

Comparative Studies of the Effects of Doping on the Electrical and Thermal Conductivities of Polystyrene.

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ABSTRACT

The electrical and thermal conductivities of polystyrene (PS) doped with graphite, charcoal, and iron III chloride (FeCl₃) have been studied. Five grams of polystyrene was mixed with varying concentrations, 0%, 0.05%, 0.1%, 0.5%, 0.75%, 1%, 1.25%, and 1.5% of each of graphite, charcoal, and FeCl₃. The mixture on melting with heat application was compressed in a wooden mold to form tablets of doped polystyrene materials. The idea behind this experiment is to find a means of reducing the cost of making conductive polymers since it is evident that tailor-made conductive polymers such as poly aniline, poly acetylene etc. do not actually have readily available starting materials and are quite expensive. On testing for the electrical and thermal conductivity of the doped polymer, its electrical and thermal conductivities were actually enhanced by the potentiating capacities of the dopant although at different degrees by the different dopant.

(Keywords: conductive polymers, thermal conductivities, poly styrene, doping, electrical conductivities)

INTRODUCTION

Most commercially produced organic polymers are electrical insulators. Conductive organic polymers often have extruded delocalized bonds (often composed of aromatic units). When charge carriers (from the addition or removal of electrons) are introduced into the conduction or valence bands, the electrical conductivity increases dramatically.

Technically almost all known conductive polymers are semi-conductors due to the band structure and low electronic mobility. However, so called zero band gap conductive polymers may behave like metals. The most notable difference between conductive polymers and inorganic semi-conductors is the mobility, which until very recently was dramatically lower in conductive polymers than their inorganic counter parts though recent advancements in molecular self-assembly are closing that gap [1].

The world electronics market has shifted its interest and concern to the use and application of conductive polymers in its production developments because of their simplicity and compactness. All hands, therefore, must be on deck to evolve highly conductive yet cheap polymers from readily available, easily sourced materials in our environment. This work was gingered by the above premise and its concern was based on how the readily available polymer, polystyrene could be electrically and thermally enhanced by doping with Iron III chloride, graphite and charcoal to help its conductivity such that it can be employed for this essential function since it is evidently clear that already made conductive polymers are not readily available and are of low cost efficiency.

Metals are characterized by the presence of free electrons and can conduct electricity; non-metals have few or no electrons and cannot conduct electricity, while semiconductors are in between the two. Plastics are generally known as good electrical insulators [2]. Insulators break down for two reasons: Firstly, the higher the voltage they must sustain, the greater the strain imposed upon their inter-atomic bonds and hence on their insulating properties.

Every insulator has a voltage at a given thickness, beyond which it will break down and conduct either across its surface or throughout the bulk of the material. Secondly, the hotter the insulator, the greater the agitation within its crystal structure and the more likelihood there will be free electrons [3].

Conductive polymers are generally not thermoplastics (i.e., they are not thermo formable although like insulating polymers they are organic materials). They have an advantage over other polymers because of their process ability which is mainly by dispersion [4]. The electrical properties of conductive polymers can be fine-tuned using the methods of organic synthesis [5] and by advanced dispersion techniques [6]. The conductivity of polymers is the result of several processes. In the traditional polymers such as polyethylene, the valence electrons are bound in sp^3 hybridized covalent bonds. Such sigma-bonding electrons have low mobility and do not contribute to the electrical conductivity of the material. Organic insulator decomposes at a temperature of a few hundred degrees centigrade, but ceramic insulators when very hot may conduct quite well. The more firmly restrained the electrons are in a material, the better its insulating properties.

At times, minute amounts of impurities or dopants may be introduced to an insulator to improve conductivity to desired amount and the process is known as doping [7]. These dopants or impurities either introduce mobile or free electrons into the insulator [8]. The conductivity of the doped material approaches the conductivity of the best available conductor, that is, silver.

