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Full Length Research Paper

Electrical, structural and thermal properties of graphite/silicone blends

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We report the results of electrical, structural and thermal investigations on graphite/Silicone blends (G/Silicone), obtained by dispersion of graphite powder in an insulating matrix of rubber silicone. The X-ray diffraction analysis showed crystalline structure for our all studied (G/Silicone) blends. Conductivity measurements were reported in the temperature range of 298 to 423 K. The blends showed percolation behaviour. It was observed that the conductivity of these blends decreases with increasing temperature indicating a metallic behaviour. In addition to the electrical study, we have made a thermal study on these blends. We found that the thermal conductivity of these blends increases when the weight concentration ("p" %) of graphite increases. In order to give a comparative analysis of both electrical and thermal conductivity of blends, we use the Agri's model which provides a good estimation of thermal conductivity of blends for all weight concentration. The scanning electron microscopy (SEM) analysis shows a good morphology for graphite concentration lower than 60%.

Key words: Polymer-matrix composites (PMCs), electrical properties, thermal properties, percolation.

INTRODUCTION

Aerospace applications as well as the leading-edge technologies in energy and biology fields etc, require a significant reduction of weight and size components, and an improvement of their electrical conductivities as well as their thermal and mechanical properties (McLachlan et al., 2005). To obey these specifications, the researchers focus their attentions on polymer-matrix composites (PMCs). Indeed, these types of materials are required increasingly in industry for their great potentialities in different fields such as the manufacture of bipolar plates for the fuel cells and photovoltaic cells. PMCs are obtained by incorporation of mineral or organic conducting inclusions in insulating matrix with a weight concentration "p". For a critical weight concentration known as the percolation threshold "p_c", an "infinite" cluster is formed. Hence, the blend's conductivity increases rapidly and a transition from an insulating state to a conducting one occurs in the composite (Khaldi et al., 2004; Ian, 2002).

To explain more the percolation behaviour, we describe two structures. The first one is the structure where the matrix surrounds the conducting inclusions at all weight concentration and the distance between them is greater than the tunnelling distance of electrons. The second one is the structure where conducting inclusions make electrical contact with each other, when the concentration fraction of Graphite reaches the percolation threshold. At this point, a conductive cluster is formed (Min and Xiaodong, 2009) and there is an abrupt change in the σ_{dc} and the current can flow through the whole system (Fatoum et al., 2008; Flandin et al., 1999).

Thermal and electrical properties play a critical role in controlling the performance and the stability of materials and they are the main fundamental properties of them. The aim of our study is to understand the effect of the graphite weight concentration on thermal and electrical properties of graphite/silicone blends (G/Silicone). We used the photo thermal method to carry out an impedance analysis at a temperature range of 298 to 423 K.

EXPERIMENTAL TECHNIQUES

Sample preparation

A micro particles of graphite (about 15 µm) obtained from Prolabo Company was mixed in an appropriate ration of silicone [synthetic

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rubber of poly dimethylsiloxane (PDMS)] at -50 and 250°C. Blends were prepared with different weight percentages “p” from 10 to 100%. Each mixture was stirred vigorously up to homogeneity for few minutes. Then, it was drowned in cylindrical Teflon mould to obtain pellets of 13 mm diameter. Samples were dried at 100°C for 1 h.

Characterisation and techniques

X-ray diffraction (XRD) measurements were carried out by using a PANalytical/X'Pert Pro MPD X-ray diffractometer with Cu Kσ radiation (λ=1.54 A°) in the 2θ range of 0 to 60°. The SEM micrographs were obtained from Quanta 2000 scanning microscope operating at 20 kV. The electrical conductivity was investigated using a HP 4192A impedance analyzer controlled by a computer and an HP view program. The conductivity was measured on pressed pellets of uniform thickness L = 3 mm and a diameter d = 13 mm at a temperature range of 298 to 423 K. We made electrical contacts by using copper electrodes of 13 mm diameter on both sides of these G/Silicone pellets adopting the sandwich geometry. Using the parallel R-C circuit model, we obtained the sample dc resistance at lower frequencies. The dc conductivity was calculated by employing the formula (Fethi et al., 2008):

$$\sigma_{dc} = \frac{1}{R}\frac{L}{S} \quad (1)$$

Where R is the bulk dc resistance of the samples; L and S are the thickness and the surface area of the sample respectively.

