

Magnetic Properties of Modified Polyvinyl Alcohol Doped with Some Lanthanides

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Abstract

Polymers are the most important in today's generation. The paper mainly focuses on basic principles of preparation techniques of modified polyvinyl alcohol with Lanthanides the newly synthesized MPVA and doped MPVA. Magnetic properties are determined by Magnetometry (VSM)

INTRODUCTION

The term "Polymer" is derived from the ancient Greek word Polus, meaning "many, much" and meros meaning "parts and refer to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. The units composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The term was coined in 1833 by Jons Jacob Berzelius, though with a definition distinct from the modern IUPAC definition [5]. The modern concept of polymerase covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger for this hypothesis. Polymers are studied in the fields of biophysics and macromolecular science, and polymer science (which includes polymer chemistry and polymer physics). Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science emerging important areas of the science now focus on non-covalent links [18]. Polyisoprene of latex rubber and the polystyrene of Styrofoam are examples of polymeric natural/biological and synthetic polymer, respectively. In biological contexts, essentially all biological macromolecules-1.e. protein (polyamides).nucleic acids (polynucleotides) and polysaccharides-are purely polymeric or are composed in large part of the polymeric compound.[1,7,8]In recent years, studies on the solid polymer electrolytes have attracted much attention in view of their application in electronic and optical devices as well as for fundamental knowledge Solid polymer electrolytes have many advantages such as no leakage, volumetric stability, ease of fabrication of thin films of the desired size, and wide electrochemical stability windows. Many studies have been made to enhance the room temperature ionic conductivities of polymer electrolytes. The conductance in polymer electrolytes. The conduction polymer electrolytes take place through distinct events[16].The first is due to charge migration of ions between the coordinates sites of the host polymer and the second is associated with polymeric chain segmental motion. ionic conductivity of polymer electrolytes is strongly affected by the degree of crystallinity, simultaneous anion motions, and the pair formation. One of the important classes of polymer electrolytes is polar polymer, like polyvinyl alcohol (PVA) which is a semi-crystalline polymer and has a very important application due to the role of OH group and hydrogen bonds. The last 50 years have seen the development of methods for the digital storage of information The current methods for the storage of digital information is predominantly through the use of

magnetic media lowering media storage density continues to be divided into particulate and continuous media. Particulate media comprises of small magnetic particles bonded on plastic tape or disk the thickness of the magnetic overcoat is typically of the order of 10000 Å. Since these are single-domain particles, the information is stored by inverting the magnetization of some of the particles. Continuous media are thin films, typically a few hundred-angstrom thickness. Particulate media are advantageous in that they are relatively simple to prepare and are chemically stable, however, their recording density is relatively low [1,2]. Magnetic materials are classified into two broad categories, soft or hard. Soft magnetic materials are characterized by large permeability and very small coercivity, typically less than 1 Oe. Hard magnetic materials are most often used in permanent magnet applications. In this chapter, the magnetic properties of MPVA and DMPVA are studied. The polymer-coated MNPs are expected to be hydrophilic exterior type having high water solubility and stability. The structural and magnetic properties as well as the spin dynamics of the $\text{NiO}_3\text{ZnO} \cdot 7\text{Fe}_2\text{O}_4$ nanoparticles which are coated by the well-known biocompatible polymer, polyvinyl alcohol have been studied. [42] The vibrating sample magnetometer (VSM), pioneered by S. Foner is a simple yet effective technique for characterizing properties of magnetic materials. Due to its straight forward design and continued use among condensed matter physicists and materials scientists, the VSM provides an ideal laboratory exercise for students in an advanced materials physics course. This setup allows exploration of a common experimental technique for measuring magnetic material properties such as hysteresis, saturation, coercivity, anisotropy. The VSM is one of a number of techniques illustrated in our material physics laboratory courses that emphasizes measurement and characterization of various materials. Polyvinyl alcohol films filled with different concentrations of CuSO_4 were prepared by casting methods, the magnetic properties of these films were intensively investigated. Magnetic nanoparticles/polymer composite was prepared via electrospinning of polyacrylic acid/polyvinyl alcohol aqueous solutions with homogeneously dispersed magnetite Fe_3O_4 nanoparticles. Thin films made from a composite of the polyvinyl alcohol and cobalt oxide nanoparticles were fabricated by spin coating.

