REVIEW ARTICLE

Theory and measurements for 0-3 $BaTiO_3$/PVDF composites

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Abstract

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This work extended the range of material properties by fabricating the $BaTiO_3$ /PVDF composite. In order to obtain the 0-3 composite without the interconnectivity of the ceramic powders, a low volume fraction of 0.3 of barium titanate ($BaTiO_3$) was filled in a matrix of polyvinylidene fluoride (PVDF) and the mixture was homogeneously stirred. The composite was shaped into a sheet form by a tape casting method. The microstructure of the composite was observed using scanning electron microscopy (SEM) which revealed that the connectivity of the composite was mainly 0-3. Subsequently, theoretical models and equations were applied to the composite for comparisons with measurements. The density and heat capacity of the composites were experimentally obtained to be 3.21103 kg/m^3 and 3021.7 J/kg ^{o}C, respectively. The composite was corona poled before the test of dielectric response. Its 1 kHz-dielectric constant and dielectric loss at room temperature were 11.5 and 0.21, respectively. The good dielectric combined with the flexibility of the material implies that the composite is attractive for electronic applications where a light, environmentally friendly, ease to fabricate and low-cost device is required.

Key words : $BaTiO_3$, PVDF, piezoelectric, dielectric, composite

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บทคัดย่อ

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ทฤษฎีและการวัดสำหรับคอมโพสิท 0-3 $BaTiO_3$/PVDF
ว. สงขลานครินทร์ วทท. พฤษภาคม 2550 ฉบับพิเศษ 2 : 413-418

งานวิจัยนี้ได้ขยายช่วงสมบัติวัสดุให้กว้างขึ้นโดยการเตรียมคอมโพสิท $BaTiO_3$/PVDF เพื่อให้ได้คอมโพสิทแบบ 0-3 โดยไม่มีการติดกันของผงเซรามิก จึงใช้แบเรียมไทเทเนต ($BaTiO_3$) สัดส่วนโดยปริมาตรต่ำเท่ากับ 0.3 ใส่ในเมตริกพอลิไวนิลลิดีนฟลูออไรด์ (PVDF) และกวนของผสมอย่างต่อเนื่อง ขึ้นรูปคอมโพสิทเป็นแผ่นด้วยวิธีการแบบเทป ตรวจสอบจุลโครงสร้างของคอมโพสิทด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกวาดพบว่ามีการเรียงติดกันแบบ 0-3 เป็นส่วนใหญ่ จากนั้นนำแบบจำลองทางทฤษฎีและสมการมาใช้ในการศึกษาคอมโพสิทเพื่อเปรียบเทียบกับการทดลอง ผลการทดลองค่าความหนาแน่น และค่าความจุความร้อนเท่ากับ 3.21103 กก./ลบ.เมตร และ 3021.7 จูล/กก. $^{\circ}$C ตามลำดับ คอมโพสิทได้ผ่านการโพลิงแบบโคโรนาก่อนการทดสอบการตอบสนองทางไดอิเล็กตริก ค่าคงที่ไดอิเล็กตริกและค่าสูญเสียไดอิเล็กตริกของคอมโพสิทที่ 1 กิโลเฮิร์ทซ์ ณ อุณหภูมิห้อง เท่ากับ 11.5 และ 0.21 ตามลำดับ การเป็นไดอิเล็กตริกที่ดีและมีความสามารถในการดัดงอได้ของสาร ชี้ให้เห็นว่าคอมโพสิทนี้น่าสนใจสำหรับประยุกต์ใช้ทางอิเล็กทรอนิกส์ที่ต้องการสิ่งประดิษฐ์น้ำหนักเบา ไม่เป็นพิษต่อสิ่งแวดล้อม ผลิตง่ายและราคาย่อมเยาว์

ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ อำเภอหาดใหญ่ จังหวัดสงขลา 90112

