Thermal Stability of Conductivity of Composite Comprising Polyaniline and MCM-41

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ABSTRACT: A composite of mesoporous silica (MCM-41) with a polyaniline (PANI) conducting polymer was synthesized by *in situ* polymerization method. PANI/MCM-41 conducting polymer composites were characterized by Fourier Transform Infrared (FTIR), UV-Vis, thermogravimetric analysis (TGA), Four-point probe for conductivity measurement and ^{13}C CP/MAS NMR. It was revealed that although conductivity of PANI was reduced after addition of MCM-41, from 1 to 10^{-1} S cm^{-1}, its thermal stability of conductivity was significantly enhanced and demonstrated the desirability which efficacy of this polymer-mesoporous silica MCM-41 composite system in relatively high temperature applications (*ca.* 150 ^{o}C).

Keywords: Polyaniline, MCM-41, sulfonic acid, thermal stability of conductivity.

1.0   INTRODUCTION

Polymers which generally comprise simply of C, H, and simple heteroatom such as N and S with π-conjugated bond would show some intrinsic conductivity. In 1967, conducting polymers such as pyrrole, thiophene and furan were characterized and the electrical conductivity of these polymers were noted [1,2]. Polyaniline (PANI) is one of the materials studied intensively due to its unique properties such as high electrical conductivity and good environmental stability in doped and neutral states. It has been generally accepted that only polyaniline with emeraldine salt structure showed electrical conductivity. Electrical properties of PANI can be reversibly controlled by charge-transfer doping and protonation. Polyaniline is environmentally stable and inert. Polyaniline has a wide range of potential technological applications including storage batteries, electrochromic devices, light emitting diodes, corrosion inhibitor and a variety of chemical sensor [3].

It has been accepted that a high conductivity of PANI need not imply a good thermal stability of conductivity. In practical applications, the latter factor might be even more critical than the former. Despite the fact that the chemical stability of PANI has frequently been investigated by thermogravimetry, studies on the thermal stability of conductivity of PANI and its composites have received much less attention [4,5,6].

It has been reported by several researchers that a good thermal stability of PANI could be improved by combining PANI with polystyrene latex [7], multi-walled carbon nanotubes [8], nano-ZnO particles [9], montmorillonite [10], graphite [11] and MCM-41 [12,13,14,15,16,17,18]. However, the thermal stability of conductivity of these composites has never been investigated. These composites have also been proven to possess a variety of unique properties such as mechanical, electrical and structure properties because of the synergistic effect owing to the intimate mixing between PANI and inorganic

or organic components at a molecular level. In this study, MCM-41 was chemically modified by functionalization with 3-mercaptopropyltrimethoxysilane (MPTS) to create sulfonic acid in order to increase the interfacial interaction between PANI and MCM-41. Further, we show that enhancement of the thermal stability of conductivity of PANI/MCM-41 composite was achieved when PANI was combined with sulfonic acid-functionalized MCM-41.

2.0 MATERIALS AND METHODS

2.1 Synthesis

The MCM-41 and PANI dodecylsulfate (PANI.DS) were synthesized according to Ref. [19] and [20] respectively. In the synthesis of PANI composite with MCM-41 loaded with sulfonic acid (PANI/MCM-41-SO$_3$H), MCM-41 was first modified with 3-mercaptopropyltrimethoxysilane (MPTS) (assay 98%, Kanto chemical) based on the procedure reported previously [21], except for the dehydration of MCM-41 at 393 K. About 3.5 g of calcined MCM-41 was evacuated overnight at 393 K, and then added to a solution of 7.4 g of MPTS (assay 98%, Kanto chemical) in 300 ml toluene (assay 98%, Kanto chemical). Toluene was dried over zeolite 4A molecular sieve before use. After 4 hours of refluxing, the powder was collected and subjected to the Soxhlet extraction for purification. The MPTS modified materials were oxidized with H$_2$O$_2$ in a methanol–water mixture. Typically, 2.0 g of aqueous solution H$_2$O$_2$ (35%) dissolved in three parts of methanol was used per gram of the material. After 24 hours, the suspension was filtered off and washed with distilled water and ethanol. The wet material was resuspended (1 wt%) in sulphuric acid (H$_2$SO$_4$; 0.1 M) for another 4 hours. Finally, the materials were extensively rinsed with H$_2$O, dried at 333 K, and stored in desiccators. The sample is denoted MCM-41-SO$_3$H. The MCM-41-SO$_3$H was dried in an oven at 120°C for 24 hours before it was combined with PANI. Aniline.HCl (assay 99.5%, Kanto chemical) dissolved in 1 M HCl (37.2 ml) was slowly added to the dried MCM-41-SO$_3$H under stirring and the suspension was stirred for 3 hours. The mixture was then heated at 90°C for 45 minutes and subsequently cooled to 0°C for 30 minutes under stirring. After 30 minutes, ammonium peroxydisulfate (APS) (assay 97%, Kanto chemical) was added dropwise to the mixture in about 2 hours and then left stirring for 24 hours. Then, 100 ml methanol was added into the mixture and stirred for 30 minutes and the final solid was filtered off under vacuum and dried at 60 ^{o}C under vacuum for 6 h. The solid obtained is denoted PANI/MCM-41-SO$_3$H.

