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Thermoelectric Behaviour of Conducting Polymer Composites: An Overview of Properties and Applicability in Fabricating Thermistors

Dr. Harindra Singh

Associate Professor
Department of Physics, CRA College, Sonipat, Haryana 131001

Abstract

Conductive polymer composites (CPCs) have garnered much interest recently due to their excellent thermoelectric and superb mechanical characteristics, besides low cost of production. With a rise in temperature the conducting channels inside CPCs experience a change, influencing their electrical conductance. This change in case of amorphous polymer matrices, is generally attributed to the change in resistance near the glass transition temperature, T_g, because of the differences in the coefficient of expansion of amorphous polymers below and above T_g. This temperature dependence of electrical conductivity in case of CPCs creates possibilities of fabrication of thermistors for various applications in electronic circuit boards. The feasibility as well as challenges involved in this area is the endeavor of the present study.

Key words: Conducting polymer composites, thermistors, sensors, PTCR, NTCR

1. Introduction:

Conducting Polymer composites (CPCs) are fabricated by adding conducting filler materials in a nonconductive polymer matrix involving various techniques [1,2]. Various properties of CPCs like corrosion resistant, less costly, light weight and ease of processability sets these apart from metals. Usually carbon family nanomaterials such as carbon black [3-7], carbon fibers (CFs) [8,9], single walled carbon nanotubes (SWCNTs) [10,11], Multi walled carbon nanotubes (MWCNTs) [1, 12-14], graphene [15-17] and graphite Nano sheets [18,19] are incorporated as fillers to make polymers conducting. All these fillers possess superb electrical conductivity as well as excellent miscibility with polymers. The amount of the filler material is gradually increased and conductivity is examined to ascertain a particular concentration of the filler at which, there is a sharp growth in the conduction through the CPC, is noticed. This particular concentration of the filler is referred as percolation threshold (ρ_c) in the literature and is governed by the equation:

$$\sigma \ \alpha \ (\rho - \rho_c)^t \text{ for } \rho > \rho_c \qquad \textbf{(1)}$$

where σ is electrical conductivity of the composite, ρ is the filler concentration and t is critical exponent decided by the volume of conductive network in PCC. As the creation of conductive network within the matrix governs the level of conductivity, even a meagre change in filler concentration can cause a phenomenal change in conduction through the composite. Dispersion of filler particles inside host polymer is shown in Fig.1. When filler amount is low, the particles are lying too much apart from one another (Zone I) and the conductivity of the composite is not improved. When the filler concentration is increased and it is near the critical concentration the inter-particle distance of filler particles decreases (Zone II) and the conductivity starts improving due to electron hopping/tunneling on applying external voltage. On further raising the filler content, formation of continuous channels of filler particles takes place (Zone III) and a sudden surge in conductivity is noticed due to of creation of a network of conducting pathways. This property of the composites is harnessed to design strain [20-22], pressure [23], temperature [24] and solvent [25] sensors to observe the external stimuli.

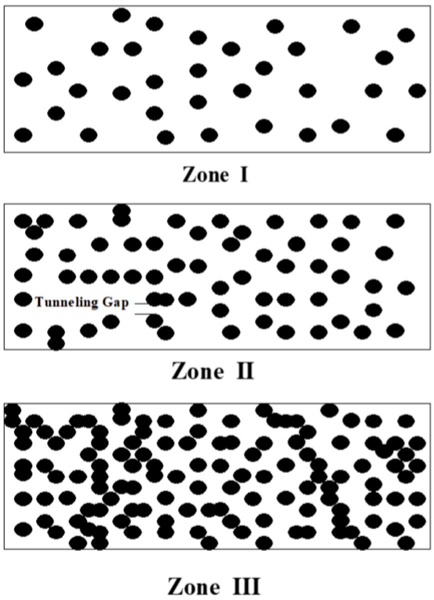

Figure.1 Dispersion of filler particles in polymer matrix

Main advantage of CPCs is their superb sensitivity. These possess a high surface area/volume ratio, which empowers them to interact with various stimuli with enhanced effectiveness, making them highly sensitive. Contrary to conventional sensors, which require sophisticated and complex machinery involving high cost for fabrication, CPCs can be manufactured involving cheap materials and simple equipment. Besides this, being lightweight and flexible, these are befitting composites for wearable gadgets. The present review is targeted to explore the potential of various CPCs for being used as thermistors in circuit boards.