PREPARATION OF POLYVINYL ALCOHOL DERIVATIVES

This chapter focuses mainly on the fundamentals and basic principles of the preparation techniques of modified polyvinyl alcohols and doped modified polyvinyl alcohol and the characterization tools which are used in the present investigation [19]. The characterization techniques include structural, thermal, fluorescence and magnetic characterization methods used to characterize newly synthesized MPVA and doped MPVA. The structural characterization includes X-ray diffraction (XRD), Fourier Transform IR Spectroscopy (FTIR), Nuclear Magnetic resonance spectroscopy (NMR), UV-Visible spectroscopy, scanning electron microscopy (SEM), Thermal properties (TGA), Electrical properties. Fluorescence properties and vibrating sample Magnetometry (VSM) is used to investigate the magnetic properties. Modification of polyvinyl alcohol is of special interest because, the introduction of these groups in polymer matrix changes the physical properties, electrical conductivity, and many other properties of PVA. Polyvinyl alcohol has excellent film-forming, emulsifying, and adhesive properties with high tensile strength and flexibility [40]. Moreover, it is nontoxic. In the present research work, synthesis and characterization of modified PVA polymer have been focus due to their wide range of applications in various fields of human interest. We have undertaken synthesis of modified polyvinyl alcohol materials by using

- Hydroxyethylation,

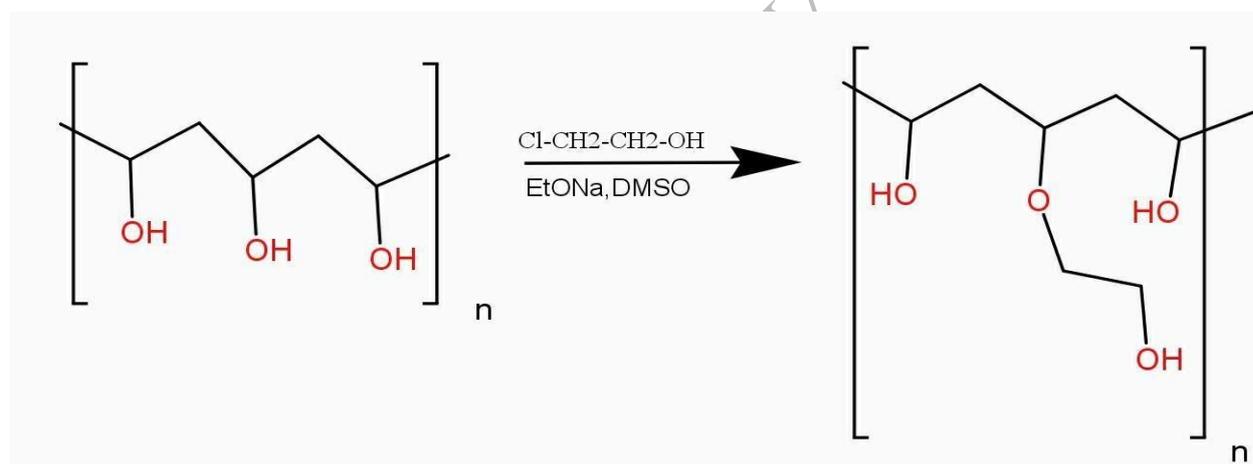
- Carboxymethylation,
- Chloroacetylation and
- Acetalysation

1. Hydroxyethylation of PVA with Chloroethanol

Chemicals Required: Na metal, ethanol, anhydrous DMSO, Chloroethanol

Procedure:

In 200 ml ethanol the amount of 10 g of Na metal was dissolved. The excess of ethanol was evaporated in vacuum. The remaining sodium ethoxide was solubilized into 200 ml of anhydrous DMSO under nitrogen, and 14 g of PVA was added. The mixture was stirred vigorously to give a gelatinous product. The residual alcohol was removed under vacuum. The resulting sodium polyvinyl alcoholate was dissolved in 200 ml DMSO and 26 ml of freshly distilled chloroethanol was added. The mixture was stirred 5 hours at 90 °C temperature. The polymer solution was precipitated into methanol to give a flocculent white solid.



