Chapter-6

STUDIES ON THE HYBRID COMPOSITES OF LDH WITH ACRYLAMIDE IN AQUEOUS MEDIUM

This chapter deals with some of the physical and chemical properties of the composites derived from acrylamide and LDH of different kinds like Ni-Al and Zn-Cr. Here in this chapter, organic-inorganic ‘hybrid gel’ approach was basically used to derive the composites. Also, the nature of the coating of such kind of derived composites over solid preforms was also studied herein.
Chapter-6

EXPERIMENTAL SECTION
STUDIES ON ORGANIC-INORGANIC HYBRID COMPOSITES DERIVED FROM ACRYLAMIDE AND LDHs IN AQUEOUS MEDIUM

6.0. EXPERIMENTAL SECTION

As reported in the Chapter-2 that the composites of inorganic layered materials and organic macromolecules have attracted considerable interest as they have adequate properties and flexible synthetic routes for development of nanoporous materials possessing different chemical functionality [344]. Basically, the organic-inorganic hybrid colloidal nanoparticles are synthesised to synergistically combine the functional properties of organic and inorganic constituents. This chapter deals with the synthesis of hybrid composites in aqueous medium containing LDHs and acrylamide oligomers. The physical characterization of such hybrid gels are also described in this chapter. Moreover, the nature of the Layer-by-Layer (LBL) thin films or coats of such hybrid gels over solid preforms was also studied herein.

6.1. Synthesis of LDHs

Ni-Al LDH and Zn-Cr LDH are prepared by the same methods already described in section 4.1.3 and 4.1.5 of Chapter-4. The Ni-Al LDH contained CO$_3^{2-}$ in the inter layers whereas in the Zn-Cr LDH the inter layers was CO$_3^{2-}$ free. The CO$_3^{2-}$ ion in the inter layers of Ni-Al LDH originated to the alkaline pH whereas in Zn-Cr LDH the inter layers was free from the CO$_3^{2-}$ ion due to the acidic pH during the synthesis of the LDH.
6.2. Synthesis of polyacrylamide (PAM)/LDHs hybrid composite gels

30 cm\(^3\) of LDH-acrylamide-water dispersion was prepared by adding 2.5\% (w/v) acrylamide, 1\% (w/v) catalyst i.e. N,N,N',N'-Tetramethylene diamine (TEMED) and polymerisation initiator ammonium persulphate to LDHs. The LDHs loading was increased from 2 to 8\% (w/v). Above four ingredients were mixed well by sonochemical shaking in high intensity ultrasonic processor (model Vibracell VCX 500, M/S Sonics and Materials Inc., USA) at 20kHz± 50Hz frequency of 33\% amplitude for 3-10 min with 3.5 sec pulsar on and 1.5 sec pulsar off mode and 1 inch (25 mm) solid titanium horn at room temperature. Total spell of sonication was for 100 min.

6.3. Flow behaviour study of PAM/LDH hybrid composite gels

The study of the flow behaviour of PAM/LDH hybrid composites were carried out with their aqueous dispersion at varied LDH content and at a fixed acrylamide concentration [2.5 (w/v) \%]. The dispersion was prepared in a high intensity ultrasonic processor (model Vibracell, VCX 500, M/S Sonics and Materials Inc., USA) with a one inch solid Titanium horn. The operating parameters of the sonicator were 20 kHz ±50 Hz frequency at 33\% amplitude for 10 min with 3.5 sec pulse on and 1.5 sec pulse off mode. The total spell of sonication was 100 min. The rheological parameters were measured in a controlled stress rheometer (model Rheolab QC, M/S Anton Paar Ltd., India) using a spindle and cup combination (model CC27-CC10) and calibration liquid (DKD-k-06901, M/S Anton Paar Ltd., India).
6.4. Conventional jar test to check the stability of the dispersed hybrid gels

To check the stability of the dispersed hybrid gels, conventional jar tests were performed. In this test, hybrid gels of two different kinds viz. Ni-Al/PAM and Zn-Cr/PAM hybrid gels were kept inside two vertical Borosil jars of 25 cm³ capacity and allowed to stay like that for 4 weeks to check the stability of the dispersed hybrid gels thus formed.

6.5. Coating of PAM/LDH hybrid composite gels over ceramic solid preforms

Prior to dip-coating the solid preforms were washed with distilled water and dried in an air oven at 110°C for 2 hours. For dip-coating, the supports were vertically hanged and coating was done at 20 mm/min dipping, withdrawing rates and the substrate was kept submerged in the solution for 1 min using a dip-coater (model KSVD from M/S KSV., Finland). The dip-coated products were dried overnight in room temperature followed by heating in an air oven at 40 and 80°C for 6 hours, respectively.

The dispersions of composite material prepared as above were coated over α-alumina tubes (manufactured by M/S Naskar Ceramics, Kolkata., India) having wall thickness 3.0 mm, length 35 mm and internal diameter 15 mm. The dried coats were calcined in air atmosphere up to 1400°C temperature at a heating profile of 5°C/min. The calcined products were allowed to cool to room temperature under normal atmosphere within the furnace.
6.6.1. The viscous average molecular weight determination of LDH intercalated polyacrylamide (PAM) formed by \textit{in-situ} intercalative polymerization

