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Abstract
Polymer-matrix composites (PMCs) with dispersed Si nanoparticles have been fabricated and investigated for their dielectric and mechanical properties for the first time. It is found that Si nanofillers significantly enhance the dielectric constant of the nanocomposites while preserve the low loss tangent of the Bisphenol E cyanate ester (BECy) matrix. Meanwhile, incorporation of Si nanoparticles effectively stiffens the polymer, as manifested by the large increase in the storage modulus. Furthermore, the AC conductivity of the composite is observed to decrease under compressive mechanical stresses due to the piezoresistive effect of Si. Therefore, these novel Si/BECy nanocomposites simultaneously display mechanical load-carrying, electric energy-storing and stress-sensing capabilities, very promising for multifunctional devices such as structural capacitors.

Keywords
Si nanoparticles, Polymer-matrix composites, Electrical properties, mechanical properties, stress sensing

Disciplines
Ceramic Materials | Manufacturing | Polymer and Organic Materials

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Novel Si/cyanate ester nanocomposites with multifunctional properties

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ABSTRACT

Polymer-matrix composites (PMCs) with dispersed Si nanoparticles have been fabricated and investigated for their dielectric and mechanical properties for the first time. It is found that Si nanofillers significantly enhance the dielectric constant of the nanocomposites while preserve the low loss tangent of the Bisphenol E cyanate ester (BECy) matrix. Meanwhile, incorporation of Si nanoparticles effectively stiffens the polymer, as manifested by the large increase in the storage modulus. Furthermore, the AC conductivity of the composite is observed to decrease under compressive mechanical stresses due to the piezoresistive effect of Si. Therefore, these novel Si/BECy nanocomposites simultaneously display mechanical load-carrying, electric energy-storing and stress-sensing capabilities, very promising for multifunctional devices such as structural capacitors.

Keywords: A. Si nanoparticles; A. Polymer-matrix composites; B. Electrical properties; B. Mechanical properties; Stress-sensing

[1] PMCs – Polymer-matrix composites
[2] BECy – Bisphenol E cyanate ester

1. Introduction

Polymer-matrix composites have been widely studied and applied as structural materials because of their excellent mechanical properties, such as high strength, toughness and stiffness. In recent years, multifunctional PMCs, materials that can accomplish multiple performance objectives in a single system, have attracted much interest worldwide because of demands for weight reduction and energy efficiency in vehicles and engineering devices. For example, structural capacitors, electrical capacitors also capable of carrying mechanical loads, can lead to remarkable weight savings in space vehicles [1-3].

The dielectric materials proposed for structural capacitors are polymer-matrix composites with various nanofillers to improve both dielectric and mechanical properties. Previous work on composite dielectrics mainly focused on polymers with ferroelectric ceramic or conductive fillers [4], where mechanical properties were usually not tested or reported [5,6]. Incorporating metal nanoparticles, such as Ni, Ag, and Al [7-9], can lead to a remarkably high dielectric constant when the volume fraction of nanofillers approaches the percolation threshold [10]. However, these composites are not expected to be effective dielectric materials due to the accompanied high dielectric loss tangent and conductivity. When mechanical properties are concerned, incorporation of carbon nanotubes is a better choice due to its high Young's modulus. But again the dielectric loss tangent and electrical conductivity in these nanocomposites are too high for capacitive applications [10-12].

In this article we report a novel polymer-matrix composite filled with Si nanoparticles. Compared to the composites mentioned above, PMCs with dispersed Si nanoparticles are expected to be an excellent candidate for structural capacitors. Firstly, Si is semiconductive and hence is expected to improve the dielectric constant of the composites. As the dielectrics in electrical capacitors, a higher dielectric constant leads to a higher energy storage volume density. Secondly, the native SiO_2 surface layer on individual Si nanoparticles is highly insulating and will block long range charge transport. As a result, a low dielectric loss tangent is expected in the nanocomposites. Thirdly, Si displays a much higher Young's modulus and a lower density than Al and Ag. Apparently, Si is more effective in stiffening the polymer matrix for structural functions while keeping a relatively low density for weight savings. Furthermore, Si displays the highest piezoresistive effect of known materials and has been widely used in mechanical stress sensors [13,14]. Recently Si nanostructrues were found to exhibit a piezoresistive coefficient ~40 times greater than in bulk Si [15]. Therefore, incorporating Si nanostructures into a polymer matrix could potentially lead to nanocomposites with a stress-sensing capability.

