INFLUENCE OF BINDERS ON THE MAGNETIC PROPERTIES OF STRONTIUM FERRITE AND NdFeB COMPRESSION BONDED MAGNETS

A THESIS

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By

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CERTIFICATE

This is to certify that the thesis entitled **"Influence of Binders on the Magnetic Properties of Strontium Ferrite and NdFeB Compression Bonded Magnets"** which is being submitted by **Mr. Himanshu Jindal** in Partial fulfillment of the requirements for the award of the degree of **Master of Technology in Material Science and Engineering** of Thapar Institute of Engineering and Technology (Deemed University), Patiala (India), is a record of the study conducted by him under our supervision and guidance and that no part of this thesis has been submitted for the award of any other degree.

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Chapter 1

Introduction

Magnets are ubiquitous in the modern society. Magnetic materials play a key role in industry. It has got many applications like ac and dc motors, stepper motors, synchronous motors, transformers, moving coil actuators, magnetic suspension, sensors, steady fields. Major application in information storage media like hard disks, communications, medical electronics & bio-engineering. Presently the global market value of these material is about 3.6 billion dollars annually which is rapidly increasing with an estimated value of 11 billion dollars by the year 2005.

Magnets attract certain metals such as Fe, Ni, Co, certain steels and other alloys. Magnet exerts attractive or repulsive force on other magnets (opposite poles attract and like poles respell). It exerts force on electrical conductors when the magnet and conductor are moving in relation to each other. It also affects the path taken by electrically charged particles traveling in free space. Actually magnet transforms energy from one form to another without any permanent loss of their own energy. e.g.

1. Mechanical to electrical in generators and microphones.
2. Electrical to mechanical in motors, loudspeaker charged particle deflection.
3. Mechanical to mechanical such as attraction or repulsion.
4. Mechanical to heat in eddy current, hysteresis torque devices
5. Special effects such as magneto resistance, Hall effect devices, magnetic resonance

Magnetic material do loose a very small strength over time i.e. less than 1% over a period of ten years [1].

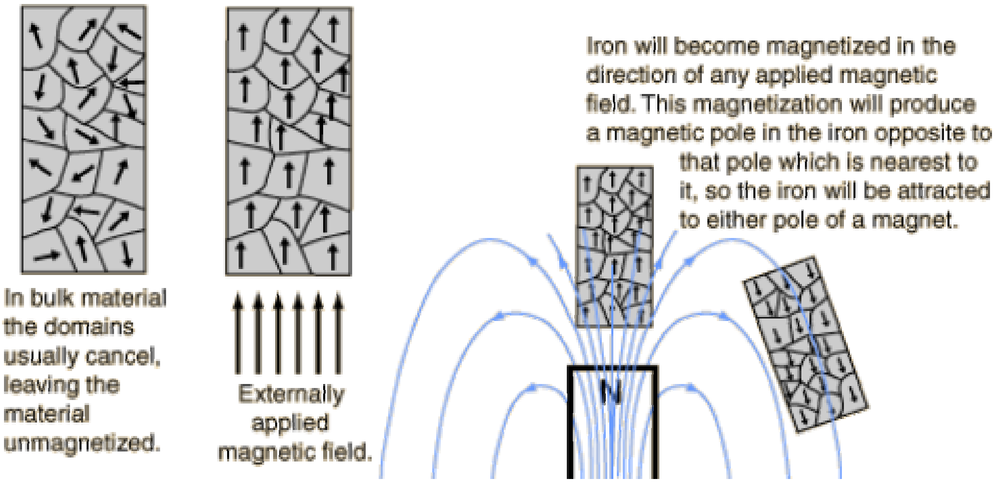


Fig 1.1 Diagram showing non-magnetized and magnetized materials

William Gilbert first realized that the Earth is a giant magnet and that magnets could be made by beating wrought iron. He also discovered that the induced magnetism was lost if the iron was heated. The magnetic behavior of earth is because it contains hot liquid centre of iron. When it moves it creates an electrical current that causes a magnetic field around earth. The earth has north and south magnetic poles. These poles are not quite aligned up with the geographical north and south poles on a map, because the moving inner core poles are always wandering around. Both pole position can wander up to 10 Km per year. Earth has a field just like magnet as it attracts things, it will attract a small magnetized needle. A needle mounted in a case that lets it move freely to the north magnetic pole. Earths magnetic field lines also attract particles form outer space as particles stream down through the atmosphere towards the magnetic pole. They cause northern lights [1].

1.1 Historical Background

The earliest magnet known to the mankind was loadstone, which mainly comprised of magnetite (Fe_3O_4) and was used for navigational purpose. At the end of the last century, plain carbon steels having about 1.5% C were developed and they remained the principal magnet alloy till about 1910. Later special steels containing some chromium or tungsten were evolved but the coercivity remained only between 3-6 kA/m. The most significant achievement in these quenched hardened steel came in 1917, when the Japanese introduced Honda Steel containing about 36% cobalt, which had a coercive force of 20 kA/m [2]. The alloyed steel essentially exploited the magnetic properties of elemental iron for which a saturation of 2 T, theoretically implied an enormous $(BH)_{max}$ of 915 kJ/m^3. But a small anisotropic field Ha ≅ 40 kA/m for iron restrained all hopes of achieving a high coercivity and at best, only a $(BH)_{max}$ of 7 kJ/m^3 could be achieved. The various additives to the steels simply served to translate the meager anisotropy field of iron into useful coercivity [3]. The coercivity in all these martensitic magnetic steels is due to the difficulty in domain boundary movement, resulting from the combined effect of non magnetic inclusion, strains, lattice defects and inhomogeneities or voids. The major drawbacks of these materials were instability of permanent magnetic properties due to aging and demagnetization with the influence of vibration, mechanical effects and weak magnetic fields [4].

An important advancement took place in Japan in 1932 with the discovery of precipitation hardened Al-Ni-Fe alloys [5]. In the following years, these formed the basis of Alnico materials which made their appearance in 1940. These magnets still continue to enjoy a considerable commercial importance. Alnicos are alloys of Al, Ni, Co and Fe with minor additions of other elements. They were the first magnets to be aptly designated as permanent, because of their resistance to stray magnetic fields, mechanical shocks and elevated temperatures. The most critical step in the processing of the Alnico magnets was the heat treatment of the alloy, which is controlled in such a way as to precipitate a dispersion of the fine, rod shaped Co-Fe particles in a weakly magnetic matrix of Al-Ni-Fe. These fine, dispersed, elongated single domain particles displayed a shape anisotropy significantly greater than their magnetocrystalline anisotropy, which was mainly responsible for the materials coercivity. The Alnico magnets were made in either oriented or unoriented form by applying a magnetic field to orient the particles during their formation. These materials also possessed high remanence and energy product as large as 60-70 kJ/m^3 could be realized commercially. However, they largely suffered from the scarcity and irregular supply of cobalt, with the problem becoming worse on account of increased production.

At the time when researchers were trying to find out a substitute material for Alnico, discovery of Barium and Strontium ferrite magnets came as a welcome relief [6]. Their constituents were much cheaper than less abundant and expensive elements of Alnico, such as nickel and cobalt. So far as practical use of permanent magnets for consumer product is concerned, where economics takes precedence over all other features, the development of ferrite magnets was epoch making at that point of time. These ferrites are hexagonal oxides and are characterized by low remanence and reasonable coercivity. Typical energy product for hard ferrites is about 30 kJ/m^3. Needless to say, discovery of ferrites is regarded as a forerunner of all the future development in this field. This is so, because hard ferrites were the first magnetic materials with the remarkable uniaxial magnetocrystalline anisotropy, resulting in very high intrinsic coercivity. It was, therefore, established that high magnetocrystalline anisotropy was the key to the development of the high performance magnets. Table 1.1 Shows the comparison of different hard magnetic materials [7]

Table 1.1 Magnetic properties of Common permanent magnets

S. No.	Material	B_r (mT)	${}_iH_c$ KA/m	$(BH)_{max}$ KJ/m^3
1.	Alnico	650	40-45	42-45
2.	Ferrites	350-400	240-320	27.5-31.5
3.	Sm Co	1050-1150	880-1360	145-160
4.	Nd-Fe-B	1200-1300	800-1200	210-250

1.2 Different types of magnets

Magnets can be classified in the following ways:

1.2.1 Temporary Magnets, Electromagnets
1.2.2 Hard Magnets and Soft Magnets
1.2.3 Bonded and Sintered Magnets

1.2.1 Temporary Magnets, Electromagnets

The materials or alloys which can be magnetized or demagnetized easily even in weak magnetic field are called temporary magnets. Soft iron and certain iron alloys such as perm alloy (a mixture of iron and nickel) can be very easily magnetized and demagnetized.

Electromagnets are the strong magnets. These are produced with the help of electricity ac or dc. These are produced by placing a metal core (usually an iron alloy) inside a coil of wire carrying current. The electricity in the coil produces magnetic field. Its strength depends upon the strength of electric current and the number of coils of wire. Its polarity depends upon the direction of the current flow. While the current flows the core behaves like a magnet, but as soon as the current stops, the magnetic properties are lost. Electrical motors, television, maglev trains, telephone; computers are the modern devices which do make use of electromagnets.

1.2.2 Hard Magnets and Soft Magnets

The magnetic materials can be broadly divided into two groups, viz., the magnetically soft and magnetically hard materials. Magnetically soft materials are easy to magnetize and demagnetize and retain their magnetization only in the presence of magnetic field and get demagnetized on removing the magnetic field. Hard magnetic materials are difficult to magnetize and demagnetize, and retain magnetization even after removing the magnetic field. Once magnetized, hard magnetic materials continue to provide a useful magnetic flux, without the aid of external electrical or magnetic input. The distinguishing characteristic of the soft magnetic material is high permeability and it is mainly this flux multiplying power that makes them suitable for their application in machines and devices. Magnetically hard materials on the other hand are made into permanent magnets, where a high coercivity is the primary requirement, because once magnetized a permanent magnet must resist the demagnetizing action of stray field including its own. The basic difference between the two types of materials is best described by the hysteresis loop i.e., the figure 1 showing hysteresis loop for hard and soft magnetic materials. The soft magnetic materials show a narrow hysteresis loop so that the magnetization follows the variation of the applied field nearly without hysteresis i.e., without significant loss. For permanent magnetic materials an exactly opposite characteristic is observed as they exhibit broad hysteresis loop, representing the amount of magnetic energy that can be stored in the material.

