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Electrical and thermal properties of polyimide/silica nanocomposite

M.J. Tommalieh[a], A.M. Zihlif[a]* and G. Ragosta[b]

[a]*Department of Physics, University of Jordan, Amman, Jordan;* [b]*Institute of Chemistry and Technology of Polymers (ICTP), CNR, Pozzuoli, Napoli, Italy*

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The electrical and thermal properties of thin films of polyimide/silica nanocomposites prepared via sol–gel process were studied as a function of nanosilica particles content, temperature and applied field frequency. It was found that the dielectric constant and dielectric loss of the nanocomposites decrease with both the frequency and the nanosilica content, while increase with temperature. The AC-conductivity measured in frequency range 200 kHz–1.5 MHz decreases with the filler concentration and increases with increasing temperature. For the (25 wt%) nanocomposite, it was found that the AC-conductivity increases with temperature, and the Cole–Cole plots showed that the calculated activation energy and relaxation time decrease with temperature. The observed thermal conductivity increases gently with temperature. The empirical universal law was used to fit the observed electrical data under the measuring conditions.

Keywords: composites; polyimide; nanosilica; dielectric constant; electrical conductivity; thermal conductivity

1. Introduction

The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines. This obviously includes polymer science and technology and even in this field the investigations cover a broad range of topics. This would include microelectronics and nanoelectronics as the critical dimension scale for modern devices is now below 100 nm. Other areas include polymer-based biomaterials, nanoparticles drug delivery, miniemulsion particles, fuel cell electrode polymer bound catalysts, layered self-assembled polymer films, electrospun nanofibres, imprint lithography, polymer blends and nanocomposites. Nanocomposites are a relatively new class of materials with ultrafine phase dimensions, typically of few nanometres. When nanoparticles are added to polymers, they create environmentally friendly polymers that can be utilised in the fabrications of advanced materials of great interest. Filled polymer nanocomposites with silica and silicates often exhibit remarkable improvement in mechanical, optical and electrical properties. For example, organic–inorganic hybrid

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*Corresponding author. Email: adzh@ju.edu.jo

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nanocomposites have novel properties to be used in photoelectronic devices, optical waveguides and conducting materials [1–4].

Polyimide is one of the varieties of thermoplastic polymers used in high temperature environment based on using fire resistant agents to improve their flame resistance; and has outstanding properties as thermal and oxidative stabilities, mechanical properties, high glass transition temperature and resistance to solvents. Polyimide structure has remarkable heat resistance, which reaches for a short time up to a temperature of 600°C. It is one of silicon polymers which are based on an inorganic silicon–oxygen structure that has organic radicals attached to silicon atoms. Polyimides nanocomposites made of hybrid organic–inorganic components are important class of new materials with tailored physical properties [5–11].

Progress in the sol–gel process was achieved in recent years to produce polyimide–silica nanocomposites with improved compatibility between the polymer and silica by increasing the interfacial interactions. The applications of the polyimide–silica nanostructured systems have been extended to opto-electronic and photonic fields, nonlinear optics, optical guides and photorefractive materials in addition to aerospace and microelectronics devices [12,13].

In this article, the electrical and thermal properties of prepared thin films of polyimide/silica composites by the sol–gel technique will be studied. Dielectric constant, AC electrical conductivity, relaxation time, thermal conductivity and thermal activation energy at different measuring conditions will be estimated as a function of frequency, silica nanoparticles content and temperature using Impedance Analyzer and thermal conductivity setup.

2. Experimental

2.1. *Nanocomposite films preparation*

Polyimides are particularly suitable for the sol–gel technique to prepare nanocomposite materials. The method of preparation of nanocomposite films made of polyimide (matrix) and nanosilica particles (filler) was described previously in full details by Musto and Ragosta using the sol–gel technique [14,15]. Briefly, the polyimide precursor was Pyre-MlRK, commercially available as a 12 wt% solution in a mixture of N-methyl-2-pyrrolidone (NMP) and xylene. The precursor was a polyamic acid (PAA) formed by condensation of pyromellitic dianhydride and oxydianiline. High purity grades of tetraethoxysilane (TEOS) and γ-glycidyloxypropyltrimethxysilane (GOTMS). Distilled water was used to induce hydrolysis of the alkoxysilane components using 32 wt% HCl solution as catalyst and ethanol as solvent. The alkoxysilane solutions used for the production of nanocomposite film (22.3 wt% silica) was prepared as follows: 3.46 g TEOS, 0.86 g EtOH, 1.20 GOTMS, 0.82 g H_2O and 1.12 g aqueous HCl solution (2.0 wt%) were added sequentially in glass vial. The mixture was magnetically stirred at room temperature, until a clear solution was obtained. The precursor hybrid solution was subsequently prepared by adding dropwise the hydrolysed alkoxysilane solution to the PAA solution, under continuous stirring for 10 min at room temperature. For the production of films, the precursors were cast on glass slides and kept at 80°C for 1 h to allow most of the solvent to evaporate. Imidisation and condensation reactions were carried out in successive isothermal steps of 1 h each, at 100°C, 200°C, 250°C and 300°C.

