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Microwave Technology In Synthesis Of Nanomagnetic Polyacrylonitrile Composites

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Abstract- An extensive work for the study of SnO_2 samples doped with x-mol% of Sb (x = 0, 6, 10, 14 and 18) is reported. The materials were prepared by the polymeric precursor method (Pechini method), calcined for 4 hrs between 800 8C and 1200 8C. The Rietveld method with X-ray diffraction data (XRD) was used to analyze the unit cell dimensions, crystallite size and microstrain. The synthesis of tin oxide nanoparticles with high thermal stability against particle growth rate was achieved by doping SnO_2 particles with Sb_2O_3. All the phases tend to have the same dimension when the temperature increases, although its values vary with x and reaches the maximum value when fired at 1100 ˚C. These variations seem to be an indication that the oxidation state of the antimony changes with the amount of Sb added to the material.

Keywords: Powders: chemical preparation; B. Electron microscopy; B. X-ray methods; SnO_2:Sb; Pigments

1.Introduction

The use of microwave irradiation as an alternative heat source is becoming more and more popular in chemistry. Its good acceptance in inorganic and organic synthesis arises from the immense increase in reaction speed, which compares favourably with conventional heating for a large number of reactions. Apart from this main advantage, significant improvements in yield, reduction of side reactions and cleaner products have been observed. A simple explanation of the above phenomena is the different mechanism of heating. Traditionally, chemical synthesis has been achieved through conductive heating with an external heat source. Heat is driven into the substance, passing first through the walls of the vessel in order to reach the solvent and reactants. This is a slow and inefficient method for transferring energy into the system because it depends on the thermal conductivity of the various materials that must be penetrated. The thermal equilibrium between the temperature of the vessel and the reaction mixture can take hours (Hoogenboom & Schubert, 2007; Sinnwell and Ritter, 2007; Chauveau *et al.*, 2008**)**.

The technological advancements in the field of petrochemical-based polymers have brought many benefits to mankind. However, it is also becoming more and more evident that the ecosystem has been considerably disturbed and damaged as a result of the extensive use of non- degradable petro-plastics. The environmental impact of plastic wastes is causing global concerns as their disposal methods are limited. Incineration of the plastic wastes produces a large amount of carbon dioxide and other toxic gases, which contribute to global warming as well as and pose serious health risks. On the other hand, satisfactory landfill sites are also limited. Thus, there is an urgent need to develop renewable resource-based environmentally benign biodegradable plastic materials, especially for short-term packaging and other disposable applications that would not involve the use of toxic components in their manufacture and would facilitate composting with the naturally occurring biodegradable products.

Degradable plastics, as defined by the American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO), are those which can go through a significant change in the chemical structure under specific environmental conditions (Kolybaba *et al*., 2003). Biodegradable plastics get degraded with the help of naturally occurring microorganisms such as bacteria and fungi. The main attraction of these polymers is their biodegradation and mineralization to benign end-products after the use of the main product by consumers and their disposal into the bio-waste collection system for composting. This whole process will finally leave behind only CO_2 and H_2O as final products.

There are two broad types of biodegradable polymers natural and synthetic. Natural polymers include polysaccharides (starch, cellulose), proteins (gelatine, wool, silk), lipid fats (fats and oil), polyesters produced by plants or microorganisms [poly(hydroxyalkanoates) PHAs], polyesters derived from bio-derived monomers [poly(lactic acid) PLA], and several miscellaneous polymers like natural rubber and composites. The second group includes non-renewable petroleum based synthetic, and biodegradable plastics such as poly(butylene succinate) (PBS) and poly(caprolactone) (PCL). There are some biodegradable polymers which do not come into either category. These are poly anhydrides and poly vinyl alcohol. The most widely studied biodegradable polymers which are likely to be the most promising replacement for petrochemical based thermoplastic are polyesters. In recent years, the application of such biodegradable aliphatic polyesters has got a boost with their increasing use in everyday use materials and medical and health care devices.

