Introduction
1.1 Introduction

The ever growing field of sensitive electronic gadgets warrants effective ways and means to shield them from all pervading electromagnetic radiations. As the electronic and optoelectronic industries make quantum leaps by showcasing highly sophisticated electronic gadgets for test, measurement and medical diagnosis, electromagnetically shielding them also require sophisticated technology and materials. Superconductors are important materials in this context not for their zero resistivity property but for their other independent characteristics, viz., Meissner effect. Also polymers can be effectively used to bypass the hindrances in utilizing superconductors for this purpose. This study is all about these two aspects.

The trend in superconductivity research has been changing gradually since Dutch physicist Heike Kamerlingh Onnes [1.1] discovered it in mercury. Since the discovery [1.2] of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor with $T_c$ above the liquid nitrogen temperature, various attempts have been made to improve two of the most critical parameters, namely, current density and mechanical or fracture strength that limit the applications of a bulk ceramic conductor. There have been different studies regarding the improvement of the latter property reported in the literature. For instance, Nies et al. [1.3] first described the preparation and properties of certain glass bonded composites of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ that showed large diamagnetic susceptibility. Fuierer et al. [1.4] reported the physical and microstructural properties of composites formed from $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and silicon rubber. A number of workers have studied [1.5, 1.6] the effects of adding silver to high $T_c$ superconducting ceramics. It has been shown that addition of silver to these ceramic materials enhanced the connectivity between the superconducting grains and increased the grain size. But mechanical property enhancement of high $T_c$ superconductor with silver addition was rather poor. These studies suggest that the practical applications of ceramic high $T_c$ superconductors are likely to be in the form of composite materials.
The goal of the current study is to investigate the Y-123/Linear Low Density Polyethylene composites for magnetic levitation and shielding applications.

The superconductivity research is ever growing. As mentioned earlier, here we are interested in its diamagnetic properties. Before going into the details of the work done, it is pertinent to have a discussion on superconductivity and its evolution.

1.2 Superconductivity

Over ten Nobel prizes being awarded so far in low temperature physics, in particular, superconductivity and superfluidity, which occur at very low temperatures, exemplify this area to be one of the most interesting areas of condensed matter physics. This goes on unabated. The Nobel Prize in physics 2003 went to Alexei Abrikosov and Vitaly Ginzburg for their work [1.7] on the theory of superconductivity together with Anthony Legget for his explanation on one type of superfluidity. In fact, the history of superconductivity started after the successful liquefaction of helium by the Dutch physicist Heike Kamerlingh Onnes in 1908. He investigated the low temperature resistivity of mercury in 1911 and found that the resistivity suddenly dropped to zero at 4.2K, a phase transition to a zero resistance state; for this Onnes was awarded the Nobel Prize 1913 in Physics [1.8]. This phenomenon was called superconductivity, and the temperature at which it occurred is called its critical temperature.

1.3 High Tc superconductor

The discovery of superconductivity in La$_{2-x}$Ba$_x$CuO$_4$ with superconducting transition temperature, $T_c$ of 30K by Bednorz and Muller [1.9] in 1986 was a milestone in the history of superconductivity. It immediately led to the discovery of a new class of high temperature superconductors having $T_c$'s in excess of 100K wherein the basic structure comprises of metallic CuO plane separated by insulating charge reservoir buffer layers. Most popular cuprate is YBa$_2$Cu$_3$O$_{7-x}$.
(Y-123) [1.2, 1.10, 1.11] with a maximum $T_c \approx 95\text{K}$ and $x$ can vary from 0 to $\sim 0.4$ (leading to variation in $T_c$ from $95\text{K}$ to 0K) [1.12 - 1.15]. Therefore, cuprate superconductor or simply cuprates were named high $T_c$ superconductor (HTSC), to contrast them with the conventional low $T_c$ superconductors which superconduct at boiling helium temperatures (4.2K). The Y-123 compound can be considered as the representative compound of the system.