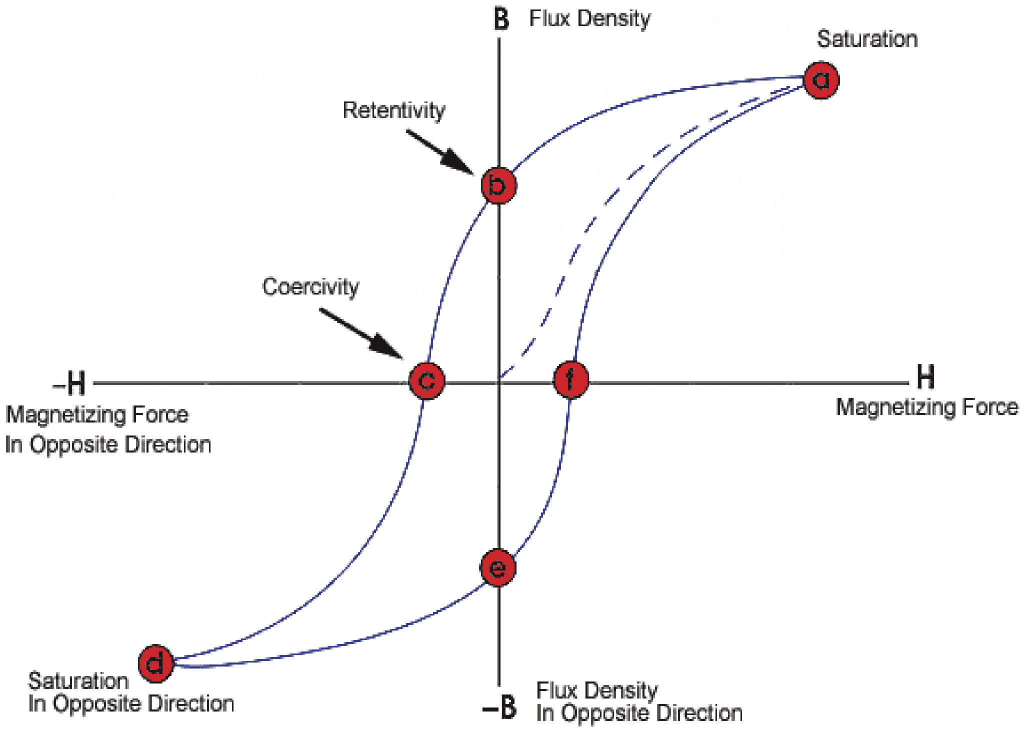


Fig. 1.2 Hysteresis loop for soft and hard magnetic materials [8]

The permanent magnets exhibit a very high resistance to demagnetizing fields and possess sufficiently high magnetic flux output to provide effective and stable magnetic fields without any operating cost. They are, within a limit, insensitive to temperature effects, mechanical shocks and demagnetizing fields. The practical importance of hard magnetic materials stems from their ability to act on other ferromagnetic materials without contact, either by attracting or repelling them.

Among the hard magnetic materials the hard ferrites and Rare earth magnets are having great importance. Hard ferrites having low cost and moderate properties and the rare earth magnets having the high magnetic properties but higher cost. Presently the rare earth magnets are used where the miniaturization is the of primary importance.

Hard magnets can be broadly classified as sintered magnets and plastic bonded magnets. Sintered magnets are produced by ceramic process involving powder preparation, shaping, firing and finishing. The bonded magnets are processed by embedding magnetic powders in non-magnetic binder.

1.2.3 Sintered Magnets

Sintered magnets are the simple magnets which are pure either hard or soft or permanent or temporary or electromagnets. These exhibit excellent magnetic properties in all respect. But in case of bonded magnets these are made from compacted high coercivity powders that are held together by non magnetic binders such as epoxy nylon and polyamide. The big advantage of bonded magnets include the cost effective net shape manufacturing process which can be held to tight tolerance. The disadvantage includes performance and lower operating temperature as compared to sintered magnets. The bonded magnet market has experienced the fastest growth of any permanent industries especially the discovery of Nd-Fe-B magnets. The flexibility of bonded magnets to achieve the desired shape and magnetic properties inherent with it contribute to their success in the market.

1.2.4 Bonded magnets

Bonded magnets were developed by Berman in 1934 in Germany using isotropic Alnico powders and phenolic resins. Bonded magnets as a subset of permanent magnet industry,is itself a very dynamic industry. Many of the fully dense permanent magnet materials, especially those that are sintered, are very hard and brittle and machining them to their final shape is often tedious. This led to an interest in bonded magnets, which are made by consolidating a magnet powder with a polymer matrix. Here machining is easy at the same time production processes also allow parts to be made directly to their final dimensions. Thermosetting binders, such as epoxy resin, are employed for use in compression-molded magnets, thermoplastic binders such as nylon are employed for injection-molded magnets, and elastomers such as rubber are used for extruded magnets.

New products like bio-magnetics, intelligent highway, PM alternator using bonded soft magnetic materials, starter-alternator hybrids are in the process of development. The major drawback to bonded magnet is the reduction in their magnetic properties, relative to those that are 100% dense with magnetic material. Polymer bonded magnets have opened a new world of application opportunities. Thermo-elastomers and thermo-plastic resins can be compounded with a variety of magnetic powders to form Injection Molded, Compression Bonded and Flexible Calendered products. Injection molded magnets can be formed into complex shapes and also can be molded directly onto other components thus reducing assembly cost. Compression bonded magnets, while of simpler geometries, offer higher magnetic output. Flexible sheet and strip is used in many applications including small motors, flexographic (printing) devices, magnetic filtering and signs.

For bonded magnets, powder magnetic properties, loading factor, and molding characteristics are important to obtain high $(BH)_{max}$ magnets. In addition to $(BH)_{max}$, the flux aging loss and thermal stability of magnets are important to applications that may be exposed to elevated temperatures. It is important to establish the thermal characteristics of both powder and polymer binder to obtain high $(BH)_{max}$ bonded magnets with desired characteristics.

Among the class of bonded magnets, bonded ferrites and bonded NdFeB is widely used. A brief description of both the bonded magnet is given below

1.2.4.1 Bonded Hard Ferrites

Bonded magnets are also called as composite materials. Hard ferrite powder is embedded in non-magnetizable magnets. In case of composite materials, the different properties of two component materials are united in one constructional element, producing new technological possibilities. Bonded hard ferrites are only used for those applications where this relatively low magnetic level is acceptable because the volume fraction of the magnetic phase is smaller than in the compact hard ferrites, thus resulting in reduced magnetic properties. Some of the advantages of composite materials (bonded ferrites) are formability, low cost and improved non magnetic properties result i.e. in terms of elasticity, strength, resistance to fracture and impact, dimensional tolerance, lower density, shaping and further processing can be fully exploited for these magnetic composite materials. Only organic materials are used for the matrix on large scale. Common materials are rubber, poly vinyl chloride (PVC), polyamides (PA), polyolefins (e.g. polyethylene and polypropylene), polystyrene, phenol and polyester resins. Inorganic materials such as metal and glass have also been proposed but there is not any practical demand for them and the use of inorganic materials is more expensive [9].

1.2.4.2 Bonded NdFeB

In the early 1980s, an important discovery was made, which modified R_2Fe_{17} to the ternary compound $R_2Fe_{14}B$, which has tetragonal crystal symmetry and strong uniaxial magnetocrystalline anisotropy. $Nd_2Fe_{14}B$ is the basic compound for the modern family of permanent magnets known as iron-neodymium-boron. Many practical applications require the properties of NdFeB magnets to be stable at higher temperatures [10]. The Curie temperature for these is slightly greater than 300 °C. For the production of NdFeB magnets reduction/diffusion methods are used widely. A melt spinning or rapid quenching method is also used for the production of NdFeB powders.

Bonded neodymium iron boron magnets are manufactured using both injection and compression molding techniques. They are composite materials consisting of melt spun NdFeB dispersed in an engineering thermoplastic or thermoset matrix.

Epoxy resins are most widely used in compression molding. The proportion of NdFeB powder to polymer matrix can be varied to achieve the desired level of magnetic performance. Very high volume fractions of the magnetic powders are possible.

Injection molding uses polyamides, or polyphenylene sulphide for higher operating temperatures. NdFeB is susceptible to corrosion, but the polymer matrix used in injection molding contributes too much better corrosion resistance when compared to fully dense sintered Neodymium. This better corrosion resistance is attributed to the fact that corrosion beyond the surface of the material is prevented by the polymer matrix, and as a result injection molded magnets do not require coatings. However, for compression molded Neodymium products, a coating is recommended because of the degree of inherent porosity.

Processing begins with the controlled mixing and dispersal of the NdFeB powder into molten thermoplast or thermoset matrix material. This mixing can be conducted using highly specialized compounding equipment due to high volume fraction of filler being used. Additives can be incorporated at this stage to influence compound properties and behavior. The resulting compound can be in palletized form as feedstock for the injection molding process and in the powder form for the compression molding process. Magnet production can be carried out on adapted injection molding machines, often operating fully automatically. Shapes with a high degree of complexity can be produced, for example, gears, snap fits and undercuts. It is possible to incorporate shafts, bushes and other inserts into the process there by greatly simplifying magnetic assemblies.

Compression molding is carried out by axial pressing. The process can be handled manually or fully automatically with statistical process under control for consistent green density. Components are thermally cured to crosslink the thermoset matrix material and to develop mechanical properties in the component. Magnetic properties can be higher than those produced by injection molding, and tooling costs are lower, although more shape complexity is possible through injection molding.

Precise dimensional control is achieved in both of these processes and usually the component does not require further machining.

