

Dielectric and Mechanical Properties of BNT-LCP Composites

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Abstract: We investigated the dielectric and mechanical properties of ceramic polymer composite xBNT - (1-x)LCP (x= 0, 10, 20, 30, 40 vol.%). The disk shaped BNT (BaNd₂Ti₄O₁₂) - LCP (liquid crystal polymer) composite samples were prepared by compression molding method. With increasing the BNT content in composites from 10 to 40 vol.%, the dielectric constant increased but the dielectric loss as well as bending strength of composites reduced. These composites were well described with modified Lichtenecker's model having $k = 0.392$ and 0.303 for the first and second ball milled BNT filled composites, which means that the BNT filler in composites are well dispersed. The dielectric constant of the composite comprised of the second milled BNT ($D_{50} = 1.39 \mu\text{m}$) was higher than that of the composite of the first milled BNT ($D_{50} = 2.45 \mu\text{m}$), which seems to be related with the different particle size and dispersion of BNT fillers in LCP matrix. The bending strength of the composite containing the second milled BNT was superior to that of the composite of the first milled BNT.

Keywords: Composite, Dielectric constant, Ceramic filler, BNT (BaNd₂Ti₄O₁₂), LCP (liquid crystal polymer)

1. INTRODUCTION

The substrate has been developed for several applications such as antenna, embedded capacitor and RF module [1-3]. In view of the technical trend of mobile devices, it is necessary that the substrate material has a high dielectric constant and low dielectric loss as well as mechanical strength for the miniaturization, high frequency and reliability of electrical devices. One of the challenges in reducing the size of any wireless communication device is the issue of antenna miniaturization. One of the most common techniques is the loading of the antenna volume with

high permittivity dielectrics to decrease the physical dimensions of the radiator. Since ceramic-polymer composite has a relatively high dielectric constant and low loss in comparison with polymer, composite can be used for miniaturization of antenna. Moreover, it is light weight, low cost and can be easily fabricated in various shapes such as sheets, 3D structure using injection molding, lamination or extrusion at elevated temperature. In this regard, ceramic polymer composites have received considerable attention as a substrate material. Ceramic-polymer composite consists of a three-dimensionally connected polymer matrix loaded with ceramic fillers. The overall properties of composite are dependent on the various factors such as the morphology (particle size, shape, etc),

Table 1. Composition table of BNT-LCP composites.

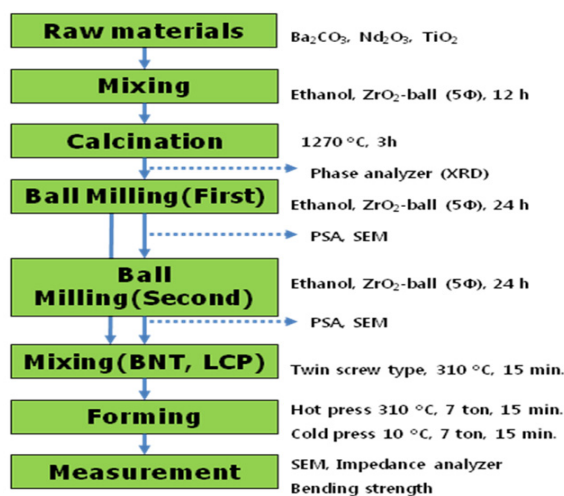
BNT/LCP (vol%)	10/90	20/80	30/70	40/60
BNT (g)	7.26	14.52	21.8	29.05
LCP (g)	22.5	20	17.5	15
BNT (cm ³)	1.38	2.76	4.14	5.52
LCP (cm ³)	12.43	11.04	9.67	8.29

volume fractions, interface area between ceramic filler and matrix polymer as well as their interfacial properties [11,12]. However, the research has mainly concentrated on epoxy-ceramic composites [4-7], thermoset polymer based composite such as polyimide [8] as well as composite including BaTiO₃ [9,10].

There are some studies concerning the effect of filler size and loading content on the microstructure and dielectric properties [13-15]. There have been few studies for the composites consisted of BNT (BaNd₂Ti₄O₁₂) filler [16] and LCP (liquid crystal polymer) in spite of the excellent dielectric properties of the microwave dielectrics BNT and thermoplastic LCP that have easy machinability. In this study, we investigated the effect of filler content and balling milling on the microstructure, dielectric and mechanical properties of the (1-x)LCP-xBNT composites (x= 0, 10, 20, 30, 40 vol.%) as shown in Table 1.