For thermal measurements, we use the photothermal method (Degiovanni et al., 1996; Adili et al., 2010) with a finite width pulse heat excitation, which is the most current method use to measure the thermal conductivity of homogeneous materials. The thermal conductivity was measured at room temperature on pressed pellets of uniform thickness of L =3 mm and a diameter of d = 25 mm.

RESULTS AND DISCUSSION

Morphological analysis

The SEM micrographs of (G/Silicone) blends at 0, 30, 50, 70, and 80% Graphite weight concentration are shown in Figure 1. A good dispersion can be deduced from the pattern of the surface morphology of these samples, in which the original traces of the embedded graphite can be clearly distinguished. Figure 1b and c shows the surfaces of the blends at lower graphite weight concentration. These images confirm that individual graphite is dispersed during processing of these blends. Furthermore, contacts between adjacent graphite occur in the blends when the graphite weight concentration becomes higher than 50%. In fact, these images show a transition from a dispersed state to an interconnected network of graphite when weight concentration increases.

X-ray diffraction analysis

We present in Figure 2a, the X-ray diffraction patterns of graphite, G (30%)/Silicone and G (80%)/Silicone blends, and in Figure 2b, the X-ray diffraction of Silicone matrix. It was clear that the peaks intensity increases when the graphite weight concentration increases. We note the crystalline structure of graphite by the presence of diffraction peaks at 2θ = 26.55, 42.38, 44.57, 50.7, 54.68 and 59.908°. This result proves that the graphite does not undergo any structural changes by dispersing in the silicone matrix and it preserves its crystalline structure.

Electrical properties

In Figure 3a and b, we present the variation of dc conductivity of our blends as function of Graphite weight concentration at room temperature and at various temperatures, respectively. The dc conductivity of all blends increases when the graphite weight concentration increases. It was observed that the conductivity of (G/Silicone) blends increases from about 8.7 10^{-3} S m^{-1} at p = 20% to 40 S m^{-1} at p = 60%.

It was found out in literature that most theoretical or semi – empirical electrical conductivity prediction models are limited to fit properly to the electrical behaviour of some kind of blends (Mamunya et al., 2002; Novak et al., 2002; Krupa and Chodak, 2001). Most of models found in the literature are of statistical percolation type. These models typically predict electrical conductivity based on the probability of particle contacts within composite. Moreover, various models take some factors into account, which can affect the conductivity of composites as well as the weight concentration at which the percolation threshold occurs (Mamunya et al., 2002; Novak et al., 2002; Krupa and Chodak, 2001). For this reason, we propose three theoretical models to correlate our experimental conductivity. The first model is where the electrical conductivity follows the Equation 2 (Novak et al., 2002; Krupa and Chodak, 2001):

$$\mathrm{Log}(\sigma_c/\sigma_i) = B(1-e^{-\alpha p})^n \quad (2)$$

Where σ_c and σ_i are respectively the electrical conductivity of composites and polymeric matrix, B, α and n are adjustable parameters. The inflexion point was identified by the percolation concentration p_c as described by Novak et al. (2002) and Krupa and Chodak, 2001):

$$p_c = \mathrm{Ln}(n)/\alpha \quad (3)$$

The second model is originally proposed by Kirkpatrick (1971) and Zallen (1983). The model proposed followed a power low equation of the following form:

$$\sigma \propto (p-p_c)^t \text{ for } p > p_c \quad (4)$$

Where, t is the critical exponent.

