A Brief Overview on Ferrite (Fe_3O_4) Based Polymeric Nanocomposites: Recent Developments and Challenges

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Abstract: In this article, we have mainly discussed about ferrite (Fe_3O_4) and its polymer based nanocomposites. Ferrite particles have become an important research material because of their vast applications in the field of biotechnology, magnetic resonance imaging (MRI), and data storage. It has been observed that ferrite Fe_3O_4 particles show best performance for size less than 10-30 nm. This happens due to the super paramagnetic nature of such particles. In super paramagnetic range these particles exhibit zero remanence or coercivity. Therefore, various properties of ferrite (Fe_3O_4) nanoparticles and its polymer nanocomposites are very much dependent on the size, and distribution of the particles in the polymeric matrix. Moreover, it has been also observed that the shape of the nanocrystals plays important role in the determination of their fundamental properties. These particles show instability over longer times due to the formation of agglomerates generated by high surface energies. Therefore, protection strategies such as grafting and coatings with silica/carbon or polymers have been developed to stabilize them chemically. Recently, silylation technique is mainly used for the modification of nanoparticles. Experimentally, it has been observed that nanocomposites composed of polymer matrices and ferrite showed substantial improvements in stiffness, fracture toughness, sensing ability (magnetic as well as electric), impact energy absorption, and electro-catalytic activities to bio-species.

Keywords: Optoelectronic, Ferroelectric, Piezeoelectric, Superparamagnetic, Nanocomposites.

1. INTRODUCTION AND SPECIAL FEATURES OF INORGANIC NANOFILLERS

1.1. Nanotechnology and Nanoparticles

In nanotechnology, we mainly study how to manipulate matter on an atomic and molecular scale [1-3]. The nanofiller include nanoparticle, nanorod, nanowires and nanotubes. Physical properties of nanoparticles in a range of 1-100 nm are different from those of non-nanoscale particles even with identical chemical composition. The important issue is that do the nanoparticles have characteristic properties affecting either exposure or hazard that are basically disparate from those with bigger particles with similar composition? So, it is still an open ended query. Nanotechnology extends from conventional device physics to totally novel methods based on molecular self assembly [4]. It provides an opportunity to develop novel materials having dimensions on the nanoscale and to establish better control on the matters in atomic scale. In 1980s emergence of nanotechnology was due to the congregation of experimental progress like creation of scanning tunnelling microscope (STM) in 1981 and the invention of fullerenes in 1985. The word "*nanotechnology*" devised by Taniguchi in 1974 was later adapted by Drexler in his book (Engines of creation, in 1986) [1]. In the recent era, we largely focused on inorganic metal and metal oxide based particles owing to their considerable importance in commercial progress and the concern of their toxicological impacts or hazard [5]. Summing up these facts and characteristics, we can say that in particular sizes (<100 nm) in which novel properties of the matter/particles originates. The nanoparticles shows diverse crystallinity depending on the size and it leads to different final properties of the particles (i.e. not shown by bulk material).

1.2. Size Effect and Thermodynamics

The particles less than 20–30 nm possess extra energy at the surface and show thermodynamic instability [1]. Therefore, different types of crystallographic transformations (i.e. lattice deformations, emergence of imperfections, rearrangements of atoms) generally occur to stabilize them. These intrinsic characteristics of nanoscale particles could influence the fundamental properties of the particles. It can be further comprehended by the size dependency of optical and electronic properties of quantum dots and thermal characteristics of particles [6]. Electric and magnetic properties are also associated with the particle size and crystallites. For example, size-dependent transition temperature for ferromagnetic particles (Fe_3O_4, $MnFe_2O_4$ and $MgFe_2O_4$) is the Curie temperature. The majority of the size effects are observed at the size below 100 nm. Moreover, surface tension (γ) of the particles below 30 nm also changes with size (r). Therefore, derivative ($d\gamma/dr$) has particular

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importance in the thermodynamic models. This fact can be easily understood by the importance of size dependency of γ in physicochemical processes (viz., dissolution and phase transformation). So, it has to be controlled for non-toxicological effects.

1.3. Nanomaterial and Polymer Nanocomposites Based on Inorganic Nanofillers

Nanomaterials are well-known for their distinctive characteristics such as mechanical, thermal, electro-magnetic, optical, specific surface including biological properties [7-9]. This categorizes them as nanostructures, nanobiomaterials, nanobioactivators, nanobiolabels etc. In 1980s, the size quantization idea was developed for semiconductors. In the size quantization process a threshold value characteristic of semiconductors could be achieved by reducing the size of semiconductor particles. This happens due to the higher energy gap (band gap) for smaller nanoparticles. Hence optical spectrum will move toward the shorter wavelength region. As a result, small size particles (< 100nm) possess unique optical and electronic properties.

Earlier the term nanocomposite was not well known and in place of it term hybrid was used. However for the improvement in the characteristics of polymer, inorganic particles had been used as additives [10]. Later term nanocomposites become more attractive field of research. Nanocomposite is a multiphase solid material and properties of nanocomposite (i.e. mechanical, electrical, thermal etc) vary distinctly from constituent materials. However, limit of dimensions for this types of properties probably be given as follows: <5 nm to favour catalytic activity, <20 nm to soften hard magnetic material, <50 nm to alter refractive index and <100 nm to achieve superparamagnetism. Basically, nanocomposites are divided into three main categories such as ceramic, metal, and polymer matrix nanocomposites. In this article, we have mainly discussed about polymer based nanocomposites. Performance of polymer matrix can be improved frequently by simply adding nanoparticles. The final properties depend on the nature and properties of the nanoscale fillers. This approach is mostly effective for the preparation of high performance novel nanocomposites, especially if good distribution of particles in the matrix is attained. Improved characteristics of high performance nanocomposites could be due to the high aspect ratio and specific chemistry of the additives. This is the main motive, why inorganic nanofillers are widely used now-a-days for nanocomposites.

In recent time, lots of works have been done to synthesis various types of polymer nanocomposites and to understand fundamental theories which in turn determine their optical, electronic and magnetic properties [11]. Polymers have importance owing to their several distinctive characteristics such as flexibility, lightweight, simple processing, low cost. The addition of inorganic nanoparticles into a polymer allows combining the characteristics of both nanoparticles and polymer. Consequently, advanced novel functional attributes could be produced towards the polymer inorganic nanocomposites (PINC) [12]. It is found in many papers that polymer-clay composites comprise superior mechanical and thermal properties in compare to pure polymers. Therefore, these types of composites turn into fashionable field of research. It was reported that the first clay based composite was clay/nylon-6 for timing belt covers purpose in Toyota car [13]. There are representative inorganic nanofillers such as metals and metal alloys (gold, silver, copper etc), semiconductors (like lead sulphide and zinc oxide), clay minerals and various oxides (titanium dioxide, silicondioxide, ferrites etc). But the choice of polymer matrix and inorganic nanofillers depends on their applications.

1.4. Optoelectronics

In optoelectronics people generally study the function of electronic devices which detect and control light. It is also called subfield of photonics [14-16]. For this function light may range from high energy (i.e. gamma rays, X-rays, ultraviolet, infrared) to low energy (visible light). Optoelectronic devices are electrical to optical or optical to electrical transducers or machines. At this juncture, we have discussed the link between optics and electronics including their uses. Mechanism that is sending from one end and receiving from other end in an electronic device makes up mainstream of optoelectronic systems. In, sending end any light producing object can be used as depend on the purpose. On the other hand, electronic device such as light emitting diode (LED), a non electronic device can be utilized as light producing object for a receiving tool [17, 18]. LED is employed for many purposes since LED device can be switched on or off many times with little consumption of current and also need low voltage. It is observed that receiving piece of equipment is much temperature sensitive. When light falls on the electronic device temperature of the concern device may vary. This could be the cause of concern for the circuit inside the device. In other words, variation in temperature inside a device is able to activate reactions in a circuit. From past two decades inorganic nanoparticles got more attention as an additive for making polymer based composites [19, 20]. In this types of composites inorganic nanoparticles provide specific optical properties and polymers are utilized to provide favourable processability as well as adequate grip between the nanoparticles [21]. Here size of the particles is crucial characteristic that influences optical properties and applications of the PINC.

1.5. Piezoelectric, Pyroelectric and Ferroelectric Fillers

1.5.1. Piezoelectric

The piezoelectric effect was discovered in 1880 by Pierre and Jacques Curie [22, 23]. They have observed that applying pressure on some crystals like a quartz or ceramic; some charge accumulates on the surface of these crystals and consequentially generates an electric voltage. Therefore, we can say that piezoelectricity is pressure generated electricity, and this effect in crystals is called piezoelectric effect. This effect can be defined as electro-mechanical interaction among the mechanical and electrical state of crystalline material [24]. The whole process is reversible in term of mechanism. For instance, lead zirconate titanate crystals shows piezoelectricity if deformed their structure by 0.1% of the initial dimension. On the other hand same crystals will show alteration of 0.1% to their initial dimension if external electric field applied on the crystals. Piezoelectric effect is useful in the production and detection of sound, generation of high voltages and electronic frequency. At present, various metal used as piezoelectric material such as barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), potassium niobate ($KNbO_3$), gallium orthophosphate ($GaPO_4$), lithium tantate ($LiTaO_3$) and sodium tungstate (Na_2WO_3) including a polymer PVDF (polyvinylidene fluoride) [22, 25]. The PVDF molecules exhibit sufficient piezoelectricity because of its intertwined long chain molecules, which attract and resist each other by applying an electric field.

1.5.2. Ferroelectricity

It is a characteristic of certain materials which possess spontaneous electric polarization that can be inverted by applying outer electric field [26-28]. The term is used parallel to ferromagnetism where material exhibits permanent magnetic moment and polarized linearly by outer electric field. This type of polarization described as dielectric polarization. However, paraelectric material shows nonlinear polarization. The direction of the spontaneous polarization can be reversed by an applying electric field in ferroelectric material. This is unique characteristic of ferroelectric materials. Normally, materials show ferroelectricity below Curie temperature T_c and become paraelectric above T_c. The nonlinearity of ferroelectric materials can be utilized for the preparation of capacitor with suitable capacitance. Hysteresis loop generated by the spontaneous polarization of ferroelectric materials can be utilized to generate memory functions. These ferroelectric capacitors could be used in medical ultrasound machines, high quality infrared cameras, fire sensors, sonar, vibration sensors etc [29, 30]. Word anti-ferroelectricity is the opposite of the ferroelectricity. The relation between these two is similar to the relation between anti-ferromagnetism and ferromagnetism. Anti-ferroelectric material consist well-organized array of electric dipoles but with adjacent dipoles oriented in opposite (anti-parallel) direction. This can be easily differentiated with a ferroelectric material where all the dipoles are unidirectional. In an anti-ferroelectric material unlike a ferroelectric the overall polarization is zero because neighbouring dipoles annul the effect. Now a day's researchers are working in another recent topic which is multiferroics [31, 32].

