DIELECTRIC & MECHANICAL PROPERTIES OF PANI COATED $Ni_{0.6}Zn_{0.4}Fe_2O_4$ FERRITE-NATURAL RUBBER COMPOSITE

[1&3]Haisel Mathew, [2]Bipinbal P.K, [3&4]Sunny Kuriakose,[3]B.Syamala Kumari
[1] Department of Physics,Little Flower College,Guruvayur,
University of Calicut ,Puthepalli P.O.,,Kerala,India
[2] Department of Polymer Science &Rubber Technology,
Cochin University of Science and Technology, Kerala,India
[3]Research Centre, Department of Physics, Maharajas College, Ernakulam,
M.G.University,. Kerala, India.
[4]Dept. of physics,Muthoot Institute of Technology and science,Varikoly,
Kerala Technological University ,Kerala,India.

Abstract

Amongst the family of conducting polymers, polyaniline(PANI) is unique due to its ease of synthesis, environmental stability, and simple doping / dedoping chemistry. Making PANI with suitable materials is a method to vary the properties of PANI. Organic–inorganic nanocomposites with an organized structure has been extensively studied because they combine the advantages of the inorganic materials and the organic polymers which are difficult to obtain from individual components. The property of composite depends on several factors such as type of filler,size of filler ,concentration and the interaction between the filler molecules and the polymer macromolecules. In the present work, The $Ni_{0.6}Zn_{0.4}Fe_2O_4$ mixed ferrite nanoparticle is prepared by Sol-Gel method. PANI coated NiZn Ferrite is prepared using Camphour sulphonic acid(CSA) as dopant, studied the frequency dependence of dielectric constant and a.c. conductivity . PANI coated NiZn Ferrite is blended with natural Rubber(NR) using Brabender Plasticorder& tried to measure the dielectric and mechanical properties of the same. The FTIR, XRD,VSM& SEM analysis of the samples were done. PANI coated NiZn Ferrite showed decrease in dieiectric constant with increase in frequency for all the samplesre. At lower frequencies electronic, ionic, dipolar rand space charge polarizations contribute towards polarization but at higher frequencies some of the polarization contributions relax out, resulting in lowering of dielectric constant. The a.c. conductivity is found to increase with increase in frequency. The formation of polarons upon the oxidation of polyaniline molecule and the combination of two close polarons to form bipolaron is the reason behind the conductive behavior.As the frequency of applied field increases, hopping of carriers also increases ,thereby increasing the conductivity.NI coated NiZn Ferrite-Natural rubber composite also showed increase in a.c. conductivity and decrease in dielectric constant with increase in frequency for all the samples. The varation in storage modulus of PANI coated NiZn Ferrite-Natural rubber composite is studied the using Dynamic Mechanical Analyser. With increase in filler content, storage modulus increased showing an increase in the stiffness of the natural Rubber.

Key words : polymers , PANI coated NiZn Ferrite ,Natural Rubber ,Dielecric constant,A.C.Conductivity,Storage modulus

INTRODUCTION

A polymer is a material whose molecule contains a very large number of atoms linked by covalent bonds, which makes it a macromolecule. Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. Electrical conductivity of conducting polymers can be tuned from insulating to metallic through proper doping. They have a conjugated structure with alternate σ and π bonds. The π bonds are delocalized throughout the entire polymer network. This results in enhanced electrical conductivity [1].Preparing conducting polymer composite is a clever way to vary the properties of of conducting polymers[2].

In the present work,the sample polyaniline coated NiZn Ferrite composite is prepared using Camphour sulphonic acid(CSA) as dopant .This composite is blended with natural Rubber(NR) using Brabender Plasticorder& tried to measure the mechanical properties of the same. The FTIR spectral analysis , XRD analysis,VSM &SEM analysis were done to characterize the prepared samples.Mechanical properties of the blend is measured using Dynamic Mechanical analyser. Mixed ferrites belonging to the series $N_{1-x}Zn_xFe_2O_4$ which ishaving spinel structure is chosen because of the availability of vast literature on the various properties of this ferrites Due to their low cost,ferrite materials are used in various devices like microwave,transformer core,memories, noise filters tc.It shows unusual physical and chemical properties when its size is reduced to nanosize.[3].