While the copper oxide superconductors (YBCO) are the system of choice here, they have the drawback that they are stoichiometrically and structurally complex. Illustrating this point will require knowledge of the crystal structure of these high $T_c$ superconductors.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y-123) is an oxygen-deficient triple perovskite oxide. The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ unit cell consists of the rare earth ion $\text{Y}$ sandwiched between Cu-O$_2$ sheets (figure 1.1). These sheets are surrounded by the charge reservoirs [1.16] which consist of the Ba-O and Cu-O chain layers. Cu-O is a one dimensional chain and Cu-O$_2$ is a two dimensional buckled plane. The oxygen of the chain layer is labile. The structural evolution of the orthorhombic from the tetragonal in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in terms of oxygen stoichiometry is interesting. Here $x$ is the variable oxygen content which undergoes drastic change in its structure and properties when its value changes from 0 to 1 [1.17, 1.18]. When $x = 0$, substance is a perfect superconductor with orthorhombic crystal symmetry and when $x = 1$, substance is a perfect semiconductor with tetragonal symmetry. To overcome the problem of oxygen loss and to form $\text{YBa}_2\text{Cu}_3\text{O}_7$ which exhibits the optimal superconducting properties, it is necessary to anneal the sample in an oxygen rich environment at temperatures around 450°C. Since the structure is stable over the entire range, $x = 1$ to 0 and the transition temperature is highly dependent [1.19, 1.20] on the oxygen level, great care must be taken to ensure that the multigrain structure is fully oxidized. The formation of the chain Cu-O layer (at $x = 0$) reduces the crystal symmetry from tetragonal to orthorhombic. The
vacancies in the Cu-O layer form channels, through which small molecules may enter or leave the structure. The structure of YBa$_2$Cu$_3$O$_y$ is shown in figure 1.1 [1.16].

![Diagram of YBa$_2$Cu$_3$O$_y$]

**Figure 1.1 [1.16]:** The crystal structure of YBa$_2$Cu$_3$O$_y$.

(Shaded area: charge reservoirs)

The copper oxide high temperature superconductors, seem to be uniquely suited for the study of LLDPE/ high Tc superconductor composites for electromagnetic shielding and levitation applications, as they exhibit diamagnetic flux exclusion and levitation properties.

### 1.4 Diamagnetic properties of high Tc superconductors

#### 1.4.1 Meissner effect

The Meissner effect is at the heart of the work presented in this dissertation as it is this effect that allows for producing superconductor/polymer composites for electromagnetic and levitation applications.

Superconductors are perfectly diamagnetic in a particular range of magnetic field strength; superconducting state will exist up to a range of temperature [1.21] and field strength. It will disappear if the specimen is raised above its critical temperature or if a sufficiently strong magnetic field is employed. In other words it expels weak magnetic fields from their interior when they are cooled below
their transition temperature. This is called as the Meissner effect and is illustrated in figure 1.2.

![Figure 1.2](image)

**Figure 1.2** [1.21]: Meissner effect in superconductors.

### 1.4.2 Levitation properties

Levitation of a magnet above a high $T_c$ superconductor is a universally observed phenomenon and it is one of the most attractive properties for superconducting applications. It could be used to construct a levitated vehicle or bearings in rotating machinery. A high speed levitating train (~500 km per hour on average) making use of a conventional liquid helium superconductor has been tested in Japan [1.22]. Japan expects to have a levitating passenger train between Osaka and Tokyo before the end of this century. There have been several studies [1.23 – 1.34] on superconductor bearings and some simple prototype bearing devices have been made. They use the levitation capability and lateral stiffness of ceramic superconductors to spin magnetic bearings at high speeds with a stable system configuration.

In HTSC, which are type II superconductors, the complete Meissner effect occurs only with magnetic field lower than the critical field. For higher magnetic field the diamagnetism arises from the shielding currents [1.35]. In fact the flux pinning [1.36] can sustain a magnetic field gradient which is related to a macroscopic current. The strong diamagnetic behavior leads to remarkable phenomenon such
as magnetic levitation. To achieve a large interaction force between a superconductor and a field source, it is important to obtain superconducting materials allowing for high current density extended to electrical paths as large as possible. Owing to the hysteretic magnetic behavior of HTSC the interaction magnetic force can be either repulsive or attractive [1.37 – 1.39] leading respectively to magnetic levitation and suspension.

