



Original Article

Electrical and mechanical properties of ternary composites from natural rubber and conductive fillers

Wiriya Thongruang¹, Churairat Ritthichaiwong², Pisanu Bunnaul², Pruittikorn Smithmaitrie¹ and Kanadit Chetpattananondh^{3*}

¹ *Department of Mechanical Engineering,*

² *Department of Mining and Materials Engineering,*

³ *Department of Electrical Engineering, Faculty of Engineering,
Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand.*

Received 26 November 2007; Accepted 3 July 2008

Abstract

Ternary composites of natural rubber filled with particulate carbonaceous and metal fillers were developed for electro-mechanical sensing purposes, while maintaining good elasticity and loading capability. The effects of filler type and composition on electrical and mechanical properties of binary and ternary conductive composites have been examined. The typical mechanical-compounding and molding processes for rubbers were used for this study. As observed, the binary composite containing 50 phr carbon black in natural rubber was the superior conductive composite for a pressure sensor based on its balance of compression set and electrical conductivity. At the same total filler content, a third metal component filler decreases the electrical conductivity of the binary composites. In addition, the third component of metal fillers deteriorates the compression set of the composites.

Keywords: ternary composite, conductive rubber, electrical conductivity, capacitance, conductive filler

1. Introduction

The demand for electrically conductive polymer composites has increased dramatically in recent years, particularly for many applications such as electromagnetic interference shielding materials (Das *et al.*, 2000), self regulated heating materials (Feller *et al.*, 2003) and pressure sensors (Job *et al.*, 2003). Among the conductive polymers, conductive rubbers are widely used (Mahmoud *et al.*, 2007, El Eraki *et al.*, 2006) because of their obvious advantage of flexibility, light weight and ability to absorb mechanical shocks. Conductive rubber composites were prepared by adding micro- and nano-size conductive fillers such as

carbon black, metallic powders and carbon nanotubes (CNTs) into rubber. Different conductive fillers such as carbon black (CB) and metallic powders (Ni, Al, Cu, etc.) have been extensively investigated to effectively improve the electrical conductivity of rubbers (Nasr *et al.*, 1999; Job *et al.*, 2003; 1999; Sasikumar *et al.*, 2006). Usually, a rather high CB content in polymers or rubbers is needed due to its low electrical conductivity compared with metallic powders. However, fillers containing copper, or a high silver content were found to prevent rubber curing.

There is evidence that the electrical properties of conductive composites depend mainly on how well of the fillers disperse within matrices (Yacobowicz *et al.*, 1990), relevant properties of the filler (e.g. particle size, surface area, aggregate structure and surface activity) and rubber-filler interactions. The number of conductive paths increases with an

*Corresponding author.

Email address: kanadit.c@psu.ac.th

increase of filler concentration, leading to a decrease of the volume resistivity of the composite. The electrical conductivity of conductive-filler filled polymers results from the direct physical contact of the fillers or the electric field effect between the conductive particles (or groups of particles) within the order of 15-100 Å. Electrons must surmount the potential barrier (gap between conductive aggregates) for hopping from one conductive aggregate to another (Medalia, 1986). It was also observed that the percolation behavior of the conductive composite depends on both shape and spatial distribution of the filler within the polymer matrix (Mamunya *et al.*, 2002). A model of conductive network formation among conductive particles is shown in Figure 1.

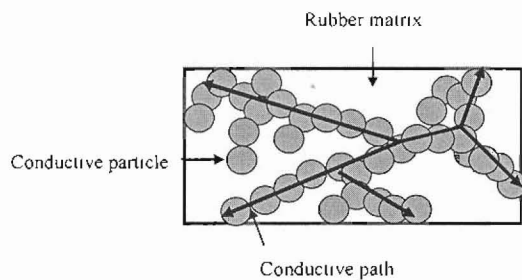


Figure 1. The model of three dimensional conductive paths formed in the conductive composites (Hussain *et al.*, 2001).