2. Literature Review

The crystallization of blends of two semi-crystalline polymers nylon-11 and poly(vinylidene fluoride) was studied. The existence of separate melting and crystallization temperatures over the whole composition range showed that these two polymers did not co-crystallize. However, blending affected the crystallization behavior of each component. Adding nylon-11 decreased the crystallization temperature (T_c) of poly(vinylidene fluoride), but increased its crystallization rate. On the other hand, the T_c of nylon-11 decreased, and its crystallization rate decreased as well when blended with PVF_2. The crystallization mechanism of both nylon-11 and PVF_2 changed in the blends compared to that in the pure states. The Ozawa index, or Avrami exponent, of poly(vinylidene fluoride) in the blend decreased from 3 to 1 as the crystallization temperature decreased from 137°C to 131°C, compared with a decrease from 2.5 to 1.3 observed in pure PVF_2 at the temperature range from 145 °C to 135 °C. The Avrami exponent of nylon-11 in the blend decreased from 2 to 1 as the crystallization temperature decreased from 159 °C to 153 °C, compared with a decrease from 2.5 to 0.75 observed in pure nylon-11 at the same temperature range **(Gao and Scheinbeim, 2023).**

Various (meth) acrylamides were synthesized in good yields directly from (meth) acrylic acid and an amine using microwave irradiation in a solvent-free environment. Under the applied conditions the (meth)acrylic function is preserved. Furthermore, the addition of an initiator like AIBN to the starting mixture leads directly to poly(meth)acrylamides in a single step **(Goretzki *et* al., 2021).**

The crystallization behavior of poly(ethylene terephthalate) (PET)/poly(ethylene- 2,6-naphthalate) (PEN) blends before and after microwave irradiation for different time intervals has been investigated by means of WAXD and DSC techniques. It was found that microwave irradiation could greatly affect the crystallization behavior of PET/PEN blends and significantly enhance their degree of crystallinity. For the PET/PEN (90/10) blends, the degree of crystallinity increased from 15 to 45% and for the PET/PEN (60/40) blends, the degree of crystallinity significantly increased, from 1 to 36%. However, with increasing irradiation time, the degree of crystallinity didn't continually increase. It reached a maximum at certain time point. The cold crystallization enthalpy Δ Hcc gradually decreased as microwave irradiation time increased and the melting enthalpy Δ Hm Vis-à-Vis the long time interval of such irradiation was decreased. In addition, the mechanism for microwave irradiation affecting the crystallization behavior of polymers is discussed **(Li *et* al., 2020).**

3. Microwave Synthesis And Medicinal Chemistry

Improving research and development (R&D) productivity is one of the biggest tasks facing the pharmaceutical industry. In the next 10 years, the pharmaceutical industry will see many patents of drugs expire. In order to remain competitive, pharma companies need to pursue strategies that will offset the sales decline and see robust growth and shareholder value. The impact of genomics and proteomics is creating an explosion in the number of drug targets. Today’s drug therapies are based solely on approximately 500 biological targets, while in 10 years from now the number of targets could well reach 10000. In order to identify more potential drug candidates for all of these targets, pharmaceutical companies have made major investments in high-throughput technologies for genomic and proteomic research, combinatorial chemistry, and biological screening. However, lead compound optimization and medicinal chemistry remain the bottlenecks in the drug discovery process. Developing chemical compounds with the desired biological properties is time-consuming and expensive. Consequently, increasing interest is being directed toward technologies that allow more rapid synthesis and screening of chemical substances to identify compounds with functional qualities.

Medicinal chemistry has benefited tremendously from the technological advances in the field of combinatorial chemistry and high-throughput synthesis. This discipline has been the innovative machine for the development of methods and technologies which accelerate the design, synthesis, purification, and analysis of compound libraries. These new tools have had a significant impact on both lead identification and lead optimization in the pharmaceutical industry. Large compound libraries can now be designed and synthesized to provide valuable leads for new therapeutic targets. Once a chemist has developed a suitable high-speed synthesis of a lead, it is now possible to synthesize and purify hundreds of molecules in parallel to discover new leads and/or to derive structure–activity relationships (SAR) in unprecedented timeframes.