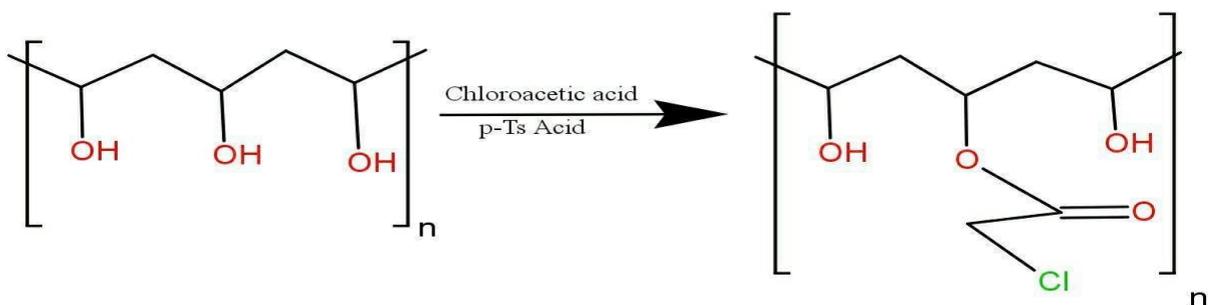
Hydroxyethylation of PVA with Chloroethanol

2. Chloromethylation of PVA with Chloroacetic acid

Chemicals Required: PVA, toluene sulphonic acid, 1,2-dichloroethane, Chloro Acetic acid, ethanol, Na₂CO₃.

Procedure:

40g PVA and 8 ml para-toluene sulphonic acid were dissolved in 200 ml 1,2-dichloroethane at 110°C. To this solution was added 70 ml of Chloroacetic acid. The mixture stirred at 90 °C for 1 hour. After cooling to room temperature, the polymer was precipitated by ethanol, dissolved in a solution of sodium carbonate in acetone and precipitated [2] several times into ethanol



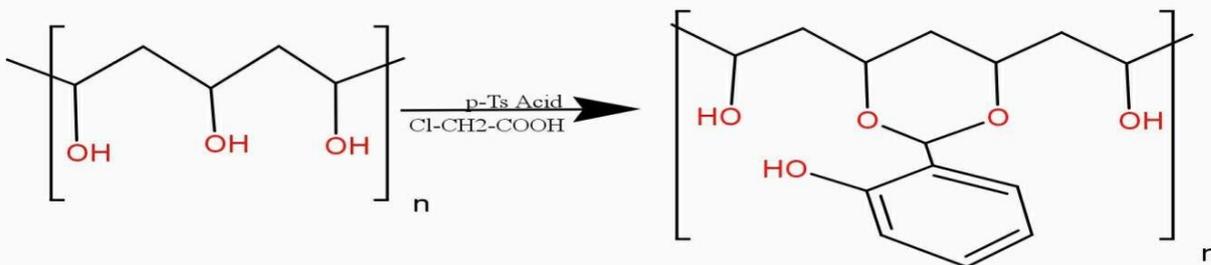
Scheme-2.2: Chloroacetylation of PVA with Chloroacetic acid

3. Acetalysation of PVA with Salicylaldehyde

Chemicals: PVA, salicylaldehyde, 5% aqueous H_2SO_4 DMSO, and methanol.

Procedure:

A mixture of 20 g PVA, 32 ml salicylaldehyde, and 20 ml 5% aqueous H_2SO_4 in 200 ml water was stirred at 60 °C for 4 hours. The precipitated polymer was filtered and dissolved in DMSO. The polymer solution was reprecipitated [2] by a large amount of methanol.[14]