In the present work, bisphenol E cyanate ester (BECy) is used as the polymer matrix to demonstrate the multifunctional nanocomposite. BECy is a high-temperature thermoset with an excellent mechanical performance and thermal stability as well as very low dielectric loss tangent [16,17]. Furthermore, the BECy monomer shows an extremely low viscosity in the range of 0.09 to 0.12 Pa·s at processing temperatures [18], a critical trait for uniformly mixing Si nanoparticles.

2. Experimental

2.1 Synthesis of Si/BECy nanocomposites

Si nanoparticles were acquired from a commercial source (Nanostructured & Amorphous Materials, Inc., USA). Since a continuous layer of SiO_2 is critical to keeping the dielectric loss low in resulting nanocomposites, the acquired Si nanoparticles were heat treated in air at 500 °C for 2 hours. This procedure removes possible organic residuals and ensures the existence of an insulating layer of SiO_2 on the nanoparticle surface. Right before the mixing with the BECy monomer, the heat treated Si-nanoparticles were dried in air at 200 °C for 10 hours to minimize the absorbed moisture [19]. The BECy monomer (TenCate Advanced Composites, USA) was mixed with an organometallic-based polymerization catalyst supplied by the manufacturer in a ratio of 100:3. The mixtures were incorporated with heat treated and dried Si nanoparticles, then sonicated and mixed at 1-2 minute intervals employing a sonic dismembrater (Model 100, Fisher Scientific, USA). Following sonication, systems were centrifuged for approximately 10 minutes to remove possible air bubbles to complete the homogenization. The slurry was passed into a 1-3 mm thick steel mold using a 10 mL syringe and cured in a rotational oven. Composites with 10, 18, and 26 vol.% of Si nanoparticles were made. The plate samples were machined and then polished smoothly for subsequent measurements.

2.2 Characterization of Si/BECy nanocomposites

The heat treated Si nanoparticles were examined by transmission electron microscopy (Tecnai F20, FEI, USA) operated at 200 kV. Thermogravimetric analysis (TGA) was conducted in order to accurately determine the Si nanoparticle loadings in the processed composites. Fracture surfaces of composite samples were examined by scanning electron microscopy (Quanta FEG 250, FEI, USA) to exam the particle dispersion in the polymer matrix. Dielectric properties of nanocomposites and neat BECy were characterized with a Novocontrol dielectric spectrometer (Novocontrol Technologies, Germany) in a frequency range from 1 Hz to 1 MHz at a series of temperatures up to 200 °C. Dielectric breakdown strength of the composites was evaluated by a CEAST Dielectric Rigidity Instrument (Instron, USA) in a voltage ramp rate of

0.5 kV/s and a current intensity of 10 mA. Dynamic mechanical analysis (DMA) was conducted using a TA Q800 instrument at a heating rate of 3 °C/min. The AC electrical conductivity of the nanocomposites under compressive stresses from 0 to 90 MPa was measured at 1 MHz with an LCR meter (Model E4980a, Agilent, USA) in conjunction with a mechanical loading frame (Model 5569, Instron, USA).

3. Results and Discussion

Figure 1 is a transmission electron microscopy micrograph of a representative Si nanoparticle used for composite fabrication. It is evident that Si nanoparticles are spherical in shape with diameters c.a. 50 nm. In addition, a continuous amorphous SiO_2 layer (~2 nm) is formed on the surface of the crystalline silicon particle. This continuous and highly insulating layer ensures that charge transport under applied electric fields is confined within individual particles. Polymer-matrix composites reinforced with Si nanoparticles of this core-shell morphology are expected to exhibit increased dielectric constant while preserving the low dielectric loss of the polymer matrix. This is an effective mechanism to elevate the composite percolation threshold in order to realize high volume fraction loadings of Si, as is demonstrated below.

Figure 2 shows the weight loss of two composites as a function of temperature during heating from 25 to 800 °C. Up to 100 °C, no obvious weight loss is observed, indicating very little moisture content in both composites. After a complete polymer decomposition at temperatures above 700 °C, the weight fraction is 18 % and 40 %, respectively, for the two composites. The two composites, therefore, contain approximately 10 vol.% and 26 vol.%, respectively, of Si nanoparticles.

