

Electrical and Thermal Conductivity of Graphite-CNT-Polymer Hybrid Composites

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Abstract. The polymer graphite composites are important for bipolar plates in fuel cells, battery electrodes in energy storage devices, self lubricated bearings etc. Although, electrical conductivity (σ) has been studied earlier in binary and hybrid polymer- graphite composites, thermal conductivity (K), which is also important parameter for stable operation of the devices, has not been studied extensively in these materials. Hence, the electrical and thermal conductivity of several polymers like PP, PPS, PES, Nylon etc. containing both graphite and carbon nanotubes (multi-wall) have been investigated by us with respect to composition. The variation of σ follows the well known percolation type behavior exhibiting sharp change of several orders of magnitude at the percolation threshold which shifts considerably to low side in the hybrid composites (see Fig. 1). The K value on the other hand exhibits large change but not by several orders in magnitude at certain concentration of the filler. There is also percolation like behavior but at much larger concentrations as compared to electrical case. There is a small distinct shift of the threshold for K value to lower side for hybrid composites. The estimation of K value with composition using several reported theoretical models shows that none of these give good fit to the experimental data. These results have been explained on the basis of charge tunneling type transport in electrical conductivity with reduction of barrier width and height for hybrid composites. On the other hand the thermal conductivity is mainly dominated by phonon scattering at the interface and reduction of this by the contact formation of the nanoparticle additive which is essential for enhancement of thermal transport in hybrid composites.

Keywords: hybrid conducting composite; thermal conductivity; percolation

Introduction

Conducting polymer composites have been extensively studied in the past for their electrical properties with several combinations of polymers and fillers [1-3]. In fact, the recent reports in market trend [4] indicate that area of conducting polymers has 1.8 billion dollar business which is expected to reach 3.4 billion dollar level by 2014. The polymer graphite composites are important for bipolar plates in fuel cells, battery electrodes in energy storage devices, self lubricated bearings etc. Although, electrical conductivity has

been studied earlier in binary and hybrid polymer- graphite composites, thermal conductivity (K), which is also important parameter for stable operation of the devices, has not been studied extensively in these materials. The effect of third component on the electrical conductivity of graphite composite was reported by Radhakrishnan et al [5] with polyether sulphone as polymer matrix. The thermal conductivity has been reported for binary composites including carbon nanotubes, graphite and other nano additives [6,7] at low concentrations < 10% but only little percolation like behavior was noted as against the sharp percolation threshold with orders of magnitude reported for electrical conductivity. Hence, we studied both electrical and thermal conductivity in the large range of combination of additives and polymers to investigate the origin for the two types of behavior.

Experimental

Materials

The polymers were commercial grade polypropylene (PP, M0030, MFI 10), (PP,H110, Reliance Industries, MFI 20), poly(ethersulfone) (PES, Gafone 3600 P, Gharda Chemicals, India) and polyamide (Nylon 6, Gujlon, GSFC, India) and poly (phenylene sulfide) (PPS, Ryton R-4, Chevron Phillips Chem. Asia) were used as such. Graphite was natural grade (better than 200 mesh size powder) obtained from Carbon Enterprises, India, and the multi-wall carbon nanotube (MWCNT) obtained from Aldrich.

Composite preparation

The composite samples were prepared by compression molding the compounded filled polymer. For incorporation of the filler + nano additive, three different methods were used so as to obtain good dispersion: (1) Powder blending (2) Solution blending and (3) Melt blending technique. The polymers which are not easy to dissolve such as PP, PPS and PES were used in powder form. The graphite powder was mixed first and then nano particles MWCNT or carbon black was added. The dispersion was achieved by suspension in methanol and ultrasonication for 1 h. These mixtures were filtered, dried, by heating at 50°C under vacuum for 1 h prior to compression molding.

Compression molding of disks

The dried powder (2.0 g) was compression molded in a single-ended compaction stainless-steel die by applying 3000 kg pressure using a hydraulic press for 5 min. The discs (3.0 cm diameter) were heated to 240°C for 1 h. For nylon composites, the strands obtained

were compression molded at 245°C under 6000 kg tonnage.

Thermal conductivity measurements

Thermal conductivity was measured using Quickline 10C, Thermal Impedance Tester, which follows guarded heat flow meter method. The upper plate temperature was at 45°C while the heat sink temperature was controlled at 3.4°C. The 17-psi pressure was applied on the specimen via upper hot plate. Computer interface gave the results after comparison with standard calibration.