This model has become the basis for many of the later

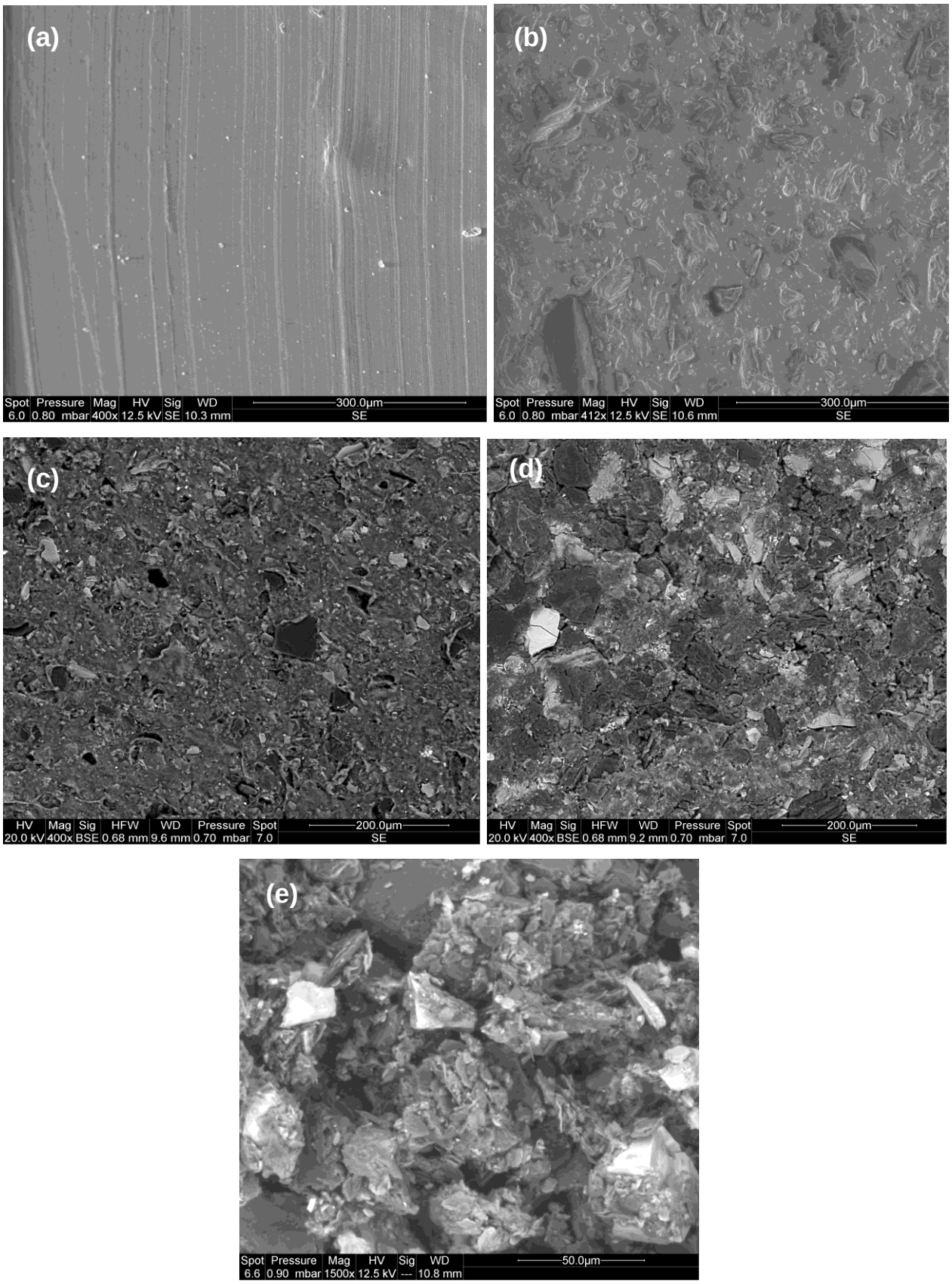

Figure 1. Scanning electron micrographs of (a) Silicone, (b) G (30%)/Silicone (70%), (c) G (50%)/Silicone (50%), (d) G (70%)/Silicone (30%), and (e) G (80%)/Silicone (20%).