Scanning electron microscopy images of the fracture surface of these two composites reveal the nanofiller dispersion in the matrix. As shown in **Figure 3**, nanoparticles disperse uniformly in the matrix in the 10 vol.% Si composite. However, some extent of nanoparticle agglomeration seems to have occurred in the composite with 26 vol.% Si loading. This may be one of the reasons for the low dielectric breakdown strength observed in this composite, as will be discussed later.

Figure 4 shows the dielectric constant ε_r and loss tangent tanδ of Si/BECy nanocomposites measured from 1 Hz to 1 MHz at room temperature (25 °C). The results of neat BECy are also included for comparison. The incorporation of Si nanoparticles increases the dielectric constant of composites. Specifically, the dielectric constant ε_r at 1 Hz of the nanocomposite with 26 vol.% Si is about 2.5 times that of neat BECy at the same frequency. The dielectric constant of neat BECy (ε_r = 2.98 at 1 MHz) shows a very weak frequency dependence. This frequency dependence is still very weak in the nanocomposite with 10 vol.% nanofillers and is slightly increased in the 26 vol.% Si nanocomposite. The maximum dielectric loss tangent of neat BECy polymer at room temperature is around 0.6 % in the measurement frequency range, despite the slight frequency dependence corresponding to dielectric relaxation in the polymer. Incorporating 10 vol.% of Si nanoparticles increases this value slightly to around 1.1% while the loss tangent is still below 1.7 % even in the nanocomposite with a Si loading of 26 vol.%. The high dielectric constant and the low dielectric loss tangent of Si/BECy nanocomposites could contribute to the potential application in electrical capacitors.

In order to evaluate the temperature effect on dielectric properties of these Si/BECy nanocomposites, dielectric characterization was further carried out in a series of temperatures from 50 to 200 °C. The results for selected temperatures are shown in **Figure 5**. It is evident that the dielectric constant ε_r of Si/BECy nanocomposites is very stable against temperature change. Most importantly, the dielectric loss tangent remains low throughout the entire test temperature range. The nanocomposite with 10 vol.% Si exhibits maximum tanδ values between 1.2 % and 1.7 % in the frequency and temperature range of test, while the nanocomposite with 26 vol.% Si displays a maximum tanδ value below 2.5 % at temperatures up to 200 °C. The high thermal stability of the dielectric properties of Si/BECy nanocomposites indicates that they are good candidates for dielectrics in capacitors at elevated temperature.

The dielectric constant (ε_r) and loss tangent (tanδ) measured at 1 kHz at room temperature (25 °C) and 200 °C are listed in **Table 1** for direct comparison. In addition, the dielectric breakdown strength (E_{br}) was measured and tabulated. A significant decrease in E_{br} is seen with the increase in Si nanoparticle loadings. This anticipated decrease is due to the intensification of the actual electric field at the interface between the conductive Si nanoparticle and the insulating polymer. Therefore, these Si/BECy nanocomposites are expected to perform well only under low electrical fields. For high power applications, surface modification of the Si nanoparticle is needed to improve the dielectric breakdown strength of nanocomposites.

For multifunctional applications, mechanical properties of the Si/BECy nanocomposite are also of interest. **Figure 6** presents the results from the dynamic mechanical analysis (DMA) tests which shows the temperature dependence of the storage modulus (E') of Si/BECy nanocomposites. The E' of neat BECy was also measured and displayed for comparison. These measurements also identify the variation of glass transition temperature (T_g) with Si loading. The E' at room temperature and T_g of Si/BECy nanocomposites and neat BECy are also listed in **Table 1**. E' at room temperature is increased by 22 % and 89 %, respectively, by incorporating 10 vol.% and 26 vol.% Si into the BECy matrix. In contrast, T_g varies only slightly with Si addition, indicating the maintained high thermal stability of nanocomposites compared with BECy matrix. The Si nanoparticle, thus, is a promising material to reinforce the BECy polymer matrix while largely preserving its thermal stability.