1.3 Synthesis techniques for bonded magnets

There are four processes for manufacturing bonded magnets. These processes are calendaring, injection molding, extrusion, and compression bonding. The first three are thermoplastic compound, which is a mixture of magnet powder and binder.

Calendaring:

It is the forming of continuous strip by processing of material between rollers. This strip may be up to several hundred feet long. Typical thicknesses are from 0.012 to 0.250 inch.

Magnet powders are mostly ferrites though some neo and ferrite/neo hybrids are also used. Applications are diverse include micro motors, printing platens, automotive transmission chip collectors, and a wide range of holding applications.

Injection molding:

It is the process of forcing the heated compound through channels and into mold cavities where it is allowed to cool and harden. The mold is opened and the parts are removed. Many magnets can be formed to precise dimensions in each machine cycle. Ferrite, neo, samarium cobalt are commonly used. Both calendaring and injection molding use magnet powder up to about 70% volume ratio and remaining is the binder. In calendar product the high binder content is required for strength and to allow bending/flexibility. In an injection-molded product, an adequate binder is required to allow plastic flow through the mold channels and to provide thorough filling of the mold cavity. Magnetic performance is reduced by the dilution effect of the binder.

Extrusion:

It is the squeezing of the compound through an orifice while controlling and heating of the profile as the compound cools and becomes either firm (flexible end product) or rigid.Magnetic loading in the rigid product can be in the 75 volume percent range. Ferrites and rare earth magnetic alloys are very abrasive. Inexpensive ferrite extrusions are used for gasketing around doors and for advertising signs especially seen on vehicles. Rare earth extruded magnets are usually rigid and are used in motor applications where a long thin walled tube is required.

Compression bonding:

In this magnetic powder is mixed with the binder, usually a thermo set epoxy, flowed in to press cavity and compacted under pressures of about 50 tons per square inch. The compacted magnet is cured at temperatures of about 150-175 °C. One advantage is that the magnetic loading can be as high as 80% by volume, resulting in higher density than calendared, injection molded, and most of the extruded magnets. Applications include motor magnets in arc, cylinder and washer shapes.

1.4 Process Flow Diagram for Processing of Bonded Magnets

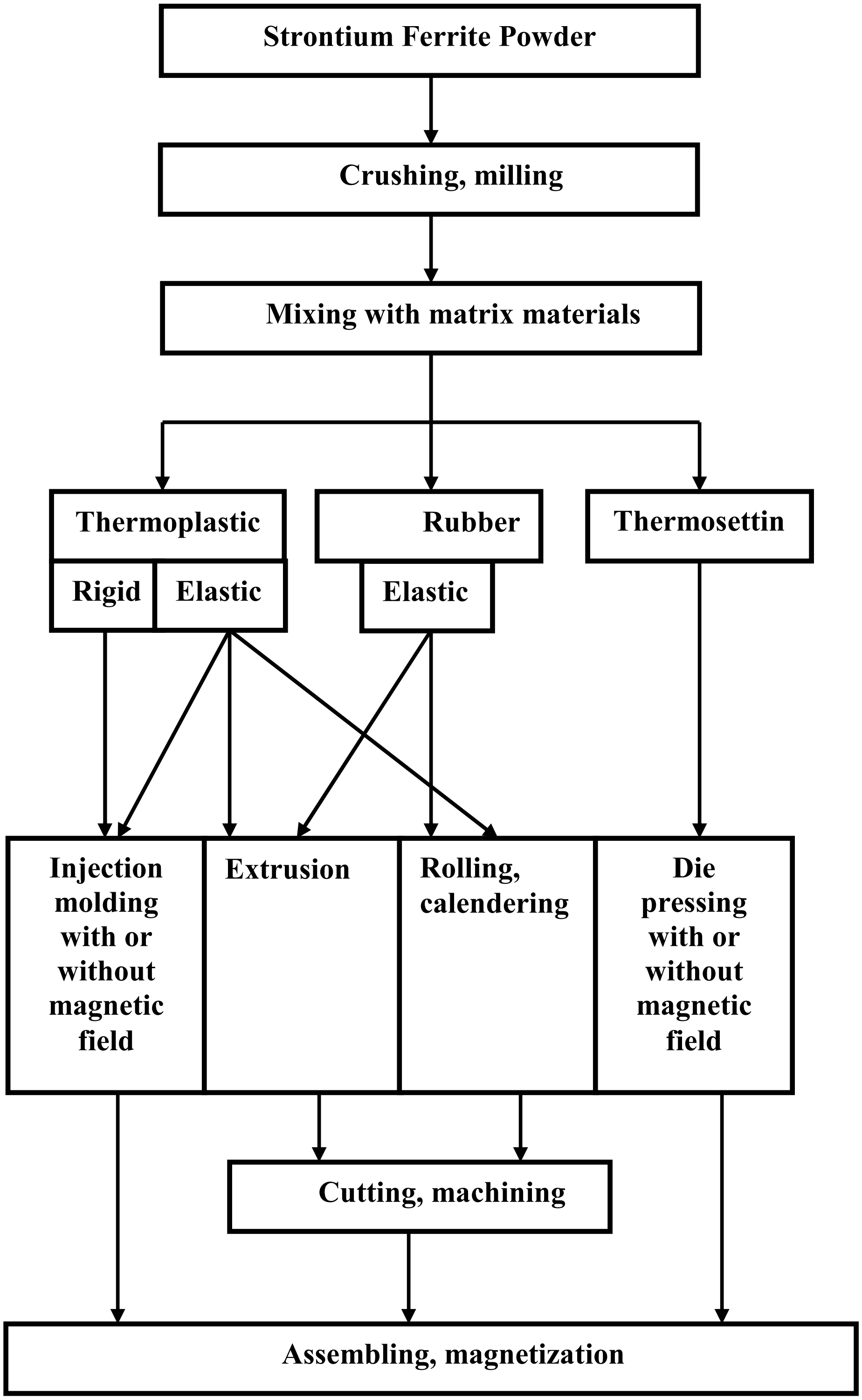


Fig. 2 Schematic process flow diagram for processing SrM of bonded magnet

1.5 Resins for compression molded bonded magnets

Although various resin systems that can be used for making compression molded bonded magnets, which may range from epoxy, acrylic, phenolic or alyllic resins, but epoxy resins are found to be more common. However, there is no information available in published literature with regard to the suitability of different resin systems for operation of magnets in different temperature resins. The typical characteristics of four types of resins viz., acrylics, allylics, phenolics and epoxy, as a class are discussed below.

Acrylics

The most widely used acrylic resins are based on polymer of methyl methaacrylate.

This primary constituent may be modified by co polymerizing or blending with other acrylic monomers or modifiers to obtain a variety of properties.

Acrylics are characterized by crystal clarity, good impact strength, formability and excellent resistance to sunlight, weather and most of the chemicals. Maximum service temperature of heat resistant is about 95 ºC

Table 1.2 Table for the typical properties of Acrylics

Property	**General Purpose Moldings**	**High Impact Moldings**
Specific Gravity	1.18 – 1.19	1.12 – 1.16
Mod. Elastic inTens. 10^5 psi	3.5 – 5.0	2.3 – 3.3
Elongation, %	3 – 5	> 25
Hardness Rockwell	M80 – 103	R100 – 120
Impact strength Ft-lb/ in. notch	0.2 – 0.4	0.8 – 3
Max. service temperature °C	75 – 105	75 - 95
Vol. Res. Ohm-cm	> 10^{14}	2 x 10^{16}
Tensile Strength 1000psi	9.5 – 10.5	5.5 – 8.0
Dielectric Strength V/mil	400	400 – 500

Allylics

Allylics are thermosetting materials. Most important of these are diallyl phthalate (DAP) and diallyl isophthlate (DAIP), which are available in the form of monomers and prepolymers (resins).

DAP resin is the first allylic polymer commercially available as a dry free-flowing white powder. Chemically, it is a relatively linear partially polymerized resin, which softens and flows under heat and pressure and crosslinks to a 3-d insoluble thermoset resin during curing. DAP undergoes an additional type of polymerization in the presence of peroxide catalyst. No water or other volatile fragments are released during the curing reaction.

Allylics exhibit superior electrical properties (insulation resistance, low loss factor, arc resistance etc.) under severe temperature and humidity conditions. Allylics resin exhibit excellent post-mold dimensional stability, low moisture absorption, good resistance to solvents, acids, alkalis, weathering, and wet and dry abrasion. They are chemically stable, have good surface finish, and mold well around metal inserts and can be formulated in pastel colors with excellent color retention at high temperatures.

Table 1.3 Typical properties of Allylics

Property	**DAP**	**DAIP**
Specific Gravity	1.27	1.26
Hardness Rockwell	114 – 116	119 – 121
Impact strength, Ft-lb/ in.notch	0.2 – 0.3	0.2 – 0.3
Max. service temperature, ºC	175	230
Vol. Res. Ohm-cm	$1.7\text{x}10^{16}$	$3.9\text{x}10^{17}$
Tensile Strength, 1000psi	4.0	4.3
Dielectric Strength, V/mil	450	420

Phenolic

Phenolic resins are used extensively as thermosetting materials, there being only a few uses as thermoplastics. The chemical configuration, in the thermoset state, is usually represented by a three dimensional network in which the phenolic nuclei are linked by methylene groups. The basic chemistry can be illustrated by the products formed from phenol and formaldehyde to form products known as resoles. These cure upon heating to form infusible, insoluble polymers commonly identified as single step resins.

The outstanding characteristics of phenolics are: good electrical properties, very rigid set, good tensile strength, excellent heat resistance, good rigidity at elevated temperatures, good aging properties, also good resistant to water, organic solvents, weak bases, and weak acids. All of these characteristics are coupled with relatively low cost.

The largest single use of Phenolic resins is in molding compounds.

The phenolic molding compounds can be divided into general purpose Phenolics or heat resistant grades on the basis of major performance. General purpose phenolics are low cost compounds with fillers such as wood flour and flock, minerals or glass filled compounds.

