Intrinsically Conducting Polymer Blends

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SUMMARY: Polyaniline (PANI) doped with different dopants (HCl, dodecyl benzene sulfonic acid, (+)-Camphor-10 sulfonic acid, dinonyl naphthalene disulfonic acid) was synthesized by chemical oxidation method. The FTIR studies indicated that the back bone structure of doped PANI was similar. Thermal stability was evaluated in nitrogen atmosphere by dynamic thermogravimetry and PANI-HCl sample showed minimum weight loss below 400°C. The electrical conductivity of PANI was not affected by the structure of dopants. The microwave absorption studies of several polymers blends containing PANI-HCl and/or carbon black were also carried out by using wave guide technique.

Introduction

Polymers, because of their light weight, easy processability and design flexibility are widely used for housing electronic appliances. However these materials are generally electrical insulators and therefore, transparent to electromagnetic radiation. The interference of radio frequency radiation (such as that from a cellular phone) with digital electronics, has necessitated the need for electromagnetic interference (EMI) shielding. The need for lightweight, formable materials that can conduct electricity and shield against electromagnetic interference (EMI) is widespread. Application ranging from molded cases for terrestrial electronics to shielding systems for satellites to low observable technology can benefit from such lightweight conductive materials.

The most economical method to enhance electrical conductivity of plastic is the incorporation of conductive filler. EMI shielding gaskets are resilient conductors based on elastomers (rubbers) filled with metals or conducting carbon black or graphite or carbon fibres. Highly conductive fillers such as silver particles are needed for attaining high shielding effectiveness while maintaining resilience[1-6]. High volume fraction of

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filler is needed if its conductivity is not high. This leads to deterioration of mechanical property and loss of resiliency. Electroless nickel coated carbon fibers (ENCF) which combine the high strength, low weight, high aspect ratio and processability of a fiber core with the conductivity and corrosion resistance of a plated nickel skin are the best conductive filler for EMI shielding.

Conductive coatings of gold, silver and aluminium on ceramic microbaloons in epoxy matrix have been reported as ultra-lightweight conductive shield material7). Shield densities significantly below 1.0g/cm^3 with electrical surface resistivities approaching those of common metals have been achieved.

Carbon black / polymer conductive compounds have been used commercially for many years. Conductive carbon black often consists of elongated aggregates (low aspect ratio) composed of very small (nanometric) primary particles sintered together. The level of particle distribution determines the conductivity8).

Polyaniline, a commercial available conducting polymer has attracted interest from researchers because of its high conductivity, low cost and stability to heat and air8) and ease of synthesis (both chemical and electrochemical)9-12). Excellent reviews and reports are available on polyaniline13-15). EMI shielding efficiency of thin polyaniline-camphor sulfonic acid films have been reported as >40dB upto ~100MHz and 39dB at 1GHz16).

Shaccklette et al.,17) reported that Versicon(Allied- Signal Inc.), a conductive polyaniline is dispersible in polar polymers such as polycaprolactone and poly(ethylene terephthalate glycol). The conductivity percolation threshold in these blends was observed in the range of 6-10% (v/v). Ikkala et al.,18) reported the electrical and mechanical properties of conductive polymer blends, prepared by blending a variety of thermoplastic polymers with a polyaniline complex, using conventional melt processing techniques. The electromagnetic interference shielding efficiency of polyaniline mixture (PANI and conducting powders such as silver, graphite and carbon black) and multilayer films has been reported to be in the range of 20 db to 50 db (frequency range 10Hz to 1GHz)[19). Very few reports are available on absorption of high frequency radiation (8GHz to 18GHz) by intrinsically conducting polymer blends (such as PANI or a mixture of PANI with other conducting fillers). It was therefore, considered of interest to study blends of thermoplastic polymers having PANI or PANI and conducting carbon black for their microwave absorption behaviour. The main objective of the present studies was to develop intrinsically conducting polymer blends based on PANI and carbon black and evaluate their performance for absorbing microwaves in the frequency range of 8-18GHz.

Experimental

Materials

Ammonium persulfate (BDH), methanol (E. Merck®), acetone (CDH), NH_4OH (CDH), dodecyl benzene sulfonic acid (AVCO), dinonyl naphthalene disulfonic acid (NACURE-155, King industries®), (+)-camphor-10-sulphonic acid (Leo), N,N-dimethylformamide (E. Merck®), dimethylsulfoxide (E. Merck®), Ketzenblack EC (Akzo Nobel) is a carbon black having a specific area of 1000m^2/g (BET). Pilene EVA 1802 (1802 vinyl acetate content = 18%, MFI = 2 gm/10min at 190°C and 2.16 Kg load, NOCIL), HDPE (Hostalene GF 7745F, MFI = 6.5 g/10min at 190°C and 2.16 Kg load, density = 0.945 g/cm^3, NOCIL), LDPE (MFI = 8 gm/10min at 190°C and 2.16 Kg load, Ladene®SABIC) and VITON GF (fluorinated elastomer from DuPont) were used as received. HDPE, EVA and LDPE were dried under reduced pressure at 65°C for 24h before use. Aniline (CDH-AR) was freshly distilled under reduced pressure and used immediately for synthesis of PANI.