The prepared polyimide/silica thin films have 1.5 mm thickness, and contain 10%, 15%, 19% and 25% by weight nanosilica particles in addition to sample of neat polyimide.

2.2. *Impedance measurements*

Impedance measurements were made, at room temperature, with HP 4194A-impedance analyzer over frequency range of 100 kHz–1.5 MHz. Calibration, short and open, of the impedance analyzer was conducted before the collection of data. Measurements were made on disc shaped specimens. Specimens were cut from the prepared composite sheets and placed between the copper plates of the test sample holder. The samples were fixed in a sample holder placed in a shielded cell designed specifically for this experiment. Two leads of the sample holder were interconnected with a terminal of the impedance analyzer [16–19].

2.3. *Thermal conductivity measurements*

In general, thermal conductivity measurement is not an easy task since the values of thermal conductivity for polymers (excellent insulators) are so small values between 0.2 and 0.3 W/m°C [20–22]. Measurements of thermal conductivity of polyimide/silica nanocomposites of different content of nanosilica particles were done by means of sending electrical pulse from a power source to transmit across double composite specimens separated by a heating current coil, all are placed in a sample holder connected to thermocouples to read the temperature measured from the specimens surfaces. Our modified setup and measuring procedure are based on that design reported by Katsure and Kamal [23]. Discs specimens of diameter 5 cm and thickness of 1.5 mm were cut from the nanocomposites for thermal conductivity measurements. All the measuring assemblies are placed in an oven, and the applied voltage and current are taken during a time interval under steady state conditions.

3. Results and discussion

It is recognised that various physical and mechanical behaviours of polymer nanocomposites are greatly influenced by nanostructure. Recent investigations of optical, dielectric and electrical properties of advanced polymer nanocomposites filled with inorganic nanofiller exhibited increase or decrease in their observed values with the filler nanoparticles concentration [10,12].

3.1. *AC-electrical results*

The used impedance analyzer reads values of the phase angle and impedance. The imaginary and real components of the impedance ($Z_\mathrm{i}, Z_\mathrm{r}$) and the dielectric constants ($\varepsilon'', \varepsilon'$) were calculated from the impedance equations reported in our previous papers [17,19]. The AC-electrical quantities were calculated as a function of applied electric field frequency, temperature and nanoparticles concentration.

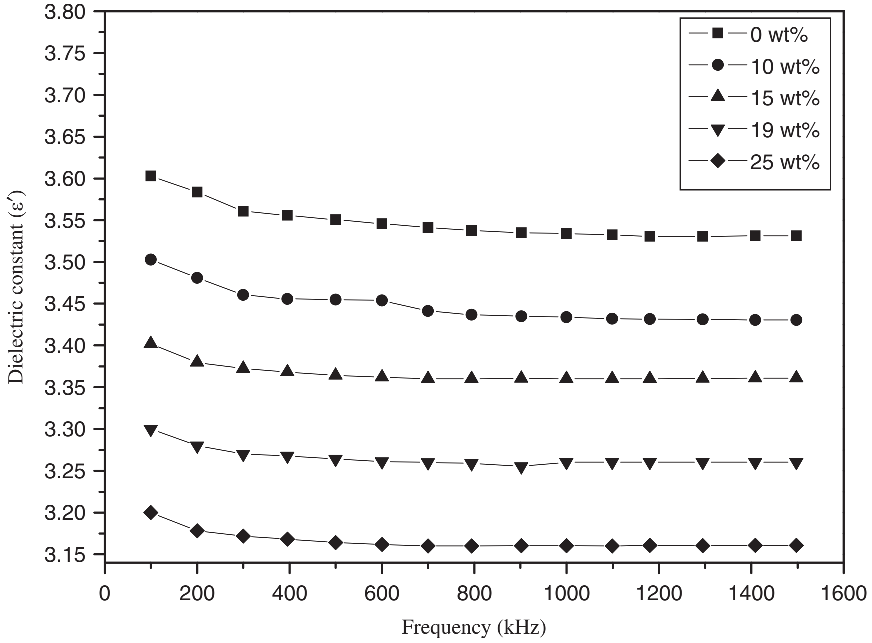

Figure 1. Variation of dielectric constant with frequency.

