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Aggregation morphology and electrical properties of particle size controlled $BaTiO_3$ filler/ polyvinylidene fluoride composites

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Abstract

Recently, because of the growth of flexible devices usage, the development of energy storage device suitable for flexible device is strongly required. One solution is the use of composite materials of ceramic powders and polymer matrices with high dielectric properties. In this study, we prepared composite films with controlled barium titanate ($BaTiO_3$, BT) particle sizes of 100 nm, 300 nm, and 700 nm and polyvinylidene fluoride (PVDF) and examined dielectric property. Additionally, cross-sectional SEM/EDS was taken and analyzed their aggregation/dispersion morphology by multifractal analysis. The multifractal structure appeared in the composite with 300 nm BT filler, and an increase in dispersion with increasing BT volume fraction was observed depending on the generalized fractal dimension $D(q)$.

1. Introduction

These days, due to the development of flexible devices such as organic light emitting diodes (OLED), there are enthusiastic demands on the development of energy storage devices compatible with flexible devices. To deal with those demands, composites of ferroelectric polymers and inorganic materials can be one of the candidates. Generally, polymers are rich in flexibility but only have a dielectric constant about 10(1). Hence, ceramic fillers are added to the polymer matrix to increase dielectric constant(1,2). In addition, the particle size and shape of ceramic filler and its aggregation affect the dielectric properties of composite devices. In this study, we prepared Barium titanate ($BaTiO_3$, BT) with controlled particle size 100, 300 and 700 nm and polyvinylidene fluoride (PVDF) composites and analyzed multifractal structures on the aggregation morphology of BT fillers in the polymer matrix. Furthermore, we examined the correlation between the electrical properties and the composite morphology.

2. Experiment

BT filler is made by mixing prepared BT powder which has particle size of 100 nm and 300 nm (BT-01, BT-03, Sakai Chemical Industry Co.), 700 nm (Fuji-Titanium Industry Co.) and polyethylene glycol (PEG1000, FUJIFILM WAKO CHEMICAL Co.) with 4 wt.% weight of BT weight with 323 K heat applied condition. Samples were kneaded BT filler and PVDF polymer at 10 rpm for 30 minutes for BT volume fractions of 0, 10, 20, 30 vol.%. The polymer composites samples were formed into thick films with thickness about 500 µm. Moreover, the thick films were observed by XRD and cross-sectional SEM/EDS, and their electrical properties were measured.

3. Results and discussion

3.1 Correlation between BT volume fraction and dielectric constant

Fig.1 represents correlation between BT volume fraction and dielectric constant ε_r at 1 kHz of the BT/PVDF composite materials. It shows ε_r increased with increasing BT filler in samples with particle size: 100, 300, and 700 nm. In addition, ε_r of 100 nm particles reached 40 at 30 vol.% indicating that the particle dispersion was improved. ε_r of 300 nm and 700 nm also increased about 10 when its volume fraction changed from 10 to 30 vol.% as shown in inset of Fig. 1. It is suggested that with the smaller particle size, there are more surfaces which create heterointerface and store higher surface energy, and this results in improved dielectric property with 100 nm particle size.

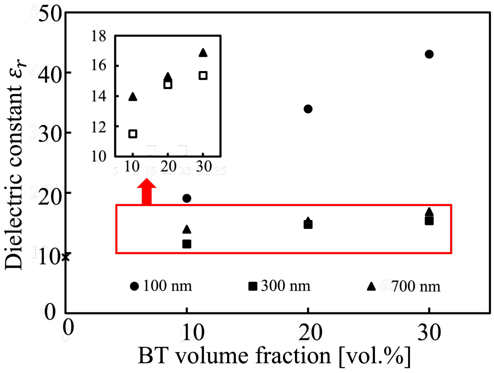

Fig.1 BT volume fraction dependence of dielectric constant.

3.2 Multifractal Analysis

According to the SEM image in Fig.2, the composite with BT particle size of 100 nm didn't reveal multifractal properties with the kneading condition in this study. Fig.3 shows multifractal spectra curves $D(q) - q$ for BT/PVDF composites with BT filler 10 and 20 vol.%. $D(q)$ represent the generalized fractal dimension and each $D(0), D(1), D(2)$ refers to capacity, information and correlation dimension. $D(0)$ of 10 and 20vol.% are 1.593 and 1.695, respectively. $D(1)$ values of 100 and 300 nm shows 1.553 and 1.666, respectively, and this indicates BT particles are less dispersed and particles agglomerate when volume fraction increased. $D(2)$ also improved from 1.534 to 1.655 as its volume fraction is raised. This indicates that an increase in the volume fraction of BT particles results in higher connectivity between each particle.

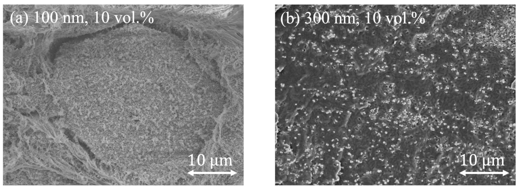

Fig.2 Cross-sectional SEM of composite film.

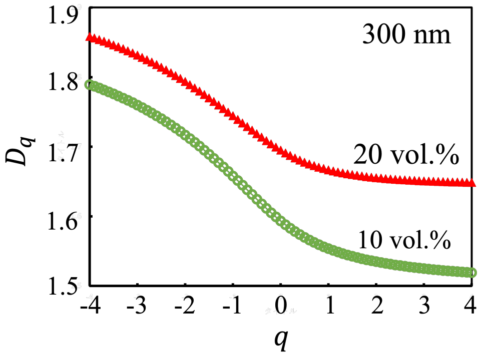

Fig.3 Results of multifractal analysis of samples with particle size of 300 nm ($D(q) - q$).

4. Conclusions

ε_r increased with increasing BT volume fraction for BT/PVDF composite samples with controlled BT filler particle size. Under the kneading conditions in this study, no multifractal structure was obtained in the composite with 100 nm BT filler. On the other hand, a multifractal structure appeared in the composite with 300 nm BT filler, and an increase in dispersion with increasing BT volume fraction was observed, depending on the value of $D(q)$.

References

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