which to a great extent, endangers the human environment. C_6H_5OH, a colourless, crystalline solid that melts at about 41°C, boils at 182°C, and is soluble in ethanol and ether and somewhat soluble in water. An aromatic alcohol, it exhibits weak acidic properties and is corrosive and poisonous. Phenol is sometimes called carbolic acid, especially when in water solution. It reacts with strong bases to form salts called phenolates. Phenol is important in industry in the

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production of certain artificial resins, e.g., Bakelite, and in the synthesis of many drugs, dyes, weed killers, insecticides, and explosives (e.g., picric acid). It is the simplest member of a class of hydroxy benzene derivatives, all of which contain a hydroxyl group attached to a benzene ring; these compounds may be thought of as derivatives of phenol and generically are called phenols.

Phenol based composite materials can provide the following key properties: high-temperature resistance, modulus retention at elevated temperature, flame and arc resistance, resistance to chemicals, high surface hardness, good electrical properties and relatively low unit costs. Significant refinements have been accomplished in compounding. Compounds for compression moulding have a lower resin content in comparison to injection grades, which have a resin level approaching 50%. In addition it is customary that each material is available in at least three types of flow: low, medium and high flow.

Composite materials have found a number of structural applications but their current use in the electronics industry is relatively limited. There are some basic idea underlying electronic composite: sum and product properties, the symmetry of composite materials (fig. 1) and its influence on physical properties, varistor action and other interfacial effects. For a sum of property, the composite property coefficient depends on the corresponding coefficient of its constituent phases. On the other hand, product properties are more interesting involving different properties in its constituent phases with the phases often causing unexpected results.

On the other hand, $BaTiO_3$(BT) - ceramic capacitor material is well known by due to its higher capacitance value averaging dielectric constant of 1500 to 2000 [2]. However, there is wide variation in dielectric properties due to deviation from $BaO:TiO_2$ ratio as well as due to presence of other phases. On the dielectric properties of composites are also influenced by the presence of impurities in the starting materials and various conditions of their preparation.

In a composite the resulting properties depend on the mass fraction and characteristics of the components and on the way in which they are interconnected. The connectivity of a composite is defined as the number of dimensions in which each component phase is continuous. The ten possible connectivity patterns of diphasic composites are shown (fig. 1).

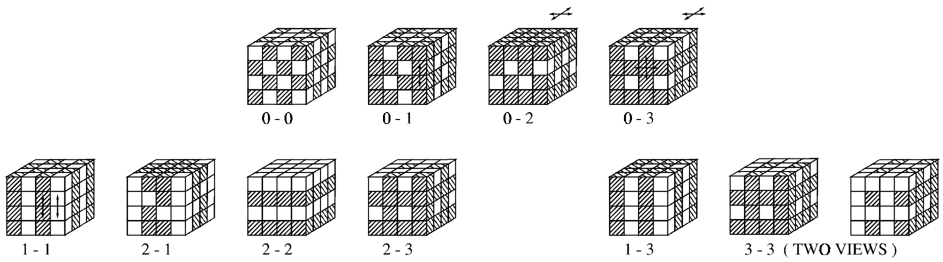


Fig. 1 The ten possible connectivity patterns of diphasic composites

In this paper, the self-development technology of the manufacturing resins on the basis of the phenols. Composites of BT ceramics and phenol resin are two-phase materials in which phenol resin phase reduces density and permittivity of the material and increases loss factor. First number is referred to an active phase – ceramic, and the second to the dimensions of connected other phase – phenol resin. The type of the composite with 2–2 connectivity has been referred to simple layer structure (sandwich) where the layer of one phase has been changed by the layer of second phase. The structure like to structure of the ceramic multilayer capacitors have such structure where layer of metal electrode has changed the layer of ceramic alternately. The properties of composites depend on the way of connectivity of their phases. It points to the particular physical or chemical properties are used to illustrate a sum, product properties or combination of properties for particular constitutive phases.

