Thermal Behaviour of Chemically Synthesized Polyanilines/Polystyrene Sulphonic Acid Composites

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Abstract   Polyanilines are synthesized by free radical chemical oxidative polymerization of aniline & o-toluidine using ammonium persulphate as an oxidant in protonic acid medium. These polymers have been introduced into polystyrene sulphonic acid (PSSA) in 2:1, 1:1, 1:2 compositions for the preparation of composite materials. The composite samples so obtained are thermally characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction, and FTIR spectra. The incorporation of polymer in PSSA has been endorsed by FTIR analysis. TGA data reveals that the (Polyaniline/Polystyrene sulphonic acid) PANI/PSSA (2:1) and (Poly o-toluidine/Polystyrene sulphonic acid) POT/PSSA (2:1) composites show better thermal stability than their 1:1 and 1:2 counterparts. Steric hindrance of –CH_3 group present in ortho position and sulphonic acid group of PSSA affects the thermal behaviour of composites. Two-step transitions are clearly reported from the DSC thermograms of polyanilines/PSSA composites and non-reversing chemical cross-linking reaction was further confirmed by X-ray diffraction and DSC thermograms.

Keywords   Polyanilines, Chemical Oxidative Polymerization, Composites, PSSA

1. Introduction

Conducting polymers have become a popular basic material for advanced applications including plastic batteries, EMI shielding, electrochromic displays and sensors[1-7]. Among conducting polymers, polyaniline (PANI) has been extensively studied for its environmental stability in the conducting form, ease of synthesis, low cost and high conductivity. Nevertheless, a few applications have been reported where conducting polymers like PANI exhibit poor physical and mechanical properties. Numerous methods have been developed to overcome such shortcomings. It has been reported that the composite system by blending PANI with a commodity polymer improves its mechanical properties[8-11]. It has also been proposed that the incorporation of side groups into the main chain[12], grafting of the conducting PANI chain to a non-conductive polymer[13] and electrochemical polymerization of aniline in a polymer matrix[14] improve their processibility and thus broaden their applicability. A large amount of PANI-inorganic composites like PANI/V_2O_5[15], PANI/TiO_2[16-18], PANI/CdS[19], PANI/graphite oxide[20] and PANI/clay[21,22], etc have been synthesized and studied to enhance the overall properties in the past few years. Similarly composites of PANI with polyacrylonitrile, Polyure thane/polymethylmeth acrylate (PU/PMMA), Acrylonitrile butadiene styrene (ABS), PVC, Polyvinyledene fluoride/ Nanocrystalline Nickel Composites, Ag-CrO_2 Nanocomposite, Polyvinyledene fluoride (PVDF) Based Composites, LiFe1/2Ni1/2VO$_4$ composite were also studied in recent years[23-28].

Here, we have developed a simple but interesting method to prepare composites of polyaniline with polystyrene sulphonic acid and poly(o-toluidine) with polystyrene sulphonic acid[29,30] to get better and some new synergistic properties which could not be attained from individual materials. The procedure involves oxidative polymerization of aniline and o-toluidine and synthesis of polystyrene sulphonic acid by the sulphonation of polystyrene separately and subsequently reinforcement of polyaniline and poly(o-toluidine) in polystyrene sulphonic acid. This paper addresses the preparation of composite samples and their thermal behaviour to explore the synergistic properties.

2. Experimental Procedure

2.1. Materials

Aniline and o-toluidine monomer were double distilled and stored at low temperature prior to use. Polystyrene of grade M110 was procured from Haldia Petrochemicals, India. All other chemicals used were procured from CDH, India.

Silver sulphate, ammonium persulphate, HCl and H_2SO_4 were used as received. Double distilled water was deionized by Millipore used throughout the studies.