The bottleneck of conventional parallel/combinatorial synthesis is typically optimization of reaction conditions to afford the desired products in suitable yields and purities. Since many reaction sequences require at least one or more heating steps for extended time periods, these optimizations are often difficult and time-consuming. Microwave-assisted heating under controlled conditions has been shown to be an invaluable technology for medicinal chemistry and drug discovery applications since it often dramatically reduces reaction times, typically from days or hours to minutes or even seconds. Many reaction parameters can be evaluated in a few hours to optimize the desired chemistry. Compound libraries can then be rapidly synthesized in either a parallel or (automated) sequential format using this new, enabling technology. In addition, microwave synthesis allows for the discovery of novel reaction pathways, which serve to expand "chemical space" in general, and "biologically relevant, medicinal chemistry space" in particular.

Specifically, microwave synthesis has the potential to impact upon medicinal chemistry efforts in at least three major phases of the drug discovery process: lead generation, hit-to-lead efforts, and lead optimization. Medicinal chemistry addresses what are fundamentally biological and clinical problems. Focusing first on the preparation of suitable molecular tools for mechanistic validation, efforts ultimately turn to the optimization of biochemical, pharmacokinetic, pharmacological, clinical, and competitive properties of drug candidates. A common theme throughout this drug discovery and development process is speed. Speed equals competitive advantage, more efficient use of expensive and limited resources, faster exploration of structure– activity relationships (SAR), enhanced delineation of intellectual property, more timely delivery of critically needed medicines, and can ultimately determine positioning in the marketplace. To the pharmaceutical industry and the medicinal chemist, time truly does equal money, and microwave chemistry has become a central tool in this fast-paced, time-sensitive field.

Chemistry, like all sciences, consists of never-ending iterations of hypotheses and experiments, with results guiding the progress and development of projects. The short reaction times provided by microwave synthesis make it ideal for rapid reaction scouting and optimization, allowing very rapid progress through the "hypotheses- experiment-results" iterations, resulting in more decision points per unit time. In order to fully benefit from microwave synthesis, one has to "be prepared to fail in order to succeed". While failure could cost a few minutes, success would gain many hours or even days. The speed at which multiple variations of reaction conditions can be performed allows a morning discussion of "What should we try?" to become an after lunch discussion of "What were the results?" (the "let's talk after lunch" mantra) [1]. Not surprisingly, therefore, most pharmaceutical, agrochemical, and biotechnology companies are already heavily using microwave synthesis as frontline methodology in their chemistry programs, both for library synthesis and for lead optimization, as they realize the ability of this enabling technology to speed chemical reactions and therefore the drug discovery process.

Since the early days of microwave synthesis, the observed rate accelerations and sometimes altered product distributions compared to oil-bath experiments have led to speculation on the existence of so-called "specific" or "non-thermal" microwave effects [11]. Historically, such effects were claimed when the outcome of a synthesis performed under microwave conditions was different from that of the conventionally heated counterpart at the same apparent temperature. Reviewing the present literature [12], it appears that today most scientists agree that in the majority of cases the reason for the observed rate enhancements is a purely thermal/kinetic effect, i.e.,a consequence of the high reaction temperatures that can rapidly be attained when irradiating polar materials in a microwave field,although effects that are caused by the unique nature of the microwave dielectric heating mechanism ("specific microwave effects") clearly also need to be considered. While for the medicinal chemist in industry this discussion may seem largely irrelevant, the debate on "microwave effects" is undoubtedly going to continue for many years in the academic world. Regardless of the nature of the observed rate enhancements (for further details on microwave effects, see Section 2.5), microwave synthesis has now truly matured and has moved from a laboratory curiosity in the late 1980s to an established technique in organic synthesis, heavily used in both academia and industry.