EXPERIMENTAL WORK

The interrelation *structure – technology – properties* was enabled the choice of optimal stable BT ceramic, (90÷96)% theoretical densities (TD), sintered at the temperature 1380°C and in the continuous time 240 minutes, for capacitive ceramics in accordance with constructor's requirements. They refer to stability of the component dielectric characteristics. Recycled ceramic, at this conditions, is characterised by constant value $\varepsilon_r = 1800$ and $tg\delta = 0.6 \cdot 10^{-4}$ in the working temperature region 25±10°C. Milling presents a conventional way of the obtaining ceramic powders. Frequently, together with milling, the homogenising process is covered. In some case, during milling the determined admixtures are added in order to improve the properties of recycled ceramic. Precursors are homogenised on the wet, as the water slip, in the ball mill (40 o/min) in time interval from 14 hours. Both, mill and balls have been made on the basis of pure (99.9%) alumina. Calcination has been carried out in the tunnel furnace at 1320°C according to the next regime: heating rate 100°C/min, cooling rate 80°C/min, time of isothermal heating at maximal temperature 30 min. On that way, the improved properties of recycled ceramic were obtained. In addition recycled material is at first crushed and later milling and sinterable BT powder is obtained [3]. Ceramic powder was analysed by the sifting method through the standard sieves and obtained powdered commercial grade BT sample, with particle size less than 100 μm.

A phenol novolac is prepared according to the following procedure. A 1 dm^3 resin kettle is charged with appropriate molar ration of phenol, and aqueous solution of formaldehyde. Also appropriate acid is added as a catalyst. The mixture is stirred and refluxed. Additional amount of acid is then introduced and refluxing is continued. In the next step a small amount of water is added and mixture cooled. The resin settles for 0.5 hour and upper layer of water decanted. Heating is then begun with the condenser modified for vacuum destilation. Water is distilled at about 10^3-10^4 Pa pressure until the pot temperature reaches 120°C. As obtained resin, brittle at room temperature, is powdered in order to obtain powder with particle size below 100 μm. As first, novolac sample (0% BT) is obtained in the form of cylinder with diameter D = 14.94 mm and thickness of d = 1.05 because of determining the electrical characteristics: C = 6.9 pF, $\varepsilon_r = 4.5$ and $tg\,\delta = 0.04$.

Fraction of powdered commercial grade BT sample with particle size below 100 μm is used as inorganic phase. Powder mixture of ceramic and novolac powders are mixed together with curing agent, and exposed to previous heat tretman. As obtained mixture with appropriate mass ration BT : novolac, in the range from approximately 95:5 to 70:30 in mass percents, is uniaxially hot pressed at 162°C / 15 MPa. Composite samples in the form of cylinders with diameter D = 15 mm and thickness of d ≈ 3.5 mm is examined according to its physical and dielectric properties [4]. Various hot-pressed composite samples are polarised at 25°C and 6 V. Dielectric properties are calculated from capacitance measured by using HP 4194A Impedance Gain Phase Analyser and HP4262 LCR-meter at 1 kHz and 1.5 kV and similar results are obtained.

Scanning electron microscopy was performed with JEOL - JSM-T20. The surfaces of BT-novolac were etched chemically by the solution of 90% HCl : 10% HF. Preventing the charge-up on the specimen under observation by covering the non-conductive material. Increasing secondary electron emission by covering the specimen surface with little secondary electron emission by covering it with a metal Au coating.

RESULTS AND DISCUSSION

The dielectric constant of BT multilayer capacitors decreases substantially under high voltage fields, often by twice or more. Selecting appropriate can exceeded mentioned shortage second (matrix) phase so that the obtained composite values for permitivity are field-independent. The interrelation structure-technology-parameters has enabled choice of optimal stable BT ceramic, sintered at the temperature 1380°C and in the continuous time 240 minutes, for capacitive ceramics in accordance with constructor's requirements. Dielectric constants and loss factors of samples sintered under various conditions are measured (fig. 2) and the compose dependencies are determined (fig. 3).