The enhanced and thermally stable dielectric and mechanical properties observed in these nanocomposites indicate that they are promising functional materials. Actually these Si/BECy nanocomposites display comparable mechanical and dielectric properties as $BaTiO_3$/BECy composites [4, 19]. However, in order to be eventually utilized in structural capacitors, these composites reinforced with Si-nanoparticles need to be further investigated for properties including fracture toughness, tensile strength, fracture strain, etc. From the point of view for mechanical reinforcement, a different morphology such as Si-nanowires, would be more effective. However, a uniform dispersion of these nanowires in the BECy matrix would be more difficult to achieve. Another issue is related to the electrical property. Utilizing one dimensional nanofillers leads to a lower percolation limit than isodimensional nanoparticles [12]. As a result, a higher dielectric loss is expected in composites reinforced with Si-nanowires.

In addition to the enhancement of dielectric and mechanical properties, the dielectric constant and loss tangent of Si/BECy composites (18 vol.% and 26 vol.% Si loading) were measured at 1 MHz under compressive stress from 0 to 90 MPa. The AC conductivity could be calculated using the equation below,

$$\sigma_{AC} = \omega \varepsilon_r \varepsilon_0 \tan\delta$$

where ω is the angular frequency, ε_0 is the dielectric permittivity of free space, ε_r is the dielectric constant and $\tan\delta$ is the loss tangent of the composite. The dielectric constant of the composites is calculated from the capacitance reading from the measurement, showing an increase with respect to compressive stresses. The loss tangent of the composites, however, displays an apparent drop with increasing stress. For neat BECy, as shown in **Figure 7**, no stress dependence of AC conductivity is observed within the test range. In contrast, a gradual decrease in AC conductivity is observed in Si/BECy composites as the compressive stress increases. At the stress level of 90 MPa, the relative decrease in AC conductivity is 4 % and 6.5 % for the 18 vol.% and 26 vol.% Si loading, respectively. This stress dependent AC conductivity in the composites is obviously originated from the piezoresistive effect in Si. Therefore, these nanocomposites also have the potential to display a stress-sensing capability, which is expected to be dramatically enhanced by higher loadings of Si nanofillers with different shapes and specified orientations. The development of Si-nanowire/BECy composites for a stronger piezoresistive effect is currently underway.

4. Conclusions

In summary, we have fabricated Si nanoparticle/BECy composites and investigated their thermal, dielectric, and mechanical properties. Incorporation of Si nanoparticles significantly enhances the dielectric constant and largely preserves the low dielectric loss, while maintaining their weak frequency and temperature dependence. Si nanoparticles have also been demonstrated to be very effective in stiffening the polymeric nanocomposites. The excellent thermal stability of the BECy polymer matrix has been maintained in the composites. These properties indicate that the novel Si/BECy nanocomposites are very promising for future structural capacitor applications. In addition, the incorporation of Si nanoparticles imparts a unique mechanical stress-sensing capability to these nanocomposites.

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References

[1] Curtis PT. Multifunctional polymer composites. Adv Perform Mater 1996;3:279-293.

[2] Thomas JP, Qidwai MA. Mechanical design and performance of composite multifunctional materials. Acta Mater 2004;52:2155-2164.

[3] Wetzel ED. Reducing weight: Multifunctional composites integrate power, communications, and structure. The AMPTIAC Quarterly 2004;8:91-95.

[4] Lu J, Wong CP. Recent advances in High-k nanocomposite materials for embedded capacitor applications. IEEE Trans Dielec Elect Insul 2008;15:1322-1328.

[5] Stefanescu EA, Tan X, Lin Z, Bowler N, Kessler MR. Multifunctional PMMA-Ceramic composites as structural dielectrics. Polymer 2010;51:5823-5832.

[6] Stefanescu EA, Tan X, Lin Z, Bowler N, Kessler MR. Multifunctional fiberglass-reinforced PMMA-BaTiO3 structural/dielectric composites. Polymer 2011;52:2016-2024.

[7] Dang ZM, Lin YH, Nan CW. Novel ferroelectric polymer composites with high dielectric constants. Adv Mater 2003;15:1625-1628.

[8] Qi L, Lee BI, Chen S, Samuels WD, Exarhos GJ. High-dielectric-constant silver-epoxy composites as embedded dielectrics. Adv Mater 2005;17:1777-1781.

[9] Xu J, Moon KS, Tison C, Wong CP. A novel aluminum-filled composite dielectric for embedded passive applications. IEEE Trans Adv Pack 2006;29:295-306.

