

LiSIPA doped polyaniline-colloidal graphite composites : Synthesis and characterization

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Aniline has been polymerized in the presence of colloidal graphite using lithium sulphoisophthalic acid (LiSIPA) as dopant, via the chemical oxidative polymerization route. The thermal stability and electrical conductivity have been improved significantly as compared to polyaniline doped with conventional inorganic dopants like HCl or H₂SO₄. The XRD and FTIR show a systematic shifting of the characteristic bands/peaks with the increase in the graphite content, which indicates sufficient interaction between graphite and polyaniline. The UV-visible spectra also show the characteristic bands of polyaniline which shows the hypsochromic shift with the increase in the graphite content. Apart from their doped counterparts, these composites also show sufficient conductivities, even in the undoped forms.

Keywords: Polyaniline, LiSIPA, Colloidal graphite, Electrical conductivity, Thermal stability, Conducting polymer, UV-Visible, XRD, FTIR

The discovery of conducting polymers in the year 1977 has revolutionized the field of material science due to their novel electronic and electrical properties. Their gamut of applications covers a wide spectrum ranging from electrode material for batteries^{1,2}, sensors³⁻⁵, anticorrosive materials⁶⁻⁸, electromagnetic interference shielding⁹⁻¹¹, electrostatic charge dissipation¹²⁻¹⁴, organic light emitting diodes¹⁵⁻¹⁸, plastic solar cells^{19,20} and supporting material for catalysis^{21,22}. However among other conducting polymers, polyaniline has been extensively studied, due to its non-redox doping, good environmental stability as well as economic feasibility, besides possessing acceptable electrical conductivity and thermal stability. Despite having a number of merits, the main issue associated with polyaniline is tendency to undergo undoping either under alkaline or elevated temperature conditions, which leads to significant decrease in the electrical conductivity. However, electronic properties of these synthetic metals can be tailored by carrying out the polymerization under controlled conditions and in the presence of specific dopants and/or fillers. Several groups have reported the use of bulky counter-ion as dopant^{23,24}, leading to polymer with improved thermal stability but reduced

electrical conductivity. The electrical conductivity can easily be enhanced by using conducting fillers like graphite. Tchmutin *et al.*²⁵ have prepared composites of graphite and conducting polymers having low percolation thresholds. Du *et al.*²⁶ have prepared nanocomposites based on exfoliated graphite. Luo *et al.*²⁷ have prepared core shell nanocomposites of polyaniline and carbon black by electrochemical route. Bourdo *et al.*²⁸ have utilized colloidal graphite for making composites having conductivities better than graphite or conducting polymer alone.

The present paper reports the use of colloidal graphite as the conducting filler and LiSIPA as bulky dopant to increase the conductivity as well as thermal stability of the polyaniline. The polymerization was carried out via the chemical oxidative polymerization route. The polymers so synthesized were characterized by the various techniques like TGA, FTIR, UV-visible spectroscopy, XRD etc. Their electronic conductivities were measured by Four-Probe technique and morphologies were observed by scanning electron microscopy (SEM).

The higher thermal stability and acceptable electronic conductivity suggests use of these polymers for melt blending with engineering thermoplastics like polyamides, polyester, polycarbonate etc. Apart from that the resistance to decrease in the conductivity due

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to undoping made these materials potential candidates for using under hostile conditions like alkaline environment and elevated temperatures.

Experimental Procedure

Materials

Aniline (Loba Chemie), HCl (35.4% s d fine-chem), Lithium sulphoisophthalic acid (LiSIPA, Eastman Chemical Company), colloidal graphite (CG, 75% solid content) and ammonium persulphate (APS, Merck) were used without further purification. Liquid ammonia (Liq. NH_3 , 30%, Loba Chemie) was used to undope the doped polymers. N-methyl pyrrolidinone (NMP, Merck) and acetone (Merck) were used for making solutions. Aqueous solutions were prepared from the double distilled water having specific resistivity of 1 M ohm cm.