Table 1.4 Typical properties for phenolics:

Property	**No filler**	**General, wood Flour and Flock**	**Shock Fabric Or Cord**	**Heat res., Glass Fiber**	**Electrical Mineral**
Specific Gravity	1.28	1.34 – 1.4	1.36 – 1.43	1.75 – 1.90	1.6 – 3.0
Modulus Elasticity inTensile, 10^5 psi	7.5 – 10	8 – 13	9 – 14	30 – 33	10 – 30
Elongation, %	-	-	0.40 – 0.55	0.2	6
Hardness Rockwell	M126	E85 – 100	E80 – 90	E50 – 70	E80 – 90
Impact strength, Ft-lb/ in. notch	Nil	0.24 - 0.50	0.6 – 8.0	10 – 33	0.32
Max. service temperature ºC	-	150 – 180	120 – 150	180 – 230	200 – 220
Vol. Res. ohm-cm	10^{11}	10^9 – 10^{12}	>10^{10}	7 – 10x10^{12}	6x10^{12}
Tensile Strength, 1000psi	7.5	5.0 – 8.5	5 – 9	5 – 10	6
Dielectric Strength, V/mil	-	200 – 425	200 - 350	200 - 370	380

Epoxies

Epoxies, known as adhesives, are premium thermosetting plastics, and are generally employed in high performance uses where their high cost is justified. They are available in a wide variety of forms, both liquid and solid, and are cured to form rigid materials by a catalyst or with hardeners containing active hydrogen. They can also be produced in flexible, resilient form. Depending upon type epoxies can be cured at either room temperature or elevated temperature, though heat cure provides better properties in a shorter time. Different curing systems can be used to provide different characteristics in the cured material. Molding compounds are available either as liquids, or as powders with various types of fillers and reinforcements. In comparison with other thermosets, unmodified epoxies are relatively expensive.

As a class, epoxies provide outstanding adhesion to both metallic and nonmetallic surfaces, excellent chemical resistance, low moisture absorption (0.01 to 0.2% in 24 hours), excellent dielectric properties, high strength and relatively good heat resistance. Maximum recommended service temperature generally ranges from 150 to 180 ºC

The different commercial resin systems are formulated by using either singly or various combinations of the following types of basic epoxy resin:

- Bisphenol A based epoxy resin
- Epoxy Phenol – Novolak (EPN) Resins
- Epoxy Cresol – Novolok (ECN) Resins
- Bisphenol F Resins
- Aromatic and Heterocyclic Glycidyl Amine Resins
- Polynuclear Phenol-Glycidyl Ether-Derived Resins

The most widely used epoxy resins are reaction products of epichlorohydrin and polyhydric phenols e.g., diglycidyl ethers of "bisphenol A" mixed with a cross linking agent (hardener) polymerize to a thermosetting liquid [11].

Table 1.5 Typical properties of Epoxies

Property	**Bisphenol a, (molded, mineral)**	**Novolac, (molded, mineral)**
Specific Gravity	1.6 – 2.1	1.7
Hardness Rockwell	101	-
Impact strength. Ft-lb/ in.notch	0.25-0.45	0.3-0.5
Max. service temperature ºC	150-260	230-260
Vol. Res. ohm-cm	$9x10^{15}$	$3x10^{14}$
Tensile Strength. 1000psi	101	-
Dielectric Strength, V/mil	350-400	280-400

1.6 Application of bonded magnets:

Applications of polymer-bonded magnets are becoming increasingly important in our daily lives. High performance bonded magnets are used in various electronic devices, office automation equipment, automotive components, hard disk drives, scanners, CDs, DVDs, sensors, magnetic bearings and other motor or motion related applications. While ferrite still dominates the market, bonded rare earth magnets are becoming more and more important due to their superior magnetic properties. Flexible bonded magnets are used for advertisements and promotional market, a typical application of the flexible magnet is fridge magnet, for this application magnetics are of secondary importance but flatness, printability, visuals are more important. Extruded magnets are used in reprographic magnetic rolls or brushes, which have very different set of performance requirements. Injection molded magnets are used in automotive applications.

1.7 Market Overview

Table 1.6 Global Bonded Market Production

	Flexible Ferrite	**Molded Ferrite**	**Bonded Rare Earth**	**Total**
Japan	$50	$130	$210	$390
US	$105	$45	$40	$190
SE Asia	$15	$40	$50	$105
China	$25	$45	$20	$90
Europe	10	$15	$15	$40
Other	$10	$30	$20	$60
Total	$215	$305	$355	$875

The global production of bonded magnets is shown in table 1.6 given above. The figures used in this table are in millions. From this table it can be concluded that Japan is the largest producer with 44% of the total. The US dominates in flexible ferrite production with 50%[12].

1.8 Outline of the Present Work

In the present work emphasis is given on the Bonded Magnets. Compression moulded bonded magnets are made from strontium ferrite and NdFeB powders. Different binders like PMMA, Fevitite, Solid Epoxy resin, Phenolic resin are tested with different percentages. Effect of different binders, effect of percentage of binders is studied. Magnetic properties like coercivity, retentivity, $(BH)_{max}$ are measured with the help of magnetometer and than compared for different binders and their percentages. Results are plotted and discussed.

Chapter 2

Literature Review

2.1 Bonded Magnet Literature Review

The works on bonded magnets are limited as compared to the sintered magnets. However, various researchers had thrown light on the magnetic properties of bonded ferrites and Bonded NdFeB. A rapidly solidified flake has been found suitable for bonded magnets. The Magnequench company of U.S.A is the main supplier of the rapidly solidified flakes. Most of the research has been carried out using Magnequench flakes. Some of the researcher studied the demagnetization curves by using various binders. Research is also carried out to study the mechanical properties of bonded compact. The present chapter briefly review the research work related to the bonded magnets.

H.Kanekiyo, M.Uehara, S.Hirosan in 1992 studied the effect of additives on microstructure investigated by means of TEM. They calculated that with the addition of Al, Si, Cu, Ga, Ag, and Au grain size reduces considerably which improves hysteresis squareness of the magnetic material $Nd_{4.5}Fe_{73}Co_{3}Ga1B_{18.5}M$. M is the additive Al, Si, Ga, Ag, Au. Material was rapidly solidified. Magnetic properties of resin bonded magnets having density 6.0 Mg/m^3 was fabricated from $Nd_{4.5}Fe_{73}Co_{3}Ga1B_{18.5}$ are B_r = 0.86T, H_{ci} = .31MA/m, $(BH)_{max}$ = 66.1 KJ/m^3 [13,14].

G.J. Tomka, P.R. Bissel, R.W. Chantrell, K.O. Grady in 1993 studied the interaction phenomena in polymer bonded permanent magnetic powders. It was studied from change in remanence curves with change in volume fraction of magnetic filler. Measurement on remanent states indicated that interaction increases rapidly with volume fraction at low volume fraction and slowly at higher volume fraction [15].

A.Z. Liu, I.Z. Rahman, M.A. Rahman and E.R.Petty in 1996 measured the properties of permanent magnets. These permanent magnets are fabricated by mixing NdFeB ribbons and binders epoxy resin under 5-tonn/cm^2 pressure. The ribbons of NdFeB alloy are prepared by melt spinning process. The performance of ribbon quenched at different rates and polymer bonded magnet are investigated by X-Ray diffraction, DTA, SEM, and VSM. The crystal lattice constant of the main phase NdFeB were found to be a=8.75Å and c=12.48 Å. They found that fabricated polymer bonded magnets show excellent physical tolerance, smooth and bright surface. Magnets can be handled for a significant period of time in air without noticeable degradation. They also investigated the effect of annealing at different temperatures and time.

In 1983 J.J. Croat produced a permanent magnet with a BH_{max} of 14 MGOe with NdFeB composition which was fabricated using the melt spinning route. From this technique magnetically hard microstructure can be quenched directly from the molten state.
The microstructure of the resulting product consist of micro crystal lattice less than .1 micrometer in diameter almost 100 times smaller than the grain size obtained in sintered materials owing to its extremely fine structure. This type of ribbon has high thermal stability and after crushing can be formed directly into a variety of bonded magnets by compression or injection moulding techniques. One inherent feature of melt spinning NdFeB is that the magnetic properties are isotropic. As a consequence the remanence and hence energy products are lower than the anisotropic or sintered magnets [16].

Influence of particle size on the magnetic properties of polymer bonded NdFeB magnets was studied by A. Handstein, K.H. Muller, R. Grossinger, H.R. Kirchmayr and R. Krewenka in 1991. They studied that particle size in polymer bonded NdFeB magnets has a remarkable influence on the magnetic properties. The difference is caused by the oxygen content of the powder. Different fractions of particle size obtained by sieving of original and milled MQI- powders were used for preparing bonded magnets were used. Coercivity of compacted powders prepared by milling of melted ingots increases with decreasing particle size. The oxygen content increases monotonously with decreasing particle size. The smaller the particles made from flakes the smaller the nucleation fields for demagnetization modes in the particles. In all cases the increasing oxygen content is accompanied by decrease of remanence [17].

NdFeB has extremely large magnetic force. This material can be obtained at low price because it contains a large amount of iron. However, this type of magnetic material is readily oxidized. Because its major component is iron, the magnetic material will corrode and rust in the presence of water. As a result magnetic force of a resin bonded permanent magnet will be greatly decreased and magnet will destroy itself. Many attempts were made to protect the magnetic powder from oxidation, but no satisfactory anti-rusting properties have been provided. Surface treated magnetic powders with excellent oxidation resistance and excellent moisture resistance is obtained by treating a rare earth iron magnetic powder with a treatment agent containing alkali modified silica particles as a major component [18].

Oxidation resistance of a magnetic material of the Nd-Fe-B type coated with silicon was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques. A special spin-coating technique was used to coat the surface of the magnetic powder NdFeB. The results of TGA and DTA indicate that the oxidation resistance of the surface treated NdFeB powder is markedly improved while its magnetic properties do not change much as compared to those of untreaed material.

The effect of the addition of ferrite powder on magnetic properties of cold pressed Nd-Fe-B bonded magnets was studied by Daniel Rodrigues, Fernando Jose Gomes Landgraf. [7]. They studied that the mixture of ferrite and NdFeB produces hybrid bonded magnets creates the possibility to produce magnets with properties and cost between NdFeB and ferrite magnets. It was concluded that addition of strontium ferrite modifies the shape of demagnetization curve and remanence is also improved considerably [19].