1.5 Electromagnetic shielding

Electromagnetic shielding is a more widespread technique [1.40] in the era of electricity and electronics, than it is usually acknowledged. Compliance to internationally agreed electromagnetic compatibility codes is an integral part of all electronic and of many electrical devices in the market. Compatibility means [1.40] that a device must comply with given limits for electromagnetic radiation to get the generated interference below the limits (in amplitude or frequency) stated by the agreed codes. Most domestic appliances, like those containing electrical motors, magnetic actuators and florescent lights, radio and television sets, computers, computer monitors and telephones etc. are in this category. From the steep increase in the preference given to optical methods for signal transmissions (example, fiber optics for telephone cables), we can understand the extent and importance of electromagnetic interference. Shielding is therefore necessary in cases where a device must be prevented from radiating electromagnetic energy by itself and protected from picking up electromagnetic energy radiated by other devices.

The type and extent of the necessary shielding will be restricted [1.41] to the case of making an electromagnetic vacuum, where the techniques based on the new materials are almost mature for applications like biomedical measurements of weak magnetic fields, electromagnetic compatibility measurements and electronic security. The solution to be adopted will depend on the size of the shield and on whether the internal temperature must be different from the refrigerator temperature or not.
A shielding surface made of high $T_c$ materials is effective because of the intergrain currents: the contribution of intragrain currents is very low, except when the full shielding properties are very modest, which is not of technological interest. The shielding currents fully depend on the stray fields, whose directions [1.40] are generally unknown and random. Therefore, with the exception of very special cases where the field direction is known, the shielding properties of the material must be isotropic.

For applications where the attainment of an electromagnetic vacuum is the aim, the use of high-$T_c$ superconducting materials showed far superior results on monolithic shields with respect to traditional high-permeability materials and a great simplification in practical use with respect to the low-$T_c$ superconducting materials. Moreover, this magnetic shielding technique is mature to scale up to the medium to large size industrial prototype stage, where it is likely to show good competitiveness with respect to the existing techniques.

Electromagnetic shielding using [1.42 - 1.44] high temperature superconductor (HTSC) is one of the large scale industrial application with peculiar requirements. It is the property of diamagnetic flux exclusion [1.45] and not the zero resistivity of the high $T_c$ superconductors makes it a potential candidate for shielding.

However in spite of all these, the difficulties involved in processing HTSC materials into desired shapes and sizes as well as their fragile nature are the main drawbacks in using these materials for shielding applications. In the next section this aspect is discussed and the role of polymer/superconductor composites as an alternative is highlighted.

1.6 Superconductor/polymer composites

High $T_c$ superconducting ceramics have an inherent brittleness which makes them difficult when they are to be molded and die-cast in to pieces of even the simple shapes, let alone the ease of fabricating it in to flexible shielding sheets. Their
mechanical properties cannot compete with those of conventional metallic superconductors. Therefore the use of HTSC material for large scale shielding or levitation has been proved [1.46] not an easy task. Further high $T_c$ superconductors are plagued with compositional instability and susceptibility to environmental degradation. These problems have impeded the development of application for high $T_c$ superconductors.

The large electromagnetic shields are generally designed with the superconducting material deposited as a thick film on a structural substrate. One of the most important criteria for the selection of any material as substrate for high $T_c$ superconducting film is their chemical compatibility with the film. The choice of the substrate, which is necessary to support a thick film causes several constraints like high cost, difficulty in refrigeration and thermal expansion mismatch.

One of the most efficient approaches [1.47 – 1.53] to circumvent these disadvantages is presumably the introduction of flexible materials like polymers as a structural support and protective matrix in to powder oxide superconductor filler to form a composite with good mechanical flexibility. Polymer matrices provide great mechanical integrity and chemical stability. Superconducting/polymer composites have superior mechanical properties, better machinability and processing flexibility in comparison with ceramics alone. Encapsulation also protects the ceramics from environmental deterioration and oxygen loss.

It has also been proved that composites formed from ceramic superconductor and polymer exhibited good magnetic levitation at liquid nitrogen temperature, though dc zero resistivity was generally lost in the composites due to poor contact between superconducting grains. Also these composites showed decent flexibility and improved toughness. Hence these composites are ideal for potential applications where zero resistivity or contact between superconducting grains is not essential to the function, such as magnetic shielding [1.54] and levitation.
Therefore it is very important to evaluate magnetic levitation properties for composite materials. Weinberger et al. [1.52, 1.53] have studied the levitation force for YBaCuO/paraffin wax composite and suggested a prototype bearing using this type of composite [1.53]. More efforts are necessary, improving the superconductor magnetic properties, to achieve higher load and stiffness capacity.