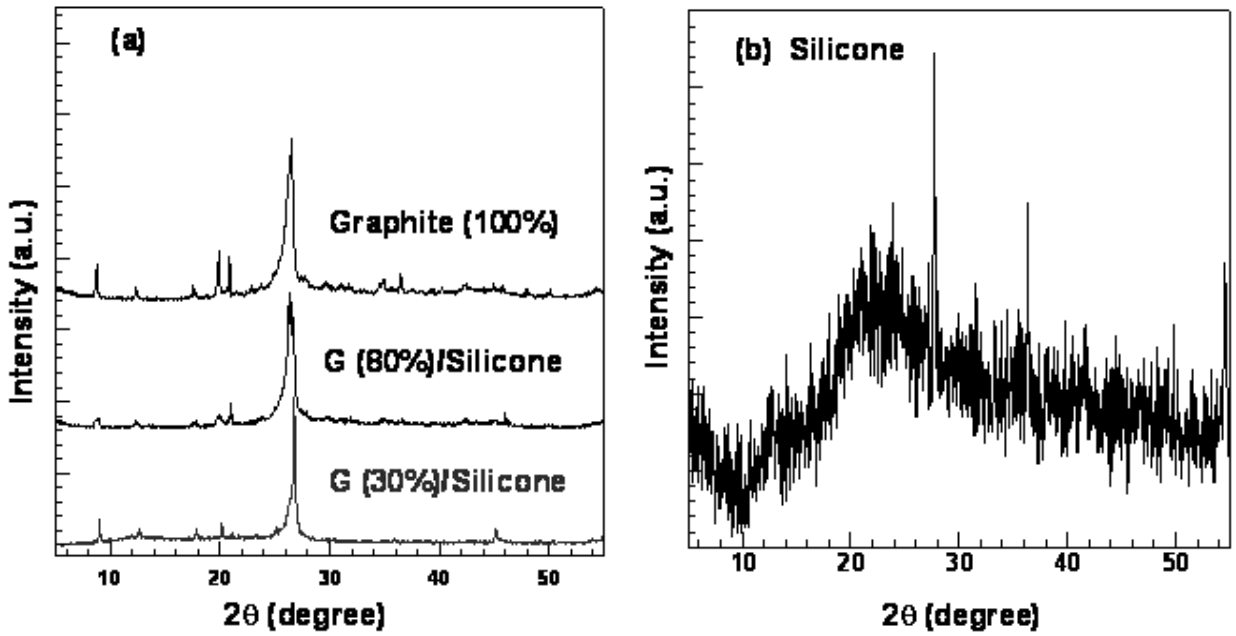

Figure 2. X-ray diffraction diagrams of (a) Graphite, G (30%)/Silicone and G (80%)/Silicone blends and (b) Silicone matrix.

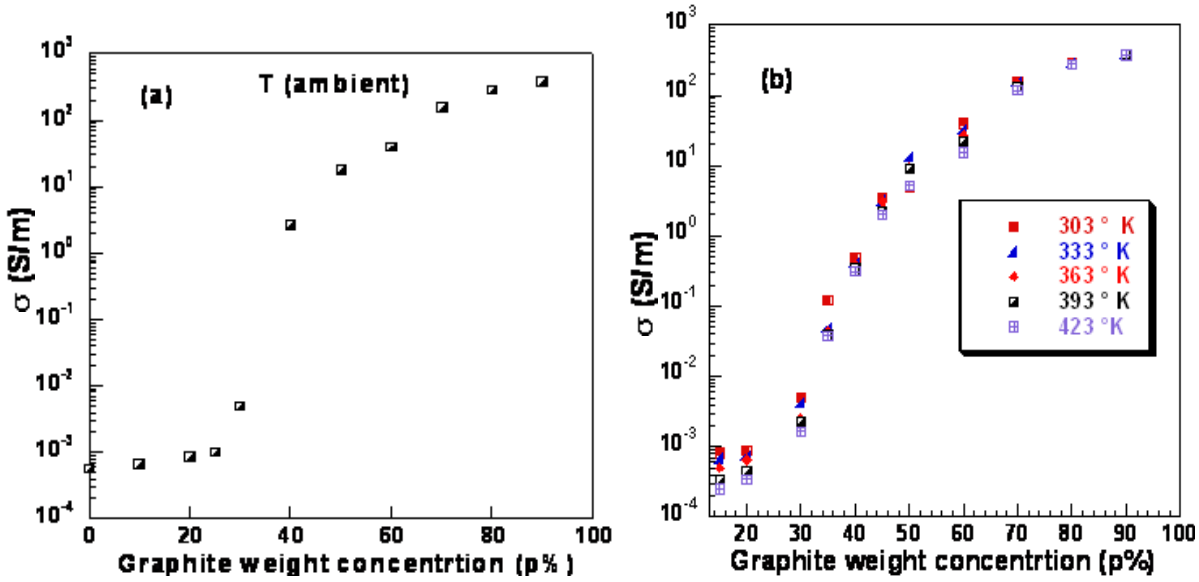

Figure 3. Weight concentration dependence of electrical conductivity for G/Silicone blends (a) at room temperatures and (b) at various temperatures (303 to 423 K).