Recently,significant scientific and technological interest has focused on the PANI-inorganic nano composite.The use of nanosized inorganic fillers like ferrites into PANI produces materials with complementary beween PANI and inorganic nanoparticles. PANI-ferrite materials can't be moulded into different shapes. When complex pattern and shape are required,,one naturally think of composites made of Natural rubber.Natural Rubber is chosen because of it's local availability possible value enhancement.Natural rubber (NR) has been increasingly used for forming composites owing to its unique mechanical properties. NR is extensively used in various products that require superior properties such as elasticity, flexibility, and resilience [4].

II.MATERIALS AND METHODS.

A. *Materials*

The materials used in the work are Aniline, Camphour sulphonic acid, Ammonium peroxidisulphate, Iron Nitrate, Nickel Nitrate,Zinc Nitrate, Ethylene glycol, Natural Rubber, ZnO, Stearic acid,TQ, Sulphur& ZDBC. All the materials except aniline were used as purchased without further purification.Aniline is distilled before the synthesis.

B. Preparation ofF $Ni_{0.6}Zn_{0.4}Fe_2O_4$ nanoparticles

Sol-gel method involves formation of an amorphous gel from a solution followed by its dehydration at an elevated temperature. For the preparation of ferrites by Sol-Gel method, the required quantity of Iron nitrate,Nickel nitrate,Zinc nitrate is taken in order to satisfy the combination of mixed ferrite as $Ni_{0.6}Zn_{0.4}Fe_2O_4$ and dissolved the nitrates in 100ml of ethylene glycol.Kept it on magnetic stirrer at room temperature for 20 to 30 minutes of stirring.Then the solution is heated till the gel is formed and the gel is heated at 120^0C till the gel turns to ash.The ash is finely powdered and sintered at 400^0C using muffle furnace for 4 hours.

C. Preparation of PANI Coated NiZnferrite

For preparing CSA doped PANI-ferrite composite, 1gm of Ni-Zn ferrite is added in 1M CSA solution.Freshly distilled aniline is added to it. Ammonium peroxide isulphate(APS) dissolved in water is added dropwise to the mixture with continuous stirring for 4-5 hrs .The precipitate obtained is filtered, washed and dried.The same procedure is repeated using 2gm and 3gm of Ni-Zn ferrite.For every composite,5ml of aniline is taken and the mass of mixed ferrite is varied.The prepared samples are named as PF1,PF2&PF3

D. Preparation of Natural Rubber- PANI Coated NiZnferrite composite

The PANI coated ferriteI conducting filler mixing with NR polymer matrix was accomplished with Brabender Plasticoder.For this PF1 powder is ued as filler.NR of the type smoked sheets, a product of Malaysia, was used in the present research..Zinc oxide (ZnO) with particle size of 20 nm, a product of Bayer Company (Leverkosen,Germany), was used as accelerator for rubber vulcanizates. The other compounding rubber ingredients were of pure grade used in industry. Typical formulation of NR composite compounds are presented in Table1.The vulcanization process of the NR-based compounds was carried out in an electrically heated hydraulic press using a special home made mould at temperature 90^0C and under pressure. The samples prepared are named as NR-PF10,NR-PF15,NR-PF30 and NR-PF70.Here phr is part per hundred rubber.