The initial slow uptake of the technology in the late 1980s and 1990s has been attributed to its lack of controllability and reproducibility, coupled with a general lack of understanding of the basics of microwave dielectric heating. The risks associated with the flammability of organic solvents in a microwave field and the lack of available dedicated microwave reactors allowing for adequate temperature and pressure control were major concerns. Important instrument innovation now allows for careful control of time, temperature, and pressure profiles, paving the way for reproducible protocol development, scale-up, and transfer from laboratory to laboratory and from scientist to scientist. Today, microwave chemistry is as reliable as the vast arsenal of synthetic methods that preceded it. Since 2001, therefore, the number of publications related to MAOS has increased dramatically.

4. **Microwave Chemical Synthesis**

Previous research has revealed several advantages from microwave-assisted wet chemical synthesis in reaction acceleration, yield improvement, enhanced physicochemical properties and the evolvement of new material phases. The study present examples that demonstrate the significance of these advantages to industrial application. In order to achieve successful industrial application there is a need to distinguish between the microwave athermal (not excited by heat) effects from the microwave-induced thermal effect (temperature rise). The optimization of this new process has to be systematically investigated, so the advantages and benefits of this new technology can be fully exploited.

Advantages and significance of Fe_2O_3 based magnetic materials

Fe_2O_3 based magnetic materials have been extensively used as recording materials because of their good magnetic properties. The emergence of nanomagnetic technology has imposed new demands upon magnetic materials. To fabricate ultrahigh density and ultrahigh speed data storage devices, which work on the magnetic -spintronic concept, magnetic materials with nanoscale particles are highly preferred [1].

Conventionally, Fe_2O_3 powders with monodispersed particles are synthesized first by means of forced hydrolysis of ferric nitrate or ferric chloride in aqueous solutions, which produces a Fe_2O_3, and then the a- Fe_2O_3 are transformed into Fe_2O_3 in a high-temperature process [2], [3]. To effectively control the particle shape and particle size, which are essential for achieving the desired magnetic properties, the hydrolysis solution must be very dilute. For producing micron- and submicron-sized particles, the concentrations of the ferric irons are generally within a range around 0.02M [2], [4], [5] and for producing nanosized powders, the ferric concentration should be much lower. In addition to dilute solutions, the conventional hydrolysis has to be carefully controlled and it generally requires 2-7 days. This means that, even based upon the shortest processing time and highest concentration, the rate for producing the nanosized iron oxide powders would be less than 0.014 gram per liter per hour. In order to use nanosized magnetic materials for industrial applications, appreciable acceleration of the process and an increase in the ferric concentration are required.

Several researchers have attempted the iron oxide synthesis via microwave-assisted hydrolysis. Komarneni et al demonstrated that under otherwise identical processing conditions, synthesis of crystalline hematite by a microwave-hydrothermal approach was 36 times faster than by conventional hydrothermal methods [6]. Our study shows the capability of controlling the particle shape and particle size with this rapid synthesis approach. Rigneau et al further shortened the processing time to 30 minutes and also increase the ferric concentration to 0.05M

[7], which could increase the production rate over one hundred times. The even more striking finding from their results was that the microwave synthesized Fe_2O_3 particles were nano scale and directly type. The significance of this finding is that it could not only remarkably simplify the synthesis procedure, but also get rid of the difficulties involved with the calcination of nano powders, and avoid the detrimental microstructure changes that accompany the transformation from a- Fe_2O_3 to ?- Fe_2O_3 in the conventional high temperature process.

Insertion electrode materials

The role of intercalation/insertion reactions in battery electrodes was first recognized about 30 years ago. From the first prototype titanium disulfide cells, the technology has more recently been commercialized in Li-ion cells using a cobalt oxide insertion cathode and a carbon insertion anode. This technology has proven highly successful in small devices. Since the conduction species intercalated in the structure exhibit very good electrical conductivity, insertion electrode materials are also considered most promising in large device and large-scale applications [8].