2. EXPERIMENTS

Ceramic filler, BNT (BaNd₂Ti₄O₁₂) was synthesized using BaCO₃ (Daejung, 99%), Nd₂O₃ (KANTO, 99.9%) and TiO₂ (high purity, 99.9%), by the following solid state reaction. Original materials were wet-mixed in a ball mill using ethanol as solvent for 24 hours. Dried powder was calcined at 1,270°C (heating/cooling rate: 5°C/min) for 3 hours and its crystal structure was analyzed by XRD (Max Science, KFX-987228-SE). Two

**Fig. 1.** Fabrication process of BNT-LCP composites.

different sized BNT fillers were obtained by controlling the number of ball milling of the calcined powder. The first and second ball milled BNT powders were prepared by one and twice milling of the calcined powders in ethanol for 24 hours, respectively. LCP (Polyplastics, E473i) was selected as a matrix polymer and had a dielectric constant of 3.7 and dielectric loss of 0.034 at 1 MHz. In order to mix BNT filler with LCP polymer, twin screw type mixer (Brabender, Plastograph) was used.

The fabrication process of BNT-LCP composites is shown in Fig. 1. LCP of a granular form was put into the twin screw type mixer, and melted by holding it for 15 minutes at 310°C. Then the ceramic filler BNT was added into the melted LCP and mixed for 15 minutes. Sample for evaluating the dielectric properties was disk shaped with 2 cm in diameter and 1 mm in thickness, which was fabricated by pressing a mixture of BNT and LCP (hereinafter, composites) with 7 tons in a mold at 310°C and cooling down to room temperature, and giving a press once more. Pressing the composites in mold at room temperature prevented a sample from

being broken by contraction at cooling and help to take it out of a mold.

The In-Ga electrode was formed on the upper and lower surface of a disk sample. The dielectric properties of the BNT-LCP composite were measured in the frequency range of 100 KHz~10 MHz with Impedance analyzer (Agilent, HP 4,194). The sample for measuring The bending strength was measured at a speed of 5 mm/min for a rectangular shaped sample (1.5 cm of width, 5 cm of length, 1 mm of height) with a universal tesing machine (Instron, Model 4,204). The microstructure of the composite was observed by SEM (Topcon, ABT-32).

3. RESULTS AND DISCUSSION

The dielectric and mechanical properties of the ceramic polymer composites are significantly affected by the morphology and amount of loading of ceramic filler in the composites. For a higher relative permittivity, higher loadings of dielectric filler are required and higher loading can give rise to the increase of viscosity as well as poor particle dispersion in a polymer matrix. Therefore, It is important to select the adequate ceramic filler for composites and BNT ($\text{BaNd}_2\text{Ti}_4\text{O}_{12}$) is selected in this study.

Figure 2 shows the XRD pattern of BNT powder calcined at 1270°C and the calcined BNT powder is a tungsten bronze structure (JCPDS-44061) [17,18]. Its lattice constant was calculated as $a = 23.86$, $b = 12.96$, and $c = 4.05$.

3.1 Microstructures of BNT-LCP composites

Figure 3 (a) is the particle size and distribution of the first and second ball-milled BNT powders by Laser scattering method (Horiba, LA-950). The median diameter of powder (D_{50}) of the first and second ball-milled BNT powders is 2.45 μm and 1.39 μm ,

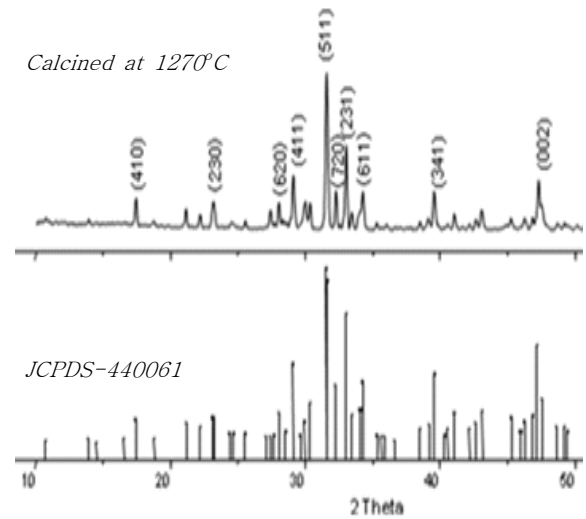


Fig. 2. XRD pattern of BNT powder calcined at 1270°C .