At room temperature, the conductivity of polyacetylene approaches the conductivity of copper on a weight basis and exists in cis-configuration at 195°K and trans- at room temperature [9]. However, in conjugated materials the situation is completely different. Conducting polymers have backbone of contiguous sp^2 hybridized carbon centers [5]. Conductive polymers are organic polymers that possess electrical, electronic, magnetic, and optical properties of a metal while retaining mechanical properties processibility commonly associated with a conventional polymer [10]. It can also be defined as any system that contains an additive to lower resistivity. The resistivity of unmodified polymers or plastics is $10^{16} \Omega\text{m}$ while conductive

additives can lower resistivity level in steps down to $10^4 \Omega\text{m}$ resistivity range [11].

This work is focused primarily on the enhancement of their crucial properties: electrical and thermal conductivities that are required of a polymer for it to be accepted for all good uses especially as a semiconductor. Commonly discarded polymers and materials from the environment were used as a means of waste control. Cost management was considered since this has served as a strong limitation for their use. These desired polymers were achieved by doping with dopants to help lower the resistivity of the polymers thus increasing their conductivities. Hence the doping process is the introduction of very small amounts of impurities example FeCl_3 , graphite or charcoal to generate charge carriers since concentrations of dopants cause certain electrons to become unpaired. Doping also leads to the formation of polarons and bipolarons and have extended p-orbital system that have more (n-type) or fewer (p-type) valence electrons to increase the conductivity of a semiconductor [12].

MATERIALS AND METHODS

Basic Theory

All the materials and equipment used for this particular research were sourced from the chemistry and physics research Lab of the Nnamdi Azikiwe University Awka, Cutix Cable Nnewi, Relief Market Onitsha, and electronic shops in Onitsha.

- White brittle pack used for protecting electronic gadgets, which is pure polystyrene
- Graphite from dry cell batteries
- Iron III Chloride from BDH Prole, England
- Charcoal from burned fire wood
- Electrical weighing balance from Mettler Toledo 2007 mode serial no 021-64852350, England
- Stirring rods and Beakers (PYREX)
- Electro thermal Heater of about 250°C from Barnstaed 2006 model, serial no 10714483 England
- Thermometer - 360°C thermometer
- Wooden mold
- Katharometer, 500 mega ohms
- MASTECH multimeter No. 005-134

5g of the polymer were weighed into a 250 ml beaker and heated at a regulated temperature of 130° C - 250° C to melt it using a thermometer and on continuous stirring to maintain a uniform temperature. During the process care was taken not to allow degradation. The dopant of known different percentage concentrations 0.00, 0.05, 0.10, 0.50, 0.75, 1.00, 1.25, 1.50 was added into the beaker containing the polymer and the two mixed thoroughly while heating respectively. The mixture was then poured immediately into the mold and compressed to form a doped tablet of polystyrene.

Table 1: Formulation of Doped Polystyrene.

Polystyrene (g)	% Concentration of Dopant		
	FeCl ₃	Graphite	Charcoal
5.00	0.00	0.00	0.00
5.00	0.05	0.05	0.05
5.00	0.10	0.10	0.10
5.00	0.50	0.50	0.50
5.00	0.75	0.75	0.75
5.00	1.00	1.00	1.00
5.00	1.25	1.25	1.25
5.00	1.50	1.50	1.50

Characterization of the Sample

(a) The electrical conductivity of the sample was carried out by using 500mega ohms MASTECH multimeter 005-1349. Each sample prepared was tested with the equipment by placing it between the two opposite rods of the multimeter and its resistance taken. Resistivity is the opposition given to flow of current per unit length of material of uniform sectional area and the reciprocal of resistivity was measured as:

$$K = I/R \quad (1)$$

Where k = Electrical conductivity
R = Resistance

(b) Thermal conductivity was carried out using Elmer 2AK kathrometer. The results were obtained from the equation below:

$$q = kdt/dx \quad (2)$$

Where q = heat flux (w/m²) dt/dx = temperature gradient (k/m)