Synthesis of Polyaniline

9.3g of distilled aniline (0.1 mol) was added to 100g analar HCl (1N) solution and the pH adjusted to 1.0 by further addition of few drops of HCl. The solution was cooled by placing the flask in an ice / salt bath. 28.52g of analar ammonium persulphate (0.125 mol) was dissolved in distilled, chilled water and slowly added to the reaction solution, which was being stirred at low temperature (0-3°C). The reaction temperature was not allowed to exceed 5°C. The reaction mixture was than left for 1.5 h with stirring. After that, the precipitated poly(aniline hydrochloride) was separated on a Buchner funnel and washed consecutively with water, methanol and acetone. Finally the polymer powder was dried in vacuum to a constant mass. Polyaniline base (polyemeraldine) was obtained by deprotonation of polyaniline hydrochloride.

Doping of polyaniline base in m-cresol was done with following dopants

a) Dodecyl benzene sulfonic acid (DBSA).
b) (+)-Camphor-10 sulfonic acid (CSA).
c) Dinonyl naphthalene disulfonic acid (NACURE-155).

FT-IR spectra of PANI samples were recorded in KBr pellets using a Biorad Digilab FTS-40 spectrometer.

Thermal stability of doped PANI samples in nitrogen atmosphere (flow rate 60 cm^3/min.) was evaluated by thermogravimetry using DuPont 3100 thermal analyser having a 951 TG module.

Preparation of blends

Conducting PANI filled thermoplastic blends having different PANI content were prepared by using a two roll mill. These blended samples were compression molded (Carver Lab. Model) at temperature above 150°C.

Microwave measurements

A rectangular waveguide, which consists of two equal halves, was fabricated for this purpose. The rectangular cavity was constructed from an aluminium waveguide of length 11 cm, breadth 4.1 cm and height of 4.1 cm. A rectangular cavity of length 11 cm, breadth 2.2 cm and height of 2.2 cm was provided in the wave guide. The inner wall of the guide has a thin slit (6 cm in length and 3 cm in breadth) in the center. Scattering parameters were measured by connecting the cavity to a Hewlett Packard network analyser (Model : 8510). The reflection and transmittance peaks corresponding to the frequencies, appeared on the screen of the analyser (Figure 1).

The sample of length 5.8 cm and 2.8 cm width was placed in the cavity and the position of the sample in the region of maximum electric field was ascertained by observing the movement of the peak on the screen of the analyser. The (reflection)S_{11} and (transmittance)S_{21} parameters were directly measured by placing the waveguide in the orthogonal direction. The concentration dependence of reflection and transmittance properties in microwave region of these blends were investigated.

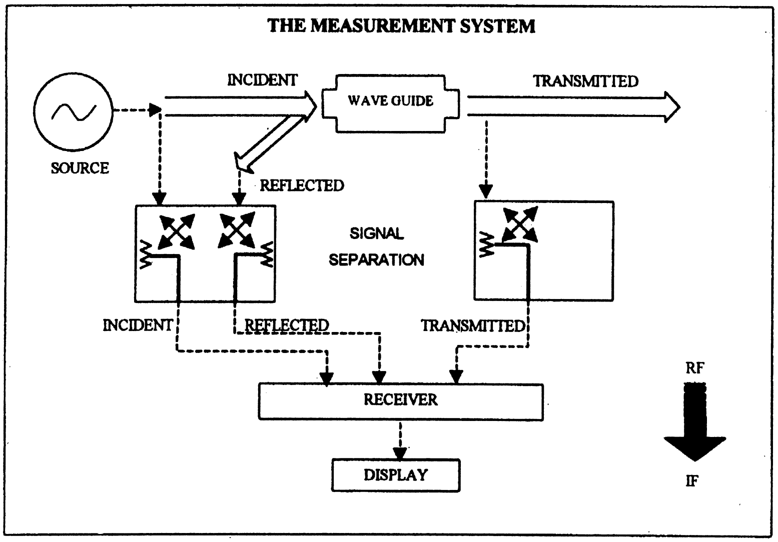

Figure 1: Microwave measurement system

Electrical measurement

Electrical conductivity of PANI and its blends was measured by four probe method.

Results and Discussion

In the IR spectra of PANI (doped with different dopants), characteristic absorption bands due to quinoid and benzenoid structure were observed at 1565±5 cm^{-1} and 1480 cm^{-1} respectively. The 1300 cm^{-1} and 1240 cm^{-1} absorption were due to C-N-C single bond. Broad absorption band centered at 1130 cm^{-1} and 830 cm^{-1} have been assigned to the aromatic C-H in-plane bending and out-of-plane bending respectively. All the spectra were similar indicating thereby that all samples have back bone structure of doped PANI. In the TG traces of PANI weight loss due to moisture (~3-5%) was observed in the temperature range of 100-150°C. Weight loss around 250-400°C has been attributed to the dopant loss while back bone degradation takes place above 530°C. In Table 1 the weight loss of PANI doped with different dopants is given. The observed weight loss below 400°C was minimum in PANI doped with HCl. No significant difference in electrical conductivity of PANI doped with different dopants was found. Therefore, PANI-HCl was used for making blends and further studies on microwave absorption.