2.2. Synthesis of Polyaniline and Poly(o-toluidine)

The polymerization of freshly distilled aniline has been carried out by free radical chemical oxidative polymerization method by using ammonium persulphate (APS) as an oxidant in non-oxidizing protonic acid like HCl. In a chemical reaction 0.1 M of aniline was mixed to precooled 1 M HCl solution at 0-5℃. An aqueous solution of APS (0.1 M) was added drop wise to reaction mixture with constant stirring for 4-5 h resulted with the stabilization of temperature of reaction mixture till the completion of reaction. The dark green precipitate so obtained was filtered and then washed repeatedly with distilled water till the pH of the filterate became neutral. This precipitate was then dried under dynamic vacuum till constant weight. The polymer was also treated with 1M aqueous ammonia with constant stirring for 3-4 h for converting it into the base/undoped form. The blue black precipitate (undoped form) so obtained was filtered and then washed repeatedly with water to neutral pH. A similar procedure is also employed for the preparation of poly (o-toluidine) undoped form and finally dried under dynamic vacuum.

2.3. Sulphonation of Polystyrene

Before going to prepare composites of PANI and its derivatives with PSSA, we prepared PSSA from polystyrene through its sulphonation. A mixture of polystyrene granules (3g), silver sulphate (0.034 g) and concentrated H_2SO_4 (44 mL) was heated at 90℃ for 2 h until it becomes dark brown and highly viscous. This liquid pours into excess of ice-cold distilled water which on constant stirring resulted into a white gummy mass. This precipitate was dissolved in distilled water to make 100 mL solution of PSSA.

2.4. Synthesis of Composites of Polyanilines with PSSA

For the preparation of composite materials, undoped PANI and POT were mixed with polystyrene sulphonic acid in different compositions, i.e., 1:2, 1:1 and 2:1 by weight. A dark green colour paste was obtained in each case, which was dried in oven at 120℃. These samples of composite materials have been abbreviated as (Polyaniline/Polystyrene sulphonic acid) PANI/PSSA (2:1), PANI/PSSA (1:1), PANI/PSSA (1:2), (Polyo-toluidine/Polystyrene sulphonic acid) POT/PSSA (2:1), POT/PSSA (1:1) and POT/PSSA (1:2) composites.

2.5. Characterization

The composite material samples along with polyanilines were thermally characterized by TGA, DSC, XRD and FTIR spectra. TGA and DSC were performed on Perkin Elmer by pursuing N_2 gas as a carrier at a flow rate of 100 mL/min within a temperature range 50-800℃ for TGA and 50-600℃ for DSC, respectively at a heating rate of 10℃/min. Wide

angle X-ray differactometer (model Philips X'pert 1830) using Ni filter and CuKα radiation as a source at 36kV and 15 mA. FTIR spectrum of all composites were taken on FTIR spectrophotometer (Model RX-I Perkin Elmer, UK) in the region of 400-4000 cm^{-1} at 4 cm^{-1} resolutions with atleast 32 scans for each sample.