In this context this proposal suggests a versatile thermoplastic Linear Low Density Polyethylene (LLDPE) to be used as a matrix for the superconducting ceramic material \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \). LLDPE is selected [1.4] for the matrix material because it has versatile properties like flexibility, good mechanical strength, elongation at break and puncture resistance compared to other branches of the polyethylene. They are readily worked at room temperature since they possess the lowest glass transition temperature of the common thermoplastics. Also they have well defined crystalline phase. Orthorhombic structure of LLDPE and the size of the crystallized domains can easily be controlled by XRD and crystallinity studies using Differential Scanning Calorimetry (DSC). \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) is selected [1.55] for the superconductor part since this ceramic material shows a more abrupt field penetration and they crystallize in orthorhombic oxygen deficient perovskite structure with a transition temperature of around 95K.

Before going into further details, a discussion on polymers would not be out of place.

1.7 Polymers

Polymer science has emerged as an active discipline of material science. This field impinges on areas of commodity, engineering and specialty polymers, thereby stimulating interest all over the globe in exploiting newer domains. There is a long history of successful development, which came from the enormous contributions of numerous people [1.56].
A polymer is a generic term used to describe a substantially long molecule. This long molecule consists of structural units and repeating units strung together through chemical bonds. These units of polymer are called monomers [1.57 - 1.59] and the process of combination is called polymerization. Polymerization is a process of reacting monomer molecules together in a chemical reaction to form three-dimensional networks or polymer chains [1.60]. The monomers are typically small molecules of low molecular weight. The monomers can be identical or they can have one or more substituted chemical groups. When the monomers are of same kind, the product of polymerization is called homopolymer and when different types of monomers are involved, the polymers are called copolymer. These differences between monomers can affect properties [1.61] such as solubility, flexibility or strength.

1.8 Copolymerization

Copolymerization is polymerization with two or more different monomers [1.62]. Copolymerization of different monomers can result in varied properties [1.63] of polymers. For example, copolymerising ethene with small amounts of hexene-1 is one way to form linear low density polyethylene (LLDPE). In LLDPE, the C₆ branches resulting from the hexene lower the density and prevent such large crystalline regions within the polymer as in HDPE. This means that LLDPE can withstand strong tearing forces whilst remaining flexible.

In this work, LLDPE has been tried as the matrix material of HTSC and a discussion on polyethylene follows this section.

1.9 Polyethylene - A highly applicable material

The discovery and development of polyethylene provides an excellent lesson in the value of observing and following up an unexpected experimental result. Polyethylene is the most popular plastic in the world. It is one of the most important polyolefins in terms of commercial production and technological
applications. Figure 1.3 shows the space filling model [1.64] of a polyethylene chain.

![Space-filling model of a polyethylene chain](image)

**Figure 1.3 [1.64]**: Space-filling model of a polyethylene chain.

Its name originates from the monomer ethene, also known as ethylene, used to create the polymer. In most scientific publications it is known as polyethylene - an indication that it is a polymer of ethylene [1.64]. Figure 1.4 [1.64] shows the three dimensional image of polyethylene.

![Three-dimensional image of polyethylene](image)

**Figure 1.4 [1.64]**: The three dimensional image of polyethylene.

Polymers formed by the repeated addition of monomer units [1.65] without the elimination of any by product molecules are called addition polymers. This occurs during polymerization, in which many monomer molecules link to each other. The monomers are unsaturated compounds and are usually the derivatives of ethene. The ethene molecule, $C_2H_4$, is $CH_2=CH_2$, two $CH_2$ connected by a double bond, as shown below.

```
H
/ \
/   /
C---C
\   \ 
H   H
```

A molecule of polyethylene is nothing more than a long chain of carbon atoms, with two hydrogen atoms attached to each carbon atom as shown below [1.64].
Polyethylene or polyethene is a thermoplastic heavily used in consumer products. This is the polymer that makes grocery bags, shampoo bottles, children’s toys, and even bullet proof vests. Its many applications include films or sheets for packaging, shower curtains, unbreakable bottles, pipes, pails, drinking glasses, and insulation for wire and cable.

Polyethylene is resistant to water, acids, alkalies, and most solvents. It has good mechanical and electrical properties, resistance to cold flow, ease of processing and an excellent cost-performance relation. These characteristics of polyethylene have generated great interest in the development of polyethylene composites with other materials so as to improve some specific property.