The ceramic of barium titanate ($BaTiO_3$, BT) is a very attractive piezoelectric material for a large area of applications such as nonvolatile memories, surface acoustic wave devices, tunable capacitors, pyroelectric detectors, etc. Modifications of $BaTiO_3$ were attempted by substituting Pb, Sr, or Ca for Ba and Zr or Sn for Ti (Ikeda, 1990; Hui-dong *et al*., 2004). However, the preparation of $BaTiO_3$ is commonly involved with high temperature parameters or processes. Polyvinylidene fluoride (PVDF) is one of the most promising polymer materials for the piezoelectric and pyroelectric effects. The effects in PVDF have been observed since 1969 (Kawai, 1969) and 1971 (Lang, 1971), respectively. The PVDF has low permittivity, low thermal conductivity and is flexible and relatively low in cost. Initial efforts were made in this work to extend the range of material properties which are desirable for applications by fabricating the composite comprising of these materials, i.e., $BaTiO_3$ and PVDF. The composites are mainly characterized by the microstructure, poling behavior, and dielectric properties. As the composite is a lead-free material, it is promising for environmental use and suitable when a low-cost and light device is required.

Theory and equations

Basically, a composite with 0-3 connectivity consists of particles connected in zero dimensions and a three dimensionally interconnected polymer matrix as shown in Figure 1.

By the use of the right proportion of the constituent materials, the composite with 0-3 configuration can be fabricated with ease. The following equations are used to prepare quantities required for mixing of ceramic and polymer (Lang and Das-Gupta, 2000).

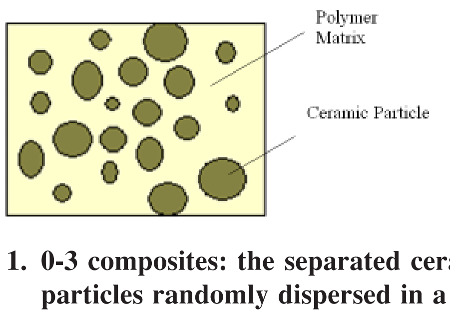

Figure 1. 0-3 composites: the separated ceramic particles randomly dispersed in a host polymer matrix.

$$M^P = M^C \frac{\rho^P}{\rho^C}\left(\frac{1-\phi}{\phi}\right) \quad (1)$$

Where M, ρ and ϕ are the mass, density and volume fractions respectively, and the superscripts P and C refer to polymer and ceramic respectively. The density ρ of the composite is determined thus,

$$\rho = \phi\rho^C + (1-\phi)p^P \quad (2)$$

and the total ceramic volume V is given by

$$V = \frac{M^C}{\phi\rho^C} \quad (3)$$

In describing composite properties with low volume fraction of the ceramic powder dispersed in the host polymer, the Pauer cube model (Figure 2) is applicable (Das-Gupta, 1994 ; Dias and Das-Gupta,1996). In this model, a unit cube represents the volume of the composite. Within this cube there is a smaller cube of dimension m which represents the volume of the ceramic embedded in a unit cube of the composite. Using this model, the ceramic grain size should not be comparable to the film thickness and then the ceramic volume fraction ϕ^C, is given by equation (4) (Das-Gupta, 1994 ; Dias and Das-Gupta,1996).

$$\phi^C = m^3 \quad (4)$$

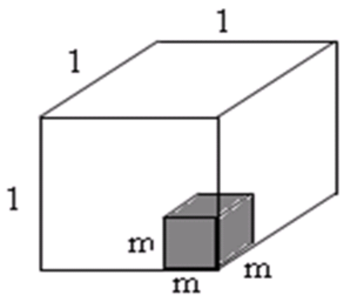

Figure 2. Pauer cube model for 0-3 composites.

For the composite used in this work, the total ceramic volume is calculated by using equation (3) to be 0.54 cm^3 and the m value to be 0.67 µm by using equation (4). This means that the total ceramic volume contains ~10^{12} ceramic cubes. Each cube is considered as a building block which can be either parallel or series connected with a matrix, depending on the respective orientation. The configuration of the ceramic cubes is commonly useful in describing electronic properties of devices consisted of composite materials which is beyond the scope of this work.