1.5.3. Pyroelectric

Pyroelectric effect was pointed out by Theophrastus in 314 BC [33-35]. Afterwards research in pyroelectricity gained more attention in the 19th century. In 1824 David Brewster explained the effect. Later William Thomson in 1878 and Woldemar Voigt in 1897 together developed a theory for the mechanism of pyroelectricity [36]. Pyroelectricity is the capacity of materials to produce momentary voltage on heating or cooling. It was observed that changing temperature the position of atoms or molecules in the crystal shifts, which in turn changes the polarization of the material and generates voltage across the crystal. The term pyroelectricity is totally different phenomena as compare to thermoelectricity [37, 38]. In pyroelectricity entire crystal changes from one temperature to another which in turn gives momentary voltage. On the other hand in thermoelectricity both sides kept in different temperature and to produce permanent voltage in the crystal. Recently, thin artificial pyroelectric films were produced to create and stabilize novel devices. Out of many other crystal lithium tantalate ($LiTaO_3$) crystals display the characteristics of both piezoelectric and pyroelectric material [39, 40].

2. MAGNETIC NANOPARTICLE-MNP (Fe_3O_4)

2.1. Introduction

Magnetism has been an intrinsic material characteristic since the genesis of this universe. Recently, magnetic nanoparticles have become important research interest because of their vast application including magnetic fluid catalysis, biotechnology, magnetic resonance imaging (MRI) and data storage [41-43]. The particles have been shown best performance when the particle sizes are below 10-30 nm that is smaller than the average size of magnetic domains. It is observed that superparamagnetic blocking temperature can be controlled by size and size distribution of the particles. At blocking temperature the time of activation over the energy barrier is higher. Then the orientation of the electrons in a specific direction might be blocked. Thus, every nanoparticle turns into single domain and shows superparamagnetism above the blocking temperature. Novel property development has also been observed in the nanometric region. Furthermore in superparamagnetic range, particles exhibit no remanence or coercively. There is no hysteresis loop in the magnetization-demagnetization curve. Moreover, properties of the nanocrystals are also dependent on the shape. Nanomaterials could also be classified according to their dimensions. The basic geometrical motif is zero dimensional (spheres, cubes and polyhedrons), single dimensional (rods and wires), two dimensional (discs, prisms and plate), three dimensional (octahedrons) [44, 45]. These particles show instability (i.e. form agglomerates) over longer times due to the high surface energies. Therefore, protection strategies such as grafting and coatings with silica/ carbon or polymers have been developed to stabilize them chemically [46, 47]. Many appropriate processes were innovated for the preparation of MNPs and can be classified into (i) physical vapour deposition (ii) mechanical attrition and (iii) chemical routes from solution.

A magnetic nanocomposite is one of the essential groups of nanostructural material. Superparamagnetic nanocomposites contains homogenously distributed superparamagnetic nanoparticles inside the polymer [48, 49]. To embed nanoparticles polymers got more attention owing to the wide-ranging properties. For instance, shape memory polymers (SMP) are very much sensitive to external stimuli. SMP having nanoparticles of magnetite can produce shape memory effect by means of inductive heating with electromagnetic fields.

2.2. Synthesis

MNPs can be synthesized by different synthetic methods. In recent time, several publications have been illustrated to synthesize shape-controlled, stable and mono-disperse MNP [46]. To synthesis high-quality MNP several methods such as co-precipitation, thermal decomposition and/or reduction, micelle synthesis, hydrothermal synthesis, and laser pyrolysis techniques were used. But here we have discussed only precipitation method briefly.

2.2.1. Precipitation Method

Precipitation method is the oldest technique for the production of MNPs from solutions through precipitation of products [46, 50]. The metal reactants are dissolved solvent (mainly water) along with a precipitating agent (ammonia, sodium hydroxide). This method yields particles having broad size distribution, crystallinity and irregular morphologies including spinel ferrites, parasites, metals and alloys. Bulk quantity production is also possible by this method. Chelating ligands (oxalate, citrate, acetyl acetonate etc.) are used to favour formation of nanoparticles as they tailor the particle size but it mainly depends on the kinetic factors [51, 52]. Mixed ferrites like barium, strontium hexaferrites are already prepared using this technique. This reaction is influenced by several controlling parameters like pH, stirring rate etc. Low metal concentration gives limited particle growth and uniformity in the particle size. Phase purity of so prepared MNPs is the key factor. This precipitation method was first reported by Massart. This group precipitated Fe_3O_4 nanoparticles using $FeCl_3$ and $FeCl_2$ at pH= 8.2. They obtained spherical nanoparticles having 10 nm diameter and irregular morphologies with 50% size distributions. Separation of nanoparticles is also a challenging task for which mainly centrifugation, filtration and magnetic separation method are mainly followed. Mixed ferrites have the problem of varying solubility of metal hydroxide which leads to non-uniformity in the particle size. Iron has the inherent tendency to oxidize forming γ-Fe_2O_3 phase [53]. In this procedure synthesized MNP posses desired crystalline structure with uneven morphologies. Moreover, prepared MNP can be modified in respect of dimension and morphology by managing factors like pH, amount of metal cation, types of precipitating agent etc. The controlling factors produce MNP with broader size distribution and roughly spherical shape. It is observed that size as well phase purity of the prepared MNP in case of mixed metal spinels is very much depending on the precipitating agent. Precipitating agent namely citric and oxalic acid form chelating complex during the reaction that in turn facilitate precipitation, and appeared precipitate is collected *via* centrifugation or filtration technique. In this method, properties of MNP are very much consistent in fixed synthetic conditions.

2.3. Functionalization of Magnetic Nanoparticle

Intrinsic agglomeration tendency of the magnetic nano particles is a challenging task during the synthesis of MNPs. We can reduce the agglomeration tendency of magnetic nanoparticle by functionalization technique. Researcher used two dissimilar ways for coating the nanoparticles with polymer: “grafting to” and “grafting from” from the particle surface [46, 54]. Recently for further modification, silylation technique is most widely used. In this process, initially Fe_3O_4/SiO_2 core shell types arrangement was produced *via* sonication assisted Stober process [55-57].

In the silylation process, firstly ferrite nanoparticles were dissolved into distilled water (100 mg/150 mL) and ultrasonicated for one hour [58]. Thereafter, 2 mL aqueous NH_3 solution was added into the solution to render it basic. Then few drops of silane (0.1 mL in 10 mL of water) were added in the solution and whole solution was stirred by mechanical stirrer (around 1500 rpm) up to six hour. Subsequently these, surface modified MNPs were washed with acetone and water and after washing particles were dried oven. A schematic representation of the structure of the silica coated ferrite particles has been depicted in Figure **1**.

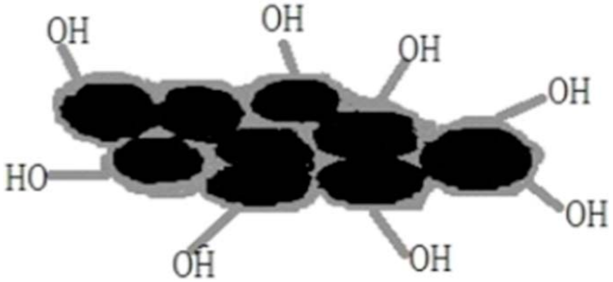


Figure 1: Schematic view of silica coated ferrite nanoparticles.

2.4. Polymer Nanocomposites Based on Magnetic Nanoparticles (Fe_3O_4)

Addition of polymers and nanoparticles together produces an elastic composite which gives valuable properties such as magnetic, electrical, optical, or mechanical properties. Recently, for the formation of sophisticated polymeric inorganic nanocomposites (PINC) researchers have started looking for the novel techniques to properly merge the characteristics of both nanoparticles and polymers. But there are number of challenges in producing PINC in which lack of price effective processes to direct the distribution of the nanoparticles into polymer matrix is the prime difficulty in the large scale production and commercialization of PINC. Therefore, it is urgent requirement that novel techniques should be created, which in turn give well dispersed particles inside the polymer matrix. Hence, it is still challenging task for us. In this review, we especially focused on the recent development of the nanocomposites prepared by Fe_3O_4 nanofillers with their applications, drawbacks and remedies.

As we know magnetic nanocomposites based on polymers are very attractive group of nanostructural material. If superparamagnetic nanoparticles dispersed in the desired polymer matrix then the resultant composite is called superparamagnetic nanocomposites. It has been shown that these superparamagnetic nanocomposites show outstanding characteristics especially if the particles were dispersed in the shape memory polymers (SMP). This is because SMP based composites can produce shape memory effect [59, 60]. Therefore, in following section, we have discussed structure, properties and applications of different polymer nanocomposites based on Fe_3O_4 nanoparticles.

2.4.1. Thermoplastic Polyurethane (TPU)/ Fe_3O_4 Nanocomposites

MNP (magnetic nanoparticles (Fe_3O_4)) can be mixed with polymers at the nano scale producing superior stable materials. It is found that TPU based nanocomposites possess unique attributes of shape memory properties [61-63]. Revolutionary activity in the field of shape memory polyurethane (SMPU) started several decades before, and it is reported that first patent on polyurethane (PU) foam came in 1966 [64]. In a series of articles, researcher such as Hayashi [65] and Tobushi and co-workers [66, 67] described the fundamental characteristics thin films and foams of SMPU. Moreover, we have seen that very limited literature is available so for on the TPU**/**Fe_3O_4 nanocomposites [68]. Therefore, considering above mentioned facts, we have prepared and analyse TPU**/**Fe_3O_4 magnetic nanocomposites in our lab. This work especially concentrated on producing and analysing nano-sized super paramagnetic ferrite based magnetic nanoparticles to prepared TPU based magnetic nanocomposites. The magnetic nanoparticles were synthesized by using co-precipitation process (mentioned above). Moreover, so prepared particles have been functionalized using novel silylation technique to improve their nanoscopic dispersion in organic media without compromising much of their magnetic properties. Finally, a few magnetic nanocomposites have been prepared with a commercial TPU matrix (grade-DP9380A, density-1110kg/m^3 at 23°C and shore hardness (method A, ISO 868) 82, purchased from the Bayer Materials, Germany) using solution casting method and the corresponding mechanical properties and magnetization behaviour of the nanocomposites have also been studied. Tensile tests were carried out according to ASTM D412-98 on dumbbell-shaped specimens with a Zwick1445 tensile testing machine (Germany) at a constant crosshead speed of 100 mm/min. The tensile tests have been carried out for five specimens for each sample.