Polymer preparation

In the present paper, the doped polyaniline was prepared by free radical chemical oxidative polymerization, through indirect routes. In a typical reaction, 0.1 mol of aniline and 1.0 mol HCl were mixed with 9.3 g of colloidal graphite dispersion in 1 L of distilled water. The above mixture was allowed to stir for 30 min and the polymerization was initiated by the drop wise addition of ammonium peroxydisulfate (0.1 mol, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 100 mL distilled water). The temperature of the mixture was maintained at $0 \pm 1.0^\circ\text{C}$ throughout the course of reaction (4-6 h). The polymer has been produced directly in the doped state as a dark green precipitate, dispersed in the reaction mixture. The precipitate so obtained was filtered to separate the polymeric precipitate and washed repeatedly with distilled water, till the pH of the filtrate became neutral. The final precipitate was then dried under dynamic vacuum till constant weight. The dried mass was then crushed to obtain the powder of the doped polymer. The doped powder was then treated with 1.0 M aqueous ammonia and stirred for 2 h to convert it to the base/undoped form (CG1-B). The CG1-B was washed repeatedly with water to neutral pH, dried under dynamic vacuum and then treated with 0.5 M aqueous LiSIPA solution and stirred for 2 h to obtain the doped form of the same (CG1-D). The doped and base forms of other composite materials, viz., CG2, CG3, CG4, CG5 and CG6 were prepared in similar fashion by keeping the amount of both HCl and aniline same as in CG1 and changing the colloidal graphite phase to 12.4, 15.5, 24.8, 49.6 and 111.6 g

respectively. The graphite percentages based on the relative amounts of aniline and graphite (75% solid content) in the feed mixtures, were found to be 43%, 50%, 5 %, 67%, 80% and 90% for CG1, CG2, CG3, CG4, CG5 and CG6 respectively.

The above-synthesized polymers were given abbreviated names on the basis of doping/undoping status and percentage of graphite and detailed descriptions of undoped and doped materials along with the abbreviations have been presented in Tables 1 and 2, respectively.

Measurements

For the conductivity measurements, pellets (length 13 mm, width 7 mm, thickness 1-2 mm) were prepared by using a hydraulic press and applying a pressure of ~ 7 Ton. The resistivities were measured by four-point probe technique using (Keithley 220 Programmable Current Source and 181 Nanovoltmeter). TGA (Mettler Toledo TGA/SDTA 851^e) was used to observe the thermal behaviour. Materials were heated from 25°C to 700°C under a constant heating rate of $10^\circ\text{C}/\text{min}$, in the inert atmosphere of nitrogen. The samples were also studied by using UV-visible spectrophotometer (Shimadzu UV-1601) after preparing solutions of their base forms in NMP solvent. FTIR (NICOLET 5700) and XRD (D8 Advance Bruker AXS X-ray diffractometer) were used to observe the characteristic peaks of these composites. Micromorphologies were observed using SEM (Leo 440, UK) at accelerating potential of 15 kV and magnification level of 10KX.

Results and Discussion

Morphological details

Figure 1 shows the SEM micrographs of the pure colloidal graphite (CG) and CG2-D respectively. The micrograph of the pure graphite clearly shows the presence flakes having layered morphology characteristic of the graphite. However in case of CG2-D composite, one can clearly see the graphite flakes coated with polyaniline particles. This may be attributed to the high specific surface area of the graphite flakes, which provides large number of binding sites to polyaniline.

UV-visible absorption spectra

UV-visible absorption spectra of base forms of composite (not shown) have been taken in NMP solvent and characteristic peaks are reported in Table 1. There are two peaks in the UV-visible range one around 320 nm is due to the $\pi \rightarrow \pi^*$ transition

Table 1 — Electrical conductivity and absorption bands of undoped polyaniline grafted on colloidal graphite

Polymer	Abbreviation	Conductivity (S/cm)	UV-visible bands in NMP λ (nm)
PANI-Undoped	PANI-B	10^{-9}	329 635
PANI-CG-Undoped (43%)	CG1-B	$1.02\text{E-}5$	324 628
PANI-CG-Undoped (50%)	CG2-B	$3.22\text{E-}5$	323 627
PANI-CG-Undoped (56%)	CG3-B	$1.48\text{E-}4$	323 626
PANI-CG-Undoped (67%)	CG4-B	0.00314	322 628
PANI-CG-Undoped (80%)	CG5-B	0.677	320 630
PANI-CG-Undoped (90%)	CG6-B	5.33	316 629

Table 2 — Electrical conductivity and FTIR bands of doped polyaniline grafted on colloidal graphite