In composites with an appreciable gap distance, there is a certain resistance R_C to the passage of charge carriers across the gap, which depends on temperature. It is assumed that the gap has a capacitance C_C . An equivalent circuit of this system is shown in Figure 2. At low frequencies, the current flows through the contact resistance since it is blocked by the contact capacitance. The total resistance of the aggregate in series with the contact region is $R_C + R_A$ (where R_A is the resistance within the aggregate). At high frequencies, the impedance of the contact capacitance is much lower than the contact resistance, and the current flows through the contact capacitance. Furthermore, since the capacitor's impedance is much lower than the aggregate resistance, the total resistance at the high frequencies is

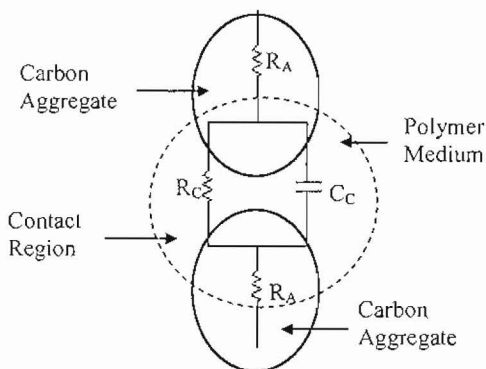


Figure 2. Equivalent resistor-capacitor circuit at the contact region of CB aggregates in a rubber matrix (Ghosh *et al.*, 2000).

approximately equal to R_A , which is lower than the total resistance ($R_C + R_A$) for the low frequencies (Yacubowicz *et al.*, 1990).

For the equivalent circuit model, as shown in Figure 2, the relationship between the electrical conductance (G) and capacitance (C_C) in term of the frequency can be written as,

$$G = \frac{1}{R} = \frac{1 + (\omega R_C C_C)^2}{R_C} \quad (1)$$

$$X_C = \frac{\omega R_C^2 C_C}{1 + (\omega R_C C_C)^2} \quad (2)$$

where X_C is the capacitive reactance and ω is the angular velocity, where $\omega = 2\pi f$ and f is the excitation frequency of the applied source.

2. Materials and Methods

2.1 Materials

Natural rubber (NR: STR5L, manufactured by Chalong Latex Industry Co., Ltd.) was used in this study. Three chosen conductive fillers are carbon black (CB: N330, supplied by Southern Excel Co., Ltd) with individual particle size of 26-30 nm, aluminum and silver powders (manufactured by Siam Prodex Co., Ltd.) with particle size of 13-20 μm and 6-10 μm , respectively.

2.2 Sample preparation

The NR/CB master batch was prepared by mixing in an internal mixer (YFM: 3 L) with a mixing time of about 1 hour to ensure the homogeneity of the composites. The NR/CB mixtures, curative chemicals and the additional conductive fillers were compounded on a typical two-roll mill for a period of time (about 30 minutes). Compounds were kept in a desiccator for 24 hours before molding at a temperature of 150°C under a pressure of 3,000 psi for vulcanization and forming into composite slaps. The time period for molding was obtained from the Moving Die Rheometer (MDR 2000). Samples were prepared at different thicknesses of 2, 4.5 and 5.5 mm. For determining mechanical and electrical properties of composites, the average value was deduced from two repeated measurements at different locations of each composite obtained from three reproducible mixing batches.

2.3 Measuring

2.3.1 Compression set testing

To determine the ability of elastomeric materials to maintain elastic properties after prolonged compressive stress, standard ASTM D395 (method B) was used to estimate the

compression set. Samples were formed into cylindrical disks with a thickness of 6.0 ± 0.2 mm, and a diameter of 13.0 ± 0.2 mm. The test was carried out at two temperatures; room temperature (25°C) and ageing temperature (70°C).

2.3.2 Compressive testing

The compressive testing was carried out according to the ASTM D575 with a Universal Testing Machine (LLOYD Model LR10K). The cylindrical specimen for this test has a radius of 28.6 ± 0.1 mm and a thickness of 12.5 ± 0.5 mm.