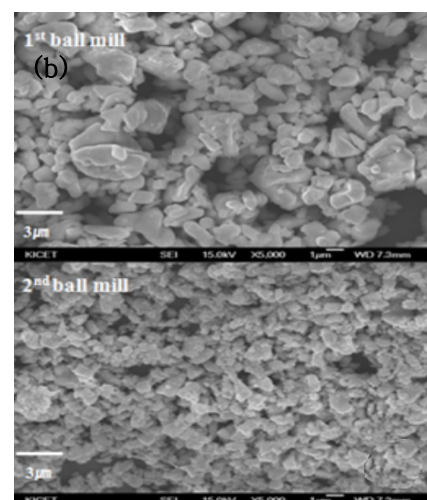
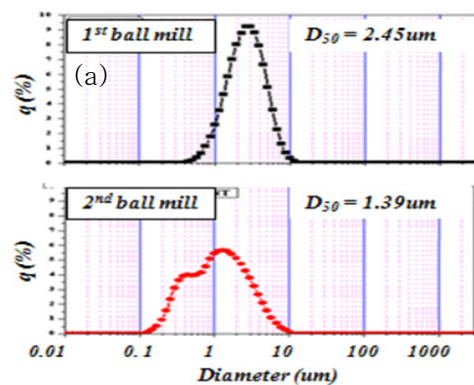


Fig. 3. (a) Particle size distribution of BNT($\text{BaNd}_2\text{Ti}_4\text{O}_{12}$) measured by laser light scattering, and (b) FE-SEM microphotograph for first and second ball milled BNT fillers.

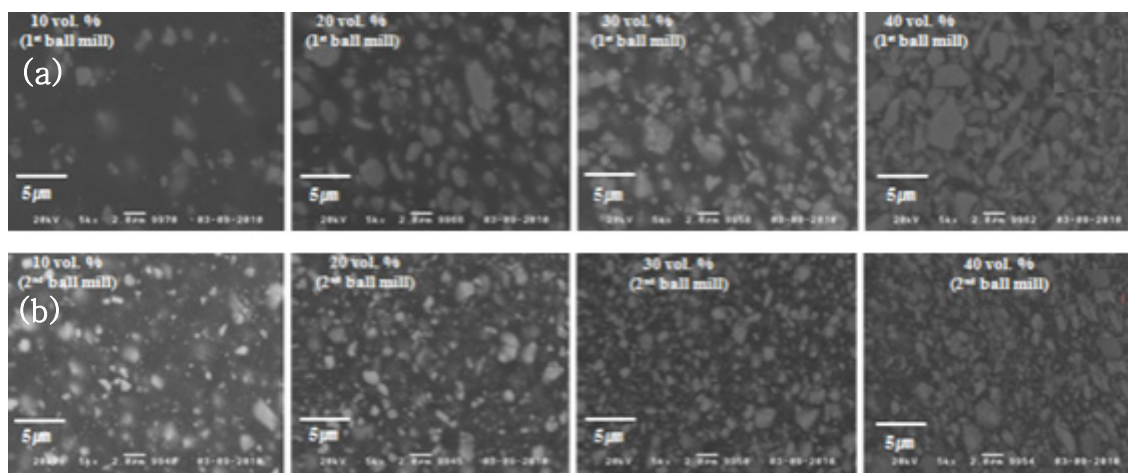


Fig. 4. SEM microphotographs of BNT-LCP composites as a function of the filler loading. (a) first ball milled BNT containing composites and (b) second ball-milled BNT containing composites.