2.2 Characterizations

The FTIR spectra of the solid samples, prepared by KBr technique, were recorded on Shimadzu Fourier transform infrared (FTIR) 8300 spectrometer. Thermal stability of the samples was measured by using DTG-50 Shimadzu under nitrogen flow (35 ml min^{-1}) and heating rate 10°C min^{-1} from room temperature to 1000°C. Solid State ^{13}C CP/MAS NMR NMR experiments were performed using Bruker Avance 400 MHz 9.4T spectrometer. The ^{31}C CP/MAS NMR spectra were recorded with a recycle delay of 5.0 s, number of transient of 6000 and spinning rate of 7 kHz. Chemical shifts for ^{13}C was referred to TMS. The UV-Vis spectra of PANI.DS and PANI/MCM-41-SO$_3$H composite were recorded using UV/VIS/NIR Spectrometer Jasco V-570. PANI and its composites were dissolved in methanol in 0.5 cm quartz cell. The absorption range of UV-Vis measurement is from 300 to 1500 nm. Conductivity measurement of the thin film of acid doped PANI and its composites, which were prepared by using solvent casting technique [20], was measured by Loresta HP (Mitsubishi Chemical) by standard four-point probe technique at room temperature, 100°C, 150°C and 200°C and measurement has been done every 15 minutes for 1 hour in order to study the thermal stability of conductivity of PANI/MCM-41

composites. Graph of conductivity versus time at constant temperature was plotted to see the trend in conductivity.

2.0   RESULTS AND DISCUSSION

The IR spectra of PANI.DS, MCM-41-SO$_3$H and PANI/MCM-41-SO$_3$H are shown in Figure 1. The absorptions in the region between 3500 and 2700 cm^{-1} in the IR spectra can be assigned to hydrogen bonded propyl and SO$_3$H groups in MCM-41-SO$_3$H (Fig. 1c). Peaks of SO$_3$H in regions 1360 to 1000 cm^{-1} region cannot be observed due to overlap with peaks of MCM-41. Although it is difficult to assign the presence of SO$_3$H in MCM-41, the absence of bands of –SH at 2600 to 2550 cm^{-1} in the spectrum confirmed that only SO$_3$H is present in the structure of MCM-41 after modification.
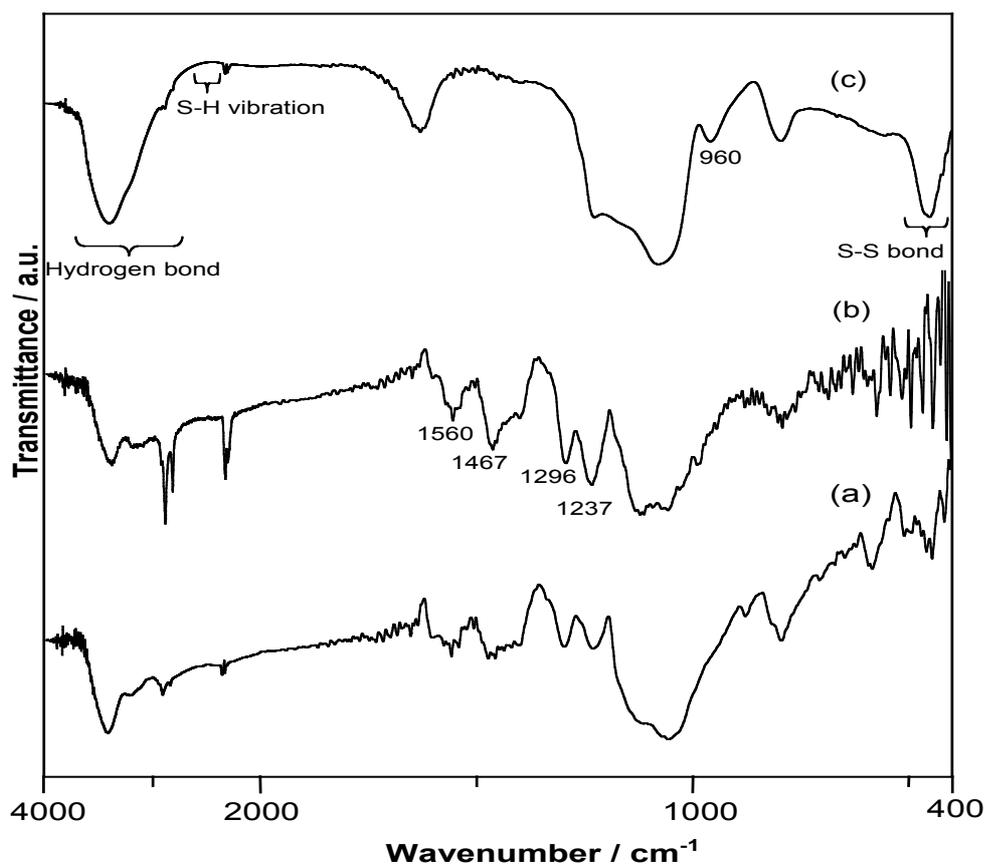
Figure 1:   IR spectra of (a) PANI/ MCM-41-SO$_3$H, (b) PANI.DS and (c) MCM-41-SO$_3$H.