3. Results and Discussion
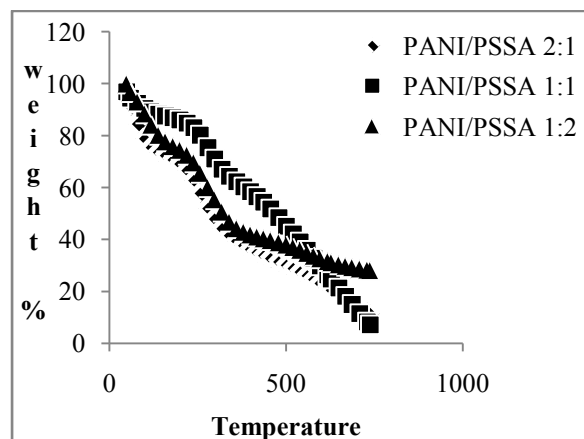
3.1. Thermogravimeric Analysis

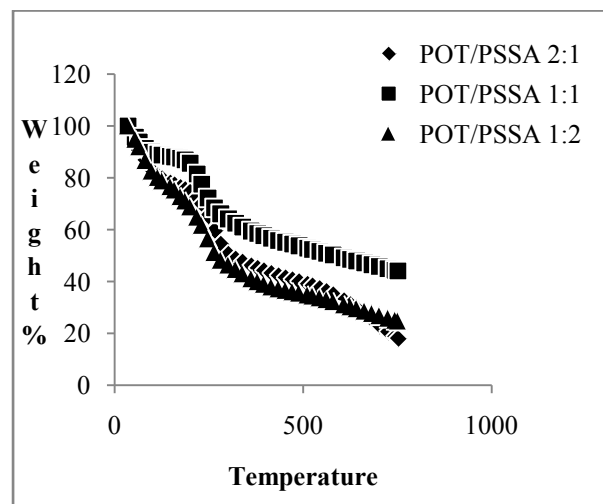**Figure 1.**   TGA thermogram of PANI/PSSA composite materials

Figure 2.   TGA thermogram of POT/PSSA composite materials

The thermogram of polyaniline emeraldine base form shows a weight loss of 7-8% upto 100℃, a weight loss of 22% from 100-450℃ and a weight loss of 40% from 450-800℃. Our data are found in good agreement with the data reported in literature[31-33], which confirms the reliability of our results. When polyaniline was mixed with polystyrene sulphonic acid in different compositions, i.e. in (2:1), (1:1) and (1:2) compositions, a different thermal behaviour with respect to the parent polymer, i.e., polyaniline is shown in Figure1. Thermogram suggests that weight loss mainly occurs in two steps. First step corresponds to the loss of water molecules, slow removal of oligomers and loss of impurities upto 120℃ with a total weight loss of ca. 6% in

PANI/PSSA (2:1) composition, upto 150℃ with a weight loss of 9% in PANI/PSSA (1:1) composition and upto 100℃ with a weight loss of 12% in PANI/PSSA (1:2) composition. Second step corresponds to the degradation of polymeric backbone and polystyrene sulphonate ions in the range of 200-400℃ (weight loss of ca. 33%) in PANI/PSSA (2:1), in the range of 160-360℃ (weight loss ca. 25%) in PANI/PSSA (1:1), in the range of 140-360℃ (weight loss of ca. 38%) in PANI/PSSA (1:2) composition. Thus, the thermal stabilities of all the composites are considerably less than that of polyaniline. This may be attributed to the decreased chain length and presence of bulky groups in the composites.

POT in its base form shows a negligible weight loss upto 410℃ and a continuous weight loss (ca. 15%) is observed upto 650℃, which is possibly due to the degradation of POT matrix in its thermogram. This implies that the base form of PANI brings about thermally more stable than undoped POT. It is possibly due to the lower steric hindrance of the –CH$_3$ group of toluidine present in ortho-position.

In case of composites of poly(o-toluidine) with PSSA a different behaviour of thermogram is shown in figure2. In case of POT/PSSA (2:1) first weight loss due to loss of moisture occurs upto 100℃, where as in POT/PSSA (1:1) weight loss occurs upto 110℃ and in POT/PSSA (1:2) composition, thermogram shows first weight loss upto 100℃. Second major weight loss due to degradation of polymeric backbone and polystyrene sulphonate ion occurs from 150-300℃ (27%) in POT/PSSA (2:1) composition, from 140-300℃ (ca. 24%) in POT/PSSA (1:1) composition and from 120-400℃ (ca. 22%) in POT/PSSA (1:2) composition.

Thus, the thermal stability of the composites depends upon the actual amount of PSSA incorporated, which in turn is governed, by the competition between reactivity and steric hindrance of –CH$_3$ group of toluidine in ortho-position.