Materials and methods

According to equation (1), one gram of PVDF powder (Fluka 81432) was dissolved in 1-methyl-2-pyrrolidone (NMP) (Fluka 69120) to obtain a PVDF solution. Care was required in designing the proportion of ceramic in order to prevent the connectivity of the ceramic particles. Finally, 1.4975 grams of $BaTiO_3$ powder (Fluka 11729) was embedded in a matrix of PVDF to form composites with 0.3 volume fraction of ceramic. The mixture was stirred by magnetic stirrer, slowly warmed until it became viscous and then agitated in an ultrasonic bath for an hour to ensure that the ceramic particles were distributed evenly in the polymer solution. The composite was formed into thin sheets on a glass plate before annealing at 120°C for 6 hrs. The density and volume of the composite were calculated using equations (2) and (3), respectively. The heat capacity of the composite, which reflects the ability of the composite to store heat, was analyzed using a Differential Scanning Calorimeter (Perkin Elmer, DSC7). The connectivity and microstructure of the composite were investigated by using SEM (JEOL JSM 5800LV).

The composite was electroded by means of the sputtering (JEOL JEEE-400). In order to make the polymer phase active, i.e., generate an electric displacement and store the electric charge, the corona poling with an DC electric field of 3.7 kV was applied to the 25 µm-PVDF at room temperature (25°C) for 20 mins (Thipmonta, 2005). In order to make the ceramic phase active, the composite was subsequently poled at 2.5 kV at room temperature for 15 mins (Limbong and Guy, 1998). Similarly to the other ceramic/polymer composites reported in the literature (Ploss *et al.*, 2001), the poling axis for each phase was kept in the opposite direction in order to enhance the dielectric properties. The dielectric constant and dielectric loss of the composite with unpoled matrix and inclusion were characterized by using the LCR meter (HP 4263B) in comparison with the composites with poled polymer matrix and with both phases poled.

Results and discussion

The SEM micrograph of 25-µm composite is shown in Figure 3. It appeared that the connectivity of the composite was mainly 0-3, i.e., the $BaTiO_3$ particles had a zero connectivity while the PVDF medium had a connectivity of 3. There was also the mixture of the other connectivities such as 1-3 or 3-3 even though the low volume fraction of the ceramic was used. An average particle size of $BaTiO_3$ is 1.0±0.1 µm which is of the same order of the calculated m value. This average grain size value was at least 10 times lower than the thickness of the composite. The Pauer cube model is therefore, applicable in describing composite properties with low volume fraction of the ceramic.

Experimental data obtained in this work are listed in Table 1. It could be seen that the measured density of $3.21x10^3$ kg/m^3 for the composite is a volumetric average value which agreed well with the theoretical value. A similar comparison by using equation (2) was done for the heat capacity and it was found that the measured value was much larger than that from prediction. This was mainly due to the elastic property of the polymer which lead to the thermal expansion while undergone the heat capacity analyzing equipment.

The variations in the dielectric constant and dielectric loss with frequency for the composite

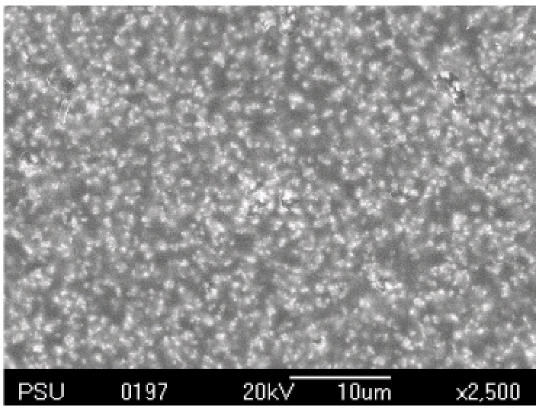

Figure 3. SEM micrograph (x2,500) of the composite with ϕ = 0.3, showing the ceramic in white and the polymer matrix in black.