The extensive research and development on new insertion materials can be recognized from Whittinghan's Work. His investigation has covered a diverse group of layered and intercalated compounds including titanium disulfide [9], [10], lithium cobalt oxide [11], tetramethylammonium intercalated vanadium oxides [12], layered-structure manganese dioxides [13] and vanadium-pillared manganese oxide structures [14]. More recently, the group is investigating vanadium oxide nanotubes, which is considered to have significant advantages due to its distinct electrical contact regions and electrolyte-filled channels [15].

The insertion materials are normally synthesized via conventional hydrothermal method. The synthesis is a tedious procedure and often takes several days to a week. The use of the microwave method has been attempted to accelerate the synthesis of layered vanadium oxide inserted with tetramethylammonium ions [12]. It was found that this method could reduce the synthesis time to minutes and also found that longer microwave hydrothermal treatment could lead to a new material structure. The adoption of the microwave method to the insertion material synthesis could not only develop a highly efficient, low cost process for synthesis of insertion materials synthesis, but also offer chances to generate new material structures that could not be obtained from conventional methods.

Molecular sieves

Crystalline molecular sieves have intraframework cages and channels of uniform microporous or mesoporous size, tailor-made acidity or basicity, and high thermal stability. Owing to these unique structures, the materials have acquired various applications in the petroleum refining and petrochemical industry [16]. The advent of nanotechnology has provided a new field for their application. The materials can be used as a high performance nanostrucutured host for preparation of advanced materials that exhibit specific optic, optoelectronic, and electrochemical properties suitable for molecular wire, quantum electronics and non-linear optical devices. A number of preparations of nanoscale materials on such a nanostructured template have been demonstrated including the synthesis of organized metal clusters, metal oxides or sulfides, isolated conducting polymers as well as confined supermolecular compounds [17-30].

The structure of the molecular sieve frameworks is of great diversity. It is sensitive to synthesis conditions. Generally, it takes several days to several weeks for obtaining the desired material. Raising the temperature may shorten the synthesis time but could result in different structures. There are often several structures concurrently in development. Although each structure may have a dominating stage, the product is more liable to mixed structures31. The process is often complicated and time-consuming for synthesizing a pure product with tailored structure.

Organometallic compounds

Organometallic compounds are generally defined as having a metal-carbon bond with properties distinct from those of inorganic compounds. Orgaometallic compounds cover a large number of varieties, which contain many kinds of metal elements. Some groups have high reactivity and reaction selectivity and are used as various kinds of catalysts or as organosynthetic reagents. Others have chemical stability and have acquired their applications in microbiocides, pesticides, anticancer agents, water repellants, octane number improvement, and antifoaming and mold releasing. Organometallic compounds are also employed as precursors for preparing ultrahigh purity metals and functional ceramics with tailored compositions and structures, such as semiconductor elements, electroconductive materials, magnetic materials, hard materials, heatresistant materials and superconductive materials, etc36.

	Microwave vs reflux			
Compound	Time (min)	Temp (°C)	Yield (%)	Rate enhancement
(dppe=)Mo(CO)4	0.5/25#	180/120	80/68	50
(dppe=)Mo(CO)4	2/180	180/155	64/55	90
(bipyQ)Mo(CO)4	0.5/90	180/110	99/88	180
(dppe)Cr(CO)4	0.5/135	180/135	86/41	270
(dppm²)W(CO)4	5/2880	180/165	62/51	576

Table 1. Synthesis of Group 6 (Cr, Mo, W) zerovalent organometallic carbonyl compounds:
synthesis method: microwave / reflux = bis(diphenylphosphino)ethane
Q 2,2’-bipyridine ²bis(diphenylphosphino)methane

5. Results

5.1 Synthesis of nanocomposites in microwave

Ferrite nanoparticles with size 15 & 20 nm were synthesized using $FeCl_2.4H_2O$ precursor at 90 ± 1^0C and ammonia (7.0 M., 17.94 mL) as precipitating agent. Synthesized ferrite nanoparticles were further reduced into Iron nanoparticles using hydrazine hydrate (99.5%) and sodium hydroxide (5.0g, 0.125 mol) at 90^0C over 12h. [Table 1]. Ferrite nanoparticles (20 nm) has shown saturation magnetization 2.754 emu/g [Fig.1 (a)], whereas iron nanoparticles (11 nm) derived from reduction of the size of ferrite nanoparticles (20 nm) has shown saturation magnetization 3.862 emu/g. [Fig.1 (b)].