3.2. Differential Scanning Calorimetry

DSC thermogram of the polyaniline (EB) form shows an endothermic peak at 50-140℃ and an exothermic peak at 185-350℃. The first peak is most likely attributed to the removal of water and the second peak may be related to the cross-linking reaction [34]. In comparison to polyaniline base form, the composite materials in different compositions show entirely different thermogram as shown in figure3.The thermogram of PANI/PSSA (2:1) composition shows an endothermic peak at 99℃, which may be attributed to the loss of water molecules present in polymer matrix. Another endothermic peak at 272℃ may be assigned to the cross-linking/oxidation of composite backbone, where as the small change above 400℃ onwards may be assigned due to the degradation of the composite backbone. In case of PANI/PSSA (1:1) also, an endothermic peak at 265℃ may be assigned to the cross-linking/oxidation of composite. A transition is observed at about 356℃, which may be attributed due to the decomposition of polymeric system, while in case of PANI/PSSA (1:2) composition, DSC thermogram shows an endothermic peak at about 140℃ due to the

evaporation of water molecules trapped inside the composite or bound to the polymer backbone. Other exothermic peak at 298℃ may be assigned due to the cross-linking/oxidation in composite backbone, whereas the change above 360℃ may be assigned due to the degradation of composite. The glass transition was not observable in these composites, because the glass transition is buried in the peak due to the removal of water and it does not exhibit hysteresis. When the polymer powder is heated, cooled and reheated, no exotherm is observed upon heating. However, if the transition is a T$_g$, it should be observed repeatedly upon heating and cooling. Cross-linking in these polymers is an irreversible chemical reaction and therefore would be observed only upon heating the polymer for the first time.
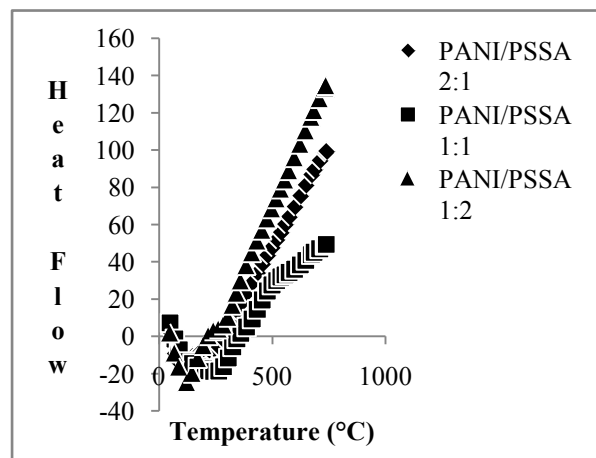

Figure 3. DSC thermogram of PANI/PSSA composite materials
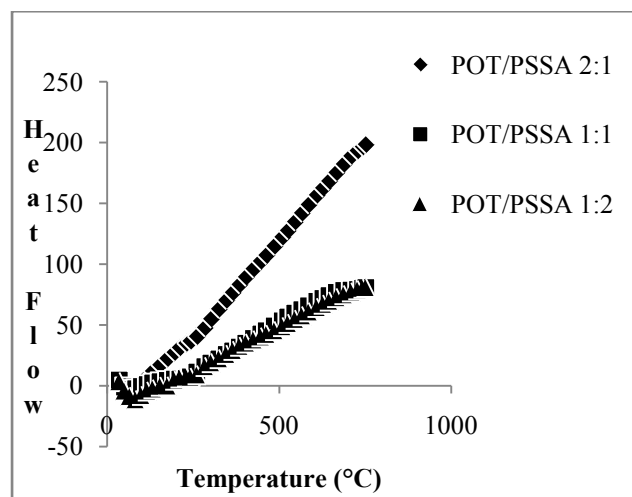

Figure 4. DSC thermograms of POT/PSSA composite materials

DSC thermogram of poly(o-toluidine) (EB) form shows an endothermic peak at 100-120℃ followed by exothermic peaks at 235 and 310℃. The exothermic peak at 235℃ may be assigned due to the oxidation or cross-linking in polymer chain whereas a change in thermogram above 310℃ may be assigned due to the degradation of composite backbone [Kumar et al 2004]. However, in the thermogram of POT/PSSA (2:1) composition as shown in fig.4, an endothermic peak at 80℃ may be assigned due to the release of