Figures 1 and 2 show the dependence of both the dielectric constant (ε') and dielectric loss (ε'') measured in the frequency range 100 kHz–1.5 MHz for different composite samples. Both ε' and ε'' decrease with increasing frequency and nanoparticles concentration. The neat polyimide has high values of ε' and ε'', where the nanocomposite of higher concentration value (25 wt%) has lower values. The decrease in ε' value with frequency is related to dispersion and polarisation processes, and decrease in ε' with increasing silica nanoparticles is due to lower value ε' of silica than that of the pure polyimide.

Figures 3 and 4 show the variations of ε' and ε'' with temperature, where both of them increase with temperature. This enhancement is attributed to the increasing charge carriers' mobility and to the activation of electron transport in the composites. Plotting the imaginary component ε'' versus the real component ε' yields what is called the Cole–Cole construction plots, which are sometimes very useful in dielectric behaviour analysis [18,22]. The plots shown in Figure 5 at different temperatures are arcs and shifted to higher values of ε' and ε'', which means that bulk resistive and capacitive components of the composite increase with temperature. The nanocomposites are still represented as parallel RC-networks connected in series. If those arcs are approximated to sunken semicircles, and by using the relation: $\omega_{\max}\tau = 1$, at the maximum values of ε'', then the relaxation time (τ) can be estimated. Table 1 shows the dependence of τ on temperature for 25 wt% composite. τ decreases from a value 1.06 to 0.26 ns with increasing temperature from 25°C to 105°C.

Figure 6 shows the variation of AC-conductivity (σ_{AC}) with the nanosilica particles content by weight measured at different frequencies and room temperature. σ_{AC} value decreases with increasing nanosilica (filler) concentration i.e. less electrical conduction.

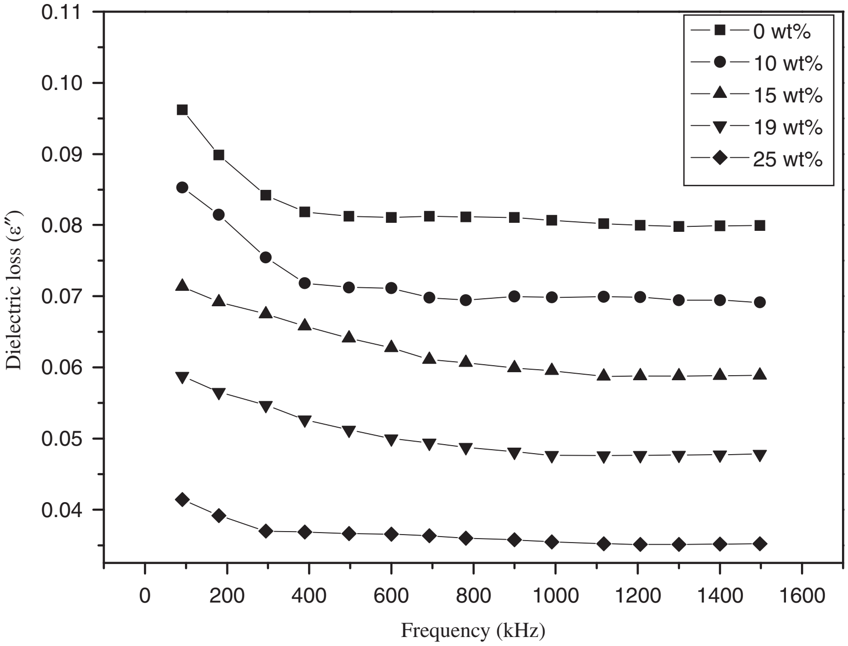

Figure 2. Variation of dielectric loss with frequency.