2.2 Recent development in bonded NdFeB magnets

Permanent magnets have been widely used in various applications for many decades to convert electrical energy into mechanical energy or vice versa. Three important features which describes permanent magnets performance are the remanence, B_r, intrinsic coercivity, H_{ci}, and maximum energy product $(BH)_{max}$. In general, magnets of higher

$(BH)_{max}$ require less volume to perform given functions. It is desirable to employ magnets of high $(BH)_{max}$ to miniaturize the design of applications.

High energy magnets based on NdFeB were first reported in late 1983. Much research activity has been devoted to the improvement of the intrinsic material properties and the development of fabrication techniques. The NdFeB type magnet can roughly be classified in two categories, the metallic and bonded magnets. The metallic magnet can either be produced by the conventional alloying casting and powder metallurgy method or by the hot deformation routes. Bonded magnets require a binder to glue to magnetic powders together. A molding step is usually required for bonded magnets.

Majority of NdFeB bonded magnets adopt the rapid solidification to produce powders. To produce bonded magnets, powders are mixed with thermal set or thermal plastic type polymers for compression or injection molding respectively. Recently, extrusion or calendaring has also been used to fabricate NdFeB magnet to serve certain application segments [20].

Chapter3

Experimental Procedure

In the present investigation, the compression molded bonded magnets of Sr-ferrite and Nd-Fe-B alloy are made. The magnetic materials used are strontium ferrite with stoichiometric composition and rapidly solidified isotropic flakes (MQP-D, of nominal composition $Nd_{12.3}Fe_{65.1}Co_{16.6}$ B_6. The Fevitite, Poly Methyl Methacrylate (PMMA), solid epoxy resin, phenolic resin are used as a binder.

The phase and particle morphology was analyzed by X-ray diffractometer (Rigaku, IIIC). and scanning electron microscope(JEOL, JSM 840 A), respectively. The processing of bonded ferrites Sr-ferrite powder is mixed with various resins percent (1-9 %) keeping the total weight percent constant. For the processing of NdFeB bonded magnets, The rapidly solidified flakes of magnequench (MOP-B and MQP-D) were ball milled using planetary ball mill for 10 minute prior to mixing. The ball to charge ratio was 5:1. The mixed charge of strontium ferrite powder and NdFeB with different binders was filled in the cavity of 5 mm diameter die and pressed under magnetic field of 2 T. The compaction pressure was to fixed 500Mpa. The curing was done in the press. The curing time used was 2 hours. The true density values used were: 7.55 gm/cc for Nd-Fe-B, 5.11 gm/cc for strontium ferrite, All magnetic measurements were done using the pulse magnetometer (TC-201). The densities were measured by using dimensions of regular pieces.

Flow Chart for the experimental procedure:

Weigh the magnetic powder and binder were used according to requirement. Let the total weight taken 1000 mg, binder used is 5 % and magnetic powder is 95 %, it implies that 5 % binder equals 50 mg and magnetic powder equals 950mg.

↓

Mix the binder and the magnetic powder properly

↓

Clean the mold cavity with acetone, apply zinc seria to avoid sticking, apply lower punch, put the mixture in mold cavity of 5mm diameter, apply upper punch, put the whole assembly in the magnetizer.

↓

Apply the load of 2 ton to compress the mixture. Before giving the magnetic pulse run water taps and water pump so as to cool the whole system of magnetizer to avoid over heating. Apply magnetic pulse twice to align the particles in the required direction.

↓

Heat the mixtures in mold cavity with the help of heater according to binder used for at most 15 minutes and allow cooling for two hours.

↓

Now before removing the sample apply one more magnetic pulse.

↓

Remove the sample carefully and measure its dimensions i.e. diameter, length, weight for calculating density.

↓

Check its magnetic properties with the help of Pulse magnetometer.

3.2 Brief description about the pulse magnetometer used for measuring magnetic properties

Specification

Functions

- TC-201C Pulse Magnetometer
- It provides a 4-quarter magnetic hysteresis loop.

- Provides the second quarter curves such as J-H, B-H, (B.H)-B.
- Provide magnetic characteristics parameters such as B_r, H_{cj}, H_{cb}, $(BH)_{max}$ in CGS and international units

Accuracy

- Accuracy: B_r: 1-3 %, H_{cj}: 1-3 %, $(BH)_{max}$: 3-5 %.

Maximum magnetizing field strength

- Maximum magnetizing field strength: 4000 KA/m or 50000 Oe

Supply power

- Supply power: 110 V 50/60 Hz 200 VA

Dimensions and weight

- Dimensions: 410*400*150 mm^3 + 410*400*150 mm^3 (except PC and printer)
- Weight: 15 Kg.

Features

- Combine pulse magnetization with measurement.
- High reliability
- Coils can be replaced
- Suitable for both powder and bar sample.
- Simple maintenance
- Enabled eddy correction and self-demagnetization field correction.
- Can measure the sample automatically.
- Can be controlled by personal computer.
- Provide graphic user interface (GUI) based in Microsoft windows.
- Low cost.

Chapter4

Results and Discussion

4.1 Characterization of raw materials

In the present work different binders are used, the properties required and the existing properties of these have been described in previous chapters. Apart from this different magnetic filler materials are used to prepare bonded magnets. The properties of these are described below. Figures 4.1(a), (b), (c) shows the XRD pattern of Strontium ferrite powder, Nd-Fe-B (MQP-B and MQP-D) respectively. The analysis of these diffraction pattern shows that the powders used in the present investigation are having single phase $SrFe_{12}O_{19}$ and Nd_2-Fe_{14}-B phase [21].

The particle size of $SrFe_{12}O_{19}$ powder is of 1μm order. The Nd-Fe-B powder is irregular in shape, with broad particle size distribution. Figure 4.2(a), (b) and (c) shows the micrograph of $SrFe_{12}O_{19}$, Nd-Fe-B (MQP-B and MQP-D) powders respectively.