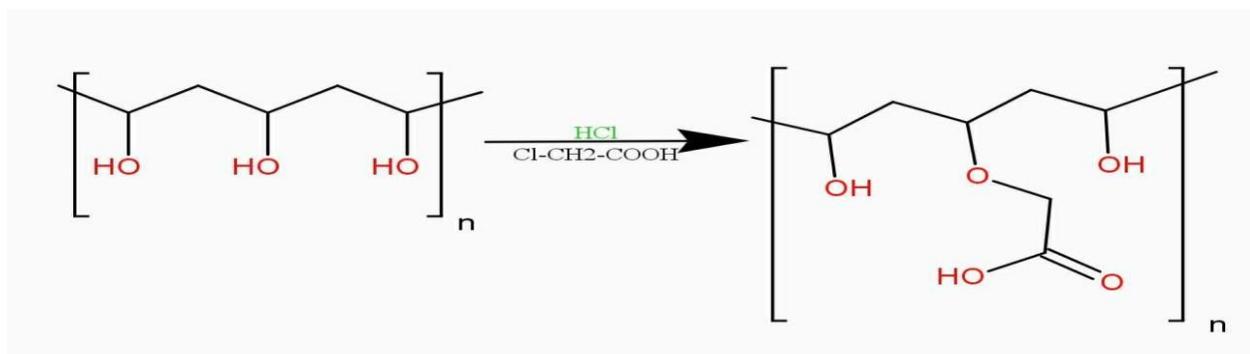
Acetylation of PVA with Salicylaldehyde

4. Carboxymethylation of polyvinyl alcohol with MCAA

Chemical Required: PVA, aqueous potassium hydroxide, monochloro acetic acid, 0.1 N hydrochloric acid, methanol.

Procedure:

The 20 g PVA was dissolved in 100 ml of aqueous potassium hydroxide solution and heated in a water bath for half-hour, 50 ml of MCAA was then added and reaction mixture was stirred at 90° C for 1.5 hours. At the end of the reaction the mixture was acidified with 0.1 N hydrochloric acid. The product was precipitated with methanol. It was then dissolved in distilled water and reprecipitated [2] from the solution using methanol. The process was repeated until the polymer became free of chloride ions.[17]



Carboxymethylation of Polyvinyl alcohol with MCAA

Doping of modified Polyvinyl alcohol

For the doping of modified polyvinyl alcohol like hydroxy ethylated of PVA (HEPVA) and carboxymethylated polyvinyl alcohol (CMPVA), La(III), Pr(III), Nd(III) and Sm(III).lanthanide metal salts (oxide) is used as a dopant. The term "doping as applied to organic semiconductors does it really to the organic semiconductor field because the processes are fundamentally different. The term widely applied to polyacetylene and other organics. Doping of the polymers may be done by the following methods [13].

1. Gaseous doping
2. Solution doping
3. Electrochemical doping.
4. Self-doping
5. Adiation-induced doping.

In gaseous doping, polymers are exposed to the vapours of the dopant under low pressure. In the solution method, the dopant is dissolved in the appropriate solvent in which all the products of doping are soluble. Only low-level doping is achieved by this method. In electrochemical doping both polymerization and doping occur simultaneously. In self-doping process, ionizable groups covalently linked to the polymer chain serve as dopants Doping can also be achieved by irradiating the polymer. High energy radiation is used to augment doping of polymer by neutral dopants, Neutrons radiation, for example, was used for radiation-induced doping of thiophene by iodine. In the presentation investigation doping of the metals can be carried out by the solution casting method [3-7].

Solution casting method for doping of MPVA:

Hydroxy ethylated polyvinyl alcohol (PVA) and carboxymethylated ial in this polyvinyl alcohol(CMPVA) were used as a matrix polymeric material in this research with high purity, the aqueous solution of this HEPVA and CMPVA was prepared by dissolving HEPVA and CMPVA in a methanol and stirred by magnetic stirrer for about one hour until HEPVA and

CMPVA were completely dissolved. La (III), Pr(III), Nd(III) and Sm(III) Lanthanide metals salts (oxide) were dissolved in methanol. Appropriate mixtures of MPVAs and lanthanides metal salts solution were mixed with stirring by a magnetic stirrer for about one hour at 90 °C. The solution was poured into a flat glass. Homogenous films were obtained after drying the solution in an oven for 24 hours. Samples of thin films of thickness of 1mm.were measured within an accuracy (+0.01mm) by a micrometre.