conductivity models. One example of a model similar in form to statistical model is the one proposed by McLachlan and Sauti (2007). This model is used extensively and successfully in literature (McLachlan and Sauti, 2007; Wu and McLachlan, 1997; Wu and McLachlan, 1998; McLachlan and Heaney, 2000; McLachlan et al., 1998; Citeme and McLachlan, 2003), where the conductivity follows the relation (Equation 5).

$$(1-p)\frac{\sigma_i^{1/s}-\sigma_m^{1/s}}{\sigma_i^{1/s}+A\sigma_m^{1/s}}+p\frac{\sigma_c^{1/t}-\sigma_m^{1/t}}{\sigma_c^{1/t}+A\sigma_m^{1/t}}=0 \quad (5)$$

Where σ_i is the insulating matrix conductivity, σ_c is electrical conductivity of the conducting load, σ_m is the composite conductivity; t and s are critical exponents,

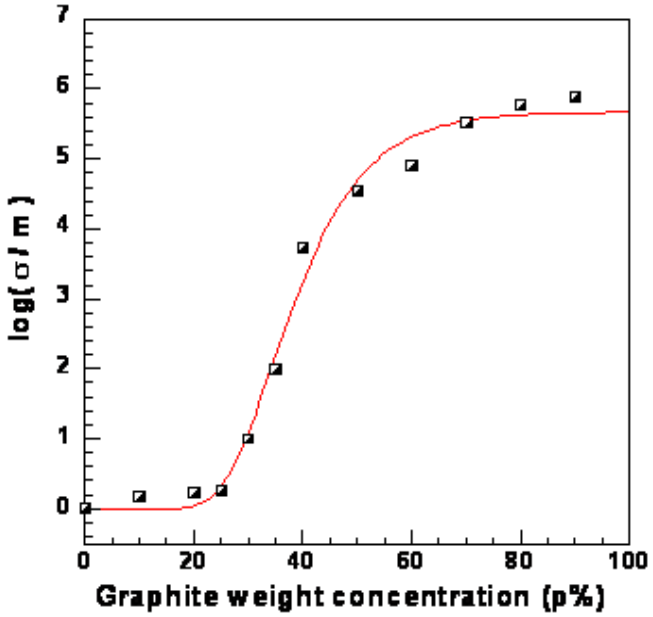

Figure 4. Electrical conductivity of G/Silicone blends versus weight concentration: experimental data and fitting using Equation 2.

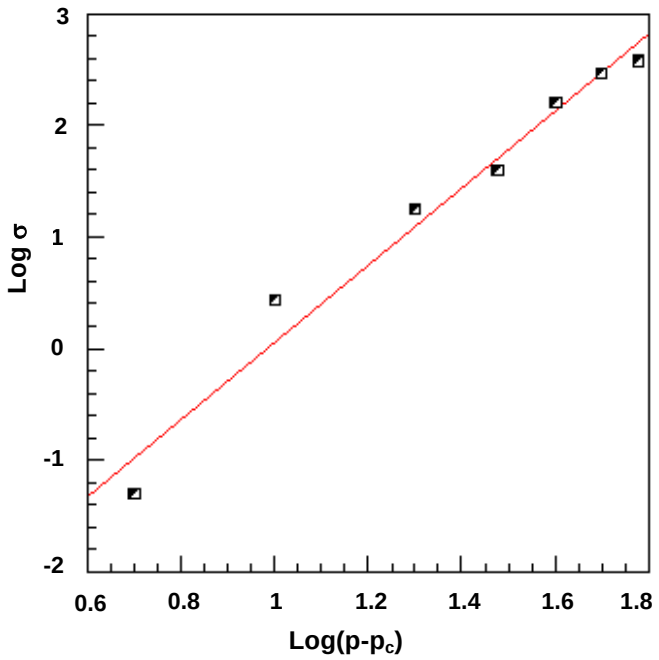

Figure 5. Plot of log (σ) versus log (p - p_c). Experimental data (square points) and fit to Equation 4 (solid line).