Table 1	
Ingredients	**Phr**
NR	100
Polyaniline –NiZn Fe2O4	10,15,30 ,70
ZnO	4
Stearic acid	2
TQ	1
ZDBC	1.5
Sulphur	2

III.CHRACTERIZATION TECHNIQUES

A. XRD Analysis

XRD patterns were employed to portray the structure of PANI , $Ni_{0.6}Zn_{0.4}Fe_2O_4$ and PANI coated $Ni_{0.6}Zn_{0.4}Fe_2O_4$ –NR composite. The patterns were obtained using a fully automated Rigaker 1710 X-ray powder diffractometer. In our set-up, filtered Cu-K2 radiation having wavelength 1.542 Ǻ is used for diffraction. The accelerating potential applied to the X-ray tube is 30 KV and the tube current is 20mA.

B. FTIR Analysis

Fourier transform infrared (FTIR) spectroscopy can be used to detect changes in coordination and configuration of molecular species in a system.The vibrations of individual bonds or groups in a molecule have the same frequency as electromagnetic radiation in the IR region FTIR spectrum is taken using an Avatar 370 spectrometer employing DTGS KBR detector

C. SEM Analysis

Scanning Electron Microscopy is similar to optical microscopy.But here electrons are used instead of photons.Electrons of high energy impinge on the sample.Secondary electrons,back scattered electrons and X-ray photons are produced.Secondary electrons form the SEM image.Using SEM ,magnification of the order of 10^6 could be achieved,which is impossible through optical microscope.Large magnification is possible because electrons have smaller wavelengths and depth of field produced is large.Scanning electron Microscopy is used for high resolution imaging.High quality low voltage images are obtained with negligible electrical charging of samples. JEOL Model JSM - 6390LV Scanning Electron Microscope was employed to check the morphology of the samples.

D. VSM Analysis

A vibrating sample magnetometer (VSM) is a scientific instrument that measures magnetic properties. VSM operates on faraday's law of induction, which tells us that a change in magnetic field will produce an electric field. This electric field can be measured and can tell us information about the changing magnetic field.Magnetization measurements were carried out on a vibrating sample magnetometer at room temperature with a maximum applied field of 15 KOe.

E. Measurement of Dielectric constant and A.C. conductivity

The dielectric properties of PANI coated $Ni_{0.6}Zn_{0.4}Fe_2O_4$ and PANI coated $Ni_{0.6}Zn_{0.4}Fe_2O_4$ –NR composite were carried out using impedence analyser . For the dielectric measurements,the sample in the form of pellet is used.The measurements are carried out using a cell assembly for holding the sample and an impedence analyser(6500B Wayne Kerr impedenceanalyser). The measurements were carried out at frequencies ranging from 100Hz to 6MHz using an impedance analyzer. Disc shaped samples were used for the measurements.. Dielectric loss and capacitance were measured for the frequency range 100Hz to 1MHz using the above system. Dielectric permittivity(έ) of the samples were calculated using the relation **έ=** Cd /6.67E-12*A**.**From the dielectric loss(tanδ) and dielectric constant,ac conductivity of the sample can be evaluated using the relation,a.c.coductivity(σ)= έ*6.67E-12* 2πf *tanδ.

Impedence analyser system

F. Dynamic Mechanical Analyser

Dynamic mechanical analyser

Dynamic mechanical analysis (DMA) is a technique used to study and characterize materials. It is most useful for studying the viscoelastic behavior of polymers. Mechanical analysis was conducted using rectangular test specimens having a dimension of 60 mm x 4mm x 2 mm with a dual cantilever clamp on a dynamic mechanical analyzer (Model Q 800, TA instruments). A sinusoidal stress is applied and the strain in the material is measured and determined the complex modulus. The temperature of the sample or the frequency of the stress are often varied, leading to variations in the complex modulus.Here,the variation in storage modulus with variation in frequency in the range 0-30Hz is studied.