2. Design, Methodology and working of thermistors based on CPCs

The change in the resistance observed with changing temperature is termed as thermoelectric behaviour. Utilizing this property of CPCs, temperature sensors or thermistors can be fabricated. The change in the resistance on rising temperature in CPCS is due to the breaking of the conducting pathways or channels due to thermal expansion. The increase in resistance with rising temperature is termed as positive temperature coefficient of resistance (PTCR) effect [26,27]. As the enhancement in resistance primarily occurs as a results of increase in the inter molecular gap of the polymer matrix, it's coefficient of thermal expansion (α) is of paramount importance. Sachdev et. al., have examined the PTCR effect in Styrene Acrylonitrile (SAN)/graphite (Gr) composite in the temperature range of 35^{o}C to 150 ^{o}C [28]. Here it is reported that composites with 1wt% and 2wt% graphite content exhibited a pronounced growth in resistivity which starts at around 100 ^{o}C [Fig2a]. In another study Sachdev et.al. [29] studied the thermoelectric behaviour of Gr filled Poly Vinyl Chloride(PVC)/SAN composites and here a sharp increase in resistivity at around 80 ^{o}C, is observed in sample having graphite concertation of 1% [Fig. 2b]. The PTCR effect may be attributed to the glass transition temperature of PVC (~ 80 ^{o}C). Dahiya et.al. examined the PTCR effect of Acrylonitrile Butadiene Styrene(ABS)/Gr composite and found that on heating the maximum change in resistivity was found in the sample having graphite concentration near percolation threshold i.e. 2.9 vol.% of graphite [30]. Low hysteresis was reported when the samples were heated up have reported presence of PTCR to 130 ^{o}C, i.e. the Tg of ABS [Fig.2c]. In case of PVC/Gr Composites Sachdev et.al [31] reported a rise in resistivity at around 55 ^{o}C, but the switching from low resistivity to high resistivity state was gradual [Fig2d]. PTCR effect in Silver (Ag) nanoscale particle were incorporated in various polymers by Rybak et.al. and the PTCR phenomenon was meticulously examined [32]. Although no perceptible PTCR behaviour was found in poly m-xylene adipamide based PCCs, may be due to its low α, however, a tenfold increase in resistance was reported in case of high density poly ethylene (HDPE)/Ag nanocomposites on increasing temperature from 25^{o}C to 75 ^{o}C.

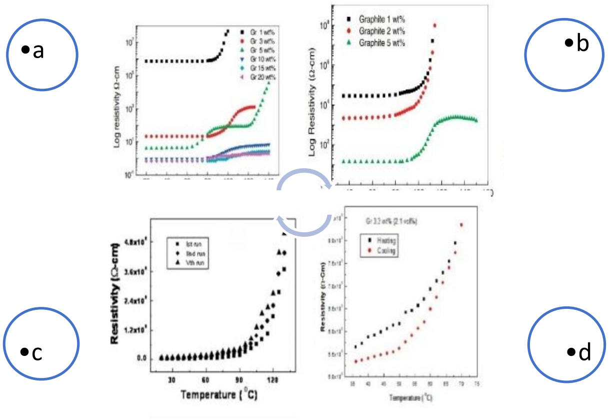

Figure. 2 (a) Log resistivity vs temperature plots for SAN/Gr composites. (b) Log resistivity vs temperature plots for SAN+PVC/Gr composites. (c) Resistivity vs Temperature plots for ABS/gr composites. (d) Resistivity vs Temperature plots for PVC/gr composite

When the temperature is more than T_g in amorphous and more than melting temperature T_m in crystalline polymer matrix, the conductance of polymer composites usually increases with rising temperature, probably because of the regeneration of conductive channels. This phenomenon is referred as NTCR effect in literature [33,34]. Upon heating, NTCR effect is always accompanied by PTCR in almost all CPCs comprising of randomly distributed filler particles in the polymer. This dual natured thermoelectric behaviour restrains many of the CPCs for being utilized as thermistors. Fabricating CPCs with a unique NTCR or PTCR effect, requires a more intricate designing avoiding formation of random distribution of conducting channels inside host polymer. Cui et.al. [35] fabricated carbon black filled cross linked Chlorinated poly (propylene carbonate) (CPPC) foamed CPCs. Here as the temperature rises, the expansion of gas caused thinning of walls of foam, resulting in reducing inter particle gap of Carbon black, consequently increasing conductivity of the CB/CPPC composite. During cooling the, the walls of foam comes back to their original, due to decrease in the amount of the gas causing decrease in conductivity. Another approach, i.e. by embedding the conducting nanoscale filler into flexible polymer matrix [36-38] is also used for making composites. This scheme is usually employed to prepare multi-function sensors such as pressure or strain. This strategy was adopted by Bae. et.al [37], where they employed reduced graphene oxide (RGO) as thermistor material and mingled it with a flexible capacitive sensor. They used parylene as substrate material and encapsulated, RGO with an optimized degree of reduction in it. This thermistor exhibited a linear and reproducible temperature coefficient of resistance of 0.83%/°C when tested in the temperature range of 22 to 70 °C. Hong et.al. [38], on the other hand, used polydimethylsiloxane (PDMS) as polymer substrate and polyaniline nanofibers as conducting filler to fabricate a film capable of sensing change in temperature, thus leading to the creation of a stretchable thermistor.