The appearance of peaks around 1560, 1467, 1296, and 1237 cm^{-1} suggested that all the polyaniline compounds have the emeraldine salt structure. The 1237 and 1296 cm^{-1} peaks characteristic of the conducting polaron structure C-N$^+$ of doped PANI associated with the oxidation or protonation states of PANI. The major peaks of MCM-41 are around 1200-1000 cm^{-1} (asymmetric Si-O-Si stretching), 960 cm^{-1} (Si-OH stretching), 800 cm^{-1} (symmetric Si-O-Si stretching) and 460 cm^{-1} (Si-O-Si bending) which can be clearly observed also for MCM-41-SO$_3$H. This indicates that the structure of MCM-41 remains unaltered after modification. This argument is supported by the fact that the X-ray diffraction patterns of the composites were identical to each other (data not shown). However, the relative intensities of the peaks were different in which the intensity of the peak around $2\theta = 2°$ assigned to the (100) reflection of MCM-41 increases with the increasing wt% of MCM-41 relative to PANI.

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Peaks in the 2900-3000 cm^{-1} region are assigned to C-H stretching vibration of alkyl groups. The reduction in intensity of these peaks is due to the lower number of alkyl groups in PANI/MCM-41-SO$_3$H compared to that of DS in PANI.DS. The peak corresponding to plane bending vibration of C-H (mode of N=Q=N, Q=N$^+$H-B, and B-N$^+$H-B) which occurs during protonation can be observed at 1120 cm^{-1} [22,23].