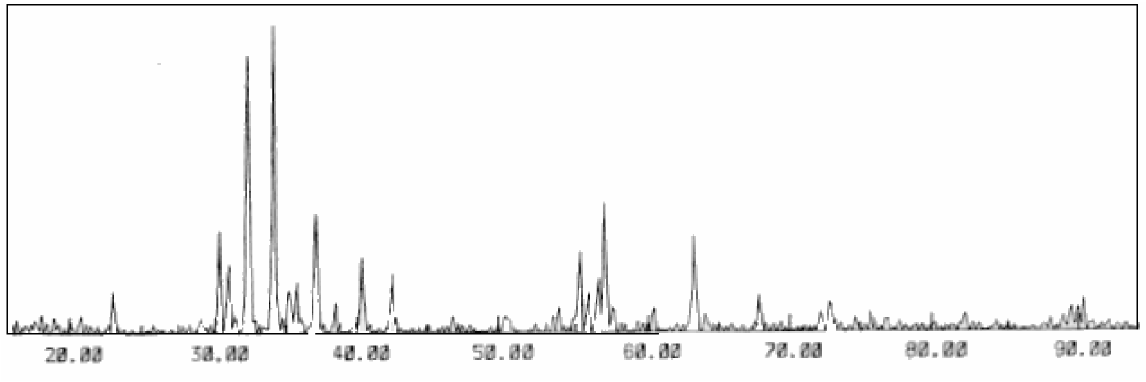


Fig 4.1(a) XRD pattern of Strontium ferrite powder

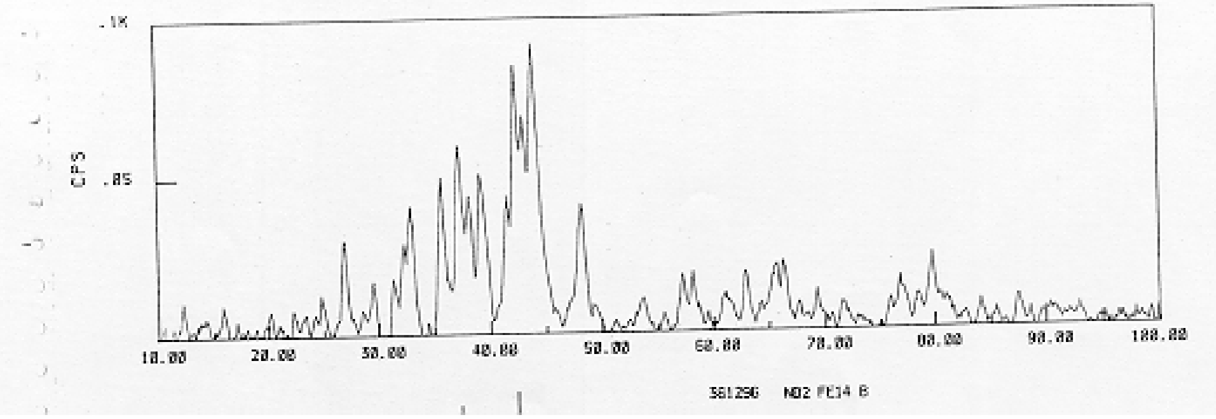


Fig 4.1(b) XRD pattern of MQP-B powder

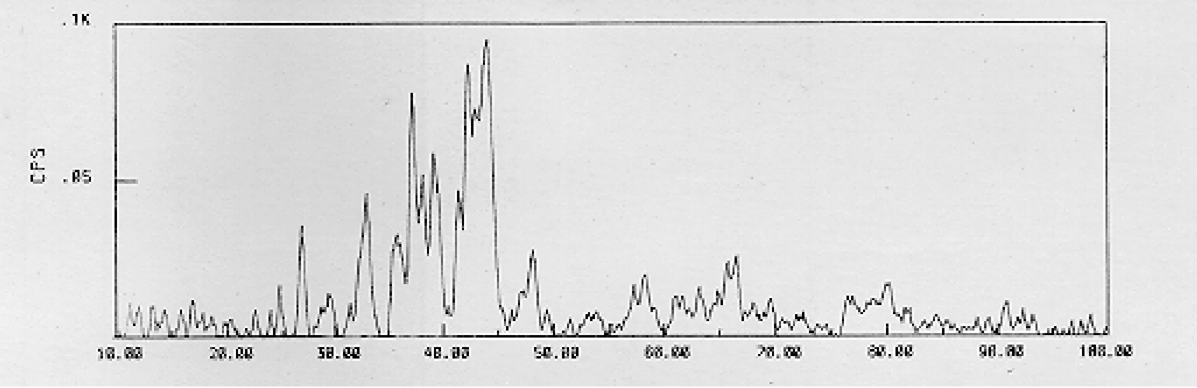


Fig 4.1 (c) XRD pattern od MQP-D powder

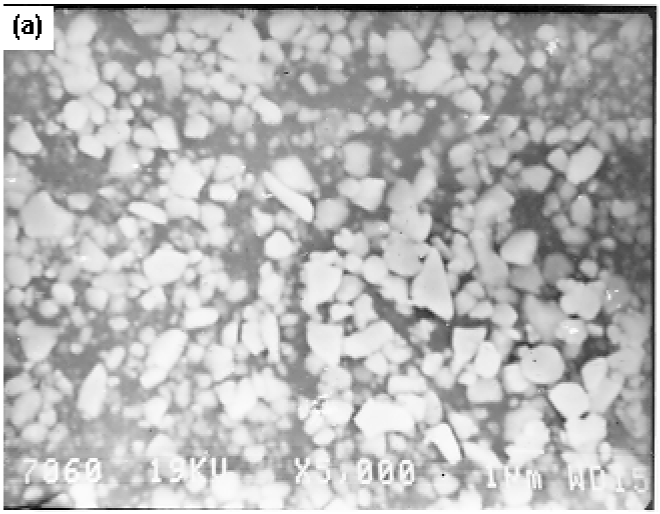


Figure 4.2(a) Micrograph of Strontium Ferrite powder

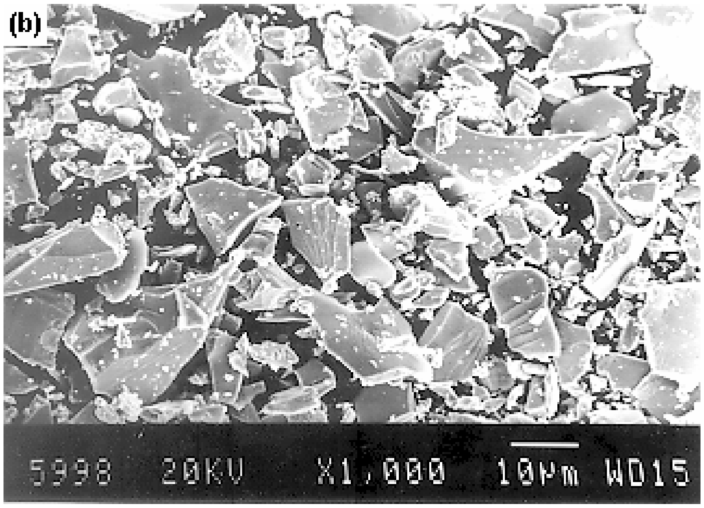


Figure 4.2(b) Micrograph of MQP-B powder

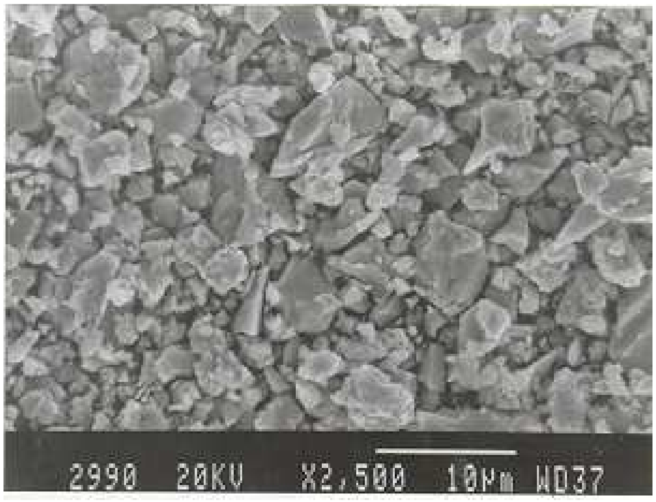


Figure 4.2(c) Micrograph of MQP-D

4.2 Particle size and morphology of Strontium Ferrite and NdFeB powders

Strontium ferrite powder was used for making the bonded magnets which are made in China whose chemical formula is $SrFe_{12}O_{19}$ and brand name is BMS-2.5H. Density of the powder is 5.2 gm/cm^3 and some other typical properties of the powder are as follows.[22-23]

Table 4.1 Magnetic properties of $SrFe_{12}O_{19}$

Magnetic properties	Typical Powders	Minimum values
Br (mT)	360.0	350.0
Hcb (kA/m)	263	247
Hci (kA/m)	302	279
(BH)max (kJ/m^3)	23.9	22.3
Powder size (μm)	.80	.90

Magnequench powders are produced through the process of rapid solidification or melt-spinning. Two grades of Magnequench powders MQP-B and MQP-D were imported and characterized. Density of MQP 'B' is 7.8 gm/cm^3 and density of MQP 'D' is 7.6 gm/cm^3. Magnetic properties of the two powders are given in Table below [24].

Table 4.2 Magnetic properties of Magnequench powders

(Properties are given in both SI units and CGS units for ready reference)

Sample Details	Br - Tesla (kG)	Hcj - kA/m kOe	Hcb - kA/m (kOe)	(BH)max - kJ/m3 (MGOe)
MQP - B	0.82 (8.15)	737 (9.26)	477 (6.00)	88 (11.80)
MQP - D	0.80 (8.0)	844 (10.60)	353 (4.43)	100 (12.5)

Table 4.3 Measured values of MQP ‘B’ and MQP ‘D’ powders

Magnetic Properties	Magnequench ‘B’	Observed Values	Magnequench ‘D’	Observed Values
B_r (Tesla)	.8200	.8310	.8000	.8011
H_{cj} (KA/m)	737	639	844	717
H_{cb} (KA/m)	477	424	353	446
$(BH)_{max}$ (KJ/m^3)	88	97.7	100	91.59
Powder size (µm)	< 5µm	< 5µm	< 5µm	< 5µm

1.3 Effect of Binder percent on the Magnetic Properties

4.3.1 Strontium Ferrite

4.3.1.1 Strontium Ferrite with PMMA Binder

Table 4.4 shows the effect of PMMA binder percent on the magnetic properties of strontium ferrite sintered magnets. Figure 4.3 shows the variation of the magnetic properties with the increasing binder percent. It is evident from the figure that the remanence is minimum at 7 binder percent. The maximum value is obtained at 3 percent. The results are on expected line, as the nonmagnetic phase increases the remanence is observed to decreases. Effect of Binder percent on the coercivities are not remarkable, it is about same for all binder percent. The energy product is found to be minimum at 7 percent. As energy product depends the remanence, so its decrease is similar to remanence.

Table 4.4 Magnetic properties at various binder percent

Binder Percent (%)	B_r (mT)	H_{cj} KA/m	H_{cb} KA/m	$(BH)_{max}$ KJ/m^3
3	154.7	148	92	3.1
5	147.3	149	85	2.7
7	114.5	146	73	1.0
9	151.1	146	91	3.2

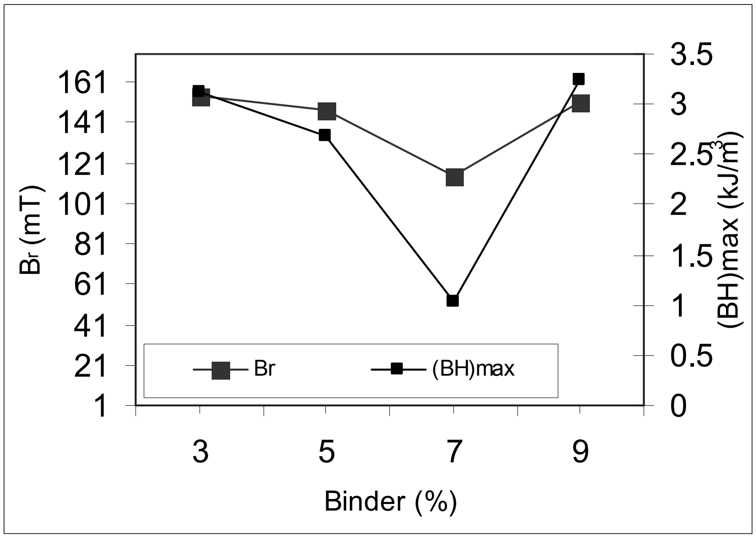


Fig. 4.3 (a) Variation of magnetic properties PMMA binder

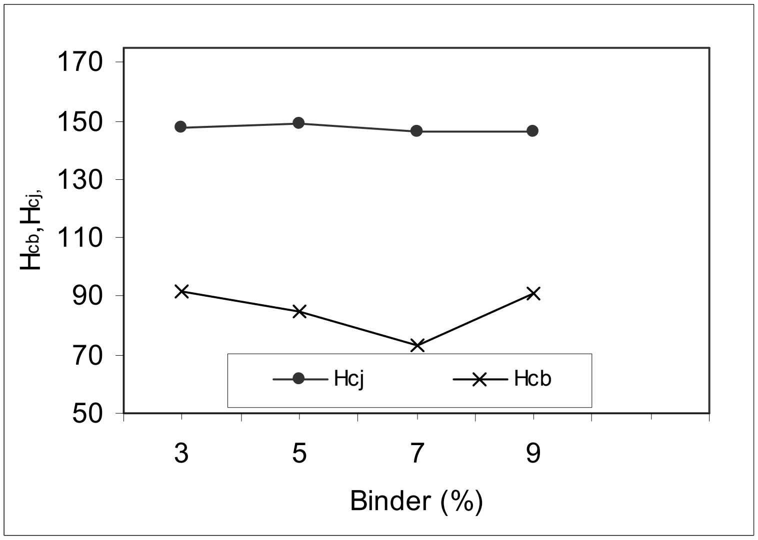


Fig. 4.3 (b) Variation of magnetic properties PMMA binder

4.3.1.2 Strontium ferrite with Fevitite Binder:

Table 4.5 shows the effect of fevitite binder percent on the various magnetic properties of strontium ferrite. Figure 4.4 (a, b) shows the variation of magnetic properties of strontium ferrite with the increasing binder percent. It can be seen from table that remanence changes abruptly with increasing binder percentage from 5% onwards. Similar pattern is followed by energy product. From the table and graph it is seen that binder percent has not much effect on coercivity. It is almost constant.