Polymer	Abbreviation	Conductivity (S/cm)	FTIR, Wavenumber (cm^{-1})
PANI-LiSIPA-Doped	PANI-D	1.1	617, 1033, 1102, 1219, 1293, 1374, 1458, 1474, 1543, 1557, 1652, 1686, 1697, 1716
PANI-CG-Doped (43%)	CG1-D	7.3	612, 1033, 1101, 1216, 1289, 1372, 1457, 1473, 1542, 1557, 1650, 1685, 1700, 1718, 1736
PANI-CG-Doped (50%)	CG2-D	8.7	612, 1032, 1098, 1216, 1290, 1372, 1456, 1473, 1542, 1557, 1651, 1685, 1718, 1736
PANI-CG-Doped (56%)	CG3-D	9.3	615, 1031, 1097, 1216, 1290, 1373, 1457, 1473, 1542, 1557, 1651, 1685, 1700, 1717, 1738
PANI-CG-Doped (67%)	CG4-D	16.92	614, 1032, 1100, 1216, 1287, 1372, 1456, 1473, 1540, 1557, 1650, 1684, 1698, 1717, 1737
PANI-CG-Doped (80%)	CG5-D	34	613, 1032, 1093, 1216, 1288, 1367, 1455, 1473, 1541, 1557, 1650, 1685, 1739
PANI-CG-Doped (90%)	CG6-D	67	613, 1032, 1092, 1216, 1288, 1366, 1456, 1473, 1541, 1557, 1650, 1685, 1739
Colloidal Graphite	CG	125	1016, 1183, 1457, 1541, 1558, 1651, 1700, 1740

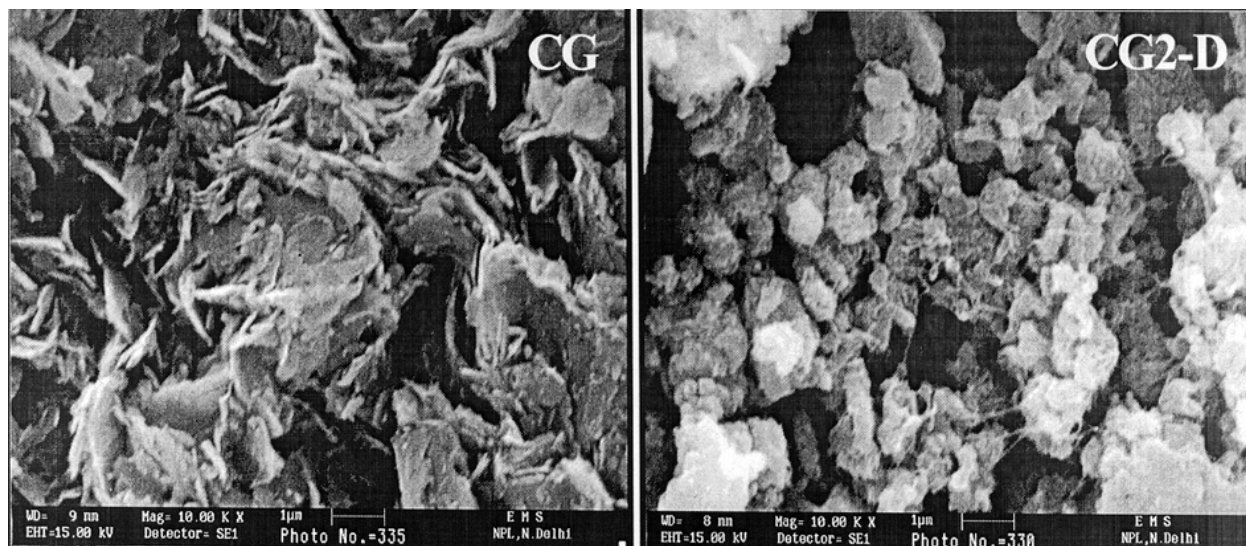


Fig. 1 — Scanning electron micrographs of the pure colloidal graphite (CG) and doped polymer CG2-D

(band-gap) and is a measure of the effective conjugation of the material. The other peak 630 nm is due to the transition between HOMO orbitals of benzenoid rings and LUMO orbitals of the quinoid rings.

The spectral data reveals that $\pi \rightarrow \pi^*$ band of the composite exhibits hypsochromic shift with respect to the emeraldine base (EB), which may be due to the reduction in conjugation lengths with the increase in the graphite content. Therefore, whereas the EB absorbs at 329 nm, CG1-B and CG6-B absorbs at 324 nm and 316 nm respectively.