The UV-Vis spectra of PANI.DS and PANI/MCM-41-SO$_3$H composites are shown in Figure 2. These samples show three characteristic absorptions at 300 – 420, 420 – 450 and 740 - 1000 nm wavelength. The first absorption band is assigned to - * electron transition within benzenoid segments. The second and third absorption bands should be related to doping level and formation of polaron, respectively [22,23]. From Fig. 2, it can be seen that the characteristic peaks of PANI.DS all appear in PANI/MCM-41-SO$_3$H composite. Although three distinctive peaks do not shift obviously, two peaks at 400 and 450 nm almost coalesce together into a peak. This implies that the presence of MCM-41 has some effect on the conjugated structure of the conducting polyaniline. In addition, the peak intensity over 1400 nm corresponding to - * transition of benzenoid segments, which is related to the number of the repeating unit of monomer in PANI, was decreased after addition of MCM-41. These results suggest that the PANI/MCM-41-SO$_3$H has relatively short conjugated PANI emeraldine salt structure due to the polymerization of PANI in the constrained space channels of MCM-41.
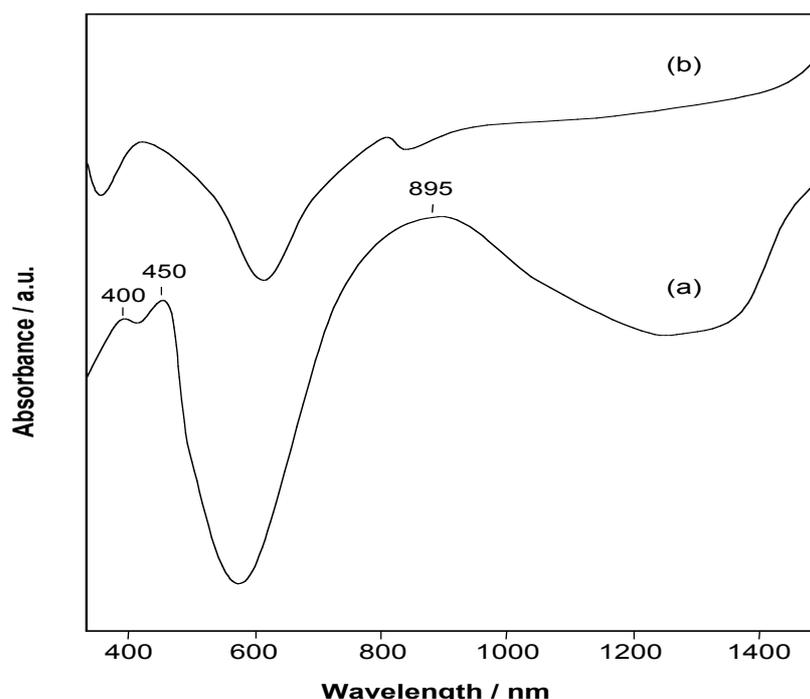
Figure 2: UV-Vis spectra of (a) PANI.DS and (b) PANI/MCM-41-SO$_3$H (the ratio of PANI : MCM-41 was 60 : 40).

Further evidence of the presence of polymer was confirmed by TGA analysis (Figure 3). The content of sulfonic acid and PANI estimated from the gravimetric analysis were *ca*. 10 % and 60% (w/w) respectively. As shown in Figure 3, the sulfonic acid and PANI start to decompose at 300 ^{o}C. The decomposition rate of the polymer when combined with MCM-41 is found to be very different from the decomposition rate of the bulk polymer. The bulk PANI emeraldine salt (PANI.DS) decomposes between 200 and 700 ^{o}C, but the polymer composite decomposes slowly from 300 to 600°C (Figure 3). This

result implies that PANI interacted strongly with the surface MCM-41-SO$_3$H, enhancing the thermal stability of polyaniline.
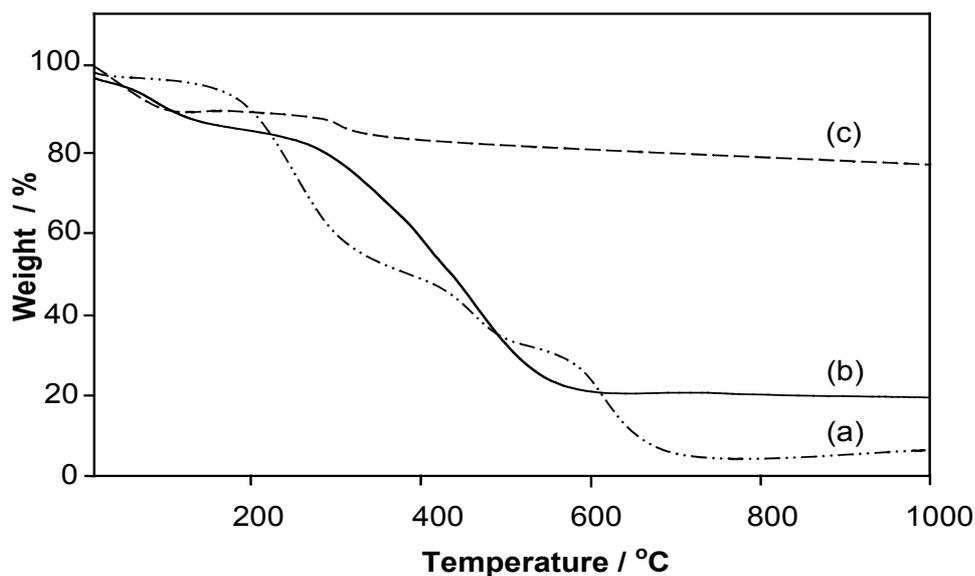
Figure 3: TGA thermograms of (a) PANI.DS, (b) PANI/ MCM-41-SO$_3$H composite and (c) MCM-41-SO$_3$H.