A= (1- p_c)/p_c, p_c is the critical weight fraction, and p is the weight concentration of conducting load in the matrix. Equation 5 yields the following two limits:

$$| \sigma_\chi | \to \infty: \sigma_m = \sigma_c [(p-p_c)/(1-p_c)]^t \qquad p_c<p \qquad (6)$$

$$| \sigma_\iota | \to 0: \sigma_\mu = \sigma_i [(p_c-p)/p_c]^{-s} \qquad p_c>p \qquad (7)$$

These equations are the normalized standard percolation results (Bergman and Stroud, 1992; Clerc et al., 1990) and characterize the exponent s and t.

This study's results have been fitted using Equations 2, 4, 6, and 7. The results are shown respectively in Figure 4, 5, and 6a and b. The fitting parameters are listed in Table 1. For the three models used, we noticed different values of p_c. In most of the cases reported in the literature, graphite percolates at around 20 wt % in G/polymer blend (Mepsted and Moore, 2003; Radwan and Jaafar, 2008) which is lower than the percolation reported in this work (around 30%). Blaszkiewicz et al. (1992) reported that for system such as G/polymer in which p_c ~ 30 to 40 wt % is greater than the predict value of about 16 wt % in percolation theory, some of the fillers particles did not make contact with their nearest neighbour particles, due to the partial wetting of the particles by the polymer.

We observed that our values, s = 0.52 and t = 2.6, were different from those obtained by computational simulation for "ideal" system $s_m \approx 0.8$ and $t_{un} = 2$ (Bergman and Stroud, 1992; Clerc et al., 1990). In fact $s<s_m$ and $t>2$; On the other hand, our results are compatible with those reported in literature ($1< t < 6.27$ and $0.33 < s < 1.28$) (Ian, 2002). In fact, t can be larger than t_{un} when the intergranular conductance of the conducting component has a very wide distribution in a continuum system (Kogut and Straley, 1979), which we suppose is the case of our graphite powder.

In fact, several models based on numerous factors were proposed to predict the electrical behaviour of blends. All models showed that percolation behaviour is dependent on polymer filler interactions, in addition to the size and shape of filler material (Boudenne et al., 2005).

On the basis of the experimental data shown in Figure 3b, we can obtain the theoretical threshold p_c by using a least-square fit through Equation 2 and 3. The fitting parameters are listed in Table 2. For all temperatures, we noticed that the percolation threshold was not affected by the temperature and still constant. It is well known that the value of the percolation threshold depends strongly on the shape of the conducting inclusions (El Malhi et al., 1999; Jonsher, 1983), the structure of the conductor particles and their morphology (Achour et al., 1996) but not on the temperature.

Figure 7 shows the variation of conductivity in the polymer-matrix composites (G/Silicone) with temperature in the range of room temperature to 423 K. A decrease of conductivity was observed with increasing temperature. These phenomena can be explained by the fact that, thermal lattice vibration perturbs the quasi-free movement of electrons, thus scattering between electrons and phonon may occur.