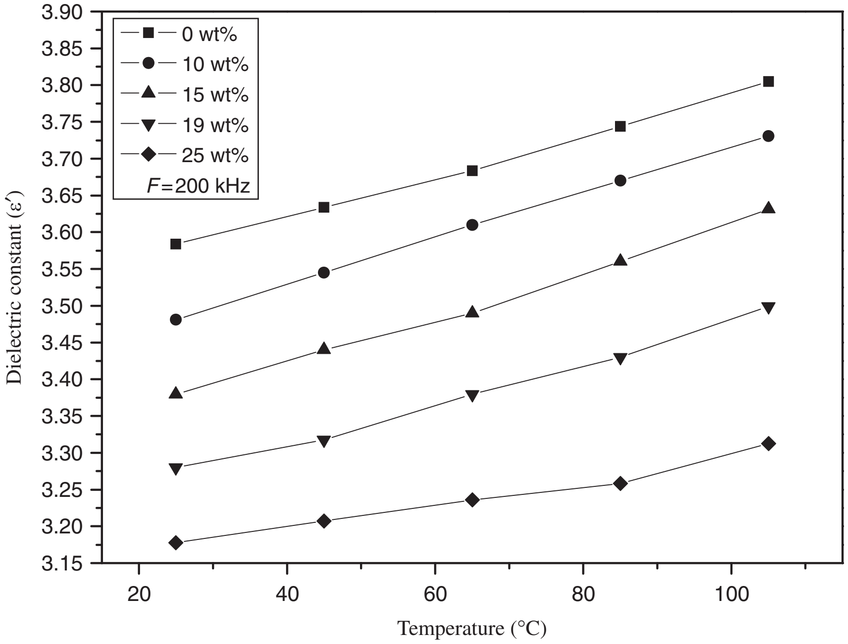

Figure 3. Dielectric constant *vs*. temperature.

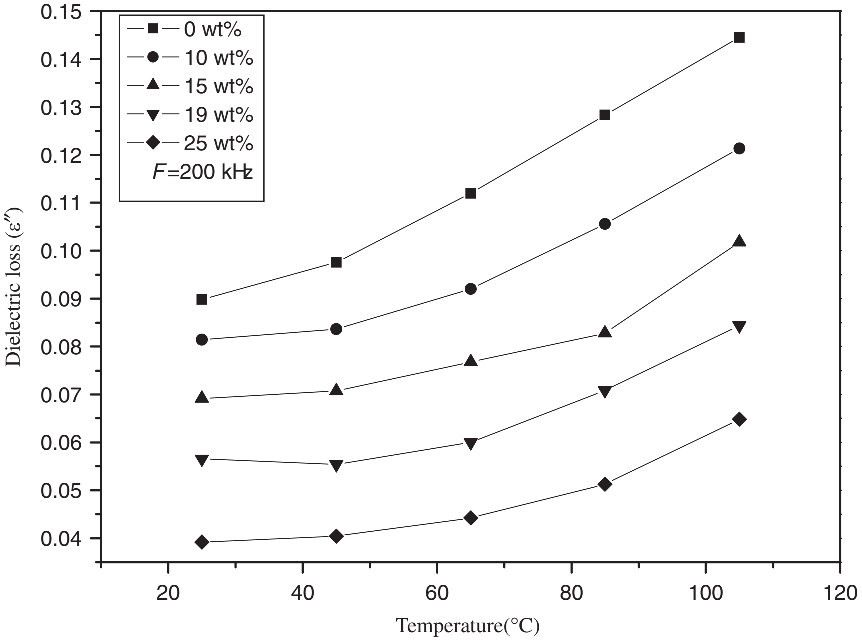

Figure 4. Dielectric loss *vs*. temperature.

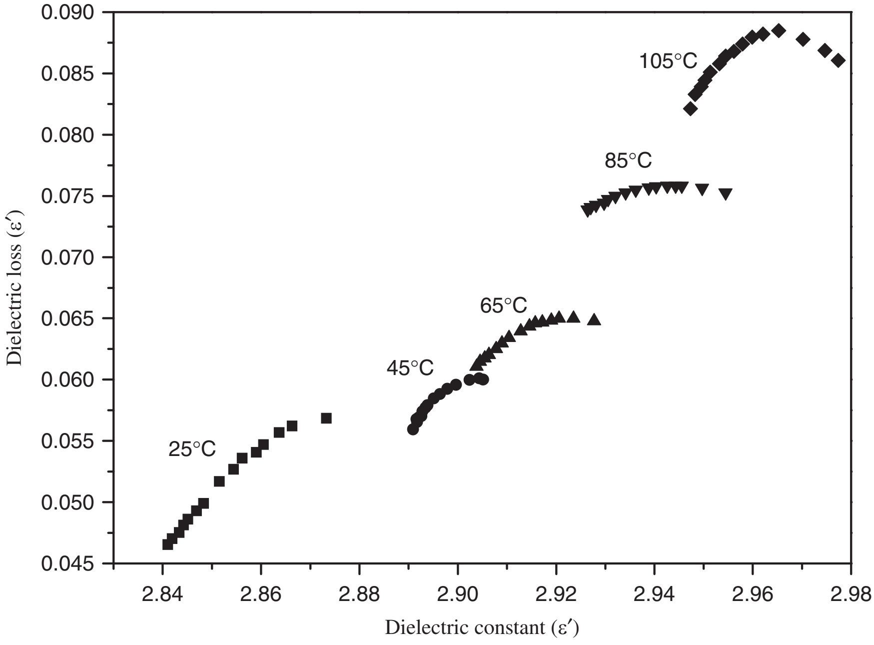

Figure 5. Cole–Cole plots for 25 wt% PI/nanosilica composite at different temperatures.

