Conductive and dielectric property of polyimide/VGCF composites in terms of thermal fluctuation-induced tunneling effect

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Abstract:

Polyimide (PI)/vapor grown carbon fiber (VGCF) composites were fabricated by *in situ* polymerization. The theoretical calculations for an increase in conductivity with elevating temperature were in good agreement with the experimental results. The results show that good heat resistance of PI/VGCF composites was attributed to few thermal fluctuation of PI chain arrangement in spite of collision between electrons flowed out from the VGCF gaps and atoms of PI chains. Real and imaginary part of complex permittivity and AC conductivity changing with frequency were obtained at different temperature. The phase lags of resistances for complex impedance were evaluated by a two-circuit model for a 3.11 vol%. The DC conductivity calculated from CPE model is almost equal with the experimental DC conductivity.

Keywords: Polyimide, vapor grown carbon fiber, tunneling conduction

Introduction:

Polyimide (PI) are candidate polymers for a variety of applications due to their useful properties such as excellent thermal stability, high glass transition temperature and radiation resistance[1,2]. To avoid accumulation of electrostatic charge on the surface of PI, conductive filler are always added into PI. The conductive and dielectric property of VGCF/PI can be analyzed by the tunneling effect established for disordered materials with large conducting regions separated by potential barriers. The demonstration must be attributed to no activation energy of relaxation processes which slightly deviated from the Debye behavior denoting asymmetric distribution of relaxation times. VGCF/PI composites show an increase on DC conductivity against temperature, indicating the occurrence of the tunneling effect for disordered materials discussed above. The best fittings between theoretical and experimental results were carried out for complex permittivity and AC conductivity. The model system contains a serial arrangement of two units that represent the contribution from the bulk composite (sample) and the contact region of the metal-semiconductor interface between the electrode and the sample. The contact phase element (CPE) is introduced to simulate and explain the dielectric behavior of the VGCF/PI composites in a more reasonable way. The experimental and calculated results indicated that the activation energy of relaxation process was almost zero. The DC component of was found to be attributed to the tunneling effect through thin barriers.

Sample preparation:

PI/VGCF composites were fabricated by *in situ* polymerization[3-5]. At first, VGCFs were pre-treated in N, N-dimethyacetamide (DMAc) under ultrasonic for 4 hours. The monomers, pyromellitic dianhydride (PMDA) and equimolar amount of 4, 4'-diaminadiphenyl ether (DADPE) were added into the DMAc solution containing VGCF. After stirring the solutions for 3 hours in the nitrogen gas, PMDA-DADPE polyamic acid (PAA)/VGCF solution was obtained. The content of

VGCF against PAA was 1.55 - 6.28 vol%. The PAA dispersed solution containing VGCF was cast onto glass and pre-cured at 120 °C in vacuum for 1 hour and then post-cured at 220 °C in vacuum for 3 hours to form PI-VGCF composite films. The thickness of the film was ca. 0.12 mm.

Results and discussion:

The resistivity decreased drastically beyond 2.72 vol% and leveled-off with further increase in the content of VGCF, indicating a percolation phenomenon. Fig. 1 shows temperature dependence of conductivity at the indicated applied electric field. The electric field was applied at room temperature and conductivity at the each fixed electric field was measured with elevating temperature by external heating in an oven with air-circulating. Interestingly, as shown in Fig. 1, the increase in conductivity with elevating temperature beyond 100 °C is quite different from positive temperature coefficient (PTC) effect denoting drastic decrease of conductivity at temperature close to their melting point of polyolefin matrix[6-8]. Such tendency is probably due to the fact that with elevating temperature, tunneling effect owing to an increase in the number of electron transfer between adjacent VGCF became much promoted than thermal expansion of the PI matrix.

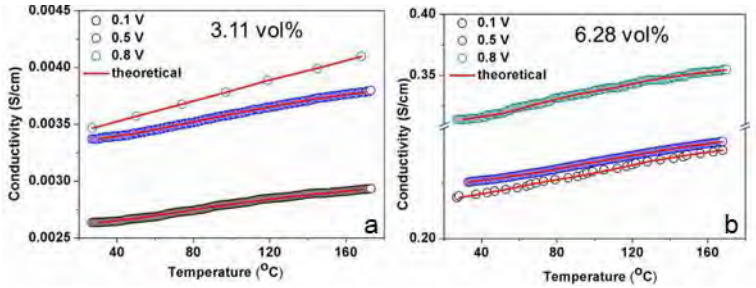

Figure 1. (a) and (b) Experimental and theoretical conductivities versus temperature for PI/VGCF composites with 3.11 and 6.28 vol% VGCF contents, respectively.