Initially, 8 % solution of TPU was prepared in THF and ultrasonicated for 15 minutes. Synthesized pristine and functionalized magnetic ferrite nanoparticles (4 wt. %) were dispersed into THF followed by 15 minutes of ultrasonication. Thereafter, these solutions were mixed together and ultrasonicated for 1 hour. Later, mixed solutions were cast on petridishes and dried at room temperature. After complete removal of the solvent the samples were kept in a vacuum oven at 70 ^{o}C till constant weights were achieved. Prepared films were used for further characterisation.

Preliminary observation shows that ferrite particles (Fe_3O_4) with silica coating shows improve dispersion in thermoplastic polyurethane (TPU) matrix (figure not shown). FTIR spectra have clearly depicts the coating of silane on particle surfaces (Figure **2**). It leads to the formation of iron-silica core shell nanoparticles. There has been a strong absorption peak at 1091 cm^{-1} in all the silane coated samples, that is because of asymmetric stretching vibrations of the Si–O–Si of silica shells. usually organic silane exhibit a doublet at 1100 and 1075 cm^{-1} including bands at 1175–1160 and 970–940 cm^{-1} for the Si–O–C stretching mode [69]. Additionally, 3-amino propyl triethoxysilane coated ferrite nanoparticles (ASF) showed a peak at 1528 cm^{-1} corresponds to the bending vibration of the amino silane.

In further analysis, it is found that thermal stability of particles also improved which is confirm by TGA analysis of different silane coated particles. From Figure **3**, it is evident that tetraethyl ortho silicate (TEOS) coated ferrites shows highest thermal stability among all. However, magnetization values decreases with surface modification of ferrites without any influence in superparamagnetic character.

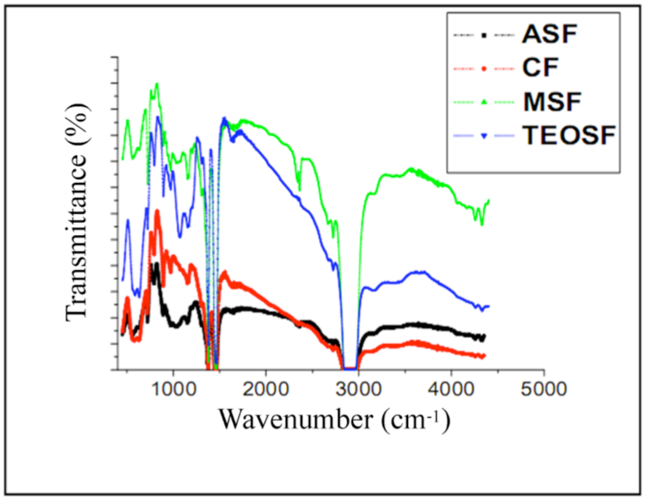


Figure 2: FTIR spectrum of 3-amino propyl triethoxysilane coated ferrite nanoparticles (ASF), pristine ferrites (CF), silyl methacrylate coated ferrite nanoparticles (MSF), and tetraethyl orthosilicate coated ferrites (TEOSF) respectively.

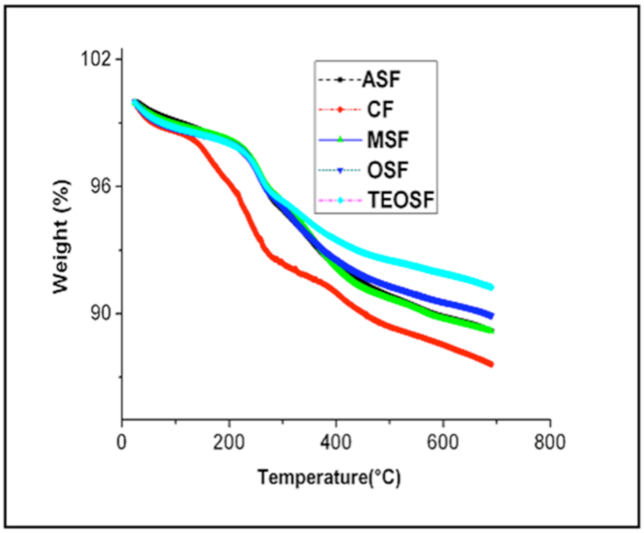


Figure 3: TGA thermogram of 3-amino propyl triethoxysilane coated ferrite nanoparticles (ASF), pristine ferrites (CF), silyl methacrylate coated ferrite nanoparticles (MSF), octadecyl silane coated ferrites (OSF) and tetraethyl orthosilicate coated ferrites (TEOSF), respectively.

We have observed that functionalized ferrite based composites displays improvement in the tensile strength compare to pristine ferrite based composite (Figure **4**). It is also observed in the magnetic analysis that functionalized ferrite based nanocomposite shows lower saturation magnetization in compare to pristine ferrite based nanocomposites (Figure **5**). This could be due to the drop of amount of ferrite per gram owing to coated outer surface and as a result magnetization (emu/g) decreased. Moreover, all nanocomposites retained superparamagnetic character except silyl methacrylate coated ferrite based nanocomposite (M4).

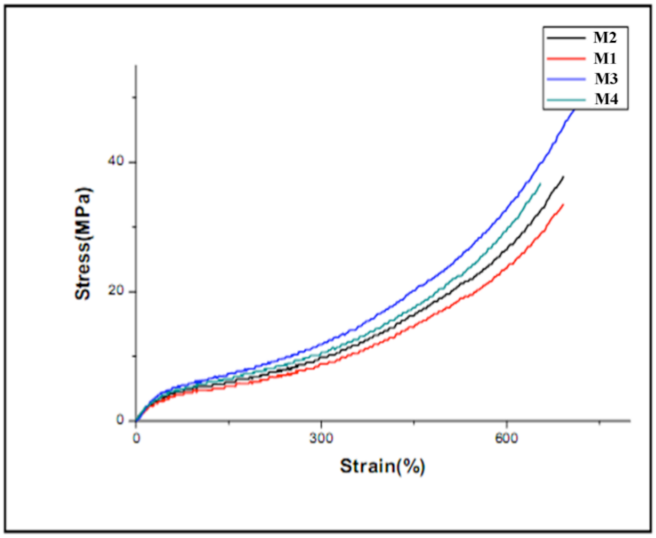


Figure 4: Stress strain graph of various ferrite-TPU nanocomposites prepared by using 4wt% of (M1) pristine ferrite, (M2) tetraethyl orthosilicate coated ferrite, (M3) 3-amino propyl triethoxysilane coated ferrite and (M4) silyl methacrylate coated ferrite.

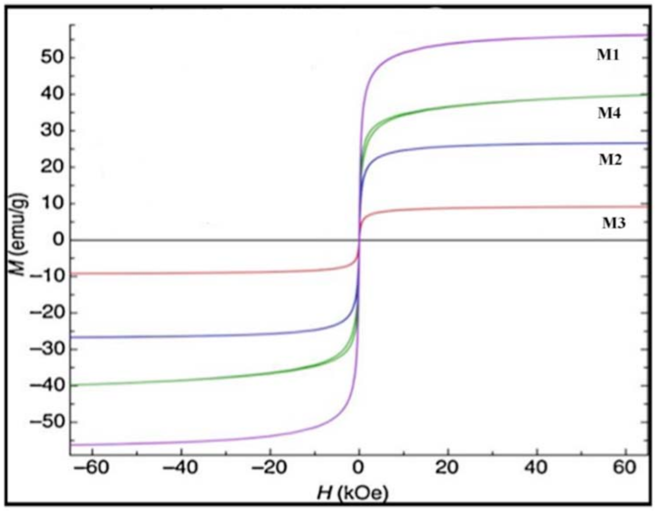


Figure 5: Magnetic properties various ferrite-TPU nanocomposites prepared by using 4wt% of (M1) pristine ferrite, (M2) tetraethyl orthosilicate coated ferrite, (M3) 3-amino propyl triethoxysilane coated ferrite and (M4) silyl methacrylate coated ferrite.

A few other researchers such as Mohsen Ashjari *et al*. also worked on TPU/Fe_3O_4 nanocomposites [68]. In this work, TPU/Fe_3O_4 nanocomposites were synthesized and studied the characteristics of the composites with respect to Fe_3O_4 nanoparticles. As compared to pure polymer authors reported significant improvement in thermal, mechanical as well as in chemical properties with the incorporation of Fe_3O_4 nanoparticles without influencing the density, toughness and processibility. But work was not much established to facilitate any industrial applications or to fabricate any practical device.

Thus from above results, we can say that TPU/Fe_3O_4 nanocomposites with different functionalized ferrite register improvement in thermal and physico-mechanical properties. These preliminary results clearly reveal that this type of smart magnetic nanocomposites can be utilized in the field of magneto-electric shape memory devices. Therefore, this field still requires more attention to stabilise the application of this type of magnetic nanocomposites. The work on TPU/Fe_3O_4 nanocomposites is still underway in our lab.

2.4.2. PVDF/Fe_3O_4 Nanocomposites

O. D. Jayakumar *et al*. developed a multiferroic hybrid PVDF/Fe_3O_4 which shows significant magneto-dielectric coupling [70]. In this work, authors formed PVDF based nanocomposites with silica modified Fe_3O_4 at room temperature. In technical analysis, it has been observed that nanocomposites formed with silica coated Fe_3O_4 demonstrate enhanced ferroelectric polarization, low leakage current together with sufficient magneto-electric coupling. The occurrence of magneto-electric coupling indicates possible tuning of dielectric constant in presence of external magnetic field. This confirms the multiferroic behaviour of the composite film and shows probable applications to develop multiferroic devices.