[10] Nan CW, Shen Y, Ma J. Physical properties of composites near percolation. Annu Rev Mater Res 2010;40:131-151.

[11] Li C, Thostenson ET, Chou TW. Sensors and actuators based on carbon nanotubes and their composites: A review. Compos Sci Technol 2008;68:1227-1249.

[12] Coleman JN, Curran S, Dalton AB, Davey AP, McCarthy B, Blau W, Barklie RC. Percolation-dominated conductivity in a conjugated-polymer-carbon-nanotube composite. Phys Rev B 1998:58:R7492-R7495.

[13] Smith CS. Piezoresistance effect in germanium and silicon. Phys Rev 1954;94:42-49.

[14] Pfann WG, Thurston RN. Semiconducting stress transducers utilizing the transverse and shear piezoresistance effects. J Appl Phys 1961;32:2008-2019.

[15] He RR, Yang PD. Giant piezoresistance effect in silicon nanowires. Nature Nanotechn 2006;1:42-46.

[16] Hamerton I, Hay JN. Recent technological developments in cyanate ester resins. High Perform Polym. 1998;10:163-174.

[17] Sheng X, Akinc M, Kessler MR. Creep behavior of bisphenol E cyanate ester/alumina nanocomposites. Mater Sci Eng A 2010;527:5892-5899.

[18] Shimp DA, Craig Jr WM. New liquid dicyanate monomer for rapid impregnation of reinforcing fibers. Proc 34th Int SAMPE Symp 1989;34:1336-1346.

[19] Chao F, Bowler N, Tan X, Liang G, Kessler MR. Influence of absorbed moisture on the properties of $BaTiO_3$/cyanate ester composites. Compos Part A-Appl S 2009:40:1266-1271.

Figure 1 TEM micrograph of Si nanoparticles after heat treated in air at 500 °C for 2 hrs.

Figure 2 Weight fraction as a function of temperature in TGA tests of the 10 vol.% and 26 vol.% Si loading composites.

Figure 3 SEM images of fracture surfaces of the (a) 10 vol.% and (b) 26 vol.% Si loading composites.

Figure 4 Frequency dependence of dielectric properties at room temperature in Si-nanoparticle/BECy composites and neat BECy polymer. (a) Dielectric constant ε_r; (b) Dielectric loss tangent tanδ.

Figure 5 Frequency dependence of dielectric properties at a series of temperatures of Si-nanoparticle/BECy composites. Dielectric constant of nanocomposites with (a) 10 vol.% and (b) 26 vol.% Si-nanoparticles; loss tangent of nanocomposites with (c) 10 vol.% and (d) 26 vol.% Si-nanoparticles.

Figure 6 Storage modulus (E') of Si-nanoparticle/BECy composites and neat BECy polymer as a function of temperature.

Figure 7 AC conductivity of Si-nanoparticle/BECy composites and neat BECy polymer as a function of compressive stress at 1 MHz at room temperature.

Table 1. Selected dielectric and mechanical properties.

	ε_r at 1 kHz		tanδ [%] at 1 kHz		E_{br} [MV/m]	E' [GPa] at 40 °C	Onset T_g [°C]
	25 °C	200 °C	25 °C	200 °C			
BECy	3.0	3.0	0.40	0.26	30	2.4	278
10 vol.% Si	4.0	4.3	1.07	0.74	16	3.0	270
26 vol.% Si	7.1	7.6	1.71	0.95	10	4.6	272