FTIR spectra

FTIR spectrums of doped forms of the composites are shown in Fig. 2. All the spectra give the characteristic bands of both benzenoid and quinoid units which confirms the presence of polyaniline in the same. The band around 798 cm^{-1} is due to the out of the plane C-H bending vibrations. Also in the region $1650\text{--}1400\text{ cm}^{-1}$, bands due to aromatic ring breathing, N-H deformation and C-N stretching are observed. The bands around 1560 and 1480 cm^{-1} are characteristic stretching bands of nitrogen quinoid ($\text{N}=\text{Q}=\text{N}$) and benzenoid ($\text{N}-\text{B}-\text{N}$) and are due to the conducting state of the polymer. The bands around 1290 and 1240 cm^{-1} are assigned to the bending vibrations of N-H and asymmetric C-N stretching modes of benzenoid rings respectively. The absorption band around 1120 cm^{-1} (C-N stretching) is due to the charge delocalization over the polymeric backbone and in the undoped polymer the intensity of this band goes down significantly. The characteristic bands of the doped forms of the composites have been recorded in Table 2.

Apart from the characteristic bands of the doped polyaniline all the composites also shows the presence of an intense peak around 1740 cm^{-1} , which may be attributed to the oxidized graphite phase and the intensity of this band goes on increasing with the graphite content. The presence of characteristic bands of both graphite and polyaniline confirms the presence of both phases in the composite. However, all these bands show a systematic shifting that indicates existence of significant interaction between polyaniline and graphite in the composite.

These interaction between graphite sheets (electron acceptor) and doped polyaniline (donor or p-type material) may be attributed to the formation of charge transfer complex and thought to be occurs due to partial transfer of lone pair of electrons of amine

nitrogen atoms to the graphite particles. As a result amine nitrogen acquires partial positive charge whereas graphite particles develop equivalent negative charge. Such complex formation between donor and acceptor molecules has been well documented in case of other conducting polymers²⁹ and also forms the basis of bulk heterojunction solar cells³⁰. The formation of such complex causes additional doping on amine nitrogen of polyaniline, leading to further enhancement in the conductivity. Such interaction has been depicted in Scheme 1.

XRD studies

Figure 3 shows the X-ray diffraction patterns of the powdered samples pure CG, CG2-D, CG4-D, and CG6-D respectively. The pattern shows a sharp peak centered on 2θ value of 26° . This sharp peak

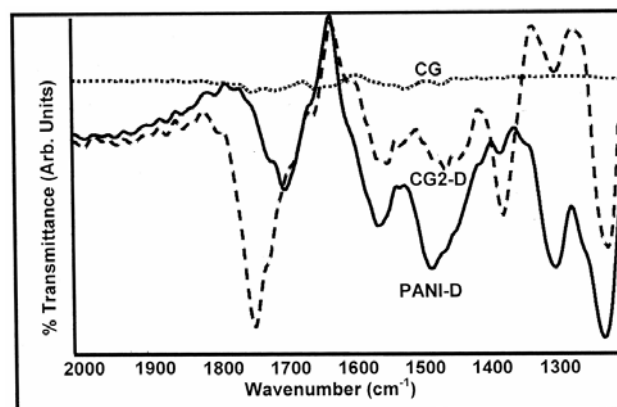
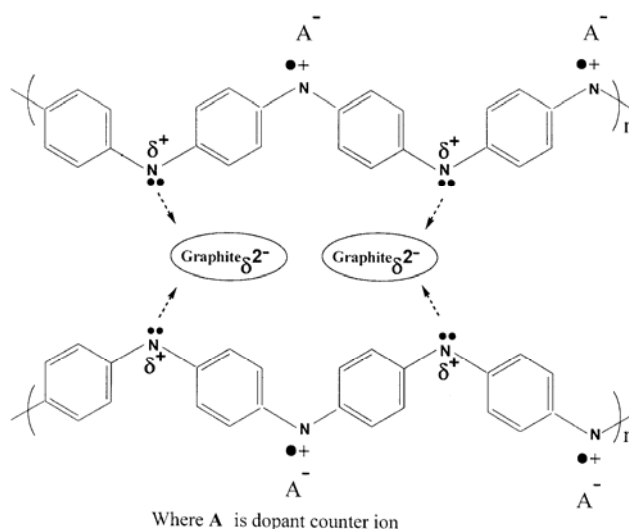


Fig. 2 — FTIR spectra of the pure CG, PANI-D and composite CG2-D



Scheme 1 —Proposed interaction mechanism between colloidal graphite and doped polyaniline