water and impurities present in composite. Another endo-thermic peak at 268°C may be assigned due to the cross-linking or oxidation of composite backbone and onset of exothermic transition above 300°C onwards attributed due to the degradation of polymeric backbone. In case of POT/PSSA (1:1) composite, the endothermic peak at 82°C appears due to the release of moisture and an endothermic peak at about 235°C may be assigned to the cross-linking/oxidation of composite backbone while an exothermic transition above 350°C shows the degradation of polymeric matrix. In case of POT/PSSA (1:2) composite, endothermic peak at 84°C may be assigned due to removal of water. Another endothermic peak at 255°C in POT/PSSA (1:2) may be assigned due to the cross-linking or oxidation of composite. The transition above 360°C onwards may be assigned due to the degradation of polymeric backbone.

Thus, on the basis of thermal profile of these materials, we can say that among polyanilines/PSSA composite materials, cross-linking or oxidative reaction starts at higher tempera-ture in PANI/PSSA rather than POT/PSSA composites, which indicates that the stability of PANI composites is higher than POT composites. These DSC results of com-posite materials are also found in good agreement with TGA results.
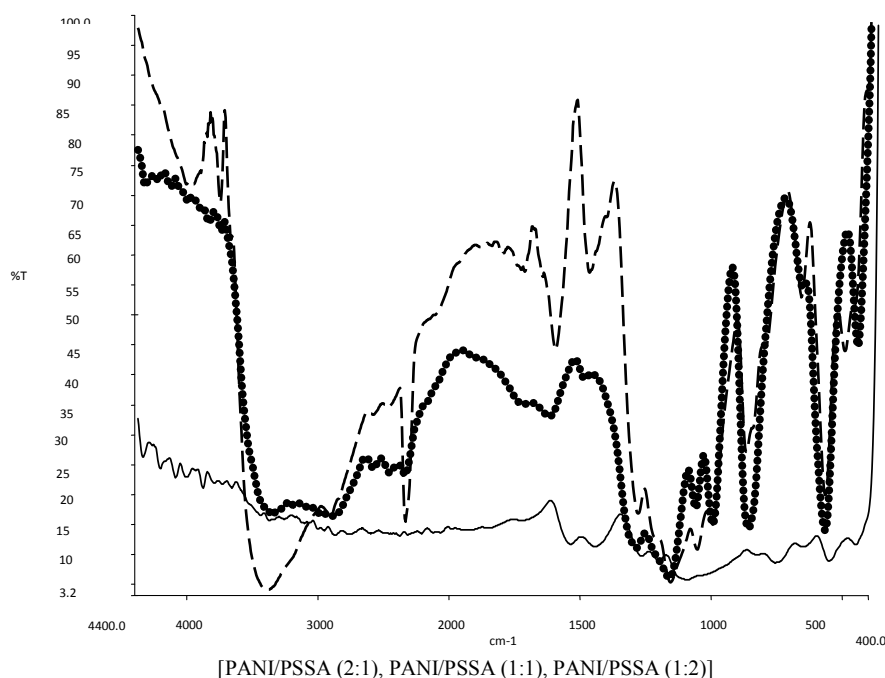
3.3. X-ray Diffraction