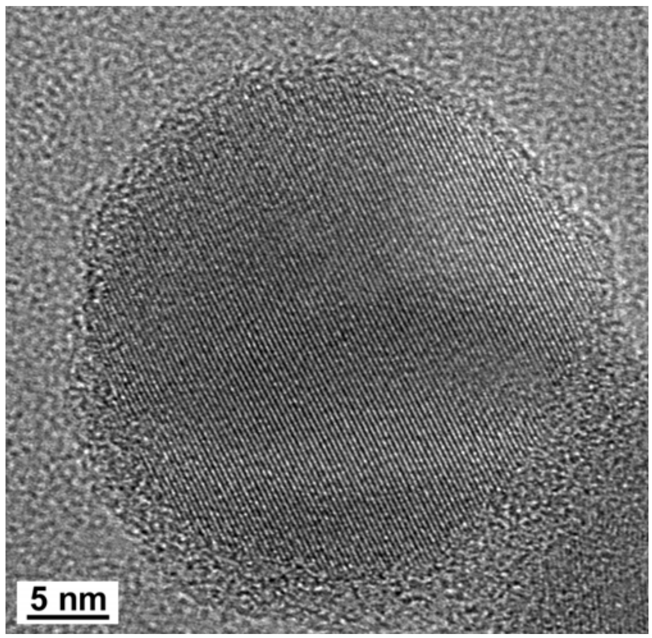

Fig. 1

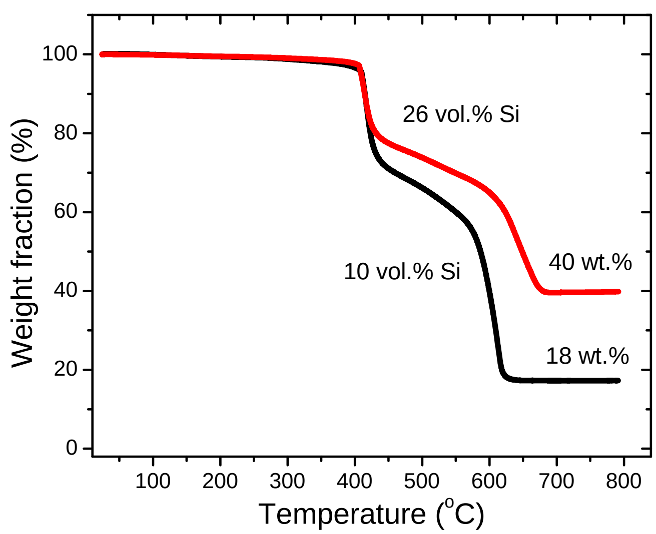
Weight fraction (%)
100
80
60
40
20
0
100
200
300
400
500
600
700
800
Temperature (°C)
26 vol.% Si
10 vol.% Si
40 wt.%
18 wt.%