T. Prabhakaran *et al*. prepared PVDF/Fe_3O_4 magnetoelectric nanocomposites films through solvent casting method with different weight fractions of Fe_3O_4 nanoparticles, and studied Fe_3O_4 loading influences on the structural, chemical, thermal, and magnetoelectric properties of the nanocomposite [71]. In this work, authors used unpoled samples of PVDF/Fe_3O_4 nanocomposite. From characterization authors claimed, enhancement of electro-active β phase by rising ferrite loading. Moreover, it is also observed that inclusion of Fe_3O_4 in PVDF chain significantly improves the thermal stability, and interfacial interaction among particles and polymer leads to improve ferroelectric polarization. The reasons behind this are: (i) ferrite particles produces additional charges which need to be balanced, (ii) secondly nanoparticles are able to behave as heterogeneous nucleating point in throughout the polarization. Additionally, excessive interfacial regions present in the composite having nanoparticles shows exchange coupling phenomena which in turn enhances ferroelectric outcome. It is observed that on rising ferrite loading (more than 0.14 wt %) leads to decrease highest polarization values. This shows the presence of particular optimum level for the ferrite loading for which superior properties (ferroelectric or piezoelectric) can be achieved. Above the optimum level ordered distribution of dipoles shattered which leads to decrease in polarization owing to restricted movement of domain wall. So, this whole process shows how Fe_3O_4 particles influence the composite characteristics. Moreover, change in strain can be easily seen by increasing temperature because magneto-striction coefficient of the filler depends on the temperature. Consequently, electro-mechanical stress is generated and shifts through the channel between the particles and polymer. This leads to increase in the polarization owing to the piezoelectric effect. Above mentioned facts clearly demonstrate the presence of ferroelectric as well as magnetic characteristics in the prepared the samples. In other word, we can say that prepared films shows magneto-electric character. Prepared films may be utilized in the field of spintronics, sensors and in memory devices.

Zheng-Qing Huang *et al*. prepared and characterized series of PVDF/Fe_3O_4 ultra filtration membranes containing Fe_3O_4 particles to get membranes having macro voids [72]. Membranes were prepared in presence of magnetic field by using the phase inversion process. The properties of both the membranes were compared. Results show 35% improvement of flux for PVDF/Fe_3O_4 membrane in the presence of magnetic field. When Fe_3O_4 content is below 65 wt%, then both Fe_3O_4 loading as well magnetic field used while the preparation of membrane shows no remarkable effect on the flux and fouling-resistance ability of PVDF/Fe_3O_4 ultra filtration membranes. However, for the 75 wt% Fe_3O_4 ultra filtration membranes (prepared in absence magnetic field) shows high pure water flux, good fouling-resistance and compaction resistance ability. This happens may be due to the fact that when Fe_3O_4 content is 65 wt%, then outer magnetic field forces Fe_3O_4 particles in a casting solution to arrange itself in the direction of magnetic field. Consequently novel membrane having lamellar macrovoids may possibly be synthesized. These novel membranes show superior properties at 70 wt% Fe_3O_4 loading in respect of pure water flux, rejection and fouling-resistance and compaction-resistance ability.

In another work, PVDF/Fe_3O_4 composite films were synthesized by spin coating technique [73]. Result shows that conductivity and magnetization properties of composite changes with Fe_3O_4 content. Moreover, magnetization values also shows increasing trend with increase in the Fe_3O_4 content. Therefore, a combined effect of conducting as well as magnetic component could be utilized for electromagnetic applications. A few other articles are reported in the literature on the PVDF/Fe_3O_4 composite which demonstrates the consequence of Fe_3O_4 particles on thermal and magnetic properties of the prepared nanocomposites [74, 75]. But more comprehensive study is still required to stabilise the work to fabricate device for practical purposes.

In view of the above mention facts, we have also worked on the PVDF/Fe_3O_4 (MNP) nanocomposites [76]. With the help of SAXS technique, we primarily studied micro or nano scale structure of PVDF/Fe_3O_4 films with respect to the surface fractal value and radius of gyration. To do this, we have prepared various samples with different concentration of ferrite (i.e. Pure PVDF, 0.5%MNP, 1%MNP, 1%MNP with silica coating and 2%MNP). Then we used SAXS technique for the determination of microscale as well as nanoscale structure of the nanocomposites. I *vs.* q plots obtained by SAXS measurements of pure PVDF and its composite with Fe_3O_4 (MNP) are shown in Figure **6**.

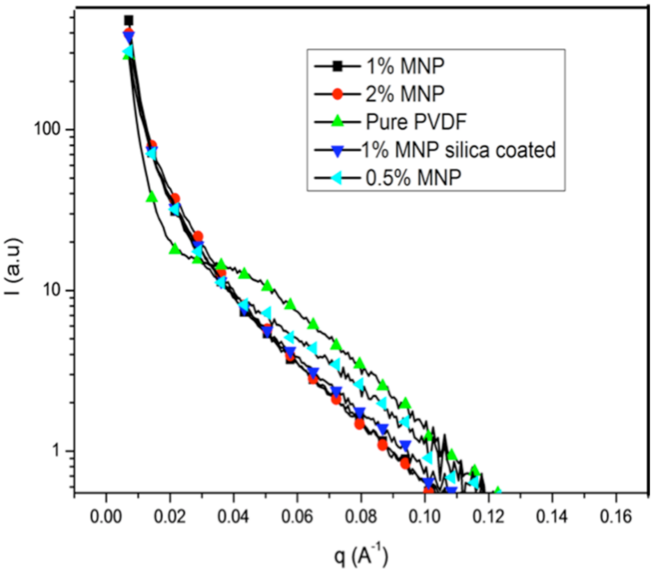


Figure 6: SAXS diffractogram (I *vs.* q) of pure PVDF and its composite with MNP [76].

Pure PVDF shows variation of slope across the q axis. Composite with 0.5% MNP follows similar trend of that of pure PVDF but extent of variation of the slope is diminished. Whereas, composites contain 1% MNP (with and without silica) and 2% MNP register similar pattern. But with 2% MNP, the composite shows higher scattered intensity (I) at low q region i.e. between 0.02-0.04 and relatively lower scattering for high q region. These indicate that some microstructural changes occur due to more entanglement and increase in secondary force in PVDF which caused reduced molecular mobility due to addition of magnetic nanoparticles at higher concentration. This has been further clarified by applying Porods and Guinier law, which gives information about radius of gyration, surface fractal and size distribution in composites. The radius of gyration (R_g), which gives idea about the interfacial area and dispersion characteristics of fillers in the matrix, has been determined by using equation (1)

$$I(q) = G \exp(-q^2 R_g^2 / 3) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where, G = Guinier prefactor, R_g is radius of gyration.

The R^2 (regression coefficient) value, > 0.9 in all cases as given in Table **1**, varies according to the order: 0.5% MNP < 2% MNP <1% MNP Silica coated <1%MNP <pure PVDF. Highest R_g value for pure PVDF, accounts for structural irregularity i.e. entanglement of polymer chain in the amorphous region and existence of crystalline domain. At 0.5% MNP, reduced R_g indicates the presence of MNP as aggregates of smaller dimension but not distributed uniformly throughout the matrix resulting in phase separation (Table **2**, also confirmed TEM not shown here). As the MNP concentration is increased to 1 %, the R_g value is also increased and resulted in increase of size of MNP aggregates. The crystalline domain size might not be affected as much as in the case of sample having 2% MNP. The reduction in crystalline domain size in 2 % MNP filled composite can be reflected in the reduced R_g value compared to 1% MNP filled samples. This signifies unformity in the nanoparticles distribution in polymer matrix and thereby gets access to influence the crystalline domain's size. In case of silica coated MNP filled sample, as expected, the lower R_g value in due to smaller aggregate size of dispersed particles than that of uncoated 1 % MNP filled sample. The surface characteristics of MNP is changed as amorphous silica creates a shell surrounding the MNP core and thus chance of interconnectivity among the aggregates in the sample, compared to that of uncoated sample, is reduced. Nanocomposites at 2% wt of Fe_3O_4 shows more regular structure with lowest surface fractal value (ds) as compare to other nanocomposites. In case of composites with 0.5% Fe_3O_4 and 1% Fe_3O_4 (with slica coating), surface fractal value comes under mass fractal which caused phase separation in composite. Thus, summing it all we can say that sample with 2wt% Fe_3O_4 loaded PVDF has been found to generate suitable crystalline structure of the matrix polymer which favour generation of piezoelectricity. These preliminary results clearly show the possibility of magneto-electric effect in this

Table 1: Guinier Fitment Over Total Ranges of q Values [76]

Sample	G	R_g(Å)	R_g(Å) (Error)	R^2
1% MNP	884.166	204.51	34.28	0.96965
2% MNP	609.169	179.31	33.41	0.95463
Pure PVDF	638.330	227.17	44.43	0.94194
1% MNP with silica coating	607.095	182.29	32.75	0.96077
0.5% MNP	426.322	163.91	31.15	0.95109

Table 2: Results of Porod Fitment for Samples (q = 0.05646 to 0.10635 $Å^{-1}$) [76]

Sample	P	Error (P)	R^2	B	Error (B)	Surface freactal (*ds*)
1% MNP	-3.1784	0.0404	0.988	1.778	0.0202	2.8216
2% MNP	-3.2543	0.0354	0.991	1.808	0.0177	2.74563
Pure PVDF	-3.0939	0.0537	0.978	2.068	0.0269	2.90608
1% MNP with silica	-2.9876	0.0453	0.983	1.740	0.0227	3.01232*
0.5% MNP	-2.7809	0.0579	0.968	1.779	0.0290	3.21901*

*****Coming under mass fractal indicating phase separation, P: Power law exponent, B: Average surface area of nanoparticles.