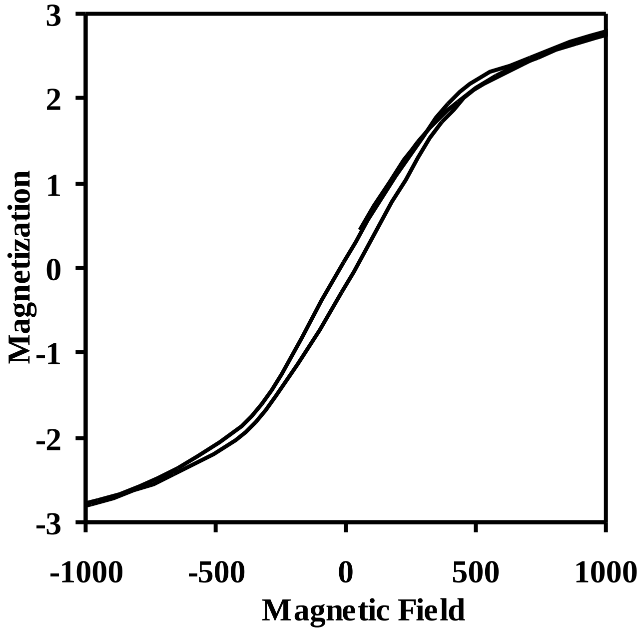

Figure 5.1: (a): VSM of Ferrite Nanoparticle (20 nm)

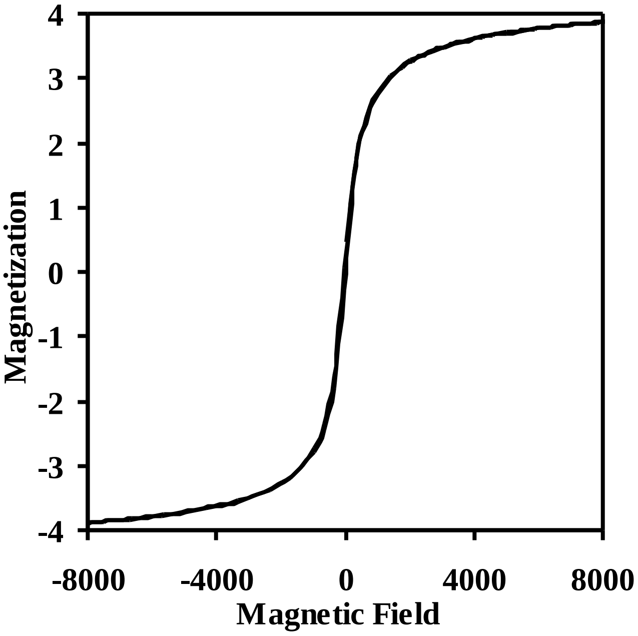

Figure 5.1: (b): VSM of Fe Nanoparticle (11 nm)

The Polyacrylonitrile (PAN) synthesized through AIBN (100 mg., 0.6089 mol.) initiated polymerization of Acrylonitrile (AN, 5.0 mL., 0.076 mol.) under microwave (10 min., 100 watt) has shown weight average molecular mass 41607 with polydispersity index 2.2075 [Fig.2].