In PANI/PSSA (2:1) composite, the XRD pattern shows sharp peaks centered on 2θ value of 15, 17 and small peak at 25°, while in case of PANI/PSSA (1:1) composition small peaks at 10, 39 and 45° and in case of PANI/PSSA (1:2) composition small hump at 10, 16, 19, 25 and 39[0] are ob-served. The intensity of above peaks decreases abruptly with the increase in PSSA content in the composite material. Thus the peaks appear as weak shoulders in PANI/PSSA (1:1) and
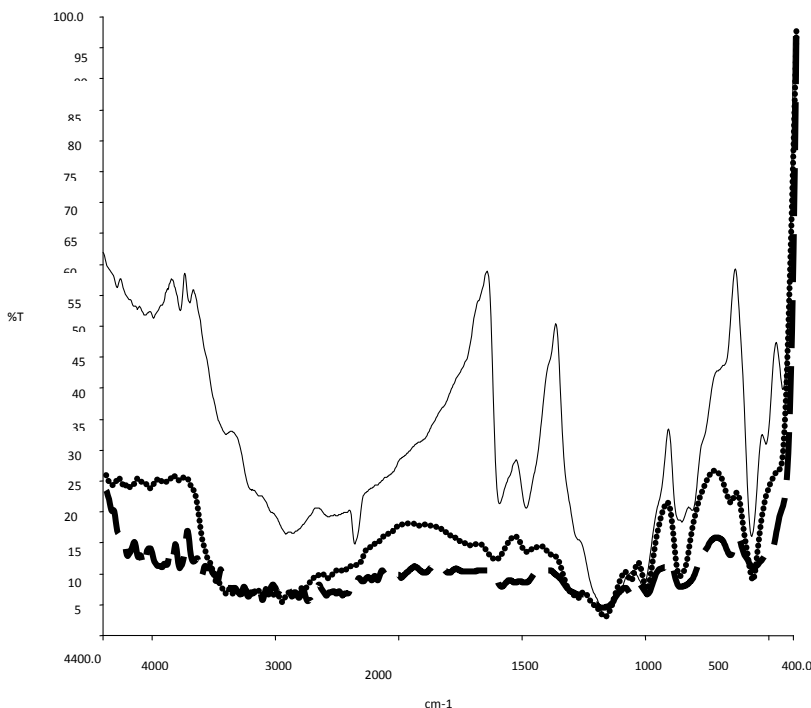
PANI/PSSA (1:2) compositions.

In POT/PSSA (2:1) composite, the XRD pattern shows sharp peaks centered on 2θ value of 14, 17 20, 39 and 45°, while in case of POT/PSSA (1:1) a small hump at 14, and a broad amorphous peak at 25 are observed. In POT/PSSA (1:2) composite, small hump at 20, 39 and 43 are observed. Thus POT/PSSA (2:1) composite is found more crystalline than POT/PSSA (1:1) and POT/PSSA (1:2) composite, be-cause as PSSA content increases in the composite material, the intermolecular chain spacing and amorphous nature of composites increases due to steric hindrance of methyl group. The amorphous nature in PANI/PSSA (1:2) and POT/PSSA (1:2) composition also attributes the reason that PSSA acts as a plasticizer and it distorts the lattice. Thus instead of en-tering inside the emplty lattice, it first forms attachment through suitable bonding at the reactive site and simultane-ously engulfs the whole polymer in a very regular manner-because of its miceller type morphology. This type of mor-phology destroys the regular arrangement of polymeric backbone and thus leads towards the amorphous character. The Bragg angles and d-spacing obtained from the wide angle X-ray diffractograms of powdered samples of com-posite materials are presented in Table-1.

Table 1.   X-ray diffractogram data of composite materials

Sample	Value of 2θ (in degree)	Value for d spacing (Å)
PANI/PSSA (2:1)	15, 17, 25	6.23, 5.23, 3.57
PANI/PSSA (1:1)	10, 39, 45	8.98, 2.33, 2.02
PANI/PSSA (1:2)	10, 16, 19, 25, 39	8.90, 5.45, 4.66, 3.55, 2.33
POT/PSSA (2:1)	14, 17, 20, 39, 45	6.30, 5.24, 4.46, 2.33, 2.02
POT/PSSA (1:1)	14, 25	6.37, 3.61
POT/PSSA (1:2)	20, 39, 43	4.47, 2.33, 2.11

[PANI/PSSA (2:1), PANI/PSSA (1:1), PANI/PSSA (1:2)]
Figure 5.   FTIR spectra of PANI/PSSA composite materials

Figure 6. FTIR spectra of POT/PSSA composite materials[POT/PSSA (2:1), POT/PSSA (1:1),POT/PSSA (1:2)]