2.3.3 Electrical testing

The AC conductance and capacitance of sample were measured with an LCR meter (HP4263B). Before measuring each specimen, a correction was made following the operating recommendation of the manual for the meter. Then, the specimen, with a diameter of 13.0 mm, was placed between the guarded (top) and unguarded (bottom) electrodes before applying the voltage of 1.0 V at various excitation frequencies of 0.10, 0.12, 1, 10 and 100 kHz. The measuring time for each excitation frequency was 60 seconds.

3. Results and Discussion

3.1 Mechanical properties

The relationship of temperature and composition with the compression set of conductive composites is illustrated in Figure 3. The compression set of a binary composite increases with increased carbon black loading. This is due to the effect of carbon black agglomeration collapse within the composites. The agglomeration collapse of a high concentration carbon black sample, as shown in the model of Figure 4, occurs easier than if the sample contained individually dispersed carbon black particles. The compression set of composites at ageing temperature (70°C) is higher than the compression set at room temperature. This result complies with the theory of increased relaxation of the rubber

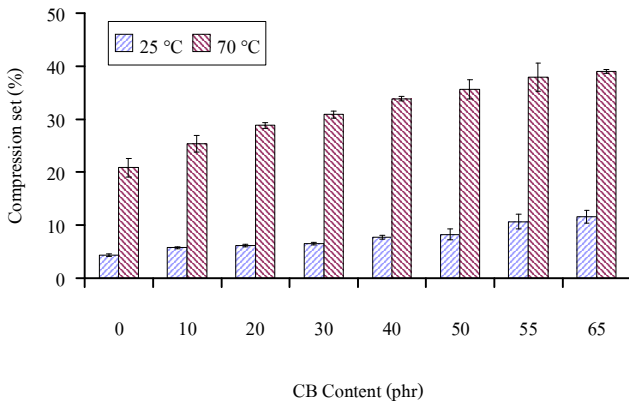


Figure 3. Compression set data of binary composites with different concentrations of CB.

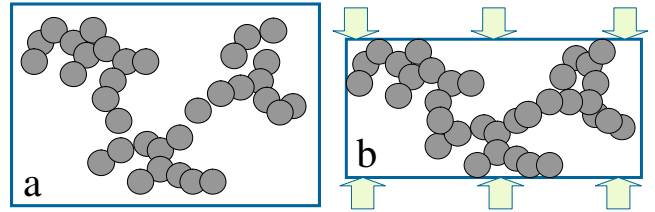


Figure 4. The agglomeration model of CB aggregates; a, without applying pressure and b, under pressure.

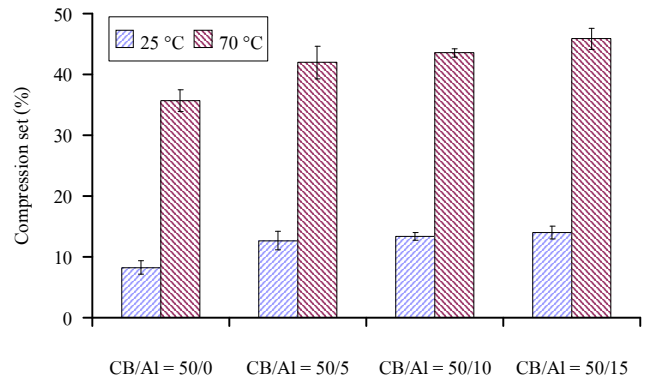


Figure 5. Compression set of the NR/CB/Al ternary composites at different Al concentrations.

molecule at higher temperatures.

Ternary composites composed of 50 phr carbon black mixed with 15 phr Al and 5 phr Ag were selected, based on the competing requirements of the electrical and mechanical properties of the material. Figure 5 represents the effect of aluminum powder content on compression set. It was found that the compression set insignificantly increases with aluminum contents. This is due to the reduction of the rubber fraction.