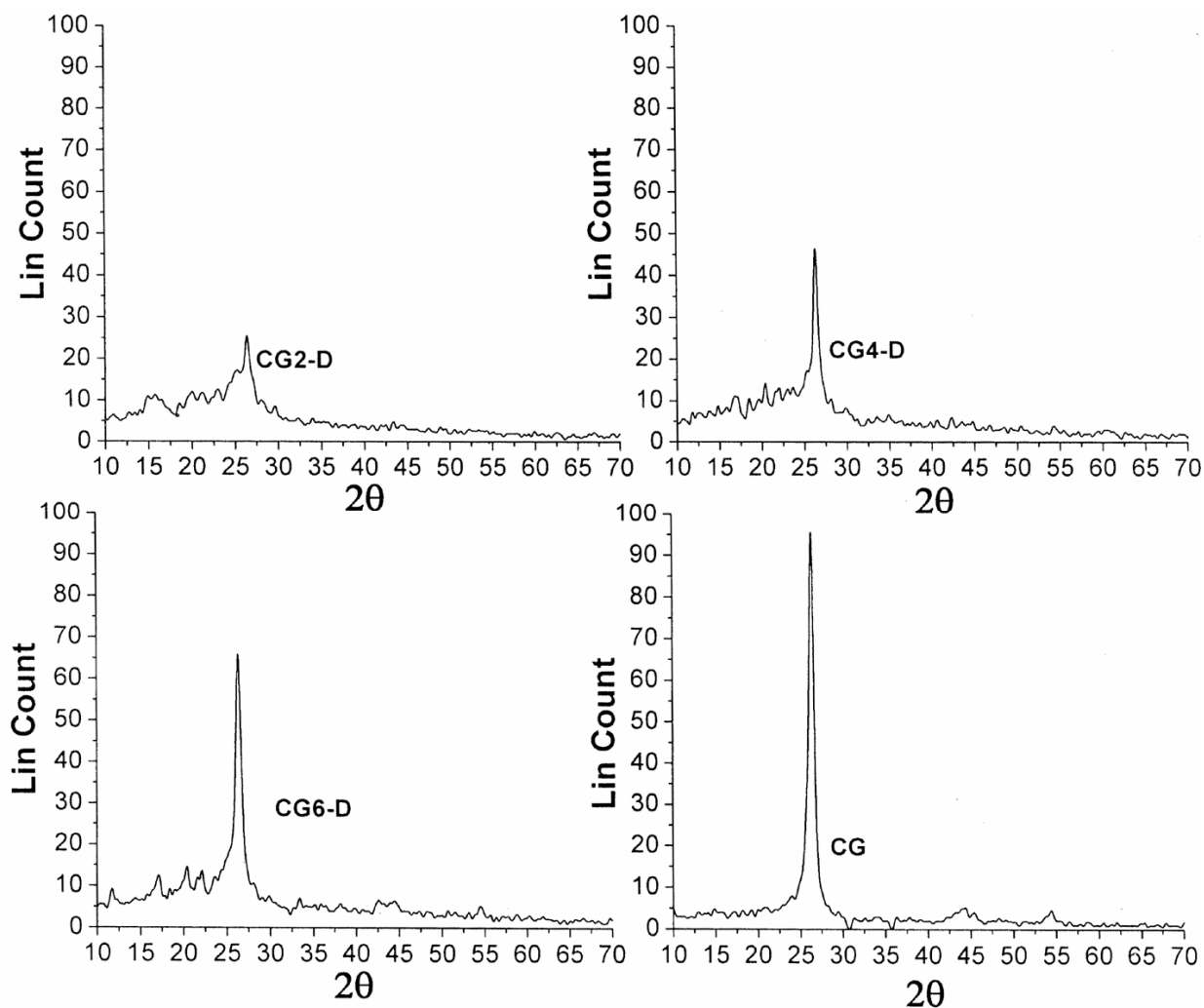


Fig. 3 — XRD patterns of the pure CG and doped materials CG2-D, CG4-D and CG6-D respectively

corresponds to the colloidal graphite phase and its intensity goes on increasing with increase in the graphite content. The composite also shows characteristic peaks of the doped polyaniline around 20° and 25° , that were absent in the XRD spectra of the pure CG. The intensity of these peaks decreases abruptly with the increase in graphite content and in both CG4-D and CG6-D 25° peak appears as a weak shoulder on the intense 26° peak of colloidal graphite phase. The coexistence of the characteristics peaks of both CG and doped polyaniline, which undergo a systematic shifting (also supported by FTIR data) with increasing graphite amount, clearly indicates the formation of composite.