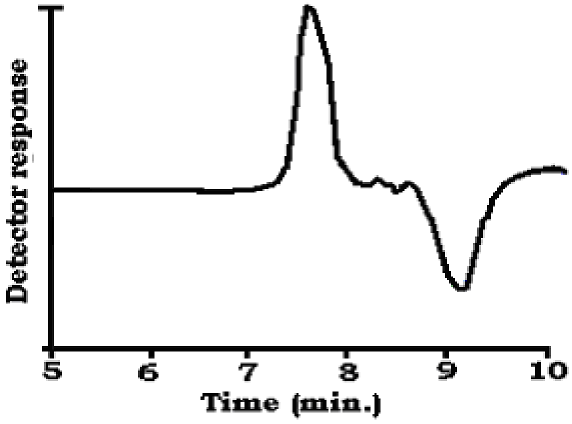

Figure 5.2: GPC of PAN

Nanomagnetic polyacrylonitrile composites (NPACs) were synthesized through AIBN (100 mg., 0.6089 mol.) initiated polymerization of AN (5.0 mL., 0.076 mol.) in presence of magnetic nanoparticles at 100W over 10 min [Table 2].

5.2. Spectra

Formation of ferrite nanoparticles, iron nanoparticles and corresponding nanocomposites has been ascertained through UV-VIS and FT-IR spectra. UV-VIS spectra of AN, PAN, ferrite, iron and corresponding Polyacrylonitrile ferrite nanocomposites [I], Polyacrylonitrile iron nanocomposites [II] were recorded in N-methyl 2-pyrrolidone. Each of the materials has shown their characteristic absorptions in Uv-vis spectra. Ferrite nanoparticles (20 nm) has shown absorption at 263 nm. Reduction of ferrite nanoparticles has provided iron nanoparticles (11 nm) with absorption at 260 nm **(Blanco *et* al., 1994).**

AN and AIBN has shown absorptions at 266 & 257 nm respectively. Polymerization of AN in presence of AIBN has provided PAN with strong absorptions at 281 nm. Such red shift in the absorption of PAN was due to n-π* transition **(Joshi *et* al., 2005).** The nanomagnetic Polyacrylonitrile composites [I] & [II] has shown absorptions at 275, 272 nm respectively. Such red shift in the absorption of nanocomposites over PAN was due to n-π* transition [Fig.3].

Each of the ferrite nanoparticles has shown common FT-IR absorptions (cm^{-1}) corresponding to the presence of atmospheric CO_2 at 2369.00 and HOH bending; 1653.45. Ferrite nanoparticles (15 nm) has shown absorption corresponding to H-O-H stretching; 3453.87, NH_2 bending; 1015.66, intrinsic stretching vibrations of the metal at the tetrahedral site ($M_{tetrahedral} \leftrightarrow O$); 585.98 and ($M_{octahedral} \leftrightarrow O$); 451.61. Ferrite nanoparticles (20 nm) has shown absence of the absorption corresponding to H-O-H stretching. NH_2 bending; 1021.84, intrinsic stretching vibrations of the metal at the tetrahedral site ($M_{tetrahedral} \leftrightarrow O$); 565.65 and ($M_{octahedral} \leftrightarrow O$); 450.21.