IV RESULTS &DISCUSSION

A. XRD Analysis

XRD spectrum of PANI „NiZn Ferrite &PANI coated NiZn Ferrite are shown in Fig1(a),Fig1(b)and Fig1(c)

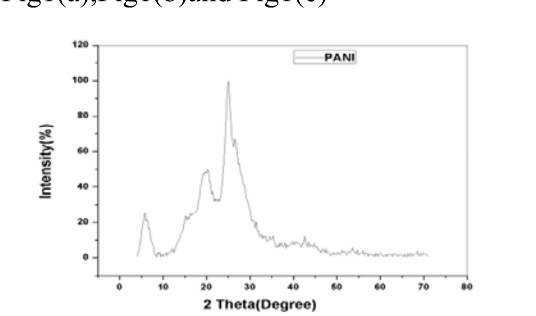

Fig1(a)XRD pattern of PANI

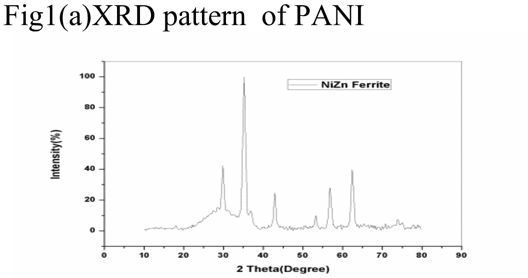

Fig1(b) XRD pattern of Ni-Zn ferrite

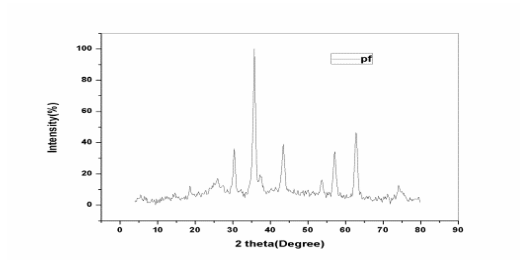

Fig1(c)XRD pattern of PANI coated Ni-Zn ferrite

The peak around 25˚in the XRD spectrum of PANI is the characteristic of π conjugation in PANI. PANI is only partially crystalline with conducting metallic islands separated by large amorphous regions as evident from the XRD spectrum. Conductivity is limited by strong disorder[5].The XRD Spectrum of NiZn Ferrite shows that the ferrite is crystalline with spinel structure. From the XRD pattern of Ferrite nanoparticles,the crystallite size was estimated using Debye-Scherrer formula and it's average size is found to be about 20nm.In the XRD pattern of composite,XRD peaks of ferrite is predominant and the broad peak of PANI is not predominant because the ferrite nanoparticles interfered with PANI chains.[6]

B. *FTIR Analysis*

FTIR spectrum of PANI doped with Camphor sulphonic acid,NiZn Ferrite &PANI coated NiZn Ferrite are shown in Fig2(a),Fig2(b)&Fig2(c)