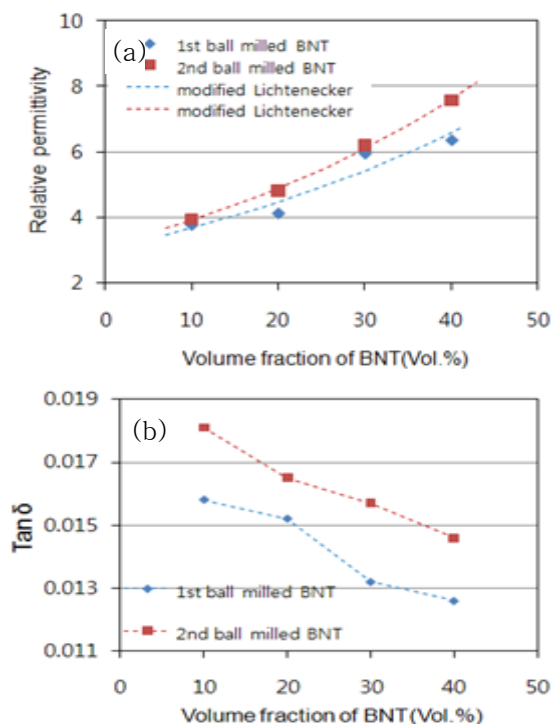


Fig. 5. (a) Relative permittivity, and (b) $\tan \delta$ of BNT-LCP composites at 1 MHz as a function of the BNT filler loading for the first and second ball milled BNT fillers.

respectively, which corresponds with SEM image of BNT powders in Figure 3(b), showing that the second ball milled powder is smaller in size in comparison with

the first ball milled powder. From SEM image of Figure 3(b), some large particles are shown for the first ball milled powder but the particle is relatively uniform in size for the second ball milled powder, which means that the double maximum and broadness of particle size distribution for the second ball milled powder in Figure 3(a) seems to be due to the agglomeration of small BNT particles.

Figure 4 (a) and (b) are SEM microphotographs of the composites including the first ball milled and second ball milled powder, respectively. There are found to be some agglomerates of BNT particles in the first ball milled BNT filled composites. For the second ball milled BNT filled composites, it is shown that there are fewer agglomerates and more uniform dispersion of BNT filler in polymer matrix. As the content of BNT filler in the composites increases, BNT filler becomes more closely packed in the matrix polymer but the dispersion of BNT filler in the LCP polymer matrix remains comparatively uniform regardless of the number of ball milling of BNT powders. From these photographs, it can be concluded that the fabrication condition of filler such as the number of ball milling considerably influences on the filler dispersion condition in the composites.

3.2 Dielectric properties of BNT-LCP composites

Figure 5 (a), and (b) represent the relative permittivity and $\tan\delta$ at 1 MHz for the first and second ball milled BNT filled composites as a function of volume fraction of BNT. With increasing the volume fraction of BNT from 10 to 40, the relative permittivity of composites gradually increased but $\tan\delta$ of composites decreased. The second ball milled BNT filled composites have comparatively higher relative permittivity and increases more rapidly than the first ball milled BNT filled composites. The difference of relative permittivity between the first and second ball milled filled composites seems to be related with the difference of not only the surface area between the first and second ball milled BNT particles, but also the distribution of BNT particles in the matrix polymer. The increase in permittivity of the second ball milled BNT powders (1.39 μm) can be attributed to the higher polarizability in comparison with the first ball milled BNT powders (2.45 μm) because more charge can be accumulated on the grain boundary of the second ball milled BNT powders due to the higher surface area. Similar observations were reported in Epoxy/SiO₂ composites [19]. It is observed that $\tan\delta$ of the second ball milled BNT filled composites is higher than that of the first ball milled BNT filled composites, which is thought to be related with the increased relaxation due to more space charge and/or the lattice strain associated with the reduction in particle size of the second ball milled BNT. Nisa *et al.* obtained the same result as described above that $\tan\delta$ of the PEEK-nanosized SrTiO₃ composites is higher than that of the PEEK-microsized SrTiO₃ composites [15].