Fig. 2

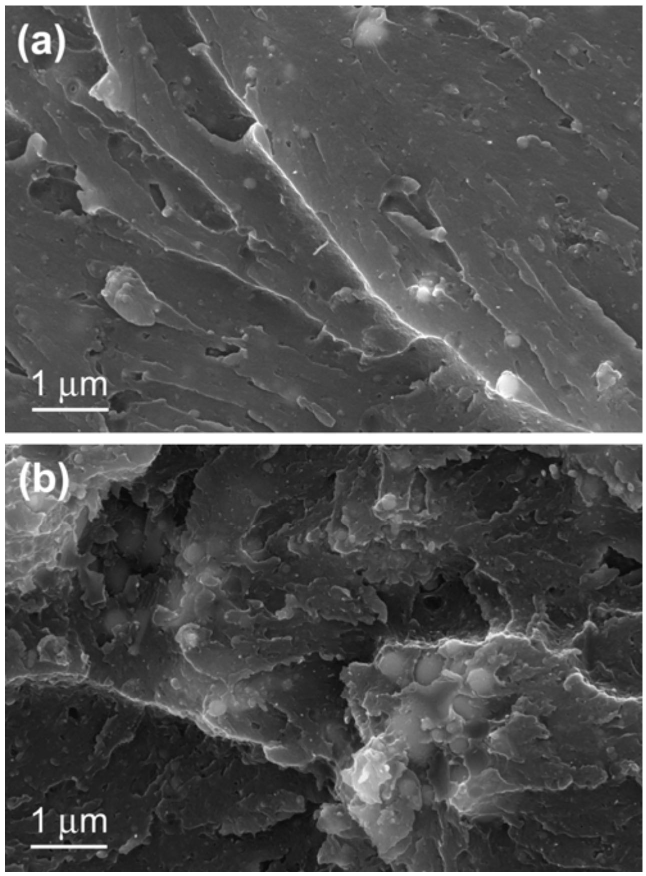

Fig. 3

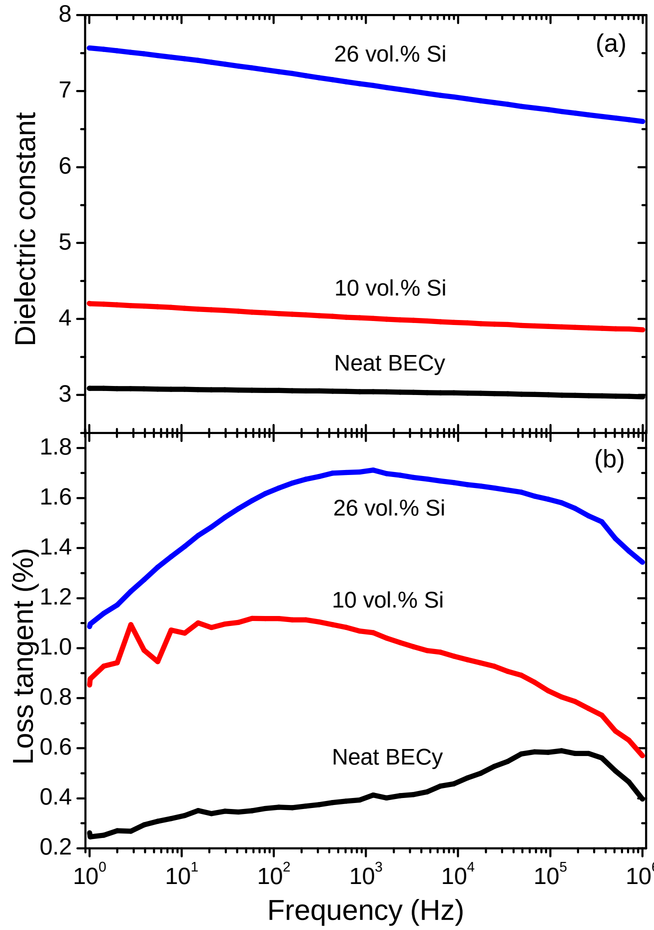
(a)
26 vol.% Si
10 vol.% Si
Neat BECy
Dielectric constant
(b)
26 vol.% Si
10 vol.% Si
Neat BECy
Loss tangent (%)
Frequency (Hz)

Fig. 4

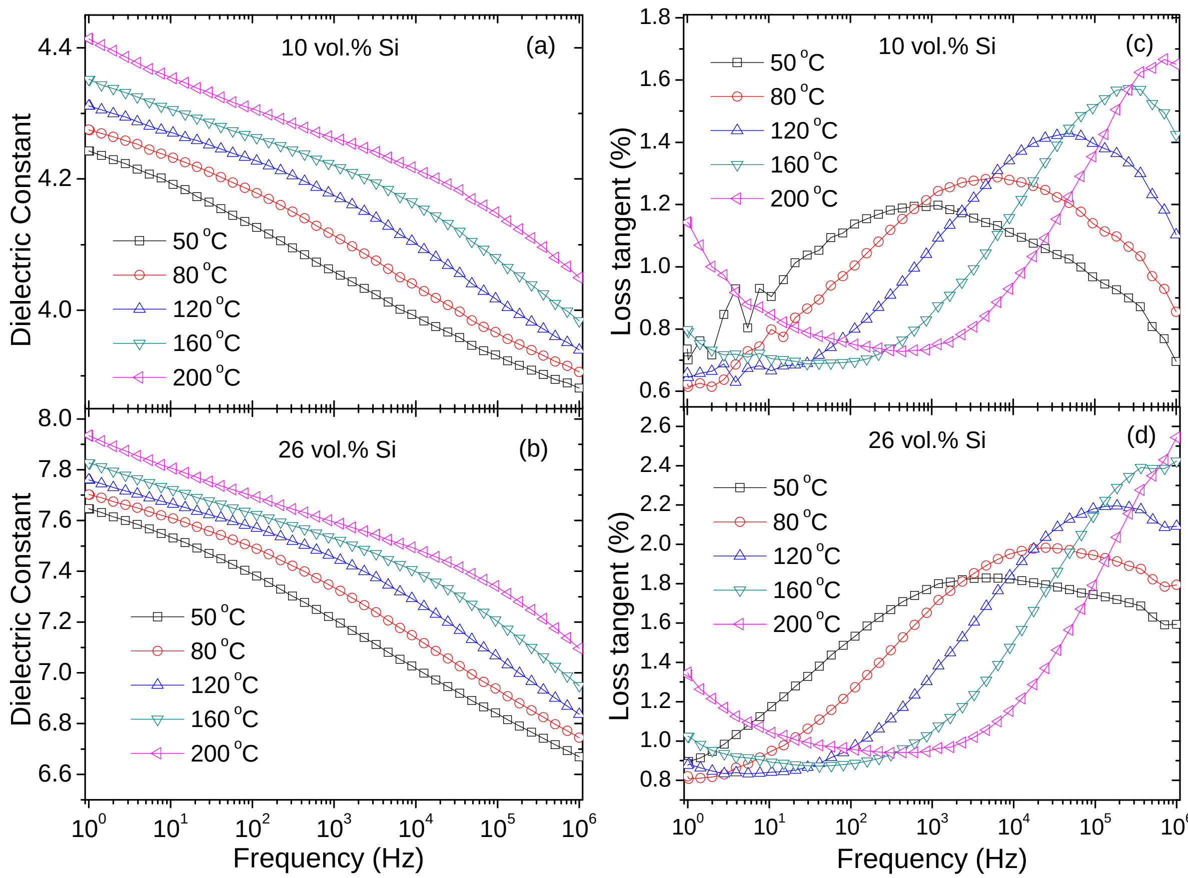
10 vol.% Si
(a)
Dielectric Constant
50 °C
80 °C
120 °C
160 °C
200 °C
26 vol.% Si
(b)
Frequency (Hz)
(c)
Loss tangent (%)
(d)