Figure 4 illustrates the effect of heating temperature on the conductivity of PANI.DS and PANI/MCM-41-SO$_3$H composite at 100, 150 and 200°C. At room temperature, the conductivity of the PANI.DS and PANI/MCM-41-SO$_3$H composites are 1.28 and 0.22 S cm^{-1}, respectively. These values are very much lower than the conductivity reported for pure PANI after being doped with HCl (12 S cm^{-1}) [17].
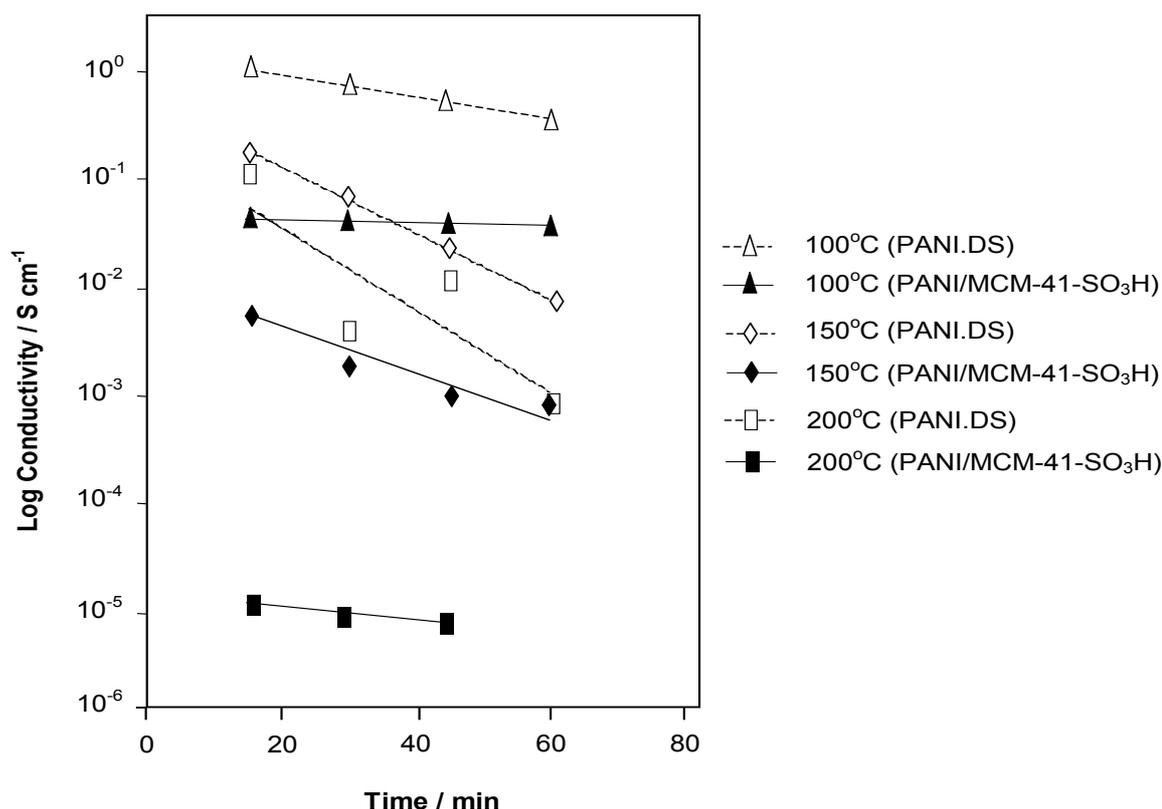
Figure 4: The conductivity of PANI.DS and PANI/MCM-41-SO$_3$H composites at 100, 150 and 200°C versus time.