RESULTS AND DISCUSSION

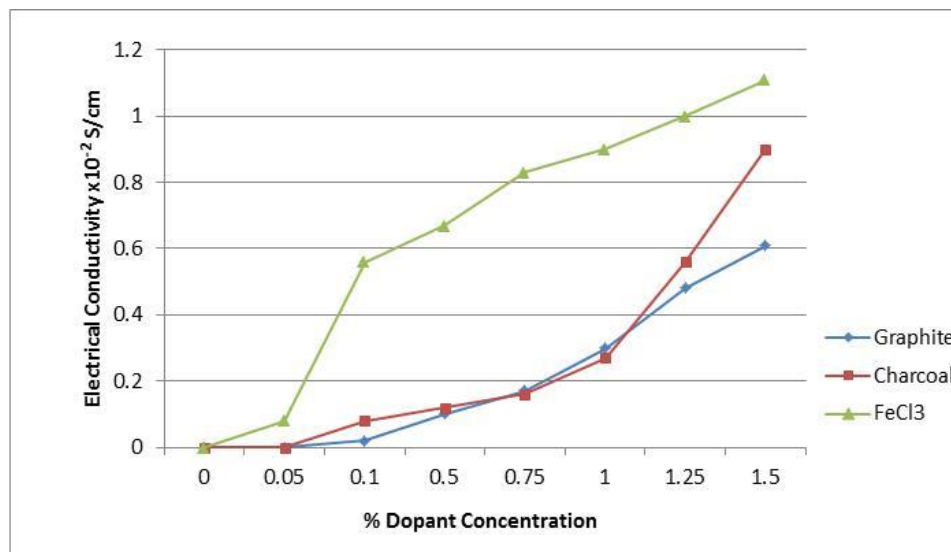


Figure 1: Effects of Doping with Graphite, Charcoal and FeCl₃ on the Electrical Conductivities of the Polymer Polystyrene.

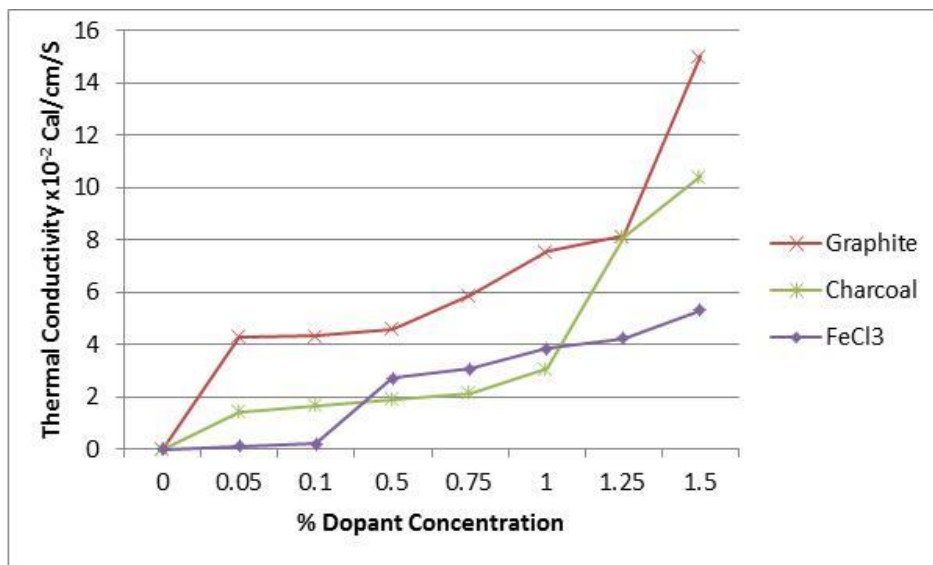


Figure 2: Effects of Doping with Graphite, Charcoal and FeCl₃ on the Thermal Conductivities of the Polymer Polystyrene.

The figures above show the effects of doping with different concentrations of charcoal, graphite and FeCl₃ on the electrical and thermal conductivities of the polymer polystyrene. Doping with charcoal produced a better result than graphite. At a high concentration it also produced more magnified effect, which could be attributed to the amorphous nature of charcoal and the demonstration of a better “island” formation in polystyrene than graphite.