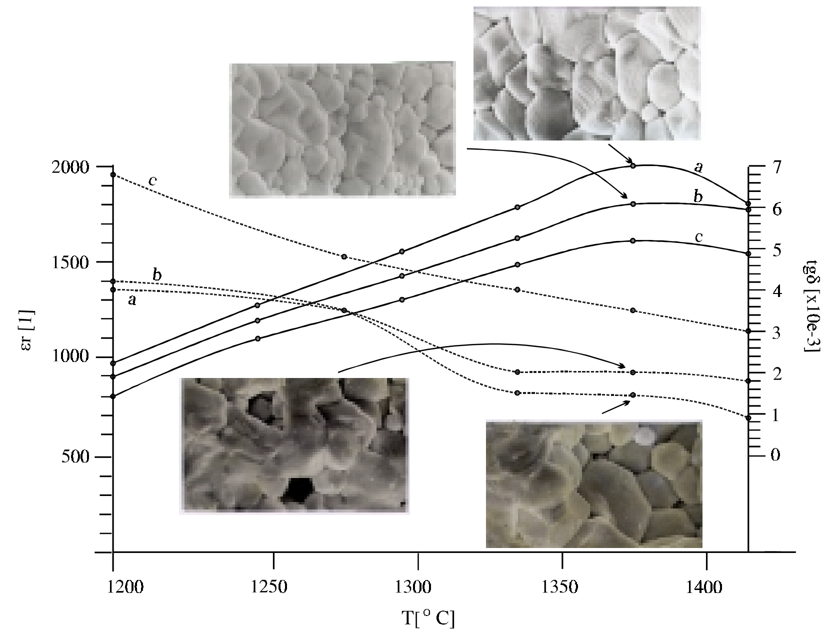


Fig. 2. Dielectric constant ε_r (full line) and loss factor tgδ (point to point line) vs. sintering temperature where the sintering time (a) 360 min, (b) 240 min, (c) 120 min, is a parameter

The parabolic dependencies are characteristics for dielectric constant (ε_r) as a function of temperature if the sintering time is taken as a parameter. On the other hand, dependence is linear function for the dielectric constant vs. time if sintering temperature is taken as a parameter. This linear dependencies point to the fact that the growth of ε_r is direct function of the middle grain size. Presence of the region of nonlinearly is the result of the pore size influence. This phenomenon can be explained by the distribution charge of electricity among the grain boundary and inside of hollows at the ceramic polarisation during determination of electric characteristics. Various sintered BT ceramic samples are polarised at 110°C and 1.5 kV/mm [5]. Values for dielectric constants ε_r and dissipation factor tgδ before and after polarisation are also measured. At polarised ceramics is noted raise of dielectric constant and capacities in the vicinity of Curie temperature and decreasing of tgδ because of increasing of resistance (fig. 4) what resulted from defect annihilation in the vicinity of grain boundaries and pores [7]. Formation of defects during ceramic polarisation follow to creating of interior fields whose prevent "hoping" effect of current conducting. Loss factor tgδ of polarised samples is lower than at non-polarised ones. This follow to obtaining of stable dielectric properties in the working temperature region 25 ± 10^{o}C.

Novolac isn't polarised and all changes connected with polarisation are the same as in the case of pure barium titanate [5], i.e. the dielectric constant ε_r has been changed insignificantly because the ferroelectric fields, in the arrays of used fields of polarisation, have the same slope (sl. 3a).

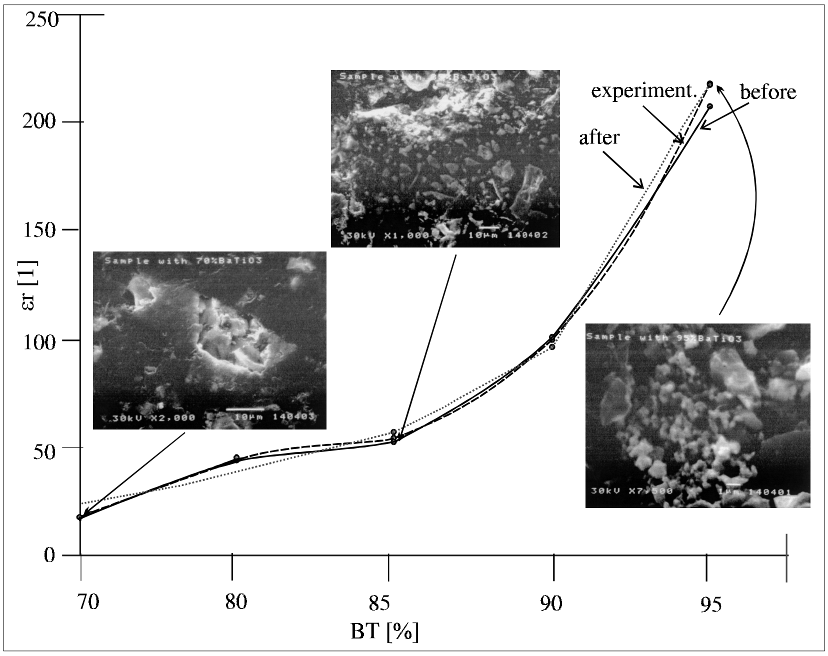


Fig. 3a. Dependence ε_r vs. BT content of hot pressed ceramic samples before and after polarisation.