Results and Discussion

The electrical conductivity (σ) in these graphite polymer composites followed the well reported non linear relationship with respect to filler volume fraction. Fig. 1 shows the variation of $\log \sigma$ with the filler concentration (ϕ) with and without the addition of third component such as MWCNT. The curve for polymer-graphite alone is typical percolation type which is described by the following equations [8]:

$$\sigma_c = \sigma_f (\phi - \phi_c / 1 - \phi_c)^n \quad \phi > \phi_c \quad (1)$$

$$\sigma_c = \sigma_m (\phi_c - \phi / \phi_c)^{-m} \quad \phi < \phi_c \quad (2)$$

where σ_c is the effective conductivity of the composite consisting of a conductor with conductivity σ_f and an insulator with a conductivity σ_m , ϕ - the volume fraction of filler, ϕ_c is the percolation threshold. n and m are critical exponents characterizing the conductivity in the conducting and the insulating phase, depend on the dimensionality of the network. It is interesting to see from Fig. 1 that, σ_c changes by tens of order of magnitude at very small concentration of filler for the ternary composite PP-Gr-MWCNT. There is a large shift in the percolation threshold with a small addition of MWCNT to PP-Gr composite. This can be explained on the basis of formation of interconnects between the graphite particle by the nano-additive as reported by us earlier [5,9].

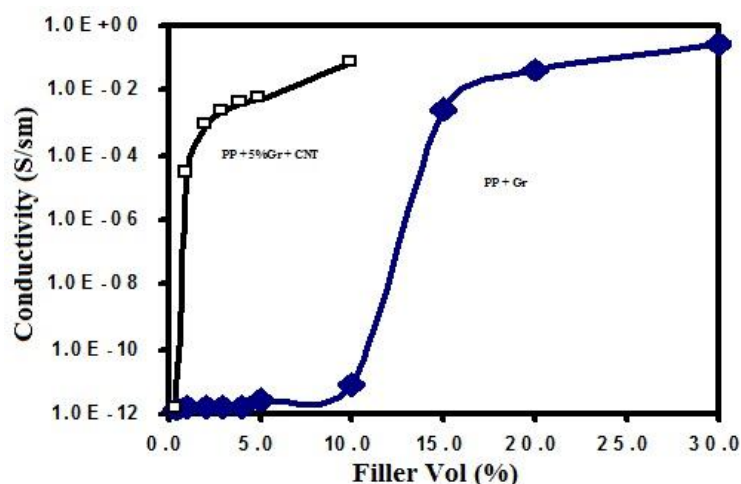


Figure 1. The electrical conductivity as a function of filler concentration in PP-Graphite and PP-Gr-MWCNT composites.

The thermal conductivity (k_c) of the composite on the other hand behaves differently. Fig. 2 depicts the k_c values obtained by us together with those reported in literature (re-plotted in the present scale) for comparison. It is seen that there is increase in the thermal conductivity value in graphite- polymer composite but large change is observed only at high concentrations. The plots of k_c / k_m relative values shown in Fig. 2 are estimated from different equations suggested for different models which are given in Appendix-1 of this paper [10-14]. It is evident that the actual experimental data does not follow any of the models through out the range of the filler concentration.

On the other hand, if the data is analyzed according to the percolation equations (1) and (2) with k_c in place of σ_c much better fit is obtained as shown in Fig. 3. The parameters for the percolation equation viz. critical volume fraction and the exponent “n” for different systems are given in Table-1. The large values of the critical volume fraction and ‘n’ suggest that the mechanism of thermal conduction could be different than percolation.

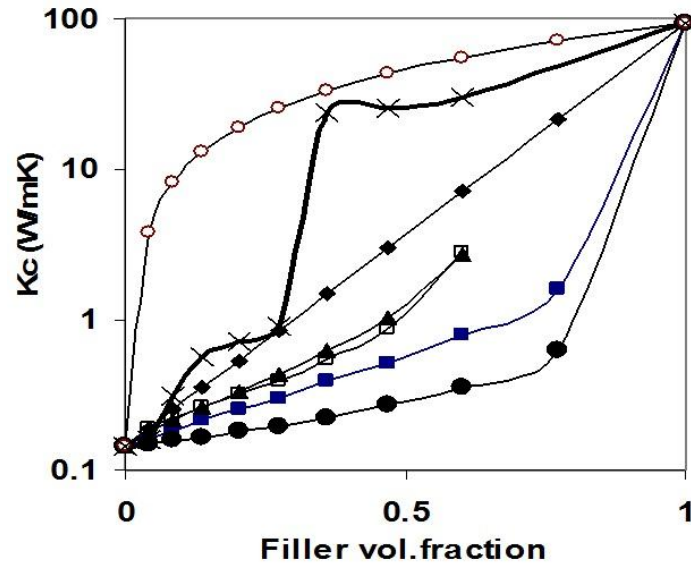


Figure 2. Thermal Conductivity of PP-Gr composite filled with graphite (X) experimental data and comparison with theoretical estimates from different models (see Appendix-1). Symbols indicated for the models: (■) Maxwell-Euchen curve; (◆) Ziebland equation curve; (▲) Lewis-Neilsen curve; (●) Parallel law of mixing; (□) Cheng-Vochev curve; (◇) Series law of mixing