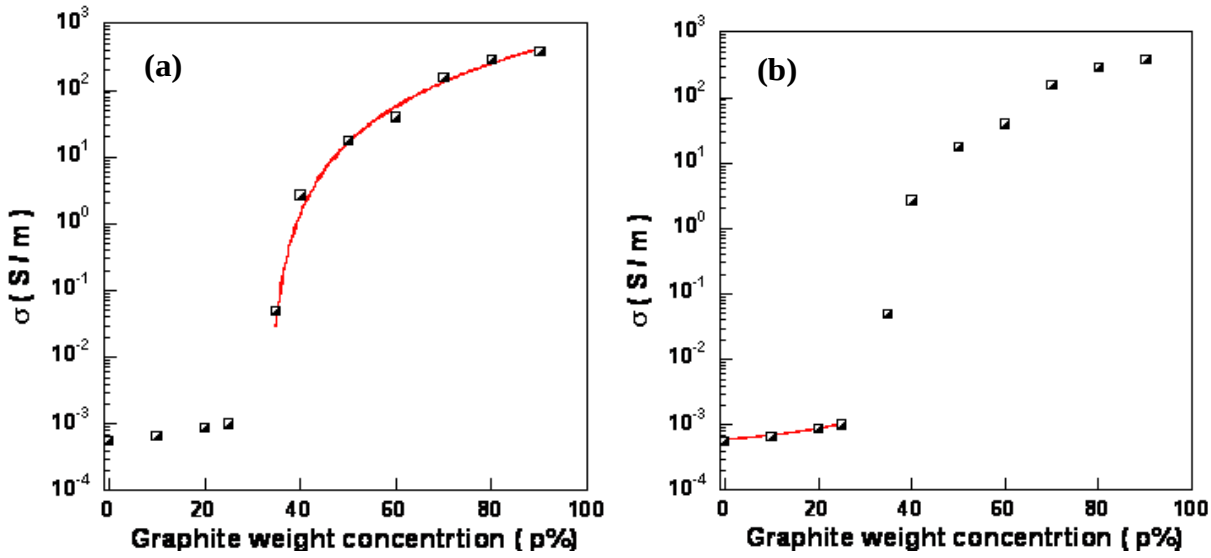

Figure 6. Best fit of electrical conductivity versus weight concentration. (a) Fit to equation (6) and (b) fit to equation (7).

Table 1. Fitting parameters: t, s and p_c using Equations 2, 4, 6, and 7.

Models	t	s	p_c (%)
Equation 3	-	-	34.420
Kirkpatrick and Zallen model	3.45	-	30
Normalized Equations 6 and 7	2.634	0.524	33.5

Table 2. Variation of fitting p_c B, n and α versus temperature, using Equations 2 and 3.

Temperature (K)	B	α	n	p_c (%)
293	5.66	0.100	39.8	34.4
303	5.79	0.080	21.7	34.9
333	5.81	0.085	21.4	35.7
363	5.77	0.088	21.7	34.9
393	5.76	0.092	24.3	34.7
423	5.78	0.090	21.8	34.3

Thermal properties

The longitudinal thermal conductivity values (κ) of G/Silicone blends are presented in Figure 8 versus graphite weight concentration. However, a non linear increase of thermal conductivity κ can be noted. The thermal conductivity increased from about 1.2 $Wm^{-1}K^{-1}$ at p=10% to 3.8 $Wm^{-1}K^{-1}$ at p=80%. This increase can be explained by the formation of thermal conducting paths (Qiuhong and Shengyu, 2007; Shen et al., 2003) in blends. Indeed, when graphite concentration is enhanced, the graphite particles with a large surface – to – volume ratio can abut and then form a connected network, resulting from the thinning of silicone joints between them. This result was not surprising, since thermal conductivity has some analogy with that of the electrical conductivity (Qiuhong and Shengyu, 2007). But in contrary to the electrical conductivity, a percolation phenomenon does not occur in the case of thermal conductivity when the graphite concentration increases in the blends (Boudenne A et al., 2005). Several models have been proposed to predict the thermal conductivity of polymer blends (Boudenne et al., 2005; Mottram and Taylor, 1991; Agari et al., 1990). Unfortunately, many of them do not have any general validity to predict thermal conductivity for medium between 15 and 30% of weight

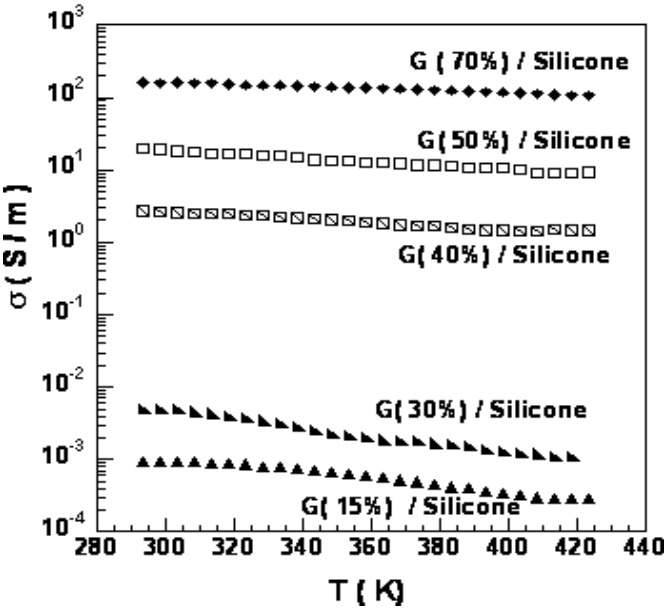

Figure 7. Variation of conductivity σ versus the temperature from 303 to 423K for various weight concentrations of graphite.