As seen in Figure 4, the increase in curing temperature reduces the conductivity of PANI.DS. However, at 100°C, the conductivity of the PANI.DS and PANI/MCM-41-SO$_3$H composites are steadily maintained with the increase of time from 15 minutes to 1 hour. The increase of temperature to 150°C causes a larger reduction rate of conductivity of PANI.DS than PANI/MCM-41-SO$_3$H composite. At 200°C, PANI.DS started to decompose which was shown in the TGA thermogram in Figure 2. This explains why the reduction rate of conductivity is the highest for PANI.DS. In contrast, the reduction rate of conductivity of PANI/MCM-41-SO$_3$H is low after the temperature was increased to 200°C. However, the conductivity of the PANI/MCM-41-SO$_3$H became so low that after 45 minutes, it could no longer be measured through the four-point probe method. The data presented in Figure 4 is sufficient to establish the high thermal stability of PANI/MCM-41-SO$_3$H composite and consequently the desirability and efficacy of this polymer-mesoporous silica system in high temperature applications.

For further confirmation of the molecular structure of sulfonic acid attached in the structure of the MCM-41, the MCM-41-SO$_3$H has been analyzed by using ^{13}C/CP MAS NMR spectrum shown in Figure 5a. The NMR spectrum shows the major signals at 54, 14 and -2 ppm which provide strong evidence for the prevalence of -(CH$_2$)$_3$SO$_3$H surface groups. The signal at 54 ppm corresponds to C3 while the next at 14 ppm and -2 ppm correspond to C2 and C1, respectively. When MCM-41-SO$_3$H was combined with PANI to produce PANI/MCM-41-SO$_3$H composite, a broad peak of PANI at around 120 ppm appeared [24], and the signals at 54 ppm, 14 ppm and -2 ppm of -(CH$_2$)$_3$SO$_3$H were shifted towards a higher magnetic field (see Figure 5b). The high field chemical NMR shift of these signals can be explained by the interaction of the free electron pairs of the nitrogen atoms of the PANI with a charged molecule on the surface of MCM-41-SO$_3$H with PANI. This argument was supported by the fact that, from thermogravimetric analysis,