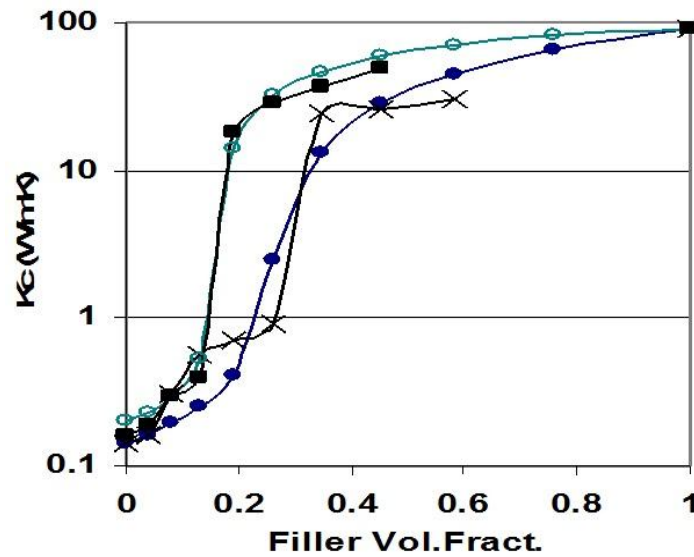


Figure 3. Thermal conductivity of PP-Gr (x) and PPS-Gr (■) composites and comparison with percolation law for the respective systems (●, ○)

Table 1. Percolation equation parameters for Thermal Conductivity.

Composite system	Critical Vol. fraction	Index 'n'
PP(I)-Graphite	0.27	0.85
PP(II)-Graphite	0.27	0.85
PPS-Graphite	0.34	0.67
PES-Graphite	0.32	0.65
Nylon-Graphite	0.40	0.27
PVC-Graphite	0.25	0.55

This becomes further clear when nano-particle additives are incorporated as third component. Fig. 4 shows the effect of incorporation of nano-additive on thermal conductivity of PPS-Gr composites. The data reported for nano-composites is also included after re-plotting in the present scale.

The nano-composite show an increase of kc value at low concentrations but the increase is not very high. Earlier reports do not indicate consistency and the upper value is limited at most to one order increase. Also, ternary composites have not been studied for thermal conductivity in the whole range of filler concentration to draw any conclusions. Although, there appears to be percolation type behavior for kc values, there is no dramatic decrease in the percolation threshold after addition of third nano-additive to polymer-graphite system as noted for electrical σ_c .

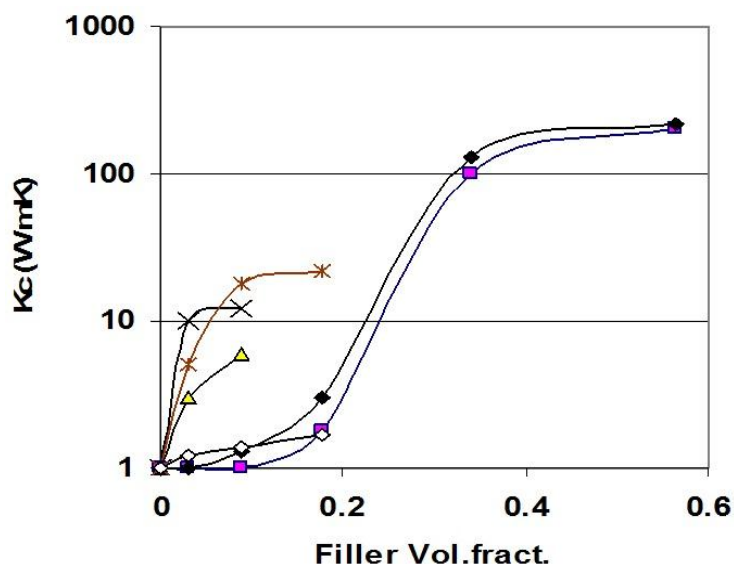


Figure 4. Thermal conductivity of polymer composites and comparison with the data reported for nano filled \square - PPS-Gr, \blacklozenge - PPS-Gr-CNT, \blacktriangle - CNT ref [6] , \times - CNT ref [7] , \ast - Graphene-Ep [15] , \blacklozenge -CNT others [8].

In order to explain these results, one has to compare the charge transport and heat transfer

processes in polymers and composite. Whereas the electron has high velocity, long mean free path, the phonons involved in the heat transfer on the other hand, have very small mean free distance [16]. Hence, the latter are not able to penetrate the barrier existing between the particles. The intergranular impedance or the Kapitza resistance is quite high for thermal conductivity [17] which is not reduced significantly by the nanoparticles. The polymer chain motion dominates the process and hence only small change is seen in k_c values for ternary nano-composites.