Magnetic Spectra and Working of VSM

When a magnetic sample is a relative motion with respect to a coil, emf is induced in the coil. Continuous vibratory motion of the sample con induces a sinusoidal electrical signal in the pick-up coil. The position of the pick up coil is usually adjusted to have a maximum induced signal with minimum noise. The induced signal in the pick-up coil is proportional to the frequency of vibrations the magnetization of the sample moves in a magnetic field, it may get retarded due to induction. So, there are possibilities for variation in time-frequency of vibration of the sample inside the pick-up coil in order to maintain a perfect simple harmonic motion with precise frequency techniques usually used to maintain the vibration of the sample boulder. This end mechanism continuously tracks the movement of the sample holder and accurately controls the vibration of the sample. This serve tech vibrating capacitor located beneath the transducer to generate control signal that varies solely with vibration amplitude and frequency. The signal, which is at the vibration frequency, is fed back to the oscillator were compared with the drive signal so as to maintain constant drive output. It is also phase adjusted and routed to the signal demodulator where it functions as the reference drive signal. The signal developed in the pick-up coil is the buffered, amplified, and applied to the demodulator. There it is synchronously demodulated with respect to the reference signal derived from the moving capacitor assembly the resulting de output is analog signal, which depend only on the magnetite of the magnetic moment, and not influenced by the amplitude and frequency drift. The cryogenic setup attached to the sample assembly can be used to study the magnetization of samples at low temperatures. The resulting de output is analog of the moment magnitude alone, uninfluenced by vibration amplitude changes and frequency density. A cryogenic setup attached to the sample permits the temperature studies. [20-25]

MAGNETIC PROPERTIES OF MODIFIED POLYVINYL ALCOHOL

The magnetic properties of modified polyvinyl alcohol (MPVA) samples clearly indicate that the magnetic characteristics are observed in the (MPVA) samples

- 1) The magnetic hysteresis of PVA and MPVA samples are shown in fig .1
- 2) It was found that increase in saturation magnetization with modification of PVA
- 3) The increasing order of saturation magnetization is given below,
CMPVA>ACPVA>CAPVA>HEPVA
- 4) Saturation magnetization of (MPVA) is summarized in Table.1
- 5) It was observed that the coercivity of the samples did not show any variation. Further the coercivity values remained nearly the same for all MPVAs as depicted in fig.2 which were the enlarged central region of the magnetic hysteresis loop.

- 6) The reason for a small enhancement in the coercivity observed in MPVAs is not clear. However, it could be due to the higher shear modulus of MPVAs.
- 7) The remnant magnetization keeps a linear variation with modification again keeping exactly the same characteristics of MPVAs.
- 8) The saturation magnetization of modified polyvinyl alcohol lies in the range of 0.48 to 0.87

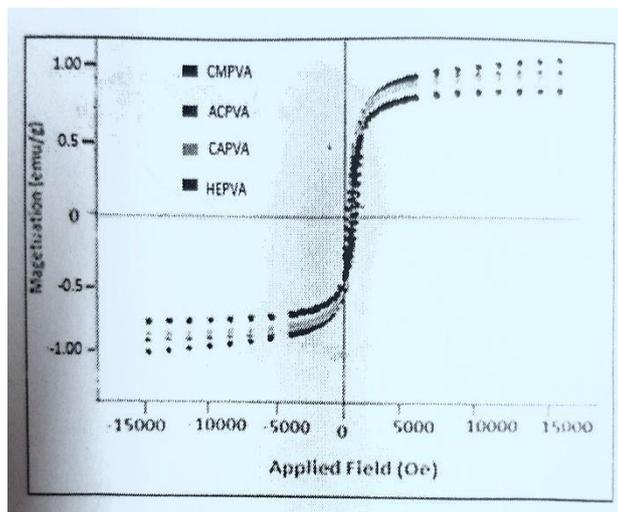


Fig-1: Magnetic hysteresis of PVA and MPVA

S.no	Samples	Calculated Magnetization (mg/g)	Observed Magnetization (emu/g)
1	PVA	0.32	0.30
2	HEPVA	0.57	0.50
3	CAPVA	0.79	0.67
4	ACPVA	0.89	0.75
5	CMPVA	0.96	0.90