The iron in iron III chloride is a transition element with a half filled d-orbital thus it is highly reactive. FeCl₃ is a deliquescent salt that on exposure at laboratory ambient conditions absorbs water from the atmosphere thus has its nature turned to be wet and will encourage ionization of the salt and thus leaving the dopant with a lot of free electrons. One can also deduce that the movement of electron from the valence band of the polymer into the partially filled conductive band of Fe³⁺ would also be efficient in explaining the excellent performance of the polymer doped with FeCl₃. The nature of FeCl₃ explained above results in formation of ‘metallic island’ concept in which case the islands of FeCl₃ would have conducted electricity through its own intrinsic property as a metallic conductor.

It is important to note that in doping with FeCl₃ there is a spiking from 0.05wt % - 0.10wt % from

which one can deduce that the rate of increase in electrical conductivity of polystyrene at lower concentration tend to be doubled and the rate decreases as the dopants concentration increases. It therefore appears like the conductive band gets saturated at a given concentration, further addition of dopants results in marginal electron transfer activity, thus causing a reduction.

On the other hand, polystyrene has a dielectric constant determined by the additive effects of electronic and dipolar polarizabilities. The latter is due to the presence of permanent electric dipoles. Polystyrene is essentially non polar with an effective dipolar moment of $6.7 - 10 \times 10^{-31}$ cm per repeating unit. These effects of the electronic and dipolar polarizabilities is increased by the presence of the dopant thereby creating dipole moments that improve conductivities through polaron assisted tunneling.

The doping with a carbon allotrope arranged hexagonally with rings formed by δ bonds and singly occupied p-orbitals perpendicular to the plane of the rings interact to form a delocalized π orbital involving all the carbon atoms in a layer. The delocalized π orbital of the graphite accounts for its intrinsic electrical properties. Electrons are delocalized along the conjugated backbone of conducting polymers through a lap of π orbitals

giving rise to the extended π -system with a filled valence bond [7].

Some dopants may introduce extra electrons (electron rich) to the π -system and are called n-doping while some will introduce holes (electron depleted) and are known as p-doping. Doping of conjugated polymers generates high conductivities by increasing a carrier concentration. Phonon helped hopping even as graphite increase the carrier concentration in polymer. Amorphousness increases the range of hopping. The increased carrier concentration bridged the wide energy gap between the full valence bond and the empty band and empty conductive band of the polymer. The graphite provides its own at a lower energy level which facilitates movement of electrons into the conductive band of the dopant from the valence bond of the polymer thus creating hole [8]. The movements of these holes cause electrical conduction within the polymer.

The electrical and thermal conductivities of the doped polystyrene increased with increase in the concentration of the dopants. The increase may be due to compactness provided by increase in concentration of the dopants which increase heat transfer through phonon. The behavior of polystyrene which was very outstanding could be because of dipolarity movement which makes a negligible contribution to the thermal conductivity of its parent form [9] but could be said to have made significant contribution to the thermal conductivity of the doped polystyrene due to its interaction with the delocalized electron in the graphite.

The density contributes to the thermal property of polystyrene. The free electrons in the graphite could have improved the dipolarity thereby increasing significantly the contribution of electron mobility in conduction through the graphite doped polystyrene. The hexagonally arranged structure of graphite would have contributed to the improvement of the polystyrene density also which will improve thermal conductivity by wave movement (phonon) or inter atomic heat transfer. The conductivity of polystyrene doped with charcoal increase at higher concentration of 1.25%. Heat transfer through electron might have played minimal role in thermal conductivity of the polystyrene doped with charcoal.

CONCLUSION

The electrical and thermal conductivity of the polymer polystyrene were enhanced and this enhancement is dependent on the nature and properties of the polymer and the dopant. It is also evident that since this is possible, discarded polymers can be employed for some industrial use when improved to the required standard.

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