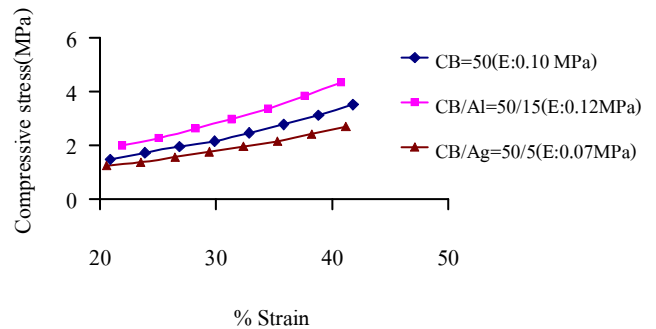


Figure 6. The compressive stress-strain of the composites containing 50 phr CB and different metal fillers (E is the compressive modulus).

Figure 6 represents the stress-strain characteristics at 20-40% strain in compression. This strain range was selected, based on the expected operating conditions for a sensor

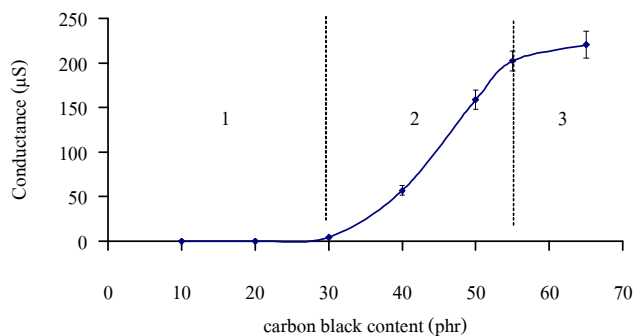


Figure 7. Conductance of the composites containing CB at different concentrations.

application. The non-linear relationship of load-compression curves (compressive stress vs. strain) of the composites from this experiment agrees well with the result from homogeneous compression of incompressible rubber which depends on the amount of filler contents (Allen *et al.*, 1967). In addition, it was found from this study that the presence of metals as the third phase in the composites containing 50 phr CB affects the composite stiffness insignificantly.

3.2 Electrical properties

Figure 7 shows the conductance data of composites with concentrations of carbon black. At low loading of carbon black (Region 1), the conductance of composite was essentially unchanged due to the deficiency of conductive fillers to form the continuous conductive paths. At carbon black content higher than 30 phr (Region 2), however, a prominent increase of conductance was found. This concentration is known as the percolation threshold concentration. At this concentration, transport of charge carriers between carbon black aggregates that are close, but not touching, is initiated (Medalia, 1986).

The dependence of electrical conductivity on the source frequency and thickness of a composite containing 50 phr carbon black are shown in Figure 8. At low excitation frequencies ($f < 1000$ Hz), there is an insignificant change in the conductivity with both the frequency and thickness. At high excitation frequency ($f > 1000$ Hz), however, the con-

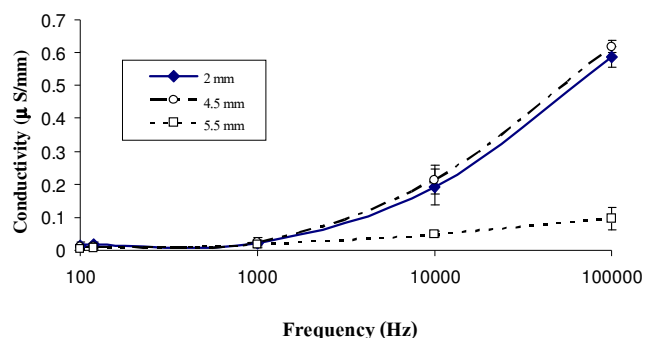


Figure 8. Conductivity of the composite containing 50 phr CB at different thicknesses and excitation frequencies.

ductivity increases significantly with the frequency. The increase of conductivity at high frequency is due to the hopping of charge carriers and agrees well with the previous studies, (Psarras, 2006; Sasikumar *et al.*, 2006; Ravikiran *et al.*, 2006; Sindhu *et al.*, 2002). When the composite sample is connected across the two terminals of a voltage source, free electrons are forced to drift toward the positive terminal under the influence of the electric field. The conductivity of the composite specimen with a thickness of 2 mm is slightly different from the one with a thickness of 4.5 mm. However, the conductivity of the specimen with a thickness of 5.5 mm is much lower than the other two samples. This may be caused from the effect of material non-homogeneity on the conductivity and permittivity due to cavities in a thick composite sample. Hence, the effect of thickness on conductivity and permittivity is observed in this study.