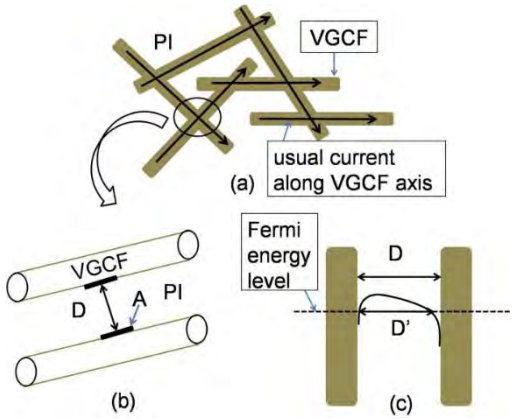

Figure 2**.** Proposed models to pursue theoretical calculation of resistivity against temperature

To represent the above concept schematically, we proposed models in Fig. 2 to pursue theoretical calculation. Fig. 2a shows the arrangement model of VGCFs through junction gaps and Fig. 2b is the enlargement model of a gap between overlapped VGCFs with distance *D*. *A* is surface area over which most of tunneling occurs. It is reasonable that most of electron transfers by tunneling effect occur between overlapped VGCFs with gap distance *D*. The schematic diagram of potential barrier is given as a well-known non-parabolic potential function shown in Fig. 2c instead of a simple rectangle potential function. Following Sheng's theory, the conductivity σ (= $1/\rho$) was calculated as a function of temperature as follows:

$$\sigma = \left(\frac{4T_1}{\pi T}\right)^{1/2}\left[\int_0^1 \sum\nolimits_0(\varepsilon)\exp\left\{-\frac{T_1}{T}\varepsilon_T^2 - \frac{T_1}{T_0}\varphi(\varepsilon_T)\right\}d\varepsilon_T + \int_1^\infty \sum\nolimits_1(\varepsilon_T)\exp\left(-\frac{T_1}{T}\varepsilon_T^2\right)d\varepsilon\right] \quad (1)$$

U_0 are parameters to form non-parabolic potential function as follows:

$$U(u,\bar{\delta}) = U_0\left[1 - \frac{\lambda}{u(1-u)} - \bar{\delta}\right] = U_o\left[1 - \frac{\lambda}{u(1-u)} - \bar{\delta}_0\varepsilon u\right] = U(u,\varepsilon) \quad (2)$$

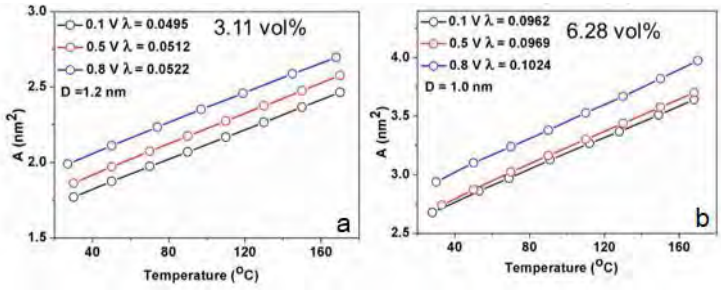

Figure 3. (a) and (b): Theoretical A value versus temperature for composites with 3.11 and 6.28 vol% VGCF contents, respectively, which were calculated by eq. 1 and 2

The best fitting between the experimental and theoretical conductivity results was obtained at D = 1.20 nm for a 3.11 vol% VGCF content and D = 1.00 nm for a 6.28 vol% VGCF content. The average gap between adjacent VGCFs for the composite with a 3.11 vol% content close to the percolation threshold is longer than that for the composite with 6.28 vol% content which is reasonable. Sheng's theory has been appropriated in many studies, in conjunction with a parabolic barrier as well as using the maximum value of the first term $-[(T_1/T)\varepsilon^2 + (T_1/T_0)\phi(\varepsilon)]$ in eq. 1 at $\varepsilon_T = \varepsilon^*$ in order to estimate the conductivity of polymer semi-conductive system as a function of the absolute temperature, T. The following simple approximation was adopted in many studies.

$$\sigma(T) \propto \exp\left[-\frac{T_1}{T + T_o}\right] \quad (3)$$

The theoretical conductivity calculated by eq. 3 are in good agreement with the experimental results by choosing T_1 and T_0 values. However, the values of D are too small to justify the average gap between adjacent VGCFs on the basis of eq. 3. That is, the values of D are obviously out of the framework of physical meaning. It must be emphasized that the theoretical estimation by non-parabolic potential barrier function in this study provides reasonable analysis in spite of complicated numerical calculation.

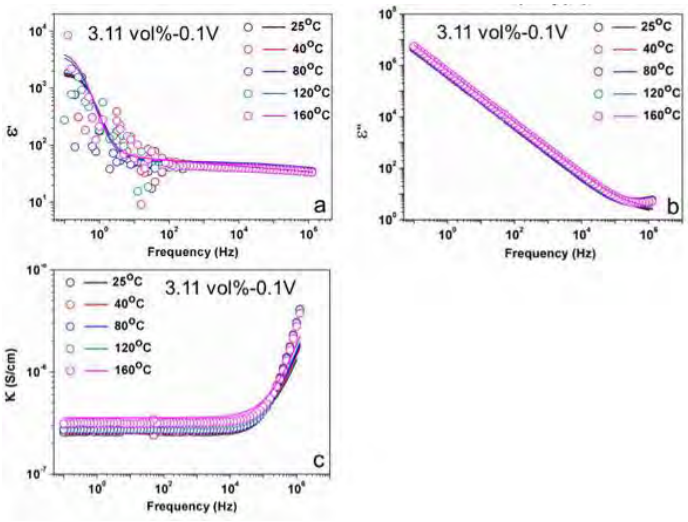

Figure 4. (a), (b) and (c): Frequency dependence of ε' , ε'' and κ , respectively. Open circles: experimental results. Solid curves: theoretical results. All results were obtained for a composite with a 3.11 vol% VGCF content.