Table 1. Temperature dependence of relaxation time for 25 wt% composite.

Temperature (°C)	Relaxation time × 10^{-6} (s)
25	1.06
45	0.53
65	0.39
85	0.31
105	0.26

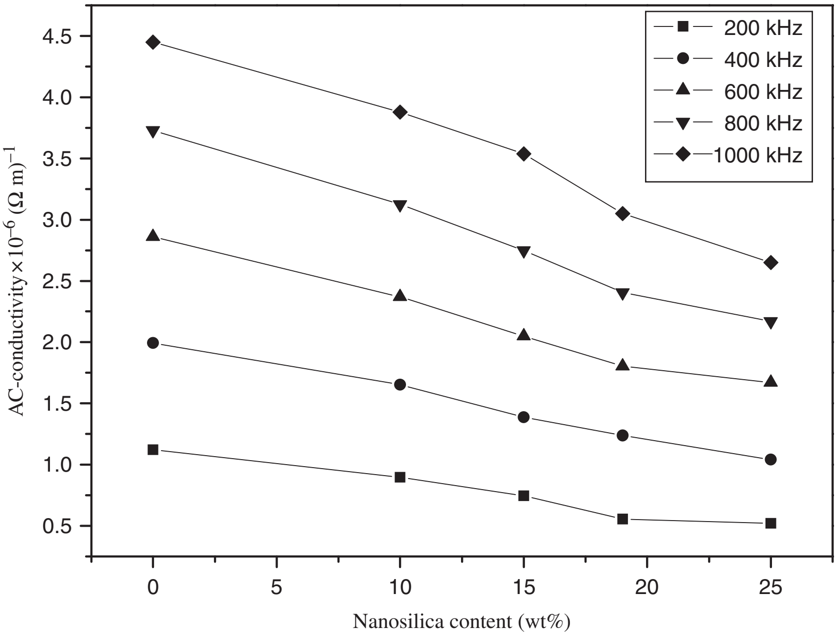

Figure 6. Variation of AC-conductivity with nanosilica concentrations.

Figure 7 shows the dependence of the AC-conductivity on temperature at different frequencies. The σ_{AC} increases when temperature increases up to 105°C. Using the Arrhenius type equation $\sigma = \sigma_0 \exp(-E_a/kT)$, the activation energy (E_a) of the conduction processes can be estimated from the linear fit of the slopes of Figure 7. Table 2 includes values of E_a obtained from the variation of σ_{AC} as a function of frequency. In this case, the activation energy has a constant value at each measuring frequency value. It can be seen that E_a values decrease with temperature from 0.5 to 0.33 eV, indicating that the energy gap of the nanocomposite becomes narrower due to creation of localised electrons states by heating, and thus electrons tunnelling and hoping take place from the valence energy band to the conduction energy band. This development in the conduction process is consistent with the observations in the dielectric behaviour.