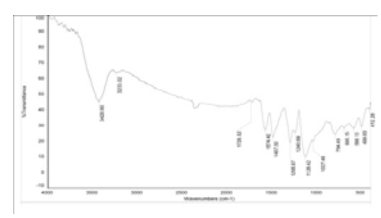

Fig2(a) FTIR spectrum of PANI

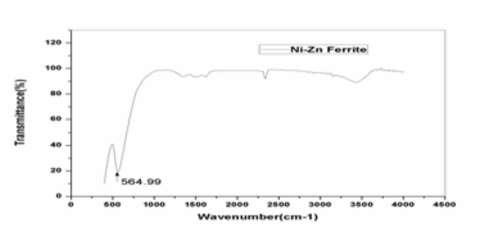

Fig2(b)FTIR spectrum of of Ni-Zn ferrite

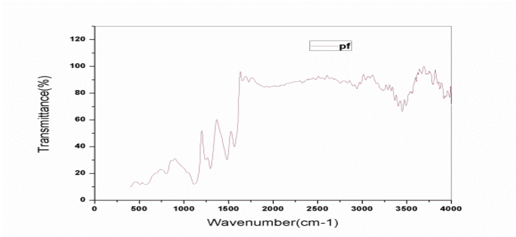

Fig2(c)FTIR spectrum of PANI coated Ni-Zn ferrite

In the FTIR spectrum of PANI (Figure2(a)), the major peaks are at around 3500/cm(N-H stretching vibration),3200/cm(O-H usually broad), 1780/cm(cyclobutanone), 1570/cm(C=N strech of the quinonoid unit of PANI),1470/cm(C=C strech of the benzoid unit of PANI) and 1100/cm(quinonoid unit of vibration of doped PANI[6].The FTIR spectra of NiZn Ferrite(Figure2(b)) shows a characteristic peak at 569.2/cm which correspond to the to the stretching vibrations of Fe-O at the tetrahedral site of the ferrite nanoparticles .This is the characteristic feature of spinel ferrite.The FTIR spectra of composite sample(Figure2(c)) shows the peaks of both PANI and NiZn Ferrite.[3]

C. *SEM ANALYSIS*

SEM images of NiZn Ferrite &PANI coated NiZn Ferrite composite are shown in Fig3(a)&Fig3(b) The SEM image shows the surface morphology of NiZn Ferrite&PANI coated NiZn Ferrite composite.SEM image of NiZn Ferrite nanoparticles show spherical shapes with high homogeneity.The composite shows a different image and the aggregation of nanopartices is found to be reduced duo to the repulsive forces between magnetic nanoparticles and PANI.[6].

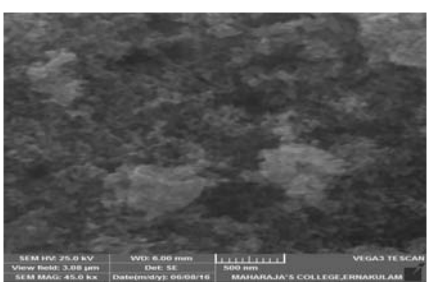

Fig3(a) SEM image of the Ni-Zn ferrite

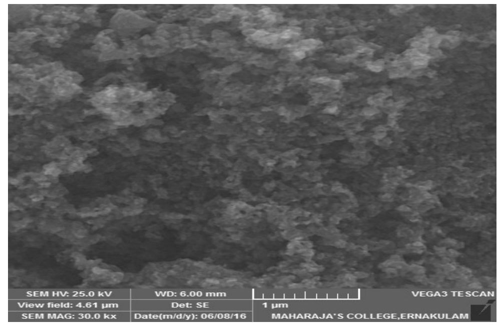

Fig3(b) SEM image of the PANI coated Ni-Zn ferrite

Figure 3(c),3(d) and 3(e) shows scanning electron micrographs of the Natural-rubber/ PANI coatedferrite composites with PANI coated ferrite at10phr,15phr and 30phr loadings. Figurereveals that PANI coated ferrite particles are well dispersed in Natural Rubber

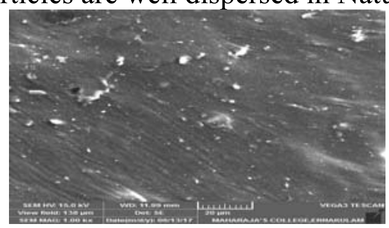

Fig3(d) SEM image of the NR-PF10

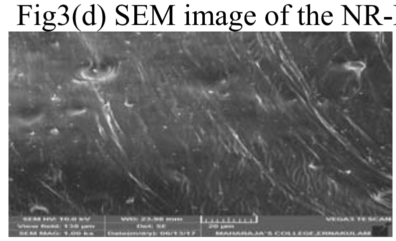

Fig3(e) SEM image of the NR-PF30

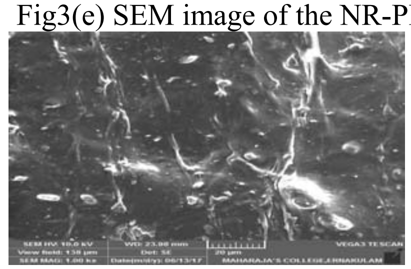

Fig3(f) SEM image of the NR-PF70

D. *VSM ANALYSIS*

Magnetization measurements were carried out on a vibrating sample magnetometer at room temperature with a maximum applied field of 15 KOe.Fig4(a)&Fig4(b) below shows the typical magnetic hysteresis loops of mixed ferrite and PANI-ferrite composite(PF1).The saturation magnetization, coercivity,Retentivity and remanent ratio of the samples are presented in table2