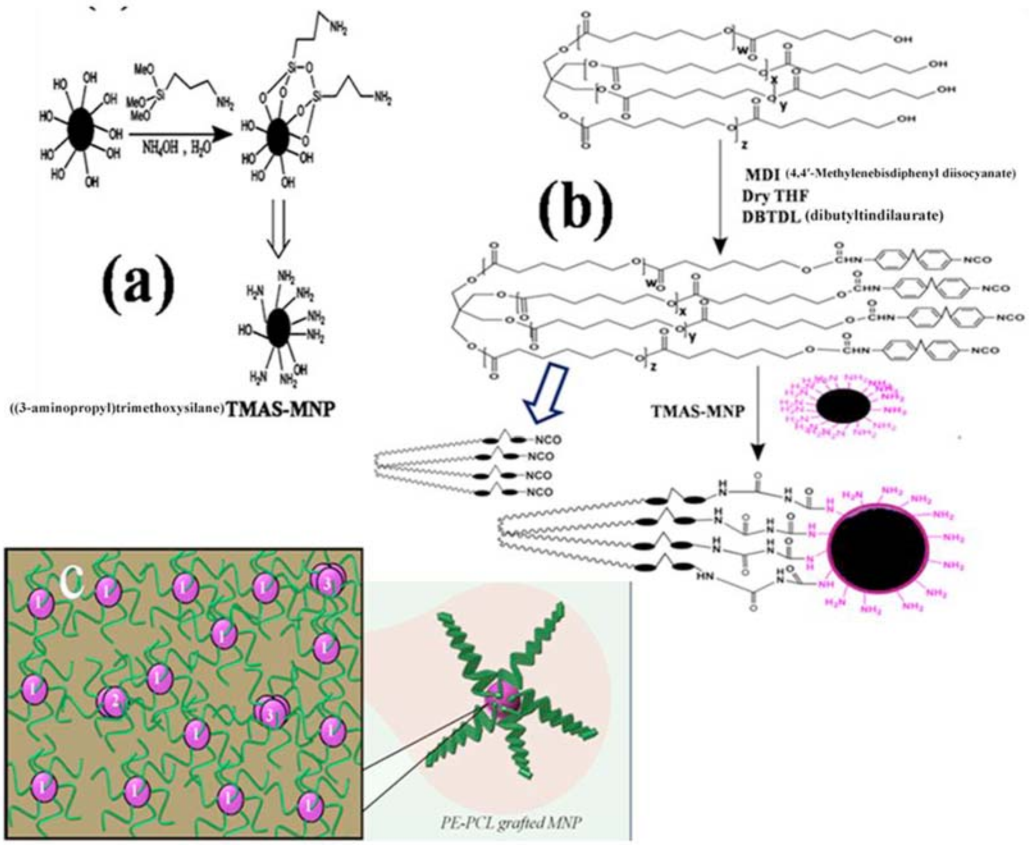


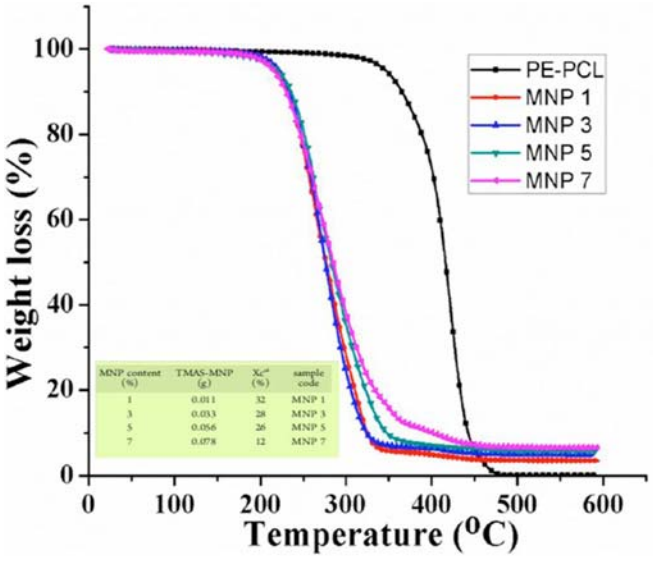
Figure 7: Schematic of (**a**) coating on the ferrite surface by tetramethyl ortho silane modification, (**b**) grafting of four armed PE-PCL [i.e. pentaerythritol (ε-polycaprolactone)] top of the tetramethyl ortho silane coated ferrites and (**c**) ferrite grafted polymer [58].

type of nanocomposites to develop magneto-electric materials (e.g. sensor, actuator etc).

2.4.3. PE-PCL Grafted Fe_3O_4 Nanocomposites

In another work, we have prepared biocompatible polymer immobilized superparamagnetic nanoparticles *via* grafting of four armed pentaerythritol (ε-polycaprolactone) (PE-PCL) on the silane modified ferrite naoparticles (Figure **7**) [58].

In this work PE-PCL was synthesized by ring-opening polymerization. We have observed considerably high grafting density of PE-PCL which in turn leads to lesser agglomeration of ferrites. Formation of four armed PE-PCL is confirmed by using spectroscopic analysis. Polymer grafted nanoparticles are biocompatible as found in MTT assay using HeLa cell line. From TGA thermograms, it has been observed that the maximum degradation temperature (Tmax) of polymer decrease from 400 °C to 265−285 °C due to the grafting on the surface of MNP (Fe_3O_4) (Figure **8**). Generally, thermal stability of polymer increases when it is grafted onto nanoparticles. But in this case thermal stability of virgin polymer was found to be higher compared to that of MNP (Fe_3O_4) grafted polymers. The decrease in thermal stability may possibly be due to the loss of crystallinity of polymer chains because of grafting onto the MNP surface.



MNP content (%)	TMAS-MNP (g)	Xc^a (%)	sample code
1	0.011	32	MNP 1
3	0.033	28	MNP 3
5	0.056	26	MNP 5
7	0.078	12	MNP 7

Figure 8: TGA thermograms of PE-PCL and MNP 1, MNP 3, MNP 5, and MNP 7 (See inset of Figure **8** for sample code) [58].

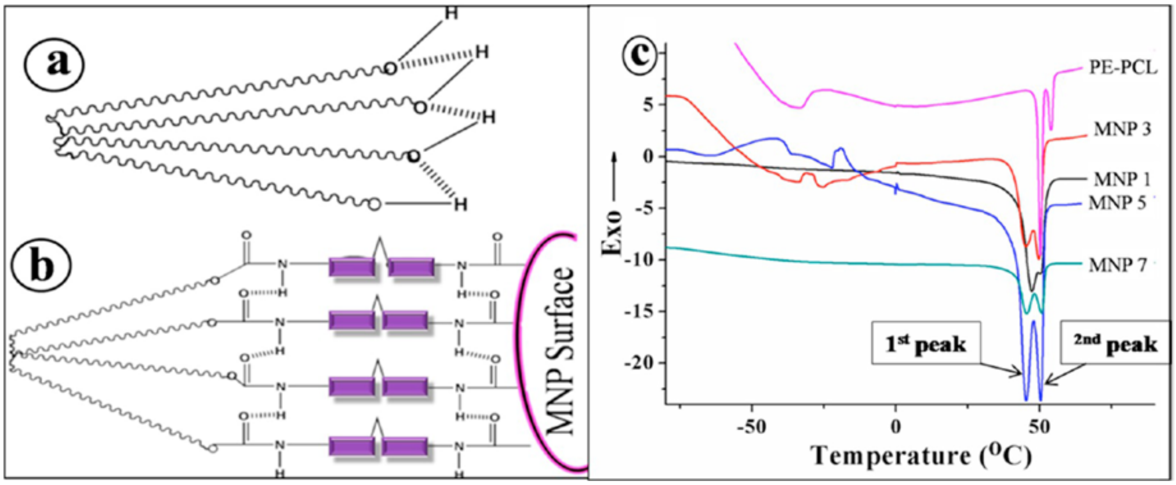


Figure 9: Schematic depiction of (**a**) intramolecular H-bonding between PE-PCL chains, (**b**) between grafted polymer chains, and (**c**) DSC thermogram of pure and grafted polymers (See inset of Figure **8** for sample code) [58].

The DSC thermogram (Figure **9c**) shows two melting peaks in the second heating cycle. These two melting peaks may correspond to two types of organization of molecules. The first melting peak originated from crystallization of linear polymeric chains and the second one as a result of intra-molecular H-bonding formed by end groups (−OH) (Figure **9a**). The intensity of the second melting peak is found to increase due to *in situ* modification of MNP. This observation is due to stacking of phenyl groups through more effective intramolecular H-bonding (Figure **9b**) that occurs between urethane groups.

To achieve the major objectives of this work that is to synthesis biocompatible nanoparticles. It is necessary to perform cytotoxicity test (*in vitro*) at different concentration of polymer grafted MNP and pristine MNP to determine whether it is cytotoxic or not. The cell viability of polymer grafted nanoparticles was performed using an MTT [3-(4,5-dimethylthiazol-2-ly)-2,5-diphenyltetrazolium bromide] assay with HeLa cells for 24 h after they had been incubated at 37 °C. Figure **10** shows polymer grafted nanoparticles MNP1, MNP 3, and MNP 5 display cell viability of about 80% at concentration of 25 µg/mL, but MNP 7 was found to be less compatible compared to MNP 1, MNP 3, and MNP 5 (about 50% cell viability at concentration of 25 µg/m). The cytotoxicity gradually reduces with decreasing MNP content from MNP 7 to MNP 1. In cell viability test, it has been observed that polymer grafted nanoparticles having less ferrite content demonstrate superior cell viability than those having higher ferrite content. Thus, these preliminary results indicates the possible applicability of new-fangled PE-PCL grafted ferrite particles in the field of magnetic targeted drug delivery and as MRI contrast enhancer.

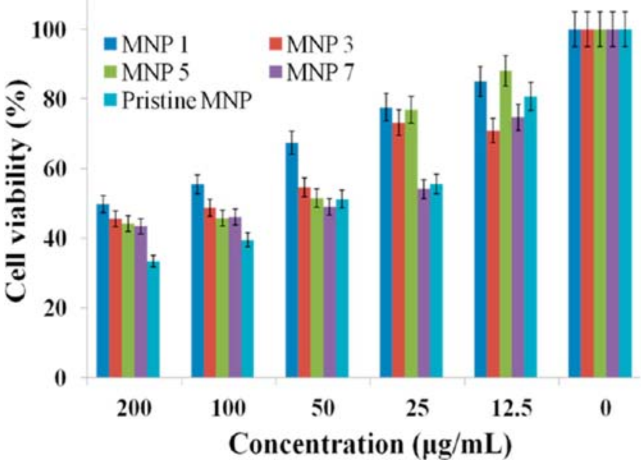


Figure 10: Column chart of *in vitro* cytotoxicity of pure MNP and polymer grafted MNP at different concentration on HeLa cell measured by using MTT assay [58].