Table 1: Thermogravimetric measurements of PANI doped with different dopants in nitrogen atmosphere.

Sample	Temperature (°C)	Weight loss (%)	T_{max} (°C)	Yc (%)
PANI-HCl	140-440 440-700	20.5 27.5	380 540	52
PANI-DBSA	250-500	65.0	328	27
PANI-CSA	164-385 385-585	27 31	290 492	41
PANI-NACURE 155	180-365 365-700	31.5 29	294 420	33

T_{max}= temperature of maximum rate of weight loss

Yc= char residue at 800°C

Electrical conductivity of Viton GF increased by incorporation of HCl doped PANI or PANI/carbon black. However carbon black was more effective in increasing the conductivity (Table 2). A three fold increase in conductivity of Viton GF containing 30 phr of PANI was observed by incorporation of 5 phr pf carbon black (CB). Further increase in CB content to 25 phr increased the conductivity by an order of magnitude.

Table 2: Electrical conductivity of Viton GF as a function of PANI or PANI/C-black concentration

PANI (phr)	Conductivity $(\text{ohm.cm})^{-1}$	PANI/C-Black (phr)	Conductivity $(\text{ohm.cm})^{-1}$
20	2.93×10^{-4}	25/05	6.76×10^{-2}
25	9.5×10^{-3}	20/10	7.4×10^{-2}
30	2.3×10^{-2}	15/15	7.6×10^{-2}
--	--	05/25	2.2×10^{-1}

The microwave attenuation of HCl doped PANI / Viton GF blends having 35 phr-50 phr of PANI was determined in 8-18 GHz region (Table 3). An increase in lossy behaviour was observed by increasing a) doped PANI content and b) at higher frequency.

Table 3: Loss measurement of HCl doped PANI/ Viton GF blends (sheet thickness=0.3mm)

Frequency (GHz)	Loss (-dB)		
	35 phr	40 phr	50 phr
8.0	0.00	0.81	0.25
10.0	0.96	2.16	1.59
12.0	0.62	2.30	2.80
14.0	1.80	1.75	3.56
16.0	2.39	3.15	4.62
18.0	2.46	3.56	5.91

In order to study the effect of PANI-HCl/Viton GF sample sheet thickness on absorption, two sheets containing 40 phr of PANI-HCl were combined and total sheet thickness of 0.58 mm was used.

Table 4: Effect of thickness of sample sheet on microwave absorption (thickness= 0.58 mm)

Frequency (GHz)	Loss (-dB)
8.0	0.05
10.0	3.19
12.0	11.92
14.0	14.38
16.0	8.14
18.0	6.38

Loss measurements on carbon black/Viton GF composites were also carried out. Better results were obtained at 20 phr of CB and at higher frequency (Table 5). An increase in CB content resulted in a decrease in microwave attenuation. This may be due to poor dispersion and agglomeration of CB particles.

Blends of Viton GF and LDPE/HDPE containing different phr of HCl doped PANI were also invetigated. Substitution of Viton GF by these low density polyolefins is expected to reduce the density of the blends. These immiscible blends may also have lower percolation threshold of PANI-HCl. By using a blend composition of Viton GF/LDPE or HDPE as 25:75 (w/w) sheets containing 5 – 40 phr of HCl doped PANI were fabricated on a two roll mill and loss measurement were carried out in the frequency range of 8-12 GHz. Maximum attenuation of 5.4 dB was observed at 9-10.5 GHz range in a sheet containing 35 phr of PANI-HCl. Further increase in PANI content did not affect the

Table 5: Loss measurements on carbon black/Viton GF composite

Frequency (GHz)	Loss (-dB)		
	20 phr (0.38 mm)	25 phr (0.8 mm)	30 phr (0.8 mm)
8.0	0.00	0.03	0.00
10.0	1.51	0.00	0.00
12.0	3.41	1.23	0.41
14.0	3.60	1.98	2.10
16.0	3.64	1.58	1.77
18.0	3.65	2.18	1.88

(Figures in parenthesis indicate the thickness of the sheet) attenuation. HDPE/EVA and PANI-HCl blends were also investigated and a loss less behaiour was observed.

The microwave attenuation increased on increasing CB concentration in HDPE/EVA and LDPE/Viton GF blends. The maximum attenuation (-46dB) was obtained in LDPE/Viton GF (75:25 w/w) filled with 40 phr CB. The HDPE/EVA filled with 40 and 50 phr CB gave attenuation of –34 and –28.2 dB respectively.

Conclusion

PANI/Viton GF blends showed a loss >10 dB in the frequency range of 12-15 GHz. However the performance of carbon black/Viton GF/LDPE composites was better. A difference in electrical conductivity of PANI/polymer blends and carbon black polymer composites was observed which may be due to difference in dispersion in melt blending and processing of these materials. In CB containing polymer blends fracturing of CB particles occur in melt processing and cooling step. On the other hand the level of fracture and dissolution of PANI in a polymer blend depends strongly on the nature of dopant. Further studies on the morphology of these blends are needed to explain the observed behaviour.

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