Complex permittivity and AC conductivity were measured at different temperature. To obtain more information about the dispersion and the structure of VGCFs in PI matrix, a simple diagram model and an equivalent circuit are established to simulate the behavior of the composite with 3.11 vol% VGCF content as shown in Fig. 4. This simple common model contains a serial arrangement of two units that represent the contribution from the bulk composite and the contact region between the electrode and the composite. Each unit is depicted by two parallel combinations of two possible electrical current composites. One is the current through the resistors and the other is the current through the capacitors. Considering the introduction of Contact Phase Element CPE, the complex impedance of the equivalent circle can be denoted as follows: $Z^* = \frac{1}{\frac{1}{R_1} + iwC_1} + \frac{1}{\frac{1}{R_2} + (iw)^{\alpha} C_2}$ (4)

C_2 is the true capacitance of the contact region. α is a constant independent of frequency. When $\alpha = 1$, the CPE becomes an ideal capacitor.

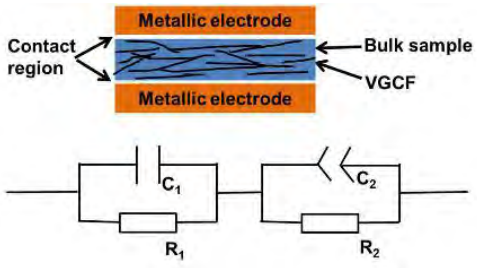

Figure 5. The diagram mode model and the equivalent circuit model of VGCF/PI composite with a 3.11 vol% VGCF content.

Table 1. The corresponding parameters in eq. 4 obtained by simulation for the composite with 3.11

	vol% VGCF				
T (°C)	25	40	80	120	160
R_1 (Ω)	30	30	30	30	30
C_1 ($F\times10^{-3}$)	89.5	89.9	90.0	95.0	100
R_2 ($\Omega\times10^4$)	1.62	1.55	1.42	1.36	0.94
C_2 (pF)	783	800	793	890	920
α	0893	0.888	0.883	0.874	0.865

Table 2. The comparison of DC component between experimental and theoretical results.

T (°C)	K_{DC} ($S/cm\times10^{-7}$) in Figure 4c (3.11 vol%)	K_2 ($S/cm\times10^{-7}$) calculated from R_2 in Table 1 (3.11 vol%)
25	2.557	3.025
40	2.703	3.041
80	2.717	3.056
120	3.066	3.362
160	3.098	3.559

In summary, the thermal fluctuation-induced tunneling conduction proposed by Sheng must be analyzed by using non-parabolic function as potential barrier on analyzing conductivity of polymer-filler composites. Because a parabolic function as potential barrier provides unreasonable values with pico-scale for barrier width and surface area over which most of tunneling occurs, especially in the case where polymer as perfect insulator. The DC component of AC conductivity was measured by complex permittivity were evaluated by a two-circuit model for a 3.11 vol% containing the Contact Phase Element (CPE) introduced to simulate and explain the dielectric behavior of the composites in a more reasonable way. The good agreements between experimental and theoretical results were established for the frequency dependence of the complex permittivity, AC conductivity. The values accorded with those obtained for the direct DC measurement, which indicated validity for the estimation about electrical current of the conductive-filler and polymer by the thermal fluctuation-induced tunneling.

References:

(1) Freilich, S. C.; Gardner, K. H.; Feger, C.; Khojasteh, M. M.; Megrath, J. E., Polyimides: Materials and characterization. Elsevier: Amsterdam, **1989**.
(2) Wilson, D.; Stenzenberger, H.D.; Hergenrother, P.M. Polyimides; Chapman & Hall: London **1990**.
(3) Jiang, X.; Bin, Y.; Matsuo, M. *Polymer* **2005**, 46, 7418-7424.
(4) Hejin Wang; Taipeng Wang; Shiyong Yang; Lin Fan. *Polymer* **2013**, 54, 6339-6348
(5) Nguyen Dang Luong; Ulla Hippi; Jukka Seppälä et al. *Polymer* **2011**, 52, 5237-5242
(6) Narkis, M.; Vaxman, A. *J. Appl. Polym. Sci.* **1984**, 29, 1639-1652.
(7) Chen, Q.; Bin, Y,; Matsuo, M. *Macromolecules* **2006**, 39, 6525-6536.
(8) Bin, Y.; Chen, Q.; Tashiro, K.; Matsuo M. *Phys.Rev. B* **2008**,77(3), 035419.