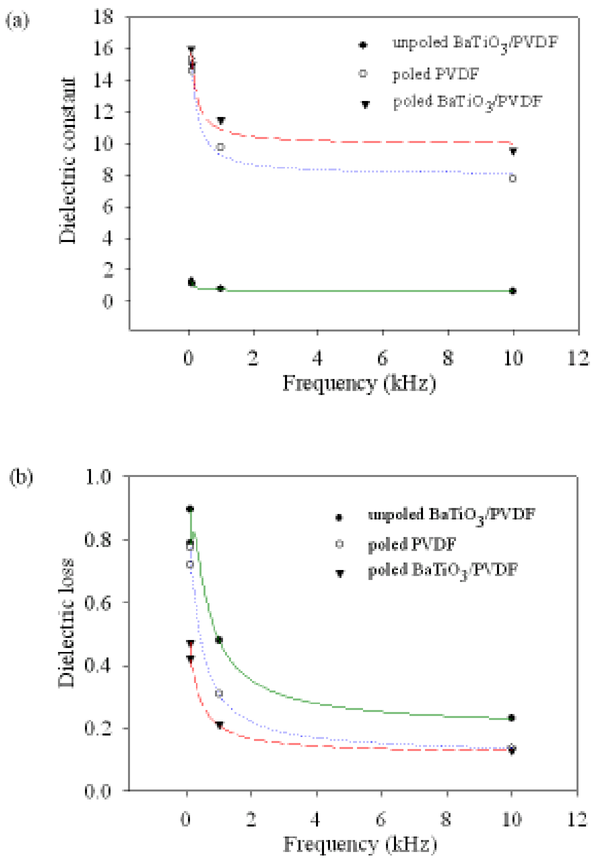

Figure 4. Experimental data of (a) the dielectric constant and (b) dielectric loss of the $BaTiO_3$/PVDF composites as a function of frequency.

Table 1. Experimental data of the density, heat capacity, dielectric constant, dielectric loss and total composite volume of the $BaTiO_3$/PVDF composites with Calculated values are given in brackets.

Materials	Density at 25°C 10^3 (kg/m^3)	Heat capacity (J/kg°C)	Dielectric constant (at 1 kHz, 25°C)	Dielectric loss (at 1 kHz, 25°C)
Poled PVDF	1.901	2322.7	8.4 - 13.51	-
Poled $BaTiO_3$	5.462	738.6	13012	-
Unpoled $BaTiO_3$/PVDF	-	-	0.8	0.48
Poled PVDF	-	-	9.7	0.31
Poled $BaTiO_3$/PVDF	3.21 (3.04)	3021.7 (1847.5)	11.5	0.21

[1] (Afifuddin, 1996)
[2] (Adisak, 2005)

are shown in Figure 4 (a) and (b), respectively.

When compared with the unpoled composite, the sample with poled polymer matrix was polarized effectively (figure 4). This was because of the relatively high value of the dielectric constant and low dielectric loss when compared with those reported in the literature (Dias and Das-Gupta, 1996;. Limbong and Guy, 1998). The composite with both phases poled oppositely showed excellent dielectric responses. The poling of the ceramic in the opposite direction did not change the polarization of the polymer and lead to an increase in the net polarization in the composites as noticed from the maximum value of the dielectric constant and a reduction of the dielectric loss over a range of frequency. However, dielectric properties of the poled composite were slightly different to those of the poled polymer and considerably low when compared with the poled ceramic. This is related to the higher elastic compliance of the polymer (Chan & Unsworth, 1989) which generally influence the electric displacement generated in the ceramic inclusions.

Conclusion

This work fabricated $BaTiO_3$/PVDF composite whose connectivity was mainly 0-3 by mixing the low volume fraction of ceramic particles in a hot polymer matrix. The composite sheets were obtained using the tape casting method. The Pauer cube model is applicable in describing composite properties and the volumetric average prediction for the density agreed well with measured value of 3.21×10^3 kg/m^3. The heat capacity and dielectric properties at room temperature for the composite should be experimentally reported and the elastic property of the polymer should be taken into account. The composite was completely poled as seen from the high dielectric constant of 11.5 and low dielectric loss of 0.21. The $BaTiO_3$/PVDF composite which is good dielectric combined with the flexibility is promising for electronic applications in a low frequency range where a light, environmentally friendly, ease to fabricate and low-cost device is required.

Acknowledgement

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