Table:1. Observed and Calculated magnetization of PVA and MPVA

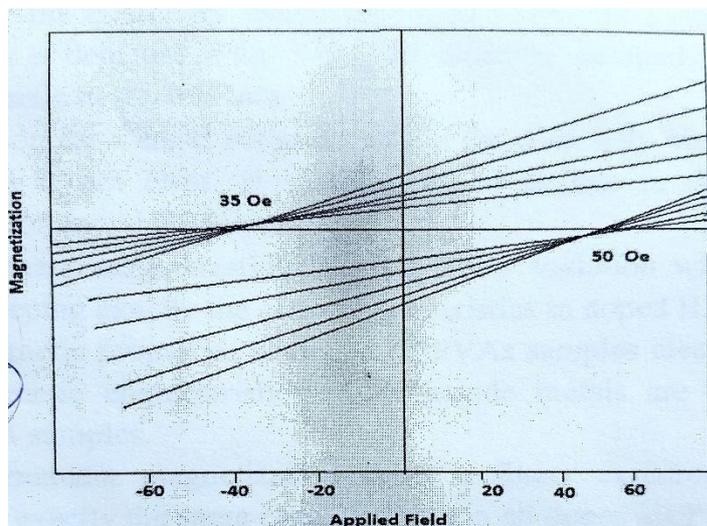


Fig-2: Central region of the magnetic hysteresis of MPVAs showing the Coercivity

MAGNETIC PROPERTIES OF DOPED HEPVA

The magnetic properties of doped HEPVAs samples clearly indicate that the magnetic characteristics are observed in the doped HEPVAs samples

- 1) The magnetic hysteresis of doped HEPVAs samples is shown in fig-3
- 2) It was found that increase in saturation magnetization with doping of HEPVAs with lanthanide metal ions.
- 3) The increased order of saturation magnetization is given,
La(III)-HEPVA > Pr(III)-HEPVA > Nd(III)-HEPVA > Sm(III)-HEPVA > HEPVA
- 4) Saturation magnetization of doped HEPVAs is summarized in Table:2
- 5) It was observed that the coercivity of samples did not show any variation. Further the coercivity values remained nearly the same for all doped HEPVAs as depicted in fig.4 which were the enlarged central region of the magnetic hysteresis loop
- 6) The reason for a small enhancement in the coercivity observed in doped HEPVAs is not clear. However, it could be due to the higher shear modulus of doped HEPVAs.
- 7) The remnant magnetization keeps a linear variation with modification again keeping exactly the same characteristics in doped HEPVAs
- 8) The magnetic properties of doped HEPVAs samples clearly indicate that the magnetic characteristics of lanthanide metals are retained in the DMPVA samples
- 9) The permanent magnetization keeps a linear variation with doping, keeping exactly the same characteristics in all doped HEPVAs [15]

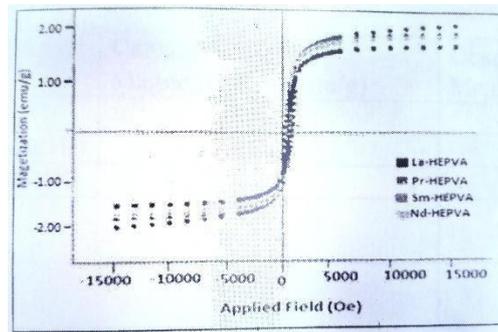


Fig-3: Magnetic hysteresis of Doped HEPVA

S.no	Samples	Calculated Magnetization (emu/g)	Observed Magnetization (emu/g)
1	HEPVA	0.57	0.50
2	HEPVA-La(III)	1.80	1.75
3	HEPVA-Pr(III)	1.60	1.50
4	HEPVA-Nd(III)	1.40	1.30
5	HEPVA-Sm(III)	1.20	1.00