Conclusion

The electrical and thermal conductivity have been measured in graphite filled thermoplastic composites with additional filler viz. multi-walled carbon nanotubes. The electrical conductivity shows a sharp transition with filler concentration as expected from the percolation theory. The thermal conductivity also exhibits a significant change but at much higher concentration of the CNT in presence of graphite. This appears like the percolation type but the change in thermal conductivity is not as high as that observed for electrical conductivity. This can be ascribed to the inter-granular impedance to phonons or the Kapitza resistance in the thermal transport in these composites.

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- [1] D. M. Bigg, *Adv. Polym. Sci.* **1995**, 119, 1.
- [2] A. Kiraly, F. Ronkay, *Mat. Sci. Forum.* **2013**, 729, 397.
- [3] I. Krupa, I. Novak, I. Chodak, *Synth. Met.* **2004**, 145, 245.
- [4] Freedomia Study No.2071, Conductive Polymers; Freedomia Group, Cleveland OH USA **2006**.
- [5] S. Radhakrishnan, B. T. S. Ramanujam, A. Adhikari, S. Sivaram, *J.Power Sources.* **2007**, 163,702.
- [6] Y. Xu, G. Ray, B. Abdel-Magid, *Composites Part A.* **2006**, 37, 114.
- [7] Z. Han, A. Fina, *Prog. Polym. Sci.* **2010**, 36, 914.
- [8] W. Bauhofer, J.Z. Kovacs, *Compos. Sci. Tech.* **2009**, 69, 1486.
- [9] B.T.S. Ramanujam, S. Radhakrishnan, *Int. J. Plast. Technol.* **2010**, 14, 537.
- [10] D. Kumlutas, I. H. Tavman, *J. Thermoplast. Compos. Mater.* **2006**, 19, 441.
- [11] S. C. Cheng, R. I. Vachon, *Int. J. Heat Mass Transfer.* **1969**, 12, 249.
- [12] T. Lewisand, L. Nielsen, *J. Appl. Polym. Sci.* **1970**, 14, 1449.
- [13] J. C. Maxwell, in: "A treatise on electricity and magnetism", Dover Inc, New York 1954, Ch.9.
- [14] Y. Agari, T. Uno, *J. Appl. Polym. Sci.* **1986**, 32, 570.
- [15] K. M. F. Shahil, A. A. Balandin, *Nano Letters.* **2012**, 12, 861.
- [16] A. S. Henry, G. Chen, *J. Comput. Theor. Nanosci.* **2008**, 5, 1.
- [17] C. W. Nan, R. Birringer, D. R. Clarke, H. Gleiter, *J. Appl. Phys.* **1997**, 81, 6692.

APPENDIX - 1

Series Model

$$\frac{1}{k_c} = \left[\frac{\phi}{k_f} + \frac{(1-\phi)}{k_m} \right] \quad (3)$$

Parallel Model

$$k_c = (1-\phi)k_m + \phi k_f \quad (4)$$

Ziebland Model

$$k_c = k_f^\phi * k_m^{1-\phi} \quad (5)$$

Cheng & Vochen Model

$$\frac{1}{k_c} = \left\{ \frac{1}{\sqrt{C(k_f - k_m)[k_m + B(k_f - k_m)]}} \right\} * \ln \left\{ \frac{\sqrt{k_m + B(k_f - k_m)} + (B/2)\sqrt{C(k_f - k_m)}}{\sqrt{k_m + B(k_f - k_m)} - (B/2)\sqrt{C(k_f - k_m)}} \right\} + \frac{(1-B)}{k_m} \quad (6)$$

where, $B = \sqrt{3\phi/2}$ $C = -4\sqrt{2/3\phi}$ for $k_f > k_m$

Lewis & Nielsen Model

$$k_c = k_m \left[\frac{1 + AB\phi}{1 - B\phi\tau} \right] \quad (7)$$

where,

$$B = \left[\frac{(k_f / k_m) - 1}{(k_f / k_m) + A} \right] \quad \tau = 1 + \left[\frac{1 - \phi_m}{\phi_m^2} \right] \phi$$

Maxwell & Euchen Model

$$k_c = k_m \left[\frac{k_f + 2k_m + 2\phi(k_f - k_m)}{k_f + 2k_m - \phi(k_f - k_m)} \right] \quad (8)$$

Agari & Uno Model

$$\log k_c = \phi C_2 \log k_f + (1-\phi) \log(C_1 k_m) \quad (9)$$

k_c = Thermal conductivity of composite

k_f = Thermal conductivity of filler/ additive

k_m = Thermal conductivity of polymer matrix

ϕ = Filler volume fraction