Fig. 5

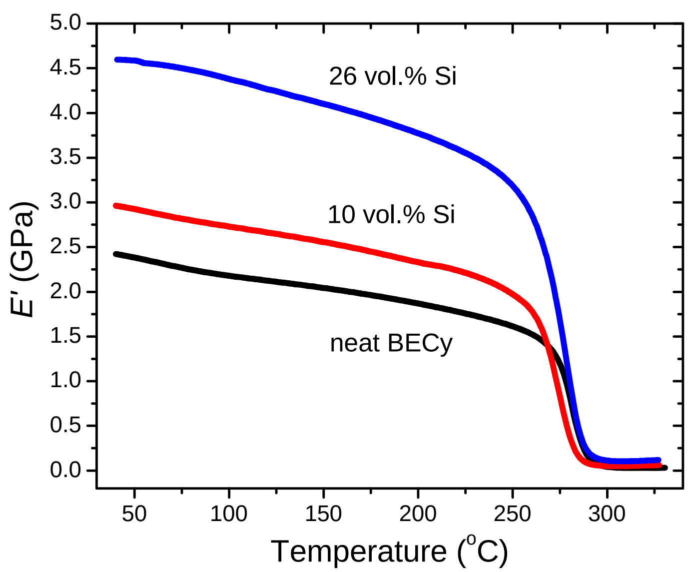
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
E' (GPa)
26 vol.% Si
10 vol.% Si
neat BECy
50
100
150
200
250
300
Temperature (oC)

Fig. 6

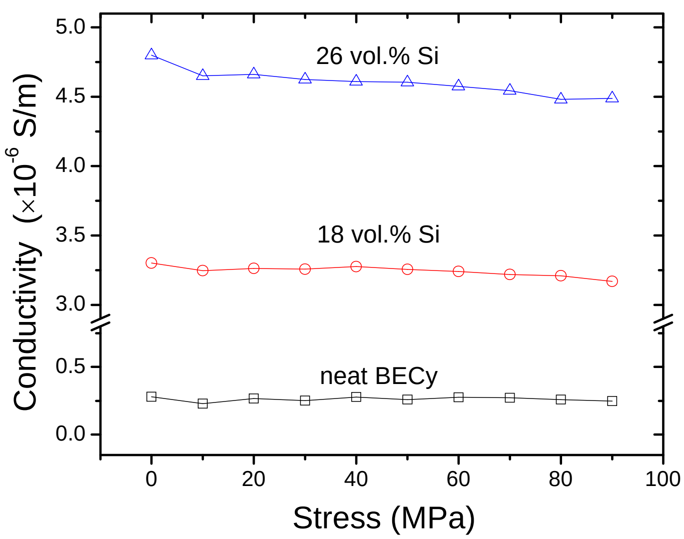
26 vol.% Si
18 vol.% Si
neat BECy
Conductivity (×10-6 S/m)
Stress (MPa)
5.0
4.5
4.0
3.5
3.0
0.5
0.0
0
20
40
60
80
100

Fig. 7