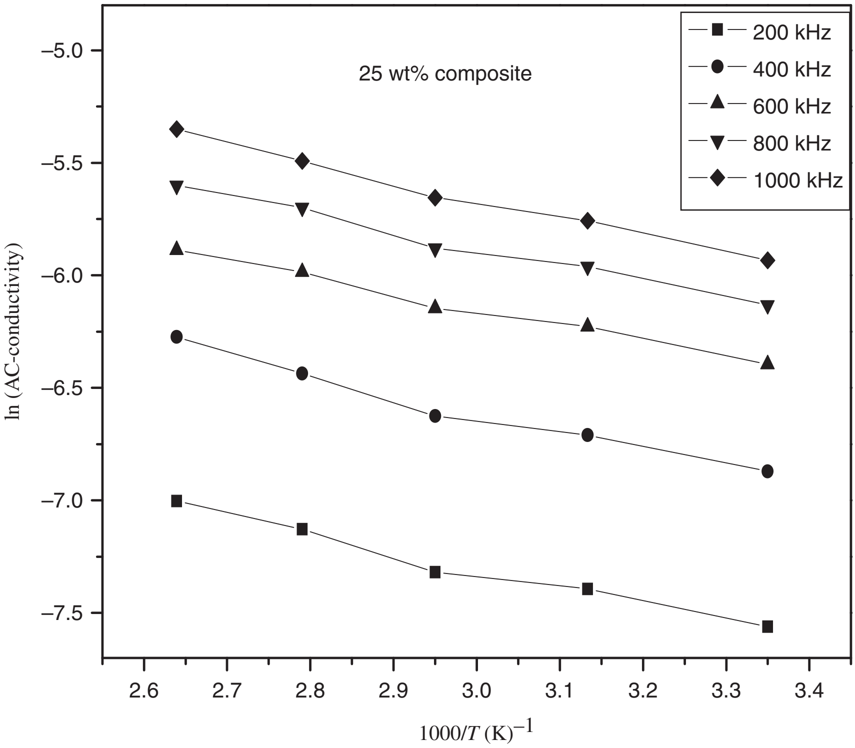

Figure 7. Variation of ln (AC-conductivity) with (1000/T) for 25 wt% nanosilica composite.

Table 2. Activation energy values for 25 wt% composite.

Frequency (kHz)	Activation energy (eV)
200	0.50
400	0.44
600	0.36
800	0.35
1000	0.33

It is general thought that the AC-conductivity is related to frequency as reported in the empirical Jonscher's [18] universal law model which is given by

$$\sigma_{AC}(f) = \sigma_{DC} + Bf^{m}, \tag{1}$$

where B and m are coefficients, f is the frequency of the applied field (Hz), σ_{DC} is the DC conductivity of the material and σ_{AC} is the AC-conductivity of the material in $(\Omega\,m)^{-1}$. At higher frequencies the conductivity increases as a power of frequency with the exponent $0 < m < 1$. In this case B and m are temperature dependents. Analysing the

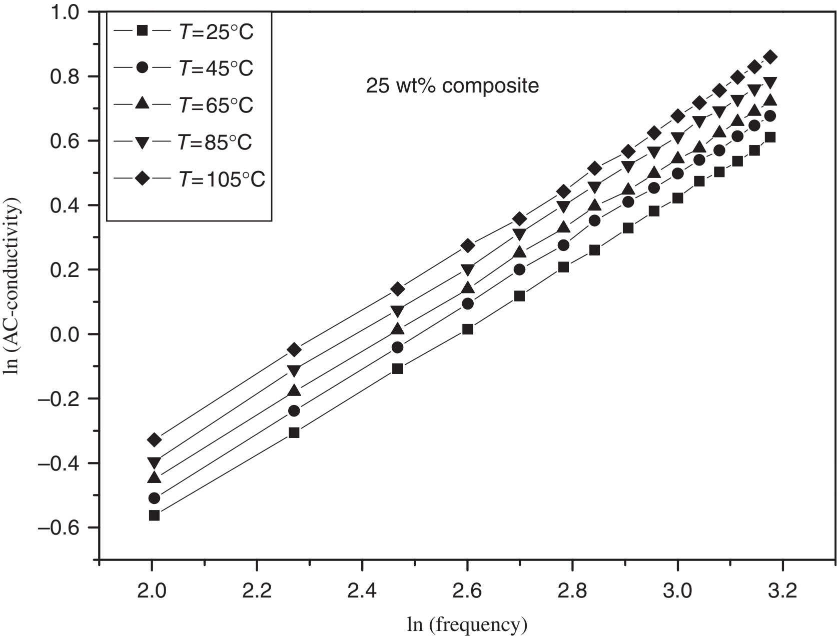

Figure 8. Variation of ln (AC-conductivity) *vs*. ln (frequency) for 25 wt% composite.

Table 3. *B* and *m* coefficients for 25 wt% composite.

Temperature (°C)	$B \times 10^{-11}$ $(\Omega\,\mathrm{m})^{-1}$ $(\mathrm{Hz})^{-\mathrm{m}}$	*m*
25	2.65	0.993
45	2.93	0.995
65	3.60	0.996
85	3.90	0.997
105	4.47	0.999

AC-conductivity results of the 25 wt% PI/nanosilica composite was done by plotting common logarithm ln (AC-conductivity) versus ln (frequency) for each temperature, as shown in Figure 8. Based on this figure, it can be assumed that the equation above can be simplified in our temperature range to:

$$\sigma \approx Bf^{m}. \tag{2}$$

From this figure the coefficients *B* and *m* are estimated and included in Table 3, where the values of *B* increase with increasing temperature and all *m* values are close to unity [17].

3.2. *Thermal conductivity results*

The thermal conduction in solids as polymer composites is produced by phonons transport (as major contributor) and from electrons and impurities existing in composites.