Table:2. Observed and Calculated magnetization of PVA and DHEPVA

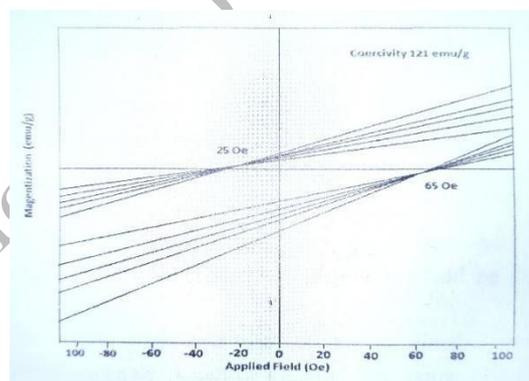


Fig-4: Central region of the magnetic hysteresis of MPVAs showing the Coercivity

MAGNETIC PROPERTIES OF DOPED CMPVA

The magnetic properties of doped CMPVAs samples indicate that the magnetic characteristics are observed in the doped CMPVAs samples.

- 1) The magnetic hysteresis of doped CMPVAs samples is shown in figs 5
- 2) It was found that increase in saturation magnetization with doping of CMPVAs with lanthanide metal ions.

3) The increasing order of saturation magnetization is given.



4) The saturation magnetization of doped CMPVs is summarized in Table:3

5) It was observed that the coercivity of the samples did not show any variation. Further the coercivity values remain nearly the same for all dopes CMPVs as depicted in graph which was the enlarged central region of magnetic hysteresis loop.

6) The region for a small enhancement in the coercivity observed in doped CMPVs is not cleared However it could be due to higher shear modulus of doped CMPVs

7) The remnant magnetization keeps a linear variation with modification again keeping exactly the same characteristics in doped CMPVs [32].

8) The magnetic properties of doped CMPV sample clearly indicate that the magnetic characteristics of lanthanide metal are retained in the doped CMPVs samples [14]

9) The permanent magnetization keeps a linear variation with doping, again keeping exactly the same characteristics in all doped CMPVs.[15]

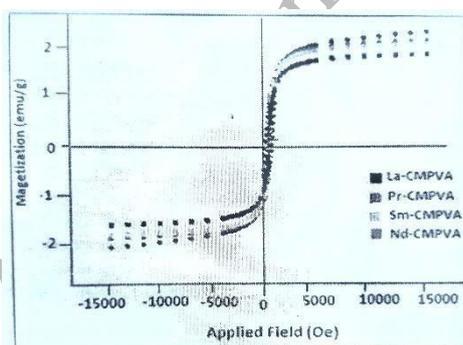


Fig-5: Magnetic hysteresis of Doped CMPVA

S.no	Samples	Calculated Magnetization (emu/g)	Observed Magnetization (emg/g)
1	CMPVA	0.90	0.87
2	CMPVA-La(III)	2.5	2.1
3	CMPVA-Pr(III)	2.0	1.9
4	CMPVA-Nd(III)	1.5	1.5
5	CMPVA-Sm(III)	1.20	1.00

Table: 3. Observed and Calculated magnetization of CMPVA

Result and Discussion:

The magnetic properties of modified polyvinyl alcohol (PVA) samples indicate that the magnetic characteristics are observed in the (MPVA samples).

1) It was found that increase in saturation magnetization with modification of PVA

2) The increasing order of saturation magnetization is given below.

CMPVA>ACPVA>CAPVA>HEPVA

3) The saturation magnetization of (MPVA) is summarized in Table: 1

4) It was observed that the coercivity of the samples did not show any variation. Further, the coercivity values remained nearly the same for all MPVAs as depicted in fig .2 which were the enlarged central region of the magnetic hysteresis loop.

5) The reason for a small enhancement in the coercivity observed in MPVAs is not clear. However, it could be due to the higher shear modulus of MPVAs.

6) The remnant magnetization keeps a linear variation with modification again keeping the same characteristics of MPVAs,

7) The saturation magnetization of modified polyvinyl alcohol lies in the range of 0.48 to 0.87

8) The increased order of saturation magnetization is given.

La(III)-HEPVA>Pr(III)-HEPVA>Nd(III)-HEPVA>Sm(III)-HEPVA>HEPVA

9) The magnetic properties of doped UPVAs samples indicate that the magnetic characteristics of lanthanide metals are retained in the DMPVA samples.

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