### 1.10 Classification of polyethylenes

Polyethylene is classified into several different categories based mostly on its density and branching. The mechanical properties of PE depend significantly on variables [1.64] such as the extent and type of branching, the crystal structure, and the molecular weight. Some of them are:

- HDPE (high density PE)
- HDXLPE (high density cross-linked PE)
- PEX (cross-linked PE)
- MDPE (medium density PE)
- LDPE (low density PE)
- LLDPE (linear low density PE)
- VLDPE (very low density PE)
1.11 Linear Low Density Polyethylene (LLDPE)

Linear Low Density Polyethylene is a linear microstructure version of the LDPE. LLDPE, defined by a density range of 915 – 925 kg/m³ is a substantially linear polymer, with unbranched chains, commonly made by copolymerization of ethylene with short-chain alpha-olefins (e.g. 1-butene, 1-hexene, and 1-octene). Branching can influence a number of physical properties like tensile strength and crystallinity. The more branched a molecule is, the lower is its tensile strength and crystallinity. LLDPE is a semicrystalline polymer and have better elongation performance and stress cracking resistance. It has glass transition temperature, \( T_g \) much less than room temperature and crystalline melting temperature \( T_m \) much higher than room temperature. At room temperature, there is a crystalline fraction that can bear load and an amorphous fraction that is mobile and adds toughness. Therefore LLDPE has very high tensile strength and crystallinity.

LLDPE are made by Ziegler-Natta vinyl polymerization, a method that uses a transition metal catalyst, like TiCl₄, to initiate polymerization. Karl Ziegler and Giulio Natta received the 1963 Nobel Prize in Chemistry for developing this method [1.66].

\[
\begin{align*}
H_2C=CH_2 & \quad \text{ethene monomer} \\
H_2C=CH & \quad \text{co-monomer} \\
\text{example: but-1-ene} \\
\text{TiCl}_3 & \quad \text{catalyst (TiCl}_3 \text{ or TiCl}_4) \\
\text{Al(C}_2\text{H}_5)_3 & \quad \text{co-catalyst (triethyl aluminium)}
\end{align*}
\]

\textbf{Synthesis of LLDPE using a Zielger-Natta catalyst}
LLDPE has higher tensile strength and higher impact and puncture resistance than low density polyethylene (LDPE). It is very flexible and elongates under stress. It can be used to make thinner films, with better environmental stress cracking resistance compared to LDPE. It has good resistance to chemicals and to ultraviolet radiation and has good electrical properties.

LLDPE is used in flexible tubing and in bags either neat or blended with LDPE. It is also used for plastic wrap, pouches, toys, lids, pipes, buckets and containers, covering of cables, and geomembranes.

Coming back to the goals and aims of this study, it must be noted here that there are reports about the studies on various superconductor/polymer composites. However optimum properties for such composites have not yet been accomplished due to various reasons like the effect of reinforcement on the polymer matrix, high insulating nature of the matrix, lack of interconnectivity of superconducting grains in the matrix etc. In this study, the preparation and characterization of LLDPE/high $T_c$ superconductor composites and further studies to bridge the gaps in the available reports on similar blends are made.

1.12 Bibliography

1.1 H. Kamerlingh Onnes, Akad. Wetenschappen, 14, 113, 818 (1911).


1.8 http://www.google.com/topic/Heike Kamerlingh Onnes biography.


Introduction

1.35 http://www.google.com/topic/levitation properties for superconductors.


1.40 Franco Pavese, Magnetic shielding using high T_c superconductors: A large-scale application with peculiar requirements, CNR, Italy (1994).

1.41 http://www.google.com/topic/superconductors electromagnetic shielding.


1.64 http://www.azom.com/topic/polymer polyethylene.


1.66 http://www.wikipedia the free encyclopaedia/topic/polyethylene LLDPE.
1.13 Index

Kamerlingh Onnes 3
superconductivity 4
high T_c superconductor 4
perovskite oxide 5
diamagnetic properties 6
Mcissner effect 6
critical temperature 4
levitation properties 7
electromagnetic shielding 8
superconductor/polymer composite 9
polymer 11
polymerization 12
copolymerization 12
polyethylene 12
linear low density polyethylene 15
Ziegler-Natta vinyl polymerization 15