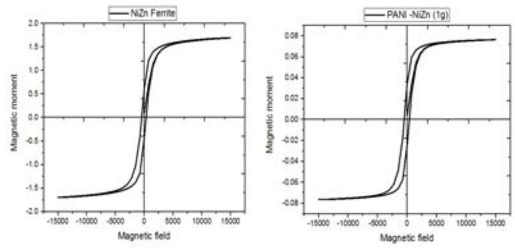

Fig4(a) andFig4(b) Hysterisis curves of ferrites and PANI coated ferrites

Table 2: VSM Analysis				
Sample	Coercitivity Hc (Oe)	Retentivity (Mr)	Magnetization (Ms)	Remanent ratio,R=(Mr/Ms)
Ni-Zn ferrite	390.26	0.52138 emu/g	1.6965 emu/g	0.30732
PANI/ -NiZn ferrite	438.04	29.648E-3 emu/g	76.541E-3 emu/g	0.38734

Pure Ni-Zn ferrite posesses greater value for retentivity and saturation magnetization than that for PANI - Ni-Zn ferrite composite.Coercivity value is greater for the composite.Remanet ratio is an indication of the ease with which the direction of magnetization reorients to the nearest easy axis magnetization direction after the magnetic field is removed.The values of the remanent ratio of the prepared samples are given in table1 and it is less for ferrite samples.[7]

Fig4 (c) shows the typical magnetic hysteresis loops of the Natural-rubber/ PANI-ferrite composites with PANI-Ferrite at10phr,15phr&30phr loadings .The saturation magnetization, coercivity,retentivity and remanent ratio of the samples are presented in table 3.

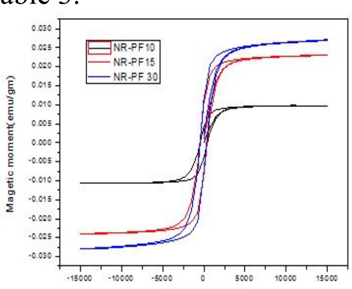

Fig4(c)Hysterisis curves of NR-PF10,NR-PF15,NR-PF30

Table3 VSM Analysis				
Sample	Coercitivity (Hc) (Oe)	Retentivity(Mr) emu/g	Magnetization(Ms) (emu/gm)	Remanent Ratio,R=(Mr/Ms)
NR-PF10	437.99	4.079E-3	10.275E-3	0.3969
NR-PF15	436.81	9.3218E-3	23.522E-3	0.3963
NR-PF 30	395.27	9.466E-3	27.55E-3	0.3435

As the loading of PANI-Ferrite in Natural Rubber increases,the value for retentivity and saturation magnetization increases.Coercivity value is found to decrease with the increase in loading.The values of the remanent ratio of the prepared samples are given in table3 and it decreases with increase in loading.[7]

E. ***Relative dielectric permittivity and A.C conductivity as a function of logf for PANI coated*** $Ni_{0.6}Zn_{0.4}Fe_2O_4$

Relative dielectric permittivity and a.c. conductivity as a function of logf for PANI coated ferrites with three different combination of anilineand ferrites i.e(pf1(5ml:1gm),pf2(5ml:2gm),pf3(5ml:3gm) are shown in Fig5(a) and Fig 5(b)