2.4.4. Polyaniline/Fe_3O_4 Composite

Chenkui Cui *et al*. prepared polyaniline/Fe_3O_4 composite using two-step oxidative polymerization of aniline monomers in the presence of Fe_3O_4 microspheres (FMS) [77]. In the process aniline oligomers oxidized by Fe^{3+} are mostly formed in the first stage and “egg-like” polyaniline aggregates were produced in the second stage (Figure **11a**). Morphology of FMS/PANI composites changes by changing the mass of PANI in Fe_3O_4 microspheres (FMS/PANIx) (here x shows the content of PANI). Pure polyaniline (FMS/$PANI_{100}$) sample shows spherical morphology (Figure **11b**) with an average diameter of about 300 nm. When PANI content increases some disordered PANI particles appeared around Fe_3O_4 microspheres with rough surfaces of microspheres. For equivalent amount of aniline monomer (FMS/$PANI_{50}$) bulky aggregates of PANI were formed on Fe_3O_4

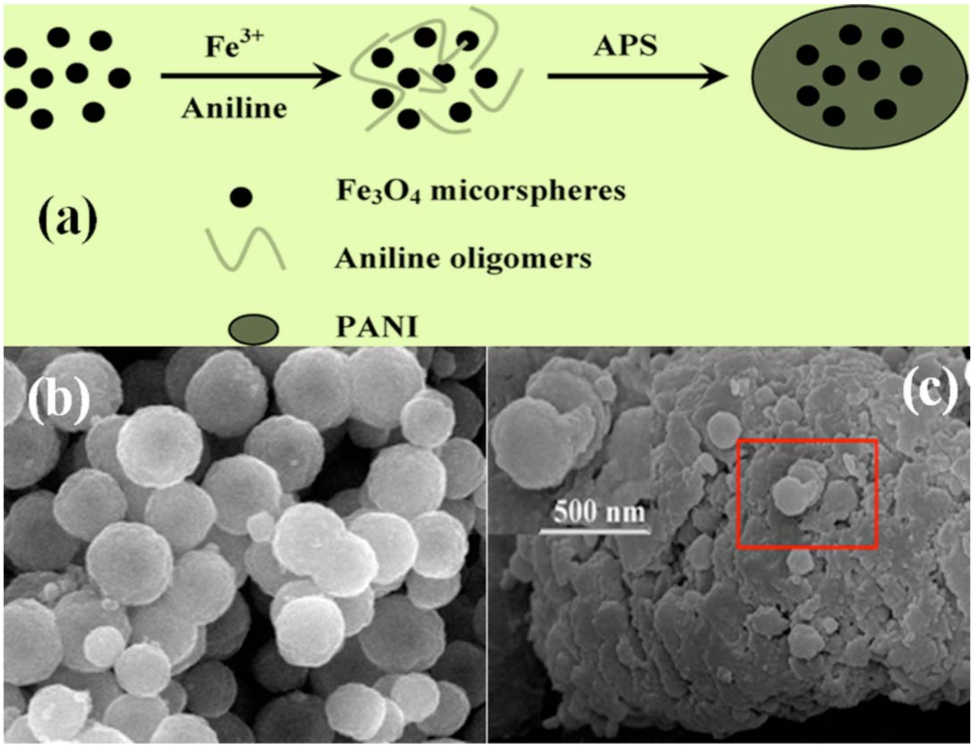


Figure 11: (**a**) Possible formation mechanism of "egg-like" FMS/PANI and (**b**, **c**) SEM images of FMS/$PANI_0$ and FMS/$PANI_{50}$ respectively [77].

microspheres giving an "egg-like" structure that is about 5 μm in length and 3 μm in width (Figure **11c**). It has been observed that further increasing in PANI amount defects on the surface appeared without any Fe_3O_4 microspheres. Therefore best result observed in case of (FMS/$PANI_{50}$) with "egg-like" structure.

It was observed that due to the addition of Fe_3O_4 microspheres impedance and reflection loss of composite enhances significantly. In all FMS/$PANI_{50}$, shows very strong reflection loss over a wide frequency range (Figure **12**). Here it has been observed that reflection loss can be modified by changing the absorber thickness. Figure **13** clearly shows the effect of thickness of absorbers on the reflection loss. Moreover, composites prepared by using two-step chemical oxidative polymerization in the presence of magnetic materials shows superior microwave absorption and environmental stability than those formed by one-step oxidative polymerization. Thus two-step method may perhaps be better route to design and prepare greatly efficient microwave absorbing materials for future research.

In another work 4-dodecylbenzenesulfonic acid-doped polyaniline/Fe_3O_4 composite films with honeycomb structure were obtained by water assisted self assembly method [78]. These honeycomb types of morphologies of the films were properly analysed by transmission electron microscopic (TEM) and atomic force microscopy (AFM). These prepared films having conducting polymers and magnetic particles shows superparamagnetic properties. Therefore, the capability to prepare 3D ordered macro-porous structures having conducting polymers and magnetic particles comprises possible applications in the field of electro-magnetic

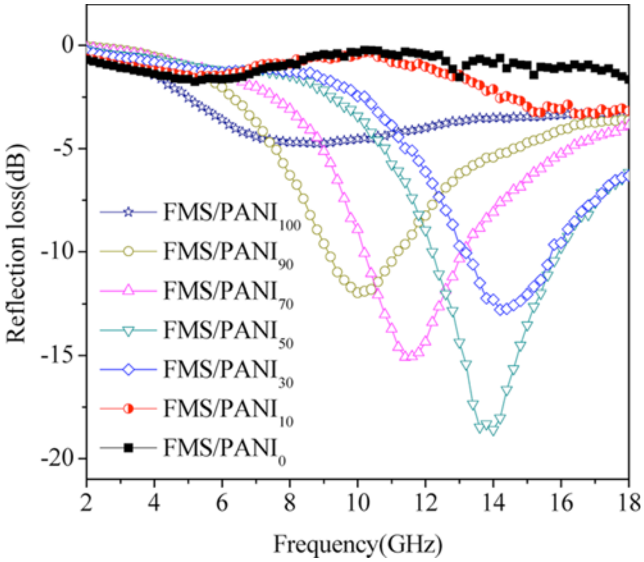


Figure 12: Reflection loss curves of FMS/PANI composites with an absorber thickness of 2 mm in the frequency range 2−18 GHz [77].

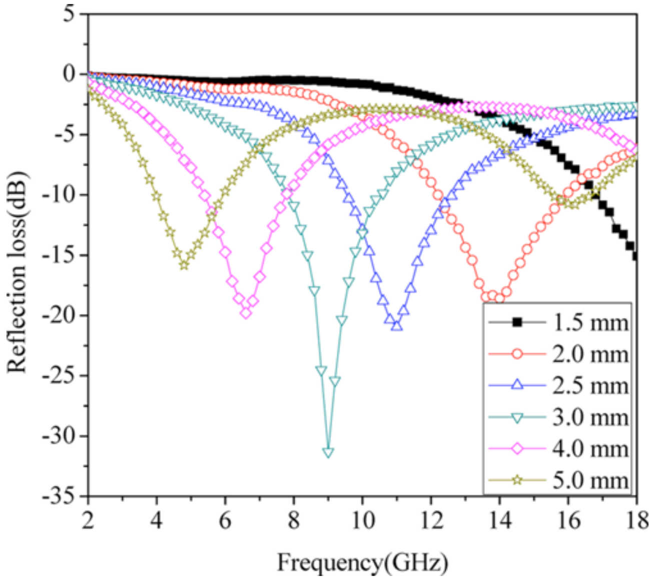


Figure 13: Reflection loss curves dependent on the thickness of FMS/PANI$_{50}$ in the frequency range 2−18 GHz [77].

materials. In another more informative article, Shouhu Xuan *et al.* tried to observe the effect of Au on the polyaniline/Fe_3O_4 nanocomposite [79]. In this article authors reported a novel process to produce magnetically responsive Fe_3O_4/polyaniline/Au nanocomposites. In the process, author's prepared superparamagnetic Fe_3O_4/polyaniline composite with well defined core/shell nanostructure *via* ultrasound assisted *in situ* surface polymerization method. Thereafter, negatively charged 'Au' nanoparticles of about 4nm diameter were successfully assembled on top of the positively charged surface of Fe_3O_4/polyaniline core shell microspheres by means of electrostatic attraction. Technical result clearly shows that so prepared Au-immobilized nanocomposites demonstrate outstanding catalytic properties. Therefore, these types of composites could be utilized as a magnetically recoverable nano-catalyst in the reduction of a selected substrate. A similar work has done by Qiaozhen Yu *et al*. in which obtained Fe_3O_4/Au/PANI nanocomposites having a rod-like morphology [80]. It has been observed that optical, electrical and magnetic properties of the prepared nanocomposites vary with molar ratio of 'Au' to Fe_3O_4, especially when the molar ratio of Fe_3O_4@Au to PANI was fixed.

2.4.5. Polypyrrole /Fe_3O_4 Nanocomposites

Hui Zhang *et al*. analyses the importance of 'Au' nanoparticles in deciding the characteristics of polypyrrole (PPy)/Fe_3O_4 nanocomposites [81]. In this work authors prepared polypyrrole/Fe_3O_4 composites nanosphere with core/shell structure *via* oxidative polymerization of pyrrole in presence of ferrite particles and assembled the 'Au' nanoparticles on the surface of prepared composite by mean of electrostatic interactions (Figure **14**). This multifunctional nanocomposites show an unforeseen combination of attributes of Fe_3O_4, PPy (conductive) and Au. It has been shown that magnetic nanocomposites can be powerfully attracted to the surfaces of electrodes by applying outer magnetic field. This in turn simplifies the complex method of preparation by conventional modified electrode. Moreover, Fe_3O_4/PPy/Au nanocomposites modified electrode exhibit exceptional electro-catalytic activities to bio-species such as ascorbic acid. Therefore, prepared nanocomposites may be used in the field of enzyme immobilization, radiation absorption and as biosensors. In another work Zhanhu Guo *et al*. find out the effect of Fe_3O_4 loading on the polymerization of pyrrole in acidic medium [82]. Technical results show that iron oxide particles notably influence morphology and other physico-chemical properties of polypyrrole. As the percentage of loading increases, thermal stability of the nanocomposite increases and found higher in case of 50 wt% loading of Fe_3O_4. It has been also observed that electrical conductivity of the nanocomposites significantly improved by adding 20 wt% Fe_3O_4. However, at greater Fe_3O_4 loading (50 wt %) conductivity decreases significantly. This reduction in conductivity may be due to the insulating behaviour of Fe_3O_4. Moreover, magnetic properties of nanocomposites are also dependent on Fe_3O_4 nanoparticles loading. In a similar work Ashis Dey *et al*. found that addition of Fe_3O_4 nanoparticles greatly

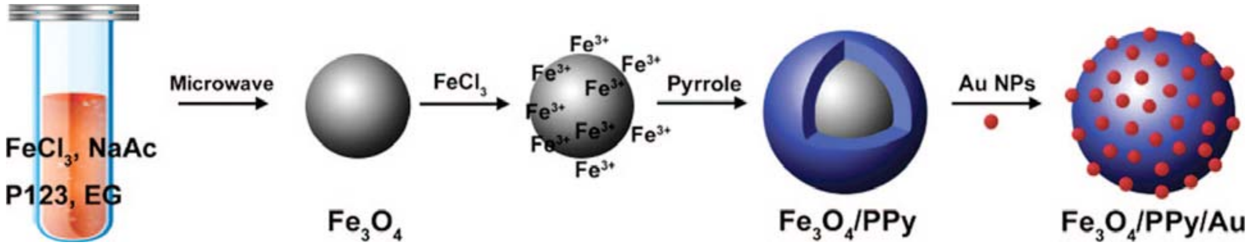


Figure 14: Schematic depiction of preparation process of Fe_3O_4/PPy/Au nanocomposites [81].

increases the dielectric constant (up to 1100) of the polypyrrole/Fe_3O_4 nanocomposite at room temperature [83]. The increase of the dielectric constant was attributed to the Maxwell-Wagner type interfacial polarisation. Large dielectric constant of the nanocomposites also indicates potential application in the field of actuator and sensors.