In the observed chemically etched surfaces of specimens BT–novolac composites, presented grains are small sizes in order to be clearly observed ones under high magnifications (here, magnifications up to 7500 are used) and correlate the effects of BT percentage in novolac with the dielectric characteristics of as obtained composites (fig. 3).

From the observed specimens are noticed particle grains of irregular form which dive into the dark–grey substance of novolac. The fracture surfaces were observed which are yielded by the fracture of sample by axis being normal to the basis. The fracture surface reveals that the grain size bulk is in the range between (1 ÷ 100) μm and those grains have so-called terrace structure. The large difference in grain size was observed at hot–pressed (162°C) samples, although the smaller grains prevail. Also several features of the observed microstructure in BT–novolac specimen should be noticed. On the photomicrographs permeating of grain boundaries are noticed as and appearance of increasing pores what is the consequence of their coalescence (fig. 3 – the photomicrograph 95% BT content).

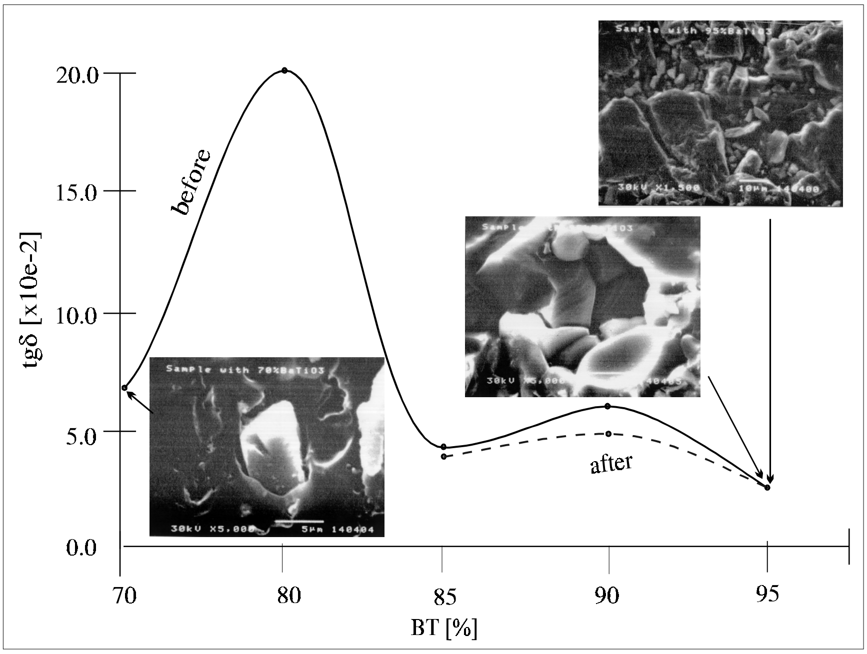
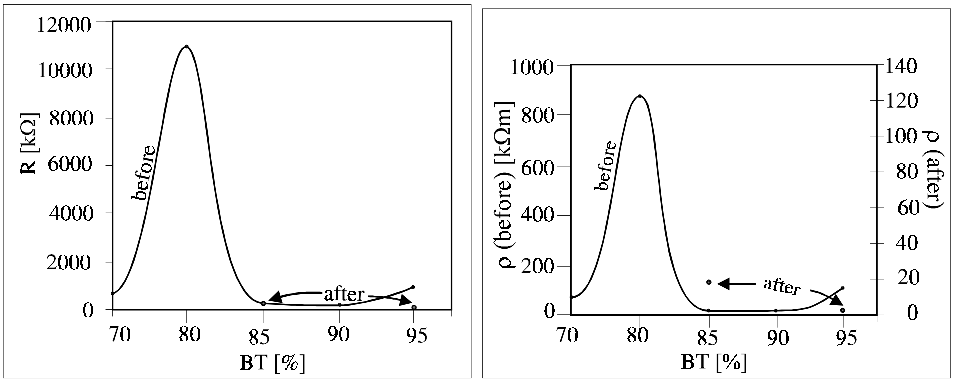


Fig. 3b Dependence tgδ vs. BT content of hot pressed ceramic samples before and after polarisation.