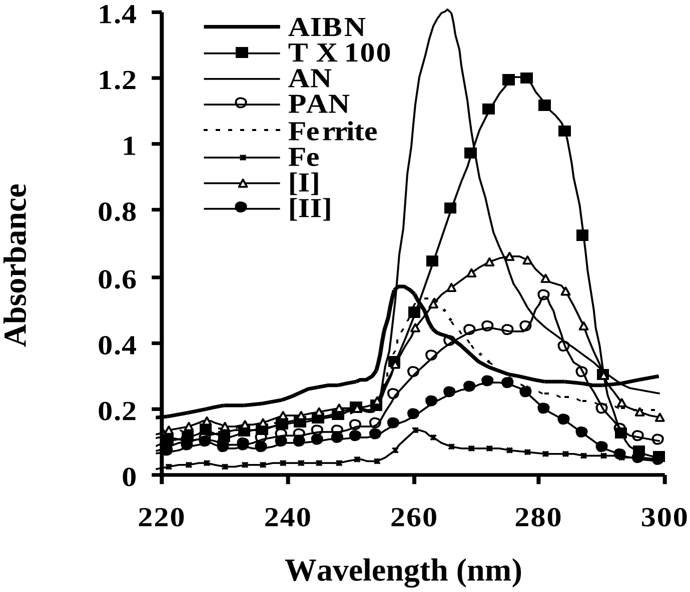

Figure 5.3: UV-VIS spectra

Reduction of ferrite nanoparticles in presence of hydrazine hydrate has rendered corresponding iron nanoparticles. Ferrite nanoparticles (15 nm) has provided iron nanoparticles (8 nm) with absorption corresponding to H-O-H stretching; 3453.87, atmospheric CO_2; 2376.00, H-O-H bending; 1653.45, NH_2 bending; 1011.98, intrinsic stretching vibrations of the metal at the tetrahedral site ($M_{tetrahedral} \leftrightarrow O$); 574.00 and ($M_{octahedral} \leftrightarrow O$); 433.17. Reduction of ferrite nanoparticles (20 nm) has rendered iron nanoparticles (11 nm) with absorption corresponding to H-O-H stretching; 3424.40, atmospheric CO_2 at 2344.65, H-O-H bending 1655.14, NH2 bending; 1019.35 **(Moensiric *et* al., 2007).**

PAN and [II] have shown common absorptions due to C-N stretching at 1248.18. PAN has shown absorptions corresponding to CH_2 stretching; 2947.40, CN stretching; 2244.60, C=C stretching; 1617.83, N=N stretching; 1512.47, CH_2 scissoring; (1458.10), CH_2 twisting; (1362.98), CH_2 wagging; 1111.76, bending due to –CH-C<; 950.61 and CH_2 rocking; 832.78 **(Tomaszewska *et* al., 2002).**

Polymerization of AN in presence of ferrite nanoparticles (20 nm) has rendered nanocomposites [I] with absorptions corresponding to CH_2 stretching; 2948.27, CN stretching; 2243.88, N=N stretching; 1511.57, CH_2 scissoring; 1458.09, CH_2 twisting; 1364.42, C-N stretching; 1248.40, CH_2 wagging; 1111.04, bending due to –CH-C<; 945.62 and CH_2 rocking; 827.64. Nanocomposites [II] derived from with iron nanoparticles (11 nm) has rendered absorptions corresponding to CH_2 stretching; 2944.64, N=N stretching; 1512.17, CH_2 scissoring; 1456.42, CH_2 twisting; 1362. 21, C-N stretching; 1248.18, CH_2 wagging; 1113.88, bending due to –CH-C<; 951.15 and CH_2 rocking; 832.06 along with a new absorption corresponding to C=N stretching at 1612.90 [Fig.4].

Conclusions

The increase of the unit cell is due to the substitution of Sn^{4+} by Sb^{3+} in the SnO_2 lattice. Sb^{3+} and Sb^{5+} coexist at higher concentration of antimony for the materials heated above 900 8C, causing the stability of crystallite size and microstrain. For the material prepared at 800 8C, the amount of Sb^{5+} increase with the addition of antimony. The HRTEM analysis showed that the undoped material is more densely agglomerated than the doped material. These results clearly show that doped antimony can be used to control particle size and stabilize SnO_2 against particle growth at high temperatures.

Heat-bodying (HB) and microwave irradiation (MI) increased the viscosity of soybean oil. Pressurized differential scanning calorimetry showed that the HB considerably improved oxidative stability over the untreated soybean oil, and oil exposed to MI had greater oxidative stability than HB. The most noteworthy finding of this studywas that HB, and to a greater extent MI, lowered the pour point considerably compared with untreated soybean oil despite having an increase in viscosity. ^{1}HNMR analysis showed no occurrence of oxidation regardless of treatment and that the pour point anomaly is most likely the result of the formation of triacylglyceride cyclic ring structures that caused an increase in viscosity. Greater friction was observed for oils treated by HB and MI than the untreated and particularly MI, which left greater wear scratches on the ball and disk surfaces used for lubricity studies. Microwave irradiation shows promise to improve the cold-flow behavior of soybean oil, butMI treatment will not produce superior vegetable oil-based lubricants.

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