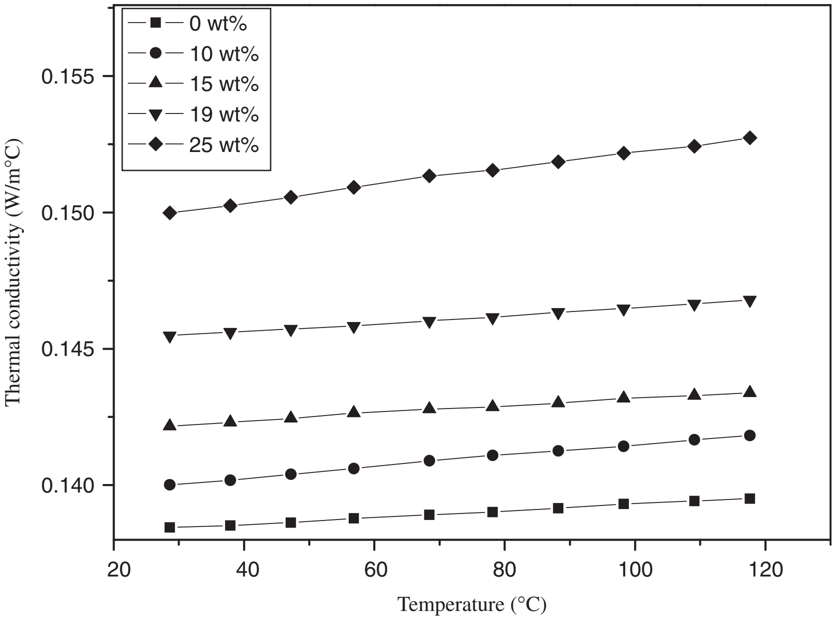

Figure 9. Variation of thermal conductivity with temperature.

Measurement of the thermal conductivity of polymeric materials is difficult since its value is relatively small and in the range (0.2–0.4 W/m°C). The thermal conductivity is very sensitive to the measuring conditions, physical and chemical structures of the polymer composite. The growing needs for materials required to thermal applications lead to the design of new composite materials with an appropriate combination of selected polymeric matrices and suitable fillers.

The thermal conductivity k for pure polyimide and four composites of nanosilica concentration (10, 15, 19 and 25 wt%) were calculated from the equation [23]:

$$k = IVL/2AT(\mathrm{W/m^{\circ}C}), \tag{3}$$

where V and I are the applied voltage and current, L is the specimen thickness, and A is the specimen area. The factor 2 refers to double specimens placed in the heating specimen holder.

Figure 9 shows the variation of the thermal conductivity with temperature and nanosilica particles content. It can be seen that conductivity increases with the temperature and decreases with the filler concentration as shown in Figure 10. This behaviour of thermal conductivity is similar to that of the electrical conductivity concerning temperature. In the case of raising the temperature, the phonons, electrons and impurities are activated and thus enhancement in the thermal conductivity is observed. Table 4 includes the variation of the thermal resistance ($R = L/k$) for the nanocomposites, where R decreases with the silica particles concentration. Thus, embedding nanosilica particles in polyimide matrix enhances the composites thermal conductivity and lowers its thermal resistance, which may be useful for thermal performance applications. Fitting the observed

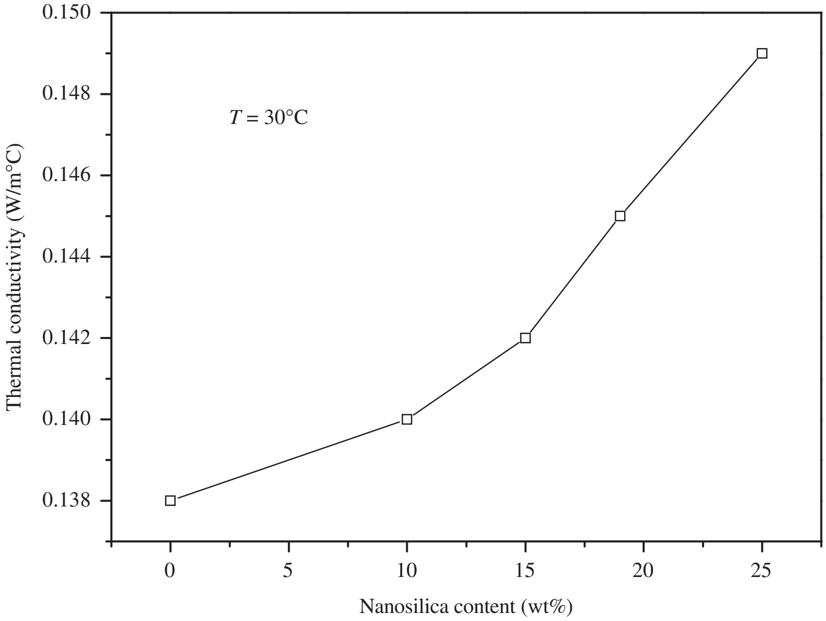

Figure 10. Variation of thermal conductivity with nanosilica concentrations.