As temperature rises, due to thermal expansion of the polymer, the conducting channels/pathways inside CPCs gets interrupted leading to enhancement in resistance. Although this PTCR behaviour amongst CPCs is quite common, utilizing these as thermistors is not free from serious challenges. In most of the CPCs the increase in resistance with temperature is non-linear as shown in Fig.1, Secondly CPCs exhibit both PTCR and NTCR behaviour with rising temperature rendering them unfit for being used as temperature sensing devices. As discussed earlier, cross-linked CPPC/CB foams can be employed to fabricate thermistors. Zhao et.al [39] have successfully developed a segregated, dual percolated system to restrain the volume expansion effect of the polymer matrix. Here graphene nano-sheets plays a pivotal role to simultaneously build up a conductive channels network, ensuring the formation of NTCR temperature sensing system. A novel scheme of synthesizing thermistors involving CPCs, is prior fabrication of a temperature sensing film and enclosing it between flexible substrates. The enclosed temperature sensing coating usually consists of polymer and conductive nanoscale particles. Based on this design strategy, Oh et al. [40 135] developed a temperature sensing film comprising of carbon nanotubes (CNTs) filled poly(N-isopropylacrylamide) (pNI-PAM)-temperature sensitive hydrogel and poly (3,4-ethylenedioxythiophene) polystyrene sulfonate, and sandwiched it between two films of PDMS. This sensor capable of sensing as small as 0.5 °C shows a sensitivity of 2.6%/°C when tested in the temperature range of 25 to 40 °C. Besides this, good repeatability was observed over large number of temperature cycles. Similarly, employing the same design approach,

Recently wearable sensors have caught the attention of researchers as these are capable of providing real time data by ensuring comfortability. Fiber based thermistors, which can be embedded in clothing, have recently been fabricated by Trung et al. [41] employed wet-spinning method and utilized in-situ reduction method to synthesize free- standing single reduced graphene oxide fiber having a diameter of ~40 um. This fiber when embedded in the clothes works as human body temperature sensing device having response time of 7s and recovery time of 20s. Besides this, the sensor displays superb repeatability over touching/un-touching cycles with human body.

Thermistors, temperature-sensitive resistors, are greatly in demand in industry due to their precise and rapid response to temperature changes. They come in two primary types: Negative Temperature Coefficient (NTC) thermistors, which decrease in resistance as temperature rises, and Positive Temperature Coefficient (PTC) thermistors, which increase in resistance with rising temperature.

3. Applications

Various applications of NTCR and PTCR thermistors are summarized in Fig.3.

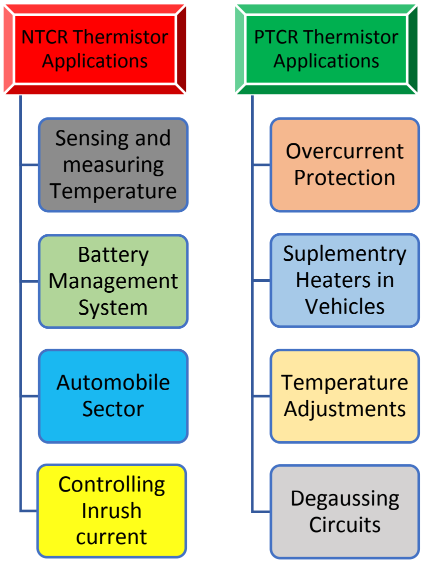

Figure. 3 Applications of NTCR and PTCR Thermistors

3.1 NTCR Thermistors

- **Sensing and Measuring Temperature:** NTCR thermistors are generally fitted in digital thermometers and domestic gadgets such as ovens and fridges to sense and adjust temperature.
- **Battery Management Systems:** NTCR thermistors keeps an eye on temperature of power storing units like battery in smartphones and electric vehicles, for proper monitoring of charging and discharging for safety of components.
- **Automotive Sector:** The temperature of fluids in radiator as well as of lubricating oil in engines of vehicles is monitored generating vital data to the electronic control unit to ensure proper health of the system.
- **Controlling Inrush Current:** In power supply systems, NTCR thermistors control inrush current by offering high resistance in the beginning which reduces as components warm up thereby safeguarding various parts from sudden spikes.