Table 4.5 Magnetic properties at various binder percent

Binder Percent (%)	B_r (mT)	H_{cj} KA/m	H_{cb} KA/m	$(BH)_{max}$ KJ/m^3
3	173.0	161	98	4.12
5	171.8	152	96	4.1
7	163.0	130	95	3.68
9	160.8	111	92	3.38

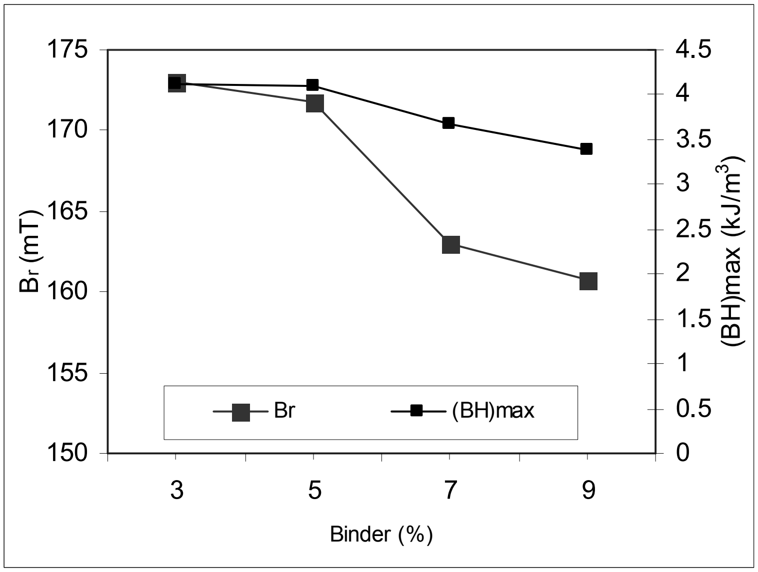


Fig. 4.4 (a) Variation of magnetic properties for fevitite binder

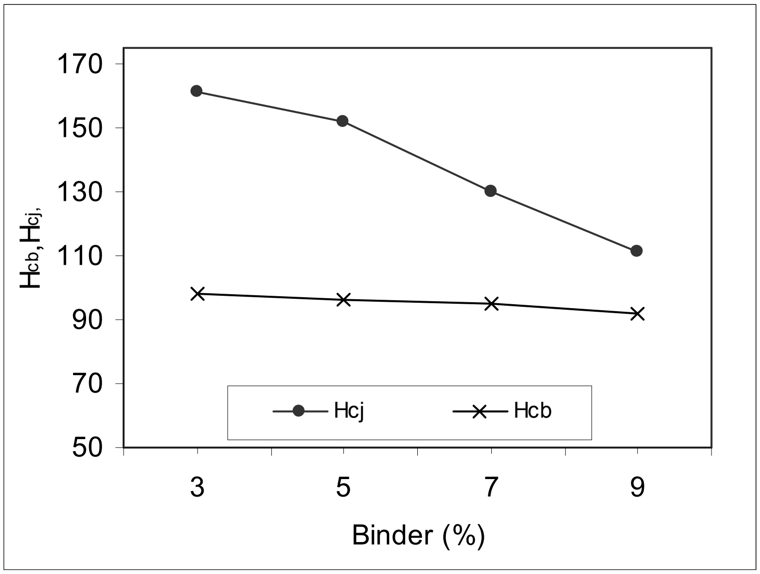


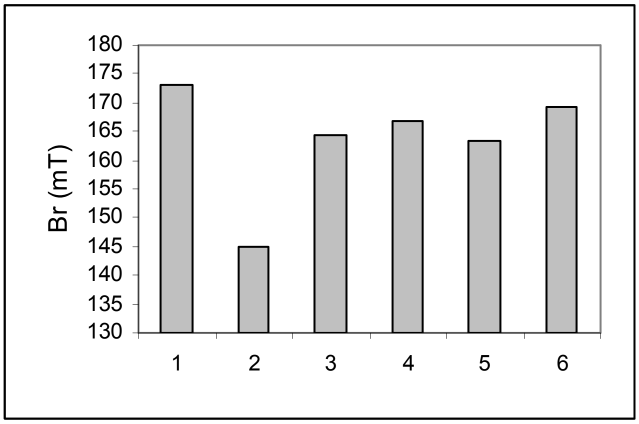
Fig. 4.4 (b) Variation of magnetic properties for fevitite binder

Effect of Different Binders on the magnetic properties

First two tables and graphs show the variation of magnetic properties with increasing binder percentage. Table 4.6 and graph 4.5 (a, b, c, d) shows the variation of magnetic properties with different binders at same percentage. Graphs and tables shows that retentivity is maximum for PMMA binder. Coercivity is maximum for CFPM binder. Energy product is again maximum for PMMA binder.

Table 4.6 Magnetic properties with various binders (5%)

Magnetic Properties	**Binders**					
	Fevitite	PMMA	Phenolic Resin	CFPM	Solid Epoxy Resin 1	Solid Epoxy Resin 2
B_r (mT)	173.0	145.0	164.5	166.9	163.2	169.3
H_{cj} (kA/m)	111.1	149	149	147	149	147
H_{cb} (kA/m)	75	86	97	99	92	99
$(BH)_{max}$ (kJ/m^3)	4.1	2.3	3.9	3.7	3.2	3.9



1- PMMA
2- Fevitite
3- Phenolic Resin
4- CFPM
5- Solid Epoxy 1
6- Solid Epoxy 2

Fig. 4.5 (a) Variation of Remanence for different binders

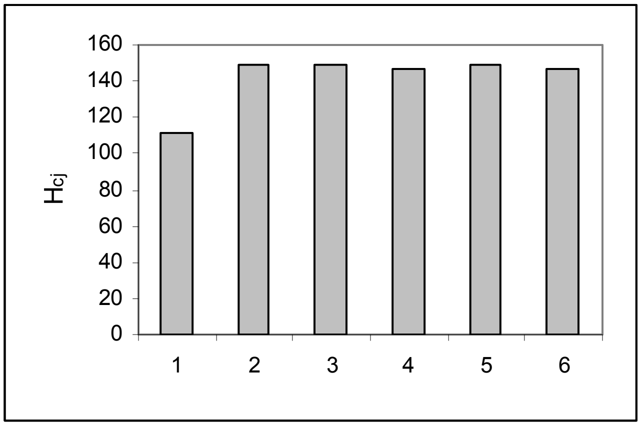


Fig. 4.5 (b) Variation of Coercivity (H_{cj}) for different binders

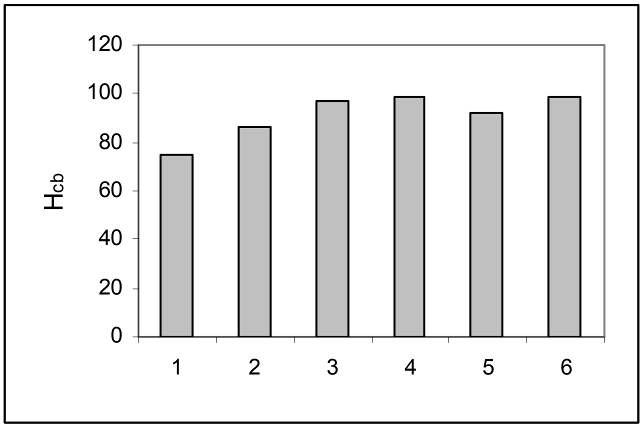


Fig. 4.5 (c) Variation of Coercivity (H_{cb}) for different binders

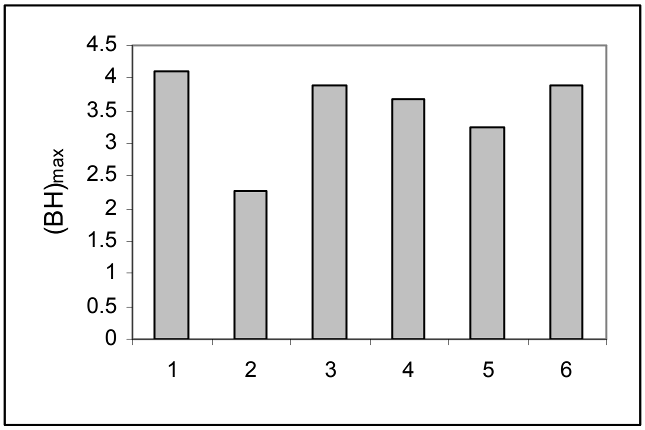


Fig. 4.5 (d) Variation of maximum energy product $(BH)_{max}$ for different binders

From graphs and tables it is seen that retentivity is maximum for fevitite and minimum for phenolic resin. Energy product is also maximum for fevitite and coercivity is maximum for phenolic resin. But when these values of magnetic properties are compared with original values of strontium ferrite powder it comes out to be comparatively very less because of dilution effect.