2.4.6. Polystyrene /Fe_3O_4 Nanocomposites

A widespread study has been done in the past for the development of superparamagnetic hybrid spheres especially to favor biomedical functions. In current study more attention paid in the preparation of more sensitive monodispersed, nanoscale spheres which encompass greater saturation magnetization. Because high saturation magnetization will provides efficient controlling and detection of magnetic signals. Some critical issues in the study are broad distribution of particle dimension during the reduction of particle size to nanometer scale and considerable reduction in saturation magnetization due to the coating of particle surface with silica. Hong Xu *et al*. renovated a novel method to produce mono dispersed superparamagnetic magnetite/polystyrene (Fe_3O_4/PS) spheres [84]. In this, work authors tried to solve the above mentioned issues. Analysis of the prepared composite showed that silica coating functionalized the surfaces of mono dispersed nanospheres to be hydrophilic. Moreover, silica modification also works as a buffer layer and protecting the magnetite nanoparticles from dissolution. In this process surface silanol groups react with variety of compounds to produce functional groups and exhibits greater saturation magnetization than in earlier reported results. Therefore, it may have application in the field of targeted drug delivery, biosensor, hyperthermia and purification or separation of biomolecules. Some other researchers also worked on the Fe_3O_4/PS nanocomposites to develop better properties but did not derive fruitful results [85, 86]. Thus, this field still needs more attention to establish the work for the biomedical applications and to form stable devices.

2.4.7. Polydopamine/Fe_3O_4 /Au Nanocomposites

Another informative work has been done in the field of biotechnology by the Min Zhang *et al*. [87]. In this work, authors prepared Fe_3O_4/polydopamine/Au composite nanoparticles. In the process, firstly Fe_3O_4/polydopamine composite nanoparticles having core shell type of arrangement were prepared by dopamine self polymerization to produce thin, surface-adherent polydopamine films on the surface of a Fe_3O_4. Subsequently, gold nanoparticles were accumulate on the exterior of Fe_3O_4/polydopamine with the reduction of Au^{3+} in the solution followed by the formation of self-assembled monolayer of MUA (i.e. 11-mercaptoundecanoic acid) on the surface of the Au nanoparticles. Then finally, iminodiacetic acid (IDA)-Cu modified Fe_3O_4/polydopamine/Au composite nanoparticles were formed by means of the carboxyl groups of MUA and react with Cu^{2+} charged iminodiacetic acid (IDA). Here IDA-Cu grouping works as fastener and linked with gold and polydopamine surface to capture target molecules. In analysis, so formed Fe_3O_4/polydopamine/Au composite nanoparticles shows strong magnetic response to an externally applied magnetic field with high specificity to protein bovine hemoglobin (BHb) and helps in the removal of abundant protein BHb in the bovine blood as well. Thus, it opens a new path for the potential future application in removing abundant protein in proteomics.

2.4.8. Polylactide (PLA)/Fe_3O_4 Nanocomposites

Gang Lv *et al.* reported a novel nanocomposite based on polylactide (PLA) nanofibers and Fe_3O_4 [88]. The MTT assay, optical microscopy, confocal fluorescent microscopy and electrochemical observations of the so formed nanocomposite (Fe_3O_4/PLA) indicates that PLA nanofibers and Fe_3O_4 particles may perhaps be utilized in the area of intracellular drug uptake of leukemia K562 cell lines in which improved gathering of anticancer drug daunorubicin (DNR) on the film of cancer cells might be observed. Confocal fluorescence microscopy shows that stronger intracellular fluorescence appeared in the target cells treated by DNR together with the Fe_3O_4-PLA nanocomposites (Figure **15**). Additionally, it was also observed that shape of the cancer cell changed which implies swelling of the majority of target leukemia cells. This clearly shows that Fe_3O_4-PLA nanocomposites provide more efficient assistance in the drug delivery than the respective nonmaterials.

Authors also explored electrochemical detection and micro culture tetrazolium studies especially to explore the consequence of nanomaterials on the drug uptake of cancer cells. The outcomes clearly shows that prepared composites may possibly promote interaction of daunorubicin with leukemia cells and surprisingly enhance the permeation and drug uptake of anticancer agents in the cancer cells. This in turn led to the induction of the cell death of leukemia cells. These preliminary results show a novel perception for the targeted therapeutic approaches of cancers.

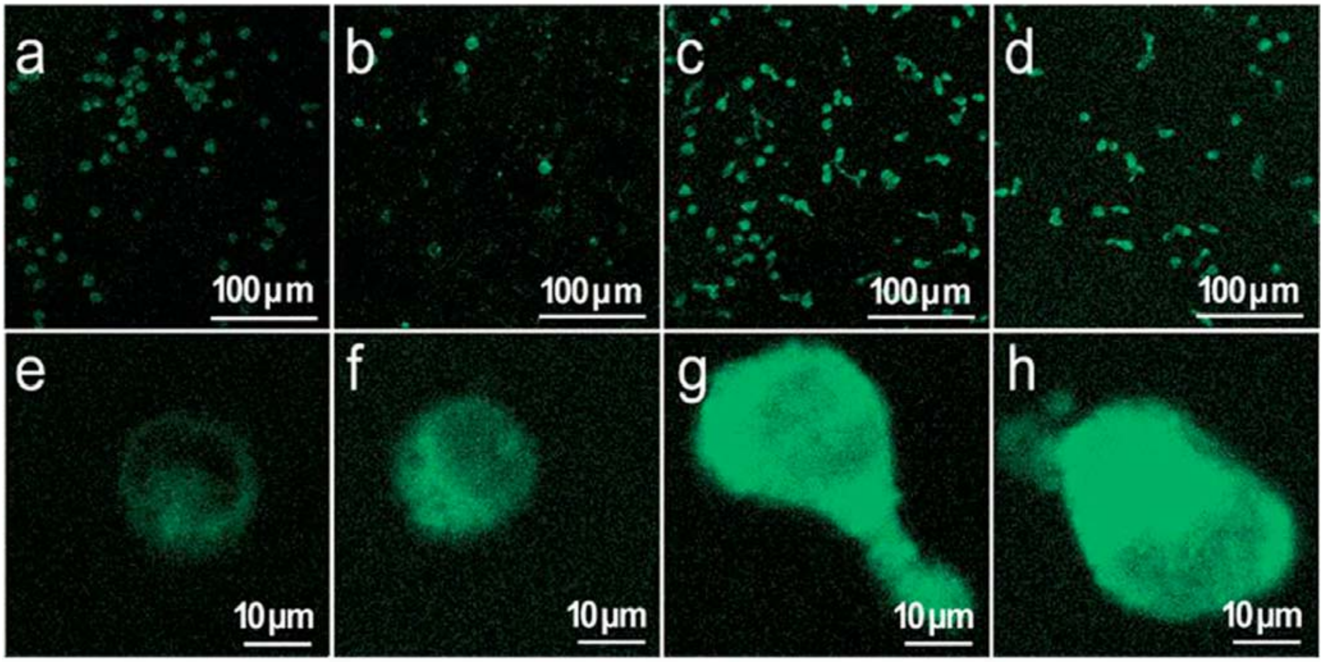


Figure 15: Confocal fluorescence microscopy images of drug-sensitive leukemia K562 cells treated with DNR (**a**, **e**), DNR and Fe_3O_4 nanoparticles (**b**, **f**), DNR and PLA nanofibers (**c**, **g**), DNR, Fe_3O_4-PLA nanocomposites (**d**, **h**) [88].

Schematic shown in the Figure **16** precisely explain the synergistic effect of the novel Fe_3O_4-PLA nanocomposites on the uptake of anticancer drug DNR in target leukemia K562 cells.

2.4.9. PMMA/Fe_3O_4 Nanocomposite

C.C. Zhang *et al.* prepared PMMA/Fe_3O_4 composite fibers and analyses permittivity and magnetic characteristics [89]. It has been shown that adding Fe_3O_4 particles leads to considerable decline in the permittivity and improvement in thermal stability of the nanofibers was observed. The permittivity of the PMMA/Fe_3O_4 composites was found very low (1.22 approximately). Low value of the dielectric constant shows that prepared composites may be used to generate ultra-low dielectric constant materials.

2.4.10. PVC/Fe_3O_4 Nanocomposites

Ovidiu Chiscan *et al*. investigated how concentration of ferrite partices affects high frequency

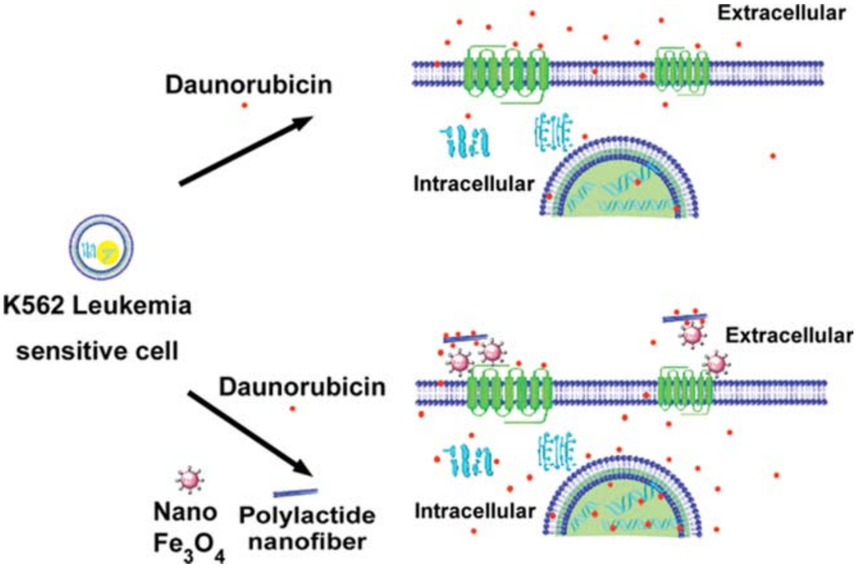


Figure 16: Schematic of synergistic effect of the novel Fe_3O_4-PLA nanocomposites on the uptake of anticancer drug DNR in target leukemia K562 cells [88].

electromagnetic fields absorption tendency of PVC nanofibers having Fe_3O_4 nanoparticles [90]. In this work, PVC/Fe_3O_4 composite nanofibers were prepared by electrospinning method with Fe_3O_4 nanoparticles embedded in the PVC matrix. Technical result shows that so prepared composite exhibits small values of the microwave transmission coefficient. Moreover, desirable absorption characteristics of the material in the X band (8–12 GHz) can be achieved by varying the loading of Fe_3O_4 particles. It is also observed that transmission loss of the prepared composites in the microwave frequency range is below −16dB (decibel). This demonstrates that PVC/Fe_3O_4 composite materials may be used as electromagnetic radiation protecting material.