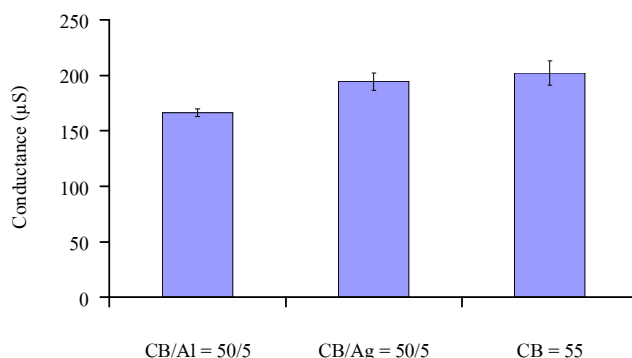


Figure 9. The conductance of composites containing the same total filler concentration.

Figure 9 shows the conductance of various composites at the same total filler concentration. It was found that the binary composite of 55 phr carbon black has a higher conductance than the two ternary composites. This is probably because both metallic powders contained in ternary composites do not form the conductive path such as carbon black alone. Further study with an X-ray diffractometer (which is not shown here) revealed that there is silver sulfide (Ag_2S) and aluminum oxide (Al_2O_3) formation in the ternary composites. That may also cause the reduction of the conductance.

Figure 10 shows the capacitance of the composites with various loadings of carbon black. At the loading range of 0-50 phr, the capacitance of the composites slightly increases due to the slight increase in the number of charge carriers or electrons. Within the range of 50-55 phr, the gap between carbon black aggregates is minimal leading to the drastic increase of the capacitance. At carbon black content higher than 55 phr, CB agglomerates are located closely to others resulting to very high capacitance. Above 55 phr the capacitance does not change significantly with CB content.

Figure 11 shows the dependence of permittivity on the excitation frequency and thickness in the frequency range of 100 Hz to 100 kHz. The permittivity decreases with the

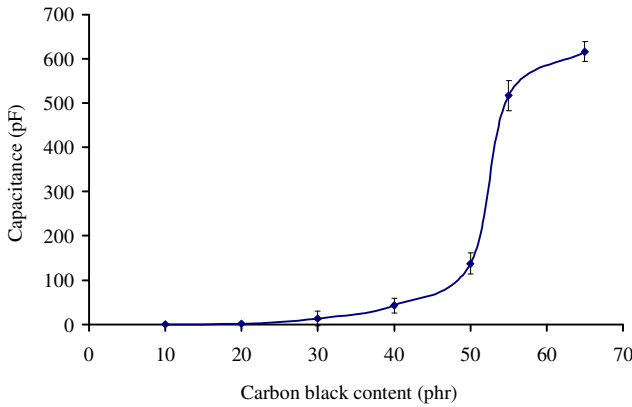


Figure 10. Capacitance of the composites containing CB at different concentrations.

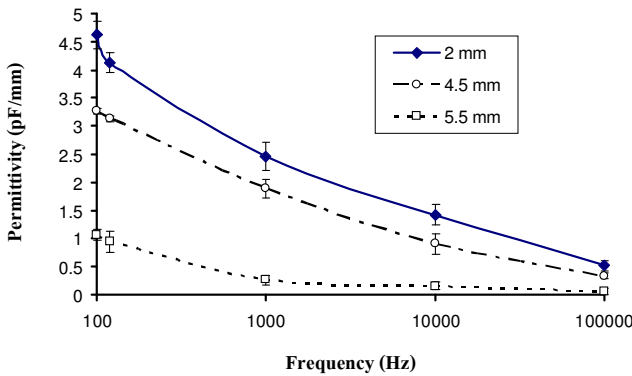


Figure 11. Permittivity of the composite containing 50 phr CB at different thicknesses and excitation frequencies.