In order to understand the physical mechanism controlling the dielectric constant of a heterogeneous system the experimental dielectric constant were compared with values predicted using modified Lichtenecker's equation (1) [20] as shown in Figure 5(a). The calculated value shows relatively better

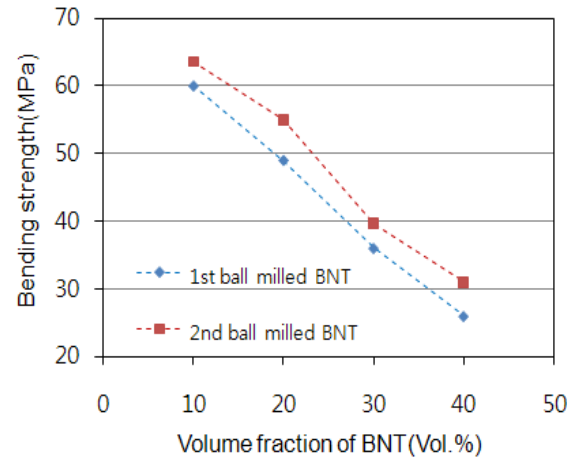


Fig. 6. Bending strength of BNT-LCP composites as a function of the filler loading for the first and second ball milled BNT fillers.

correlation with experimental results. Lichtenecker's model describes the composite system consisting of randomly oriented spheroids inside a continuous matrix [21].

$$\text{Log } \varepsilon = \text{Log } \varepsilon_p + v_b(1-k)\text{Log } (\varepsilon_b/\varepsilon_p) \quad (1)$$

where ε is the relative permittivity of the composite, k is an empirical fitting constant of the composites, v_b is the volume fraction of the ceramic, and ε_p and ε_b are the relative permittivity of the matrix polymer and the ceramic filler, respectively. In the case of this study, ε_p and ε_b are 3.7 and 90 at 1 MHz, respectively. From the curve fitting of the measured data with equation (1), values of k of 0.392 and 0.303 were obtained for the first and second ball milled BNT filled composites, respectively. The parameter k of the modified Lichtenecker's equation is considered to be dependent on the type of polymer and ceramic filler employed. The composites filled with the second ball milled BNT powders seems to be well dispersed seen from the report that k has a value around 0.3 for most well-dispersed composites [20]. This result indicates that the parameter

k is dependent on the dispersion state of the composite. The second ball milled BNT filled composites have comparatively higher relative permittivity than the first ball milled BNT filled composites, which corresponds with the result that longer ball milling time can enhance the relative permittivity of a ceramic - epoxy composite [22].

3.3 Mechanical properties of BNT-LCP composites

The bending strength of BNT-LCP composites was studied using a universal testing machine (Instron, Model 4204) and the results are shown in Figure 6. The bending strength shows a decreasing trend with increase in filler loading. This can be attributed to the fact that when more and more BNT particles is loaded within LCP, the deformation area in the matrix polymer decreases and hence reduces the bending strength. Composites with the second ball milled BNT particles shows better bending strength compared with first ball milled BNT filled composites, which is likely to be related with the difference of the interface area and dispersion between BNT particles and matrix polymer. In comparison with the first ball milled BNT filled composites, the larger interface area and better dispersion between filler and polymer in the second ball milled BNT filled composites improve adhesion between the filler and the matrix, which appears to result in the enhanced bending strength. A few mechanical strength data for the ceramic and polymer composites have been reported and in most cases, filler or CNT was added to high molecule in order to improve the mechanical characteristics. In this study, the bending strength data for BNT-LCP composites may be meaningful for the further studies.

4. CONCLUSION

In this work, we have fabricated the BNT-LCP

composites and investigated their microstructure, dielectric and mechanical properties according to the filler loading and the number of ball milling. The median diameter of powder (D_{50}) of the first and second ball-milled BNT powders is 2.45 μm and 1.39 μm , respectively. The relative permittivity of the composite comprised of the second milled BNT ($D_{50}=1.39 \mu\text{m}$) is higher than that of the composite of first milled BNT ($D_{50}=2.45 \mu\text{m}$), which seems to be related with the different particle size and dispersion of BNT fillers in LCP matrix. The bending strength of the composite containing the second milled BNT is superior to that of the composite of single milled BNT.

Therefore, it is useful to reduce the BNT filler size for improving the dielectric and mechanical properties of BNT-LCP composites. With increasing the BNT content of BNT-LCP composite from 10 to 40 vol.%, the relative permittivity increases, but the dielectric loss as well as bending strength of composite reduces. BNT-LCP composites were well described with modified Lichtenecker's model having $k=0.392$ and 0.303 for the first and second ball milled BNT filled composites, which means that the BNT filler in composites are well dispersed. This BNT-LCP composite is expected to be a promising substrate material.

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