2.5. Application of Magnetic Nanoparticles (Fe_3O_4)

Magnetic nanoparticles display extraordinary behaviours because of size effects [41]. Numerous novel possible applications (Figure **17**) of ferrite nanoparticles are reported especially in the field of information storage and biomedical applications. Biomedical applications include MRI, hyperthermia, targeted drug delivery, cellular imaging etc [42, 43]. But for drug delivery applications particles comprising drugs are injected in the body. Therefore, it is necessary to recognize the biocompatibility of the particles and possible coating materials for drug delivery purposes [46]. So, conclusively we can say that preparation of ferrites nanoparticles with desirable dimension and biocompatibility is an essential area of research in the field of nanotechnology.

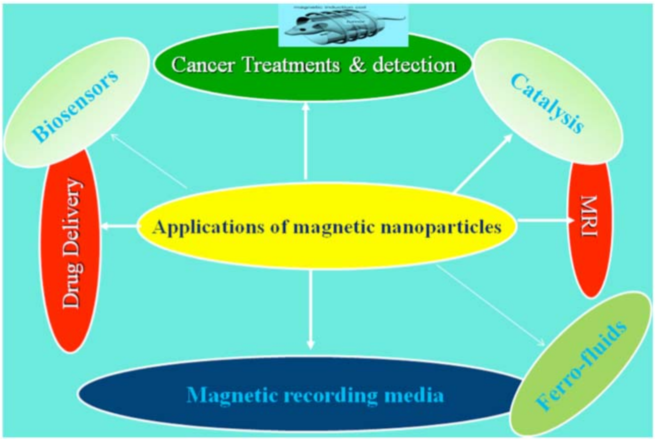


Figure 17: Schematic showing possible applications of ferrite (Fe_3O_4) nanoparticles.

3. FUTURE WORK AND SCOPE OF THE FERRITE NANOFILLERS (MNPs)

The development of biodegradable materials and their polymer composite by using renewable resources having excellent material characteristics is still an important task to fulfil the need for the polymer industries. Recently environmental impact of waste polymers (plastic or rubber) is the rising global concern. So, novel techniques must be innovated to make the polymers and their composite biodegradable. An alternative for this is bio-nanocomposites (i.e. materials of biological origin that are biodegradable materials). However, many types of nanofiller with their polymer composite play important role but has some disadvantages as well. Magnetic nanoparticles including ferrites, meghamite and mixed iron oxides finds many fold applications, but it has got some inherent disadvantages. Poor thermal properties and low magnetization, inferior dispersibility makes it a sort of back bencher in the class of high performance smart materials. As a result of it, incorporation of such magnetic nanoparticles into the polymeric matrix is a challenging task due to inherent agglomeration tendency of such particles. Thus, dispersibility and stability of nanofillers are to be improved in future. In present time, application of magnetic characteristics of polymer inorganic nanocomposites in the electromagnetic wave absorption and electromagnetic (EMI) shielding gained additional interest. Polymer inorganic nanocomposites may also be used as dynamic component in the field of optoelectronic and magneto-optics. But important points concern with PINC are dispersibility of nanofillers, specific size range of nanofillers, thermal stability and composite behaviour in different condition. Hence in further work related with PINC, one has to take care of these points. We observed that not much work has been done on conducting polymer based magnetic nanocomposites. Thus, it will also be the broad area of research in future to investigate the magneto-electric properties of composite and to develop new magneto-electric sensors, actuators and other superconducting material based on conducting polymers. Therefore, number of challenges along with development still exists with magnetic nanoparticles and their composites. Therefore, we need to solve these problems for further modification and developments.

4. CONCLUSIONS

On the basis of above description it is found that magnetic nanoparticles (Fe_3O_4) are acting as superior filler for many polymer matrix and their hybrid composites exhibit drastic improvements in conductivity, magnetism, optical, fatigue resistance, thermal stability, sensing ability and mechanical properties as well. The improvements are mainly owing

Table 3: Overview of Preparation Methods, Characteristics and Applications of Fe_3O_4 Nanoparticles and its Polymer Nanocomposites

Types of filler/polymer composites	Synthesis methods	Advantage	Limitations	Applications	Related references
Fe_3O_4 nanoparticles	Coprecipitation, hydrothermal, sol-gel	Superparamagnetism, no remanence or coercivity, easy to coat by silane agents, suitable magnetization	Instability over longer times, poor thermal properties, biocompatibility, agglomeration tendency	Magnetic fluid, catalysis, sensors, MRI, targeted drug delivery, cellular imaging etc.	[42, 43, 46]
TPU/Fe_3O_4 nanocomposites	Solvent casting, physical mixing	Made into thin film or foam, shape memory properties, improved tensile strenght and saturation magnetization, Biodergradable by fungus	Poor thermal properties, acid like HCl causes decomposition	For smart application.	[62, 68]
PVDF/Fe3O4 nanocomposites	Solvent casting, physical mixing	Significant magneto-dielectric coupling, enhanced ferroelectric polarization, low leakage current, suitable conductivity and magnetization properties, generation of piezoelectricity	Poor dispersion of particles, poor process ability, difficult to achieve beta phase of PVDF	To develop multiferroic devices, piezoelectric applications	[70-74]
PE-PCL grafted/Fe_3O_4 nanocomposites	Ring-opening polymerization of caprolactum	Biocompatible, higher cell viability, suitable magnetization	Need homogeneous dispersion of Fe_3O_4 particles, hydrophobic nature of caprolactam	Magnetic targeted drug delivery and MRI applications.	[58]
Polyaniline/Fe_3O_4 nanocomposites	Two-step or one step oxidative polymerization aniline in presence of Fe_3O_4	Producing egg-like or honeycomb morphology, improved characteristic impedance and reflection loss, better microwave absorption and envirnmental stability, show superparamagnetic, catalytic properties with Au.	Pure conductive Polymers have relatively high complex permittivity and quite low complex permeability, Need more attenuation of incident electromagnetic waves	To prepare greatly efficient microwave absorber materials, to develop electromagnetic, devices, recoverable nano-catalyst with Au	[77-80]
Polypyrrole/Fe_3O_4 nanocomposites	Chemical oxidative polymerization	With Au it exhibits exceptional electrocatalytic activities to bio-species such as ascorbic acid, simplifies the tedious preparation process of the conventional modified electrode, enhance thermal stability, increase electrical conductivity and dielectric constant	Need to chemical relativities and aggregation of particles	In biological separation, enzyme immobilization, radiation absorption, actuator and as biosensors	[81-83]
Polystyrene/Fe_3O_4 nanocomposites	Double-mini emulsion polymerization with sol gel technology	Efficient control and detection of magnetic signals, higher saturation magnetization	Difficulty lies in the interrelated effects in synthesis and assembly such as coating of particles may reduce magnetization	Targeted drug delivery, biosensor, hyperthermia and purification or separation of biomolecules	[84-86]

(Table 3). Continued.

Types of filler/polymer composites	Synthesis methods	Advantage	Limitations	Applications	Related references
Polydopamine Au/Fe_3O_4 nanocomposites	Self polymerization	Good magnetic response to an externally applied magnetic field, vary specific to protein bovine hemoglobin (BHb) and helps in the renoval of abundant protein BHb in the bovine blood	Need more attention to control thickness of the polydopamine shells, steric hindrance among the bound molecules, need to reduceside reaction or non specific bindings	In removing abundant protein in the proteomic analysis	[87]
Polylactide (PLA)/Fe_3O_4 nanocomposites	Fe_3O_4 nanoparticles were prepared by electro chemical deposition under oxidizing conditions and PLA nanofibers were fabricated by electro spinning techniques	Favorable effects on intracellular drug uptake of leukemia K562 cell lines, enhance the permeation and drug uptake of anticancer agents in the cancer cells, polylactide (PLA) is one kind of biocompatible and biodegradable material	Need to control the size of nanoparticles and reduction of side effects	For the targeted therapeutic approaches of cancers	[88]
PMMA/Fe_3O_4 nanocomposites	Electro spinning method	Improvement in the thermal stability of the nanofibers, dielectric constant found very low low	High loading may destroy the polymer intrinsic properties and increase aggregation tendency of the particles	To generate ultra-low dielectric constant materials	[89]
PVC/Fe_3O_4 nanocomposites	Electro spinning method	Low value of the microwave transmission coefficient, controlled absorption properties of the material in the X band (8-12 GHz), transmission loss found below-16dB (decibel)	Increasing the concentration of Fe_3O_4 inside the nanofibers, the distance between the enclosed nanoparticles decreases and they tend to agglomerate may leads to poor properties	In the electromagnetic radiation protecting material and for high-frequency electronic applications	[90]

to the greater surface area of the nanoparticles, specific chemistry, compatibility with polymer and enormous interfacial adhesion between nanoparticles and matrix polymer. However, these properties still depend on filler loading, size of fillers, compatibility and dispersibility of filler in polymer matrix. It has been many times observed that composite shows superior properties, if the amount of loading of nanofillers is less. Magnetic nanoparticle shows superior properties and their composite behaves like shape memory materials when incorporated to polymer matrix but have poor dispersibility and stability up to long time. Additionally, surface of the magnetic nanoparticles has to be functionalized to avoid aggregation. But the main requirement is to assure biocompatibility of the particles as well as possible coating materials to improve the final characteristics. Overall all, we can say that the preparation of ferrite particles and their composites are essential area under discussion in the field of nanomaterial science and technology.

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