increasing of frequency. This can be explained on the basis of a distribution of localized states in the band gap of the amorphous polymer (Tagmouti *et al.*, 1997) along with the relationship of permittivity and frequency, $\epsilon \propto \frac{1}{f}$. That is, at low frequency, the energy band gap is wider than at high frequency. Thus, the capacitance at low frequency is higher than at high frequency. The permittivity of the composite specimen with a thickness of 2 mm is slightly higher than the one with a thickness of 4.5 mm. However, the permittivity of the specimen with a thickness of 5.5 mm is much lower than the other two samples. Again, this may be described from the effect of material non-homogeneity as in the case of the conductivity result.

3.3 Morphology

SEM micrographs of the composites were shown in Figure 12. The composite containing only CB filler (Figure 12 a) shows highly uniform dispersion of the filler. The platelet like fillers of Al and Ag were shown in Figures 12b and 12c, respectively. The localized dispersion of the metallic particles was observed in the composites with cavities which resulted in the reduction of the conductance and the

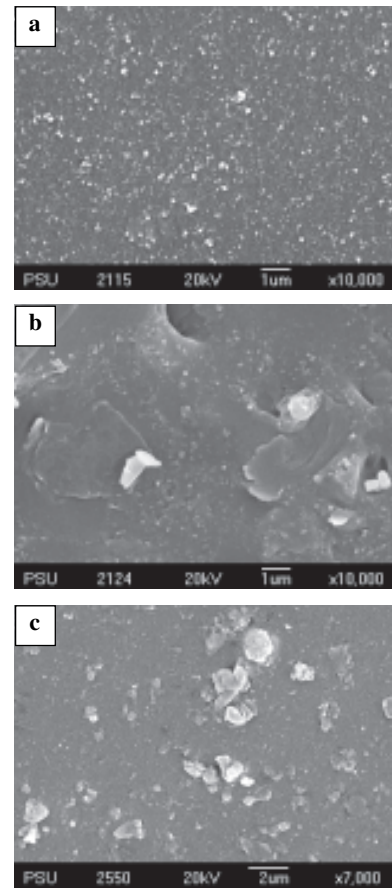


Figure 12. SEM micrographs obtained from NR composites (round and small particle refers to CB while plate like and large particle refers to Al and Ag): a) 50 phr CB, b) 50 phr CB mixed with 5 phr Al and c) 50 phr CB mixed with 5 phr Ag.

compression set.

4. Conclusions

Electrical and mechanical properties of ternary composites of natural rubber, carbon black and metallic powders were studied. Aluminum and silver powders were chosen due to their high conductivity and their benign effect on the curing behavior of the rubber. The composites were developed for use as load or stress sensors. It was observed that the conductance of composites at high excitation frequencies is higher than at low frequencies. Sample thickness affects the conductivity and permittivity due to the material non-homogeneity, in which a thin composite sample has a higher conductivity and permittivity than a thick one. The capacitance decreases with the increase of frequency and thickness. The compression set of binary and ternary composites increases with the total filler content. For potential use as a pressure sensor, the binary composite composed of 50 phr carbon black is superior due to its balance of the compression set and electrical conductivity. The third-additional com-

ponent of metal powders in the composites does not improve the electrical and mechanical properties compared with the same total filler contents of carbon black-rubber binary composites.

Acknowledgement

The authors would like to thank the Physics department and Mechanical Engineering Department, Prince of Songkla University for providing the LCR and mechanical testing equipment, as well as Dr. C. Dechwayukul for technical assistance on mechanical testing.