3.2 PTCR Thermistors

- **Overcurrent Protection:** PTCR thermistors act as current-limiters, safeguarding electrical and electronic circuitry by raising resistance appreciably during fault/short circuit situation, keeping current within safety levels.
- **Supplementary Heaters in Vehicles:** PTCR thermistors are deployed as supplementary heaters in vehicle compartments, particularly in diesel operated vehicles to pre-heat fuel in cold areas to solve engine start problems.

- **Temperature adjustment:** In electronic circuits boards, PTCR thermistors sense and adjust temperature within specified limits to resolve temperature fluctuation issues, ensuring proper functioning of components.
- **Degaussing Circuits:** These are employed in CRT monitors and televisions for the purpose of degaussing coils to eradicate remaining/ leftover magnetic fields, enhancing quality of watching

Thermistors are also utilized in medical equipment, HVAC systems, and industrial automation for accurate temperature monitoring and control, highlighting their versatility and importance in modern technology.

4. Conductive Polymer-based Thermistors: Challenges and Future Perspectives

Although conductive polymer composites sensors possess innumerous merits over conventional temperature sensing gadgets, yet serious limitations still exists, which need to be tackled. The biggest challenge is to improve the sensitivity and selectivity of these. Whereas, conductive polymers possess good sensitivity, it is seriously affected by surrounding environmental parameters e.g. strain, pressure, humidity, solvents and pH. Thus in spite of big strides in improving the thermoelectric parameters of CPCs there are still innumerous challenges in the arena of CPCs- based temperature sensors for their applicability as thermistors. Another big challenge in CPCs is generation of stable and reproducible data. The characteristics of CPCs experience a change depending upon the development and production techniques resulting in inconsistent sensor performance. A linear, repeatable and consistent temperature coefficient of resistance is essential for CPCs-based thermistors. Nonlinear and presence of hysteresis during heating/cooling cycles renders these CPCs-based devices unfit for application as temperature sensors and thermistors. Self-healing is another great aspect of CPCs-based temperature sensors which deserves consideration as is capable of enhancing their lifespan and durability. Consequently, researchers all over the globe are involved in fabricating CPCs with improved reproducibility and consistent performance.

To overcome all these shortcomings and limitation, development of innovative CPCs with improved sensing capabilities is required. It is possible by revamping the chemistry of the existing CPCs or by formulating altogether new composites. Besides this, incorporating CPCs based sensors in clothing and accessories to make wearable devices is desired so that data pertaining to physiological aspects can be generated and transmitted to the health care providers at a faster pace, for taking corrective measures.

5. Conclusions

Thermoelectric behavior is observed in CPCS during heating/cooling cycles can be harnessed to fabricate temperature sensors/thermistors for applicability in different areas. In CPCs usually conductive fillers are randomly dispersed in the polymers and thus both PTCR and NTCR effects are noticed as temperature changes. This feature renders the dual natured conventional filler loaded CPCs unfit for practical applications as temperature sensors/thermistors. Composites with segregated distribution of fillers such as foamed structure, can be employed for synthesizing CPCs which exhibit either only PTCR or NTCR effect during heating/cooling cycles. Another approach of fabricating CPCs by incorporating materials such as conductive nanoparticles, nanofibers, and conductive polymers etc. in host polymer is capable of generating sensors with improved sensitivity and repeatable temperature sensing properties. To enhance comfortability, such devices are made involving fibers and embedded in clothing to fabricate a wearable temperature sensor/thermistor.

Research spread over the last few decades led to the development of different types of CPCs. Both the sensitivity and repeatability of the fabricated sensors have phenomenally improved during this period. Superb flexibility and outstanding bendability coupled with miniature size of these CPCs have made these temperature sensors befitting gadgets for applications like current limiters, poly-fuses in electronic circuit boards, electronic skins (e-skins) and for health monitoring purpose. Thus fabricating CPCs with a linear coefficient of resistivity, ensuring flexibility without compromising performance and curtailing cost of production will ensure their large scale utility for various applications.

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