Conductivity

The room temperature conductivities of the composites were determined by studying the current-

voltage (I - V) characteristics of the materials. The linear regions of the I - V plots have been selected to utilize the ohms law for deducing the resistance of the materials. Therefore, the slope of the straight line between I - V plots gives the resistance " R " of the samples, which ultimately gives the conductivity by taking into account dimensions of the samples. The conductivity σ of the pellet is given by the following relation:

$$\sigma = L/RA$$

Where L is the length of the pellet, R is resistance and A is cross-sectional area of the pellet.

The calculated conductivity values for undoped and doped materials have been reported in the Tables 1 and 2 respectively. The conductivity of both doped and undoped materials increases with the increase in

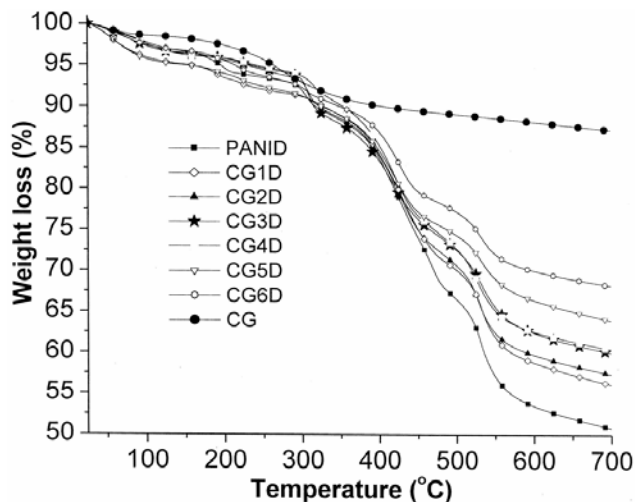


Fig. 4 — TGA graphs of pure CG and doped materials PANI-D, CG1-D, CG2-D, CG3-D, CG4-D, CG5-D and CG6-D respectively

the graphite content despite being decrease in conjugation length, which may be attributed to the highly conducting nature of graphite that acts as conducting bridge between the metallic islands of the polyaniline. The composites show significant conductivities even in undoped forms, which could be increased just by doping with a protonic acid. This provide us a way to control and tune the conductivity of the resultant composite and depending on the graphite content and degree of doping almost any value of conductivity is possible between highly conducting graphite and insulating emeraldine base. These materials may be quite useful particularly for sensors, actuators and electrochromic devices as response time and reversibility could be improved dramatically due to acceptable conductivity even in the undoped state. Further these composites also shows less decrease in the conductivity due to undoping of the materials affected either by slightly alkaline environment or elevated temperatures.

Thermogravimetric analysis

Figure 4 shows the thermo-gravimetric analysis (TGA) of the doped materials. These plots show that weight loss occurs in five systematic steps each corresponds to the loss of particular species. First a minor loss occur upto 140°C, which may be attributed to the loss of adsorbed water molecules, volatile compounds and traces of monomers, oligomers and initiator etc. Minor loss in the 150-275°C is related to some changes in the dopant and graphite phase. These loss steps involve the loss of sulphonic acid group and

carboxylate group of the dopant molecule and onset of degradation of polyaniline phase. The fourth and fifth loss steps are connected with the breakage of the polymeric backbone and dopant moieties. The composites show very little weight loss between the 550-700°C and the residues remaining in this region are mainly thermally stable inert materials like minerals and metallic impurities, graphite and the carbonized polymeric and dopant fragments. Since the amount of residue increases with the increasing graphite fraction, it could be used to determine the amount of actually incorporated graphite content.

The TGA data also revealed that these composites have good thermal stability even in vicinity of 300°C, which envisages them as a good candidate for melt blending not only with conventional thermoplastics (polyethylene, polypropylene, polystyrene etc.) but also with engineering thermoplastics like polyamides, polyester, polycarbonates etc.

Conclusions

Highly conducting composites of polyaniline and colloidal graphite have been prepared by *in-situ* polymerization technique. These materials show significant conductivities even in the undoped forms and are resistant to the conductivity degradation under alkaline or elevated temperature conditions. This envisages the use of these composites for sensing and electrochromic applications. Morphological details reveal presence of layered structure in pure CG and globular particles in composites. UV and FTIR data shows significant shifting of the characteristic bands/peaks, indicating significant interactions between different phases (polyaniline and CG) of the composite. These interaction between graphite sheets and doped polyaniline were attributed to the formation of charge transfer complex and thought to be occurs due to partial transfer of lone pair of electrons of amine nitrogen atoms to the graphite particles. XRD patterns also show the characteristic peaks of both polyaniline and CG. Thermal data suggests that composites have good stability even in the vicinity of 300°C and thus could be used for melt blending with engineering thermoplastics.

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