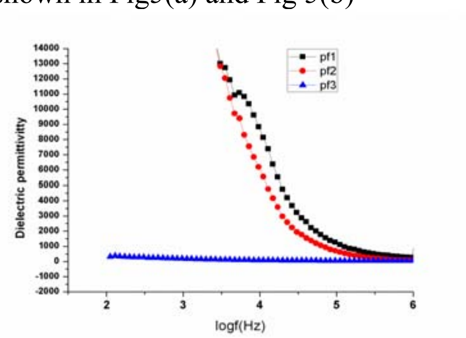

Fig5(a) έ as a function of logf for PANI coated $Ni_{0.6}Zn_{0.4}Fe_2O_4$

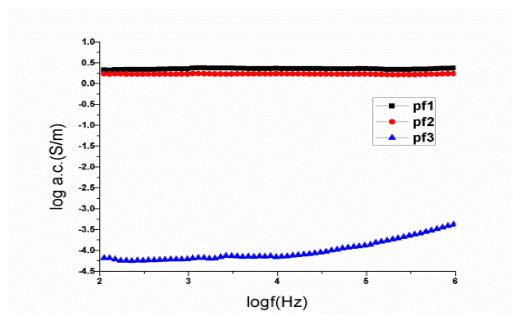

Fig5(b) loga.c as a function of logf for PANI coated $Ni_{0.6}Zn_{0.4}Fe_2O_4$

It can be seen that the dielectric constant decreases with increase in frequency for all the samples.The mechanism of polarization is attributed to four different types of polarisations i.e.electronic,ionic,dipolar rand space charge polarizations. At lower frequencies all these contribute towards polarization but at higher frequencies some of the polarization contributions relax out, resulting in lowering of dielectric constant[8].As the content of ferrite particles increases,the dielectric constant is found to decrease. The ac conductivity increases with frequency according to the relation, Ϭ= ἑ*6,67E-12* 2πf *tanδ. The formation of polarons upon the oxidation of polyaniline molecule and the combination of two close polarons to form bipolaron is the reason behind the conductive behavior. As the frequency of applied field increases, hopping of carriers also increases ,thereby increasing the conductivity. A.C.conductivity increases with frequency in small polaron hopping. So it is confirmed that conduction is due to small polaron hopping .The AC conductivity profiles are similar to those of the real part of dielectric permittivity which also decreases with increase in ferrite content[9].

F. Relative dielectric permittivity and A.C conductivity as a function of logf for PANI coated ferrite-Natural rubber composites

Relative dielectric permittivity and A.C conductivity as a function of logf for PANI coated ferrite-NR composites with PANI coated ferrite(PF) at10phr,30phr&70phr loadings are shown in Fig6(a)&Fig6(b). pf1 is ued for the composite preparation**.**