Table4.7 Magnetic properties with various binders (10%)

	Fevitite	PMMA	Phenolic Resin	CFPM	Solid Epoxy Resin 1	Solid Epoxy Resin 2
Br (mT)	160.8	151.1	137.7	157.2	148.6	148.6
Hcj (kA/m)	150	146	153	145	147	149
Hcb (kA/m)	94	91	86	93	90	89
$(B*H)_{max}$ (kJ/m3)	3.397	3.2	1.96	3.684	3.06	3.17

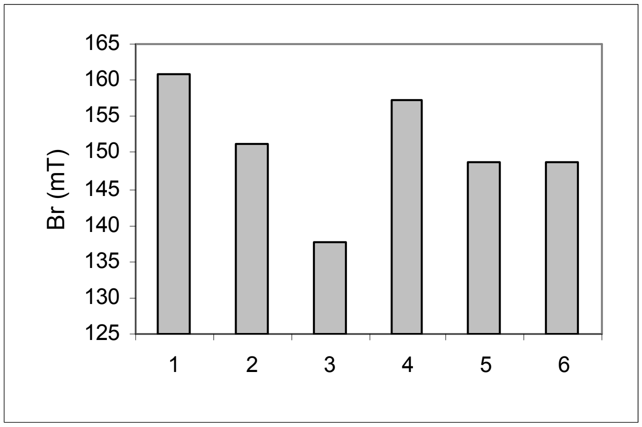


Fig. 4.6 (a) Variation of Remanence for different binders

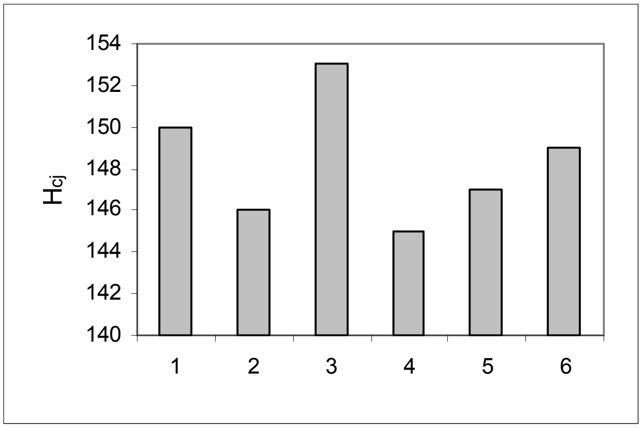


Fig. 4.6 (b) Variation of Coercivity (H_{cj}) for different binders

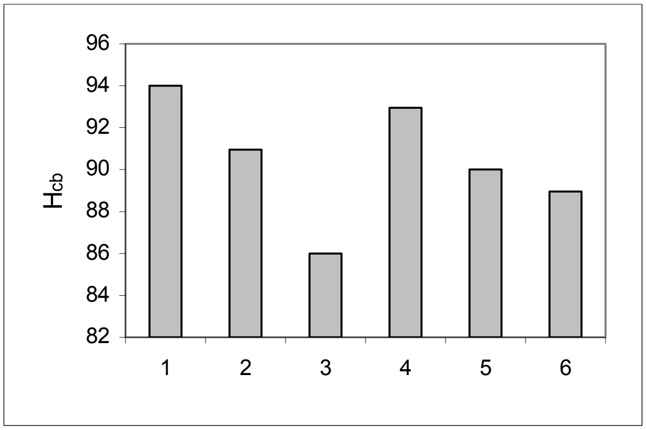


Fig. 4.6 (c) Variation of Coercivity (H_{cb}) for different binders

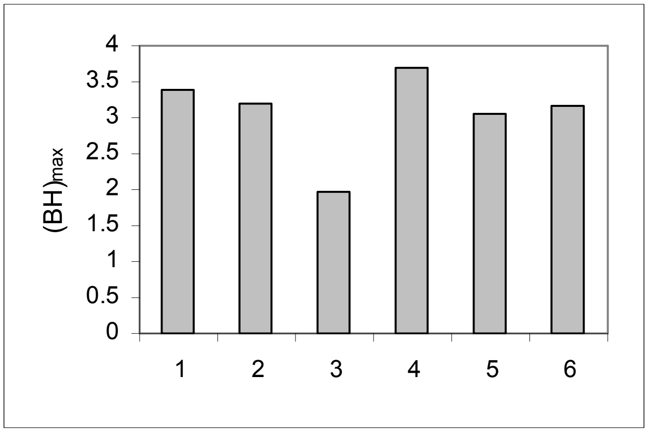


Fig. 4.6(d) Variation of maximum energy product $(BH)_{max}$ for different binders

4.3.2 NdFeB Bonded Magnets

As the rapid solidified NdFeB flakes are expensive, it is not quite feasible to carry out the study with various binders and different percentage. Keeping the above fact we restricted our study with only two binder percent i.e. 5 and 10 %. However, we tried to withdraw the conclusion from the limited experimentation.

Table 4.8 and figure 4.8 (a, b, c, d) shows the variation of magnetic properties of NdFeB with the addition of various binders. It is seen that retentivity is maximum for CFPM binder at 5% and energy product is maximum for solid epoxy. Coercivity is seen to be maximum for PMMA at 5%. These values of magnetic properties are comparatively very less as compared to original values of NdFeB powder.

Table 4.8 NdFeB with different binders and different %age of binders

Magnetic Properties	CFPM		Solid Epoxy		PMMA	
	5%	10%	5%	10%	5%	10%
Br (mT)	577.6	517.9	578.8	487.4	536.3	503
Hcj (kA/m)	517	558	533	527	610	600
Hcb (kA/m)	282	279	287	258	301	276
(B*H)max (kJ/m^3)	41.20	36.82	42.11	31.73	39.87	32.51

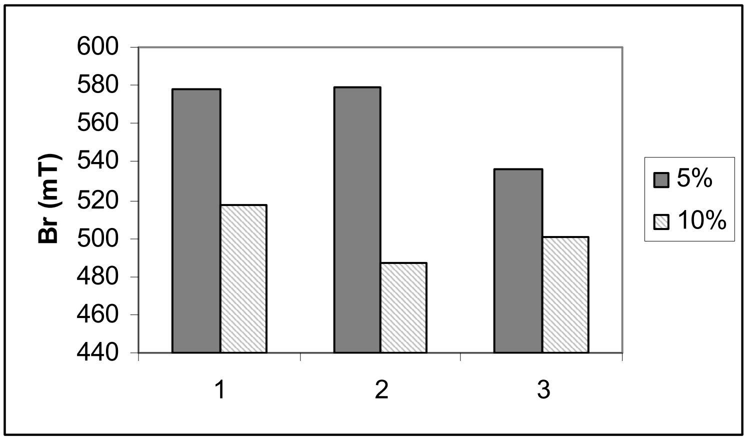


Fig. 4.7 (a) Variation of Remanence for different binders

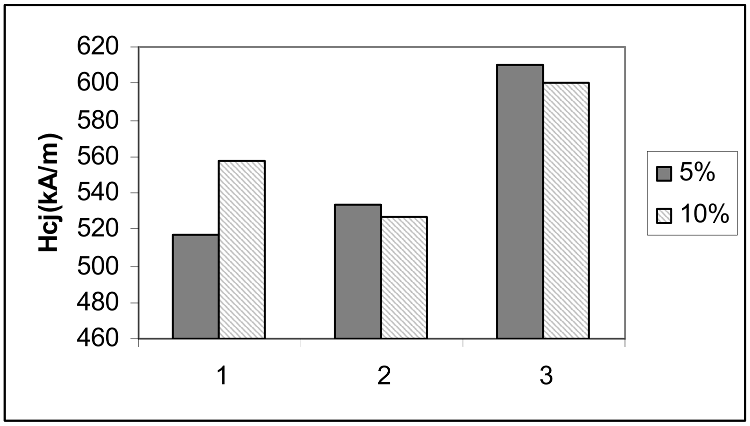


Fig. 4.7 (b) Variation of Coercivity (H_{cj}) for different binders

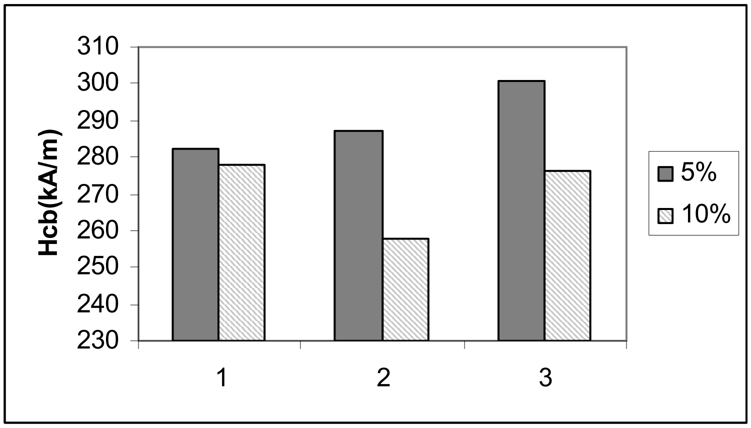


Fig. 4.7 (c) Variation of Coercivity (H_{cb}) for different binders

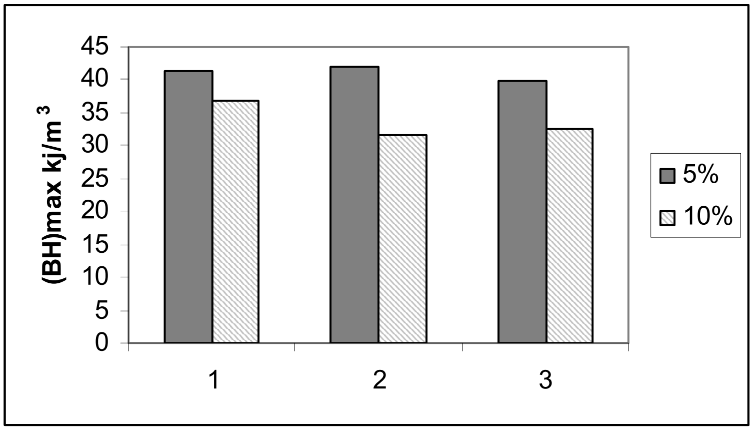


Fig. 4.7(d) Variation of maximum energy product $(BH)_{max}$ for different binders

CONCLUSION

From all above tables, graphs and discussions it can be concluded that magnetic properties of the strontium ferrite and NdFeB bonded magnets decreases considerably with dilution effect. Increasing percentage of binder reduces the magnetic properties. Whatever may be the binder used it reduces magnetic strength of the magnetic material considerably. With increased percentage of binders generally above 5 % magnetic properties mainly retentivity and energy product decreases abruptly. Bonded magnets should be used where one can compromise for its magnetic strength and where magnetic properties are of less importance.

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