3.4. FTIR Analysis

The FTIR spectra of emeraldine base form of aniline are observed in the range of 1650 cm^{-1} to 1220 cm^{-1}, which arises due to the aromatic ring breathing, -NH- deformation and due to the -C-N- stretching. The bands at 1577 cm^{-1} and at 1484 cm^{-1} are the characteristic bands of N- quinoid and benzenoid rings and their presence shows a prominence in the conducting state of the polymer. The absorption band at 1227 cm^{-1} arises due to C-N benzenoid ring stretching in the polymer. The peak at 818 cm^{-1} attributes due to the para coupled ring while peak at 886 cm^{-1} represents the deformed vibrational mode of benzene ring, which is caused due to attachment of specific group present on the ring. Figure5. Shows the FTIR spectra of composite materials prepared by reinforcement of polymer, i.e. polyaniline to PSSA in different compositions such as PANI/PSSA (2:1), PANI/PSSA (1:1) and PANI/PSSA (1:2) compositions. The FTIR studies reveal the formation of composite materials and help to obtain their compositions qualitatively. In case of composites, the out of plane H deformation, i.e. para coupling was observed at ~ 800 cm^{-1}. The band at 1470-1490 cm^{-1} corresponds to C=C ring vibrations of benzenoid ring. The peak at 1130-1140 corresponds to sulphonic acid group in all these compositions, i.e. due to the symmetric $-SO_3$ stretching. The intensity of this band goes on increasing with the increase in PSSA content. The characteristic bands of both PSSA and PANI confirms the presence of both phases in composite materials, but all these bands shows a systematic shifting that indicates existence of significant interaction between PANI and PSSA in the composite material.

The FTIR spectra of poly(o-toluidine) giving peaks at 1591 and 1491 cm^{-1} are due to the C=C vibration of quinoid and benzenoid rings. The characteristic peak at 1304 cm^{-1} has been attributed due to C-N in Q-B-Q sequence. The peak at 807 cm^{-1} attributes to the para coupled phenyl ring and a strong peak at 878 cm^{-1} appears due to the methyl group attached to phenyl ring. The band at 1155 cm^{-1} could be attributed to the $-CH_3$ rocking mode. The FTIR spectra of composite materials are shown in figure6. The C=C vibrations of quinoid ring is observed at 1590-1620 cm^{-1} in all composites. The peak due to C=C vibration of benzenoid ring is observed at 1485-1510 cm^{-1} in composite materials. The peak due to methyl group attached to the phenyl ring is observed at 850-870 cm^{-1}. The characteristic peaks observed at 1170-1190 cm^{-1} are due to symmetric stretching vibrations of $-SO_3$ (polystyrene sulphonic acid). The peak at 3100-3400 cm^{-1} shows the presence of N-H stretching vibration in all compositions. The intensity of these peaks goes on increasing with the increase in PSSA content.

4. Conclusions

Polyaniline and poly(o-toluidine) have been reinforced into PSSA in 2:1, 1:1 and 1:2 compositions for the preparation of composite material. TGA-DSC result show that thermal stability of PANI/PSSA (2:1) and POT/PSSA (2:1) is higher than their 1:1 and 1:2 compositions, respectively. In all thermograms, the first peak is observed due to loss of water/moisture and oligomers while the second peak may be due to the crosslinking/oxidation followed by degradation of composite material. From XRD pattern, we infer that crystallinity of PANI/PSSA (2:1) and POT/PSSA (2:1) is higher than their 1:1 and 1:2 conuterparts. PANI/PSSA (2:1) and POT/PSSA (2:1) compositions find an easy way to attack on

the suitable sites of polymer, which facilitates the easy movements of polyaniline and poly(o-toluidine) molecular chain, ultimately causes a change and contributes towards the higher crystallinity. The FTIR data demonstrated the interaction between PSSA and polyanilines with the presence of sulphonic acid peaks in all composites. The characteristic bands of PSSA, PANI and POT also confirm the presence of both phases in the materials.

ACKNOWLEDGEMENTS

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