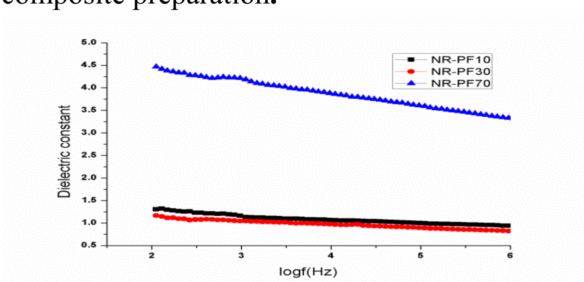

Fig6(a.) ἑ as a function of logf for NR- PF

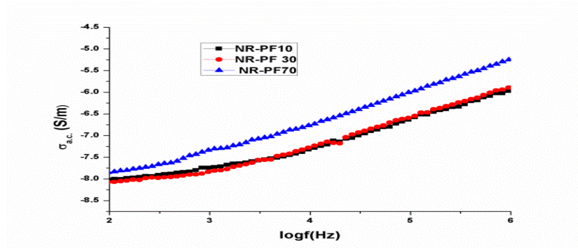

Fig6(b) log a.c.as as a function of logf for NR-PF

It is observed that the dielectric constant continuously decreases with increase in frequency. Incorporation of PANI and ferrite causes dipoles to be formed in the composites which contribute to the dipolar polarization. Difference in conductivity between NR and PANI coated ferrite causes the space charges to be accumulated at the interfaces when an electric field is applied leading to interfacial polarization. The dipolar and interfacial polarization account for the dielectric constant of the composites. At higher frequencies these polarizations will not be able to keep up with the alternating field which decreases the dielectric constant. The mechanism of conductivity is the three-dimensional hopping of electrons inside the NR elastomer matrix.The incorporation of PANI coated ferrite into the NR matrix improved the quality of the molecular structure and increased the charge carrier's transport within the NR matrix. As the frequency of applied field increases, hopping of carriers also increases ,thereby increasing the conductivity. A.C.conductivity increases with frequency in small polaron hopping. So it is confirmed that conduction is due to small polaron hopping[10].

E. Mechanical properties of PANI coated ferrite –NR composite

Fig7(a) and Fig7(b) shows the dynamic mechanical properties of the PANI coated ferrite-Natural rubber composites with PANI-ferrite at10phr,15phr&30phr loadings.

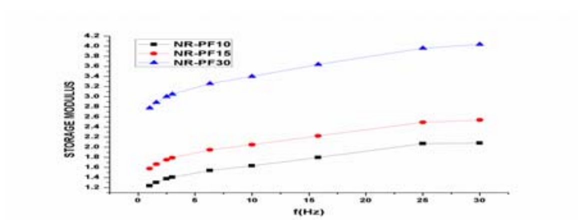

Fig7(a).Storage modulus as a function of freq. for NR-PF

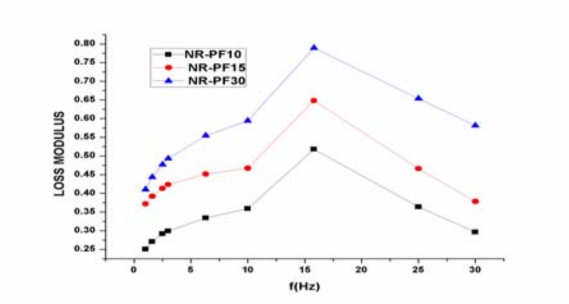

Fig7(b).Loss modulus as a function of freq. for NR-PF

Fig.7(a) shows the frequency dependence of the storage modulus of the composites. With increase in filler content storage modulus increases showing an increase in stiffness of the composites .For all composites, beyond 10 Hz, the increase in stiffness is more pronounced. Increase in frequency in a dynamic mechanical test is equivalent to a decrease in temperature. So the increase in stiffness beyond 10 Hz can be equated to the transition region in a temperature sweep test, where the temperature is so reduced that the material becomes glassy. A corresponding trend is observed in the loss modulus graph (Fig 7(b) of the composites. Due to the adherence of the filler to the polymer phase there is increase in stiffness of the polymer chain The results indicate the inherent reinforcing potential of Pani-ferrite composite is arising from the filler filler and filler rubber interactions [11].

The incorporation of PANI coated Ferrite into the NR matrix improved the quality of the molecular structure and increased the charge carrier's transport within the NR matrix. As the frequency of applied field increases, hopping of carriers also increases ,thereby increasing the a.c conductivity.With the increase in filler content storage modulus increased showing an increase in stiffness of the composites Due to the adherence of the filler to the polymer phase there is increase in stiffness of the polymer chain .The results indicate the inherent reinforcing potential of Pani- coated ferrite is arising from the filler rubber interactions. The results obtained refer to that specific properties can be tailored in the nanocomposites by mixing different proportions of PANI coated ferrite in natural rubber and the different proportions of filler can vary the the mechanical property of the Natural Rubber.Thin sheet of this composite can be tested for application like electromagnetic WAVE niterference shielding.The electrical and magnetic properties of the filler is a faourable factor to improve the shielding effectiveness.As the filler improves the mechanical property of natural Rubber,the composite may act asa mechanically strong shield. Conducting Polymers and their composites have been developed to replace or supplement typical metals for EMI shielding applications, which have merits such as light weight,physical flexibility, and easy control of electrical properties.

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