Table 4. Thermal and electrical conductivities (30°C).

Nanosilica composite	k (W/m°C)	R (m°C/W)	$\sigma_{AC} \times 10^{-6}$ $(\Omega\,\text{m})^{-1}$
0 wt%	0.138	7.2	1.2
10 wt%	0.140	7.1	1.0
15 wt%	0.142	7.0	0.8
19 wt%	0.145	6.9	0.7
25 wt%	0.150	6.7	0.5

increase in the thermal conductivity of the nanocomposites with the filler volume fraction (Figure 11) exhibits a linear dependence, which is in agreement with that reported by Agrawal et al. [24] of their measurements on the thermal conductivity of styrene–butadiene composites.

There is a point which is essential to be clarified. In general, good electrical conductors are also good thermal conductor as normally observed in metallic solids. But the observed electrical and thermal behaviours of the studied thin films of nanosilica composites are different. Electrical conductivity decreases and the thermal conductivity increases with nanosilica concentration as shown in Table 4. It is known that phonons are major thermal conduction contributors. It seems that the nanosilica particles are effective in thermal

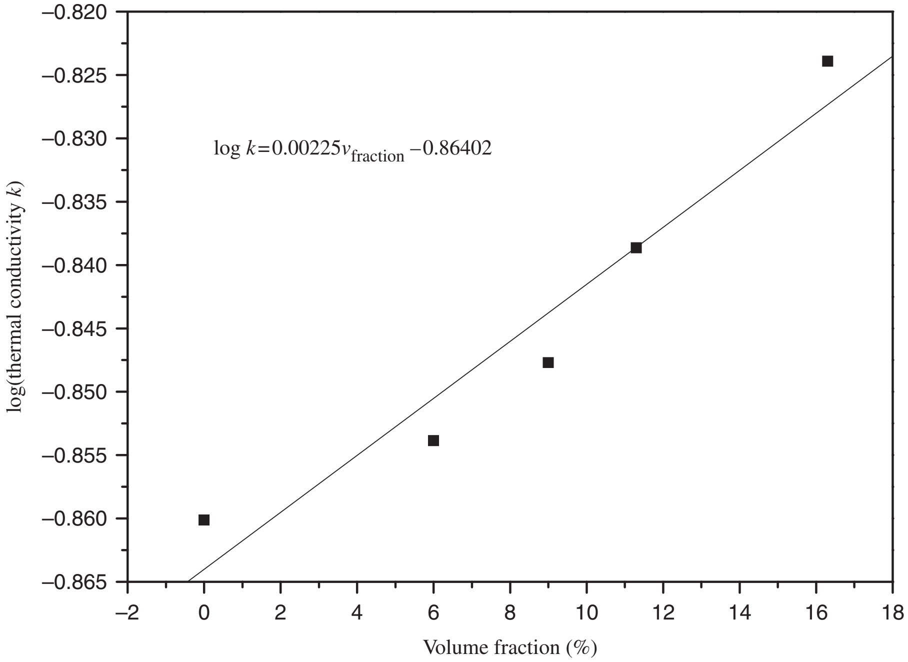

Figure 11. Agrawal model of the observed thermal conductivity vs. composites volume fraction.

transfer due to their small sizes and huge surface area. So it is expected that the heat transport increases with the nanosilica concentration, where a great amount of phonons reflection and transmission takes place. But in the case of electrical conduction, the electrons contribution is small since both polyimides and silica are insulating substances, and the electricity transport suffers decay from increasing charge absorption and decreasing conductive paths density with increasing nanosilica concentration.

4. Conclusion

In this study, the AC electrical and thermal properties of a set of nanocomposites of polyimide polymer (matrix) and nanosilica particles (filler) were investigated as a function of applied field frequency, temperature and nanosilica concentrations: 10, 15, 19 and 25 wt%. It was found that the dielectric constant and dielectric loss of the nanocomposites decrease with the frequency and the nanosilica content, while increase with the temperature. The measured AC-conductivity decreases with increasing filler concentration and increases with increasing temperature. The electrical conductivity of the 25 wt% nanocomposite was studied as a function of temperature. It was found that it increases with temperature. Analysis of the constructed Cole–Cole plots showed that the estimated activation energy and relaxation time of thermally activated process decrease with temperature. The observed electrical results fit approximately the reported empirical universal law concerning the AC-conductivity measured under different applied frequencies. The observed thermal conductivity increases slightly with increasing temperature.

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