By observing specimens micrographics it can be concluded that the dark–grey substance of novolac "wet" the grains and the most part of sample the grains are separable (fig. 3b–the photomicrographs 70% BT content). Non-homogenity in composition point to differences in hardness of particular regions. Larger and smaller irregular regions of solid matter like agglomerates can be also observed (fig. 3a). With increasing percents of the BT content in composite it's noticed the pores which round, nearly regular form.



(a) (b)

Fig. 4. Dependence (a) R and (b) ρ vs. BT ‡ novolac composite before and after polarisation

Analysing in mind experimental data, an empirical relation is suggested between mass fraction of BT (X_{BT}) and $ln\varepsilon_c$ at as obtained composites. Linear empirical relation can fit in with:

$$ln\ \varepsilon_r = 0.0450013\ X_{BT} + 0.8884.$$

for ceramic mass contents approximately ranging from 0.70 to 0.95 mass fraction of BT what is in agreement with earlier examinations [6].

Logarithmic value has showed that the dielectric constant of BT ceramics greatly depends on the grain size and grain size distribution in the sintered BT samples. Mentioned is important for the more precise defining the properties of as obtained BT- phenolic resin composite [8]. On the other hand, further examinations can also be conducted in the sense of the synthesis of phenolic resins with optimal characteristics from the standpoint of its dielectric characteristics and compatibility by disperse active BT phase. Some examinations have pointed that resolve types of phenolic resins have some advantages at synthesis of this type of composite.

CONCLUSION

Recycled ceramic materials are convenient for application in electronic components what are reduced an expense. Using phenol, which performs trash in many industries, the depositing and solving the poison in the rivers and ground are prevented. The dielectric properties of BT–novolac composite are determined by ferroelectric properties of polycrystalline BT. On the basis of analysing condition influence of obtaining on the properties for pure or recycled barium titanate, the optimal conditions of its synthesis and processing were determined. Since BT has a wide region of application, the understanding of relation between microstructure features and dielectric characteristics, as the dielectric constant, dielectric dissipation loss factor and specific resistively, are a very important because of the same expectation for the composite.

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KOMPOZITI BAZIRANI NA KAPACITIVNOJ RECIKLIRANOJ KERAMICI

Violeta Dimić i Dragan Mančić

U ovom su radu razmatrane mogućnosti korišćenja prirodno otpornih i neuništivih recikliranih materijala, kao što su keramički materijali, smole i rastvarači, za sintezu kompozitnih kapacitivnih materijala. U vezi s tim, prikazali smo rezultate sinteze kompozita na bazi recikliranih sirovina, barijumtitanata i novolaka. On se ne može predstaviti kao prost kompozit, tj. kao keramička faza uronjena u matricu novolaka, s obzirom da i disperzna faza i matrica imaju aktivnu ulogu. Primenom principa prognoze kompozitnih kapacitivnih materijala na bazi barijumtitanata i novolaka (fenolformaldehida) istraživali smo mogućnosti njihove primene za izradu elektronskih komponenti. Disperzna BaTiO3 faza karakterisala se nepravilnim oblikom čestica veličina manjih od 100 μm, raspoređenih u homogenoj organskoj matrici. Ispitujući promene dielektrične konstante, i ugao dielektričnih gubitaka sa promenom koncentracije keramičkog praha, praćenjem promena mikrostrukture kompozita istog sastava, analizirali smo korelaciju električnih i mikrostrukturnih svojstava. Dobijeni rezultati, na taj način, omogućuju prognozu u skladu sa relacijama sastav (tehnologija) - mikrostruktura - dielektrična svojstva.

Ključne reči: *barijumtitanat, novolak, reciklirana keramika, sinterovanje, toplo presovanje, električna svojstva*