there is a shift to a higher temperature of the decomposition of PANI in PANI/MCM-41-SO_3H compared to PANI.DS (Figure 3). On the basis of these results, a model of the interaction of polyaniline with MCM-41-SO_3H in PANI/MCM-41-SO_3H composite is proposed (see Figure 6).
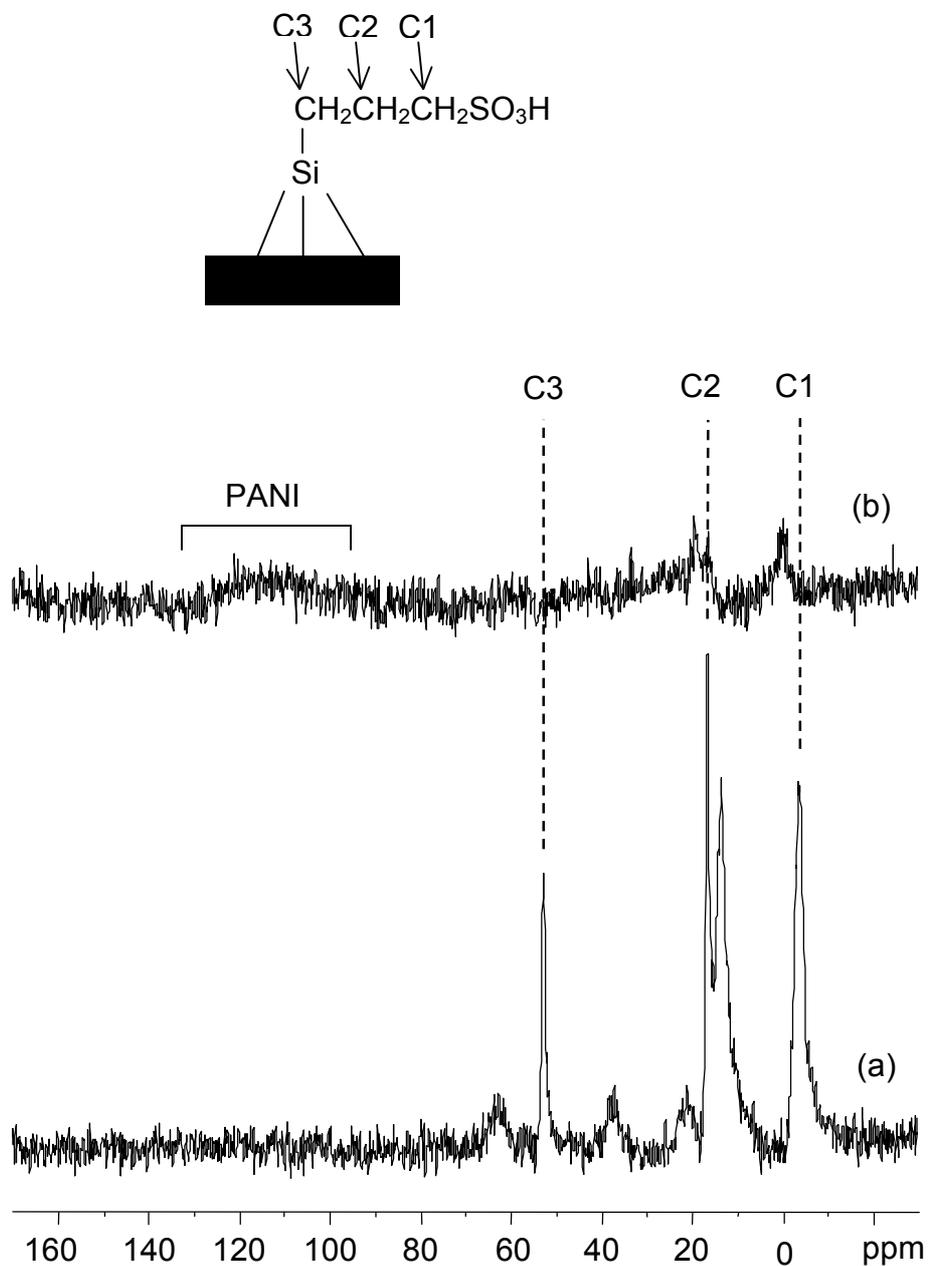
Figure 5: ^{13}C CP/MAS spectra of (a) MCM-41-SO_3H and (b) PANI/MCM-41-SO_3H.
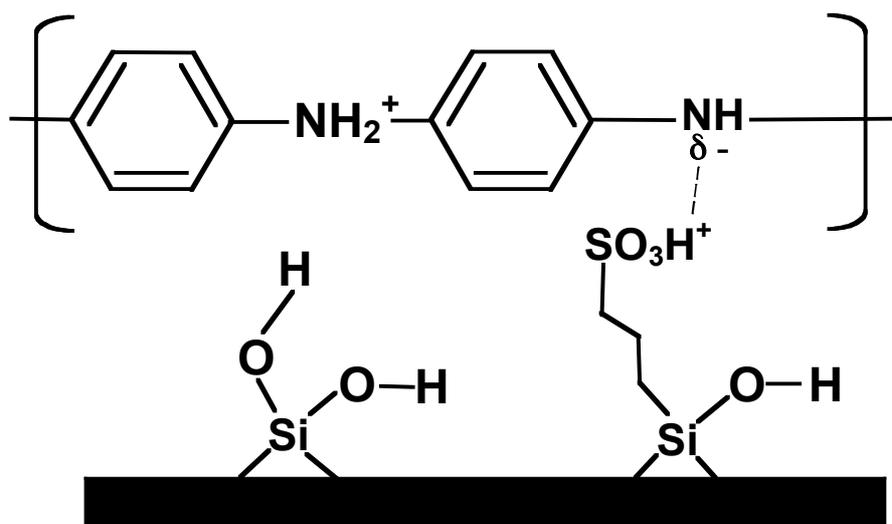
Figure 6: The proposed interaction between polyaniline and MCM-41-SO$_3$H in PANI/MCM-41-SO$_3$H composite.

4.0 CONCLUSION

PANI/MCM-41-SO$_3$H composites were successfully synthesized by *in situ* polymerization technique in the presence of aniline.HCl monomers as starting material. It is revealed that the long order integrity of MCM-41 remains intact after encapsulation of PANI. FTIR spectra of PANI in PANI/MCM-41-SO$_3$H composites show that they are in the emeraldine salt form. Although PANI/MCM-41-SO$_3$H composites show lower conductivity compared to PANI.DS, they show a higher thermal stability of conductivity than that of PANI.DS, because there is the interaction of the free electron pairs of the nitrogen atoms of the PANI with a charged molecule on the surface of MCM-41-SO$_3$H with PANI. As a global guide for future actions, this work opens new perspectives for the use of PANI/MCM-41 composite as a conducting material at high temperature.

5.0 REFERENCES

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