References

- Allen, P.W., Lindley, P.B. and Payne, A.R. 1967. Use of Rubber in Engineering, Maclaren and Sons LTD., London.
- Das, N. C., Khastgir, D., Chaki, T. K. and Chakraborty, A. 2000. Electromagnetic Interference Shielding Effectiveness of Carbon Black and Carbon Fibre filled EVA and NR based Composite. *Composites*. 31(A), 1069-1081.
- El Eraki, M.H., El-Lawindy, A.M.Y., Hassan, H.H. and Mahmoud, W.E. 2006. The physical properties of pressure sensitive rubber composites, *Polymer Degradation and Stability*, 91(7): 1417-1423.
- Feller, J. F., Chauvelon, P., Linossier, I. and Glouannec, P. 2003. Characterization of Electrical and Thermal Properties of Extruded Tapes of Thermoplastic Conductive Polymer Composites (CPC). *Polymer Testing*. 22: 831-837.
- Ghosh, P. and Chakrabarti, A. 2000. Conducting carbon black filled EPDM vulcanizates: assessment of dependence of physical and mechanical properties and conducting character on variation of filler loading. *European Polymer Journal*. 36: 1043-1054.
- Hussain, M., Choa, Y. -H., and Niihara, K. 2001. Fabrication process and electrical behavior of novel pressure-sensitive composites. 32: 1689-1696.
- Job, A. E., Oliveira, F. A., Alves, N., Giacometti, J. A. and Mattoso, L. H. C. 2003. Conductive composites of natural rubber and carbon black for pressure sensors. *Synthetic Metals*. 135-136: 99-100.
- Mahmoud, W.E., El-Lawindy, A.M.Y., El Eraki, M.H. and Hassan, H.H. 2007. "Butadiene acrylonitrile rubber loaded fast extrusion furnace black as a compressive strain and pressure sensors", *Sensors and Actuators A: Physical*, 136(1): 229-233.
- Mamunya, Y. P., Davydenko, V. V., Pissis, P. and Lebedev, E.V. 2002. Electrical and thermal conductivity of polymers filled with metal powders. *European Polymer Journal*. 38: 1887-1897.
- Medalia, A. I. 1986. Electrical Conduction in Carbon Black Composites. *Rubber Chemical Technology*, 59: 432-454.
- Nasr, G.M., Osman, H.M., Abu-Abdeen, M. and Aboud, A.I. 1999. Material Properties: On the percolative behavior of carbon black-rubber interlinked systems, *Polymer Testing* 18: 483-493.
- Psarras, G.C. 2006. Hopping conductivity in polymer matrix-metal particles composites. *Composites Part-A*. 37: 1545-1553.
- Ravikiran, Y.T., Lagare, M.T., Sairam, M., Mallikarjuna, N.N., Sreedhar, B., Manohar, S., MacDiarmid, A.G. and Aminabhabvi, T.M. 2006. Synthesis, characterization ad low frequency AC conduction of polyaniline/niobium pentoxide composites. *Synthetic Metals*. 156: 1139-1147.
- Sasikumar, K., Suresh, G., Thomas, K.A., John, R., Natarajan, V., Mukundav, T. and Vishnubhatla, R.M.R. 2006. Magnetoactive elastomeric composites: Cure, tensile, electrical and magnetic properties. *Bulletin of Materials Science*. 29: 637-640.
- Sindhu, S., Anantharaman, M.R., Thampi, Bindu.P., Malini, K.A. and Kurian, Philip. 2002. Evaluation of a.c. conductivity of rubber ferrite composites from dielectric measurements. *Bulletin of Materials Science*. 7: 599-607.
- Tagmouti, S., Oueriagli, A., Outzourhit, A., Khaidar, M., Ameziane, El.L., Yassar, A., Youssoufi, H.K. and Garnier, F. 1997. Electrical and Structural properties of Refractory metal Mo/Poly(3-Methylthiophene) Schottky Barrier Diodes. *Synthetic Metals*. 87: 109-113.
- Yacubowicz, Y. and Narkis, M. 1990. Electrical and Dielectric properties of Segregated Carbon Black-Polyethylene Systems. *Polymer Engineering and Science*. 30: 459-468.