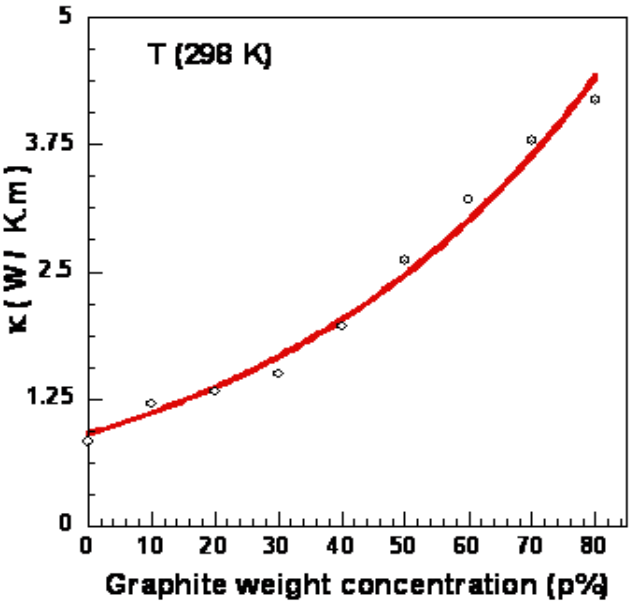

Figure 8. Thermal conductivity versus graphite weight concentration for the G/Silicone blends. Solid lines are the fitted curve to the Equation 10.

concentration (Mottram and Taylor, 1991; Agari et al., 1990) which is the case of graphite blends. However, Agri develop a semi-empirical model (Agari et al., 1990, 1991), which yields better results than the theoretical ones. The logarithmic equation of Agri is given by Equation 8.

$$\log \kappa_c = pC_2 \log \kappa_f + (1-p)\log(C_1\kappa_m) \quad (8)$$

Where κ_c, κ_m and κ_f are respectively: the thermal conductivities of the composite, the polymer matrix and of the fillers; “p” is the weight concentration on Graphite, and C_1 and C_2 are obtained by fitting experimental data. According to Agri, C_1 represents the effect of particles on the polymer structure, while C_2 represents the ability of fillers particles to create continuous paths (Agari et al., 1990; Agari et al., 1991). This model has the advantage that to correlates thermal conductivity with electrical conductivity. Indeed, Agri assume that there is a relationship between C_2 and the weight concentration “p_c“ at electrical percolation threshold when the polymeric matrix is filled with conducting particles. Moreover, if the crystallinity of the polymer does not change in the presence of filler particles, then $C_1 = 1$ (Agari et al., 1990, 1991) and Equation 8 becomes:

$$\log\left(\frac{\kappa_c}{\kappa_m}\right) = pC_2 \log\left(\frac{\kappa_f}{\kappa_m}\right) \quad (9)$$

Finally, Agri showed that C_2 remains a curve fitting parameter that can be used to detere the electrical percolation concentration threshold “p_c” using Equation 10 (Krupa and Chodak, 2001).

$$C_2 = \log(1/p_c) \quad (10)$$

Assuming that C_1 equals one, the parameter C_2 values (Table 3) are obtained from fitting of experimental data of thermal and electrical measurements. From this table, it can be observed that C_2 and p_c are closely linked. Indeed, C_2 and p_c values obtained from thermal and electrical measurements exhibit a bit different values. It is clear that the Agri’s model provides a good estimation of thermal conductivity of blends for all weight concentration.

Conclusion

The polymer-matrix composites of G/Silicone were investigated in this work. The dc conductivity of our blends showed percolation behaviour. For the three models used in this work, we noticed different values of p_c. In fact, this difference is due to the factors taken into account by these models, which can affect the weight concentration at which the percolation threshold occurs.

However, p_c is still constant when we expose blends at various temperatures. For all blends, the conductivity decreases when the metals temperature increases. The thermal study showed that the thermal conductivity improves greatly when graphite concentration increases. This increase can be explained by the transmission of thermal agitation between graphite loads. In order to give

Table 3. Values of fitting parameters: p_c in Equation 3 and C_2 in Equation 10.

Measurements	C_2	p_c (%)
Electrical	0.46	34.4
Thermal	0.50	31.6

a comparative analysis of both electrical and thermal properties of blends, we use the Agri's model which provides a good estimation of thermal conductivity of blends for all weight concentration.

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