The viscous average molecular weight of the \textit{in-situ} polymerized acrylamide was determined by the single-point method [345]. For the determination of the viscous average molecular weight, a hybrid gel was prepared using 4\% (w/v) Zn-Cr LDH, 5\% (w/v) acrylamide, 1\% (w/v) ammonium persulfate as initiator and 1\% (w/v) TEMED as the catalyst. The composite hybrid gel was centrifuged at 10,000 RPM in a research centrifuge (model Remi R24). The filtrate part mainly containing non interlayer polyacrylamide was kept separately for its molecular weight analysis. The residue part was collected and suspended in water by shaking in a magnetic stirrer. The dispersion was treated overnight in 1M Na$_2$CO$_3$ to exchange interlayer species with CO$_3^{2-}$ ion. The carbonate exchanged dispersion was again centrifuged at 10,000 RPM. Collected the filtrate and discarded the residue. The filtrate obtained was rich with exchanged polyacrylamides from the interlayer space. The polyacrylamide portion was extracted by adding equal volume of methanol. The separated polyacrylamide was centrifuged and dried at 40°C. A portion of the dried interlayer polyacrylamide was weighed and redissolved in 1M brine solution to get a clear dispersion of known solid concentration. The viscosity of the dispersion was then measured in Ubbelohde viscometer and calculated the viscous average molecular weight by using standard equation and corresponding Mark-Houwink constants [345].

The filtrate obtained from the first centrifugation was treated with purified methanol to make an approximately 1:1 ratio of water and methanol. These extracted
external surface polyacrylamides were then separated and dried at 40°C. A weighed out portion of the dried polyacrylamide was redissolved in 1M brine solution to get a clear dispersion. The viscosity of the dispersion was measured in Ubbelohde viscometer for determination of molecular weight of non-intercalated polymers as described above.

6.6.2. Gel Permeation Chromatography (GPC) of the prepared hybrid composites

The Gel Permeation Chromatography (GPC) of the experimental samples was carried out in Water 110213 using Empower software for 35 min retention time with 50 µl sample.

6.7. Physico-chemical characterisation of PAM/LDH hybrid composites by powder XRD, TG-DTA-DTG-DSC, FT-IR, XPS, TEM, SEM etc.

The chemical characterization of the prepared LDHs was carried out by Ion Chromatography (model Metrohm 881 IC Compact Pro1), ICP-AES (model JY-2000) and TG-DTA (model SDT Q600) analysis, CHN analysis (model Perkin Elmer 2400). The TG-DTG-DTA characterization of the hybrid gels and the polymers extracted from them were carried out by using thermal analyser (model SDT Q600 from M/S Waters., India) from RT to 800°C in argon atmosphere at the heating rate of 10°C/min. The DSC characterization of the interlayered polyacrylamide derived from the LDH derived acrylamide hybrid gels were carried out by using DSC (model TA DSC 2010) from 50 to 200°C in argon atmosphere at the heating rate of 20°C/min. The powder XRD characterizations of different products were carried out using Cu kα radiation with wavelength of 1.54056 Å at a scan rate of 0.2° 2θ/min (model Rigaku-Ultima IV., Japan).
The Fourier Transform Infrared (FT-IR) spectra were recorded in spectrophotometer (model Perkin-Elmer 2000 System) in 400-4000 cm\(^{-1}\) range at a spectral resolution of 4 cm\(^{-1}\) using KBr pellets.

The XPS spectra were recorded in a KRATOS AXIS 165 dual anode (Mg and Al) apparatus using the Mg K\(_\alpha\) anode. The pressure in the spectrometer was about 10\(^{-9}\) Torr, for energy calibration the carbon 1s binding energy was taken to be 284.6 eV. The location and full width at half maximum (FWHM) for a species was determined using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as a pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples in general were reproducible to within ± 0.1 eV.

The Transmission Electron Microscopy (TEM) was carried out by placing a drop of the hybrid dispersions on C coated copper grids, allowing the solvent to evaporate. The qualitative characterization of hybrid dispersions were performed on a FEI Tecnai F 12 (Philips Electron Optics, Holland) instrument operated at 100 kV.

The Scanning Electron Microscopy (SEM) studies of the samples were carried out in a Hitachi S-520 SEM unit, for this samples were mounted on an aluminium support and were coated with Au in HUSGB vacuum coating unit.
Chapter 6

RESULTS & DISCUSSION
RESULTS AND DISCUSSION

This chapter provides an account of the synthesis, characterization of the synthesised compounds and correlation of the results. The characterizations are based on powder X-ray diffraction, FT-IR analysis, SEM, TEM, XPS, thermal analysis (TG-DTG-DTA-DSC) and also the flow behaviour properties of the composite gels.

6.8. Chemical characterization of the LDHs

The chemical characterization of the prepared LDHs after fitting with the standard formula given by Allmann [9] gave their formulae as (details described in Chapter-4 section 4.5.2 and 4.5.5) \([\text{Ni}_{0.7}\text{Al}_{0.3}(\text{OH})_2](\text{NO}_3^-)_{0.02}(\text{CO}_3^{2-})_{0.28}.3.23\text{H}_2\text{O}\) and \([\text{Zn}_{0.6}\text{Cr}_{0.4}(\text{OH})_2](\text{Cl}^-)_{0.4}.2.657\text{H}_2\text{O}\) respectively.

6.9. Synthesis of hybrid gels of acrylamide monomer and LDHs under sonochemical activation

Acrylamide monomers underwent polymerisation after intercalation in the interlayer slabs of the inorganic host LDHs (Ni-Al and Zn-Cr) under sonochemical activation. The polymerisation was initiated by the persulphate initiator and TEMED acting as the catalyst. The polymerisation of the acrylamide monomers occurred in the hybrid gel matrix also.
Figure 6.9. Figure showing the synthesis of hybrid gel of acrylamide monomer and LDHs under sonochemical activation and its coat over solid ceramic preform.
6.10. The viscous average molecular weight determination of the LDH intercalated polyacrylamide (PAM) formed by \textit{in-situ} intercalative polymerization

Two types of polymers were formed in the composite of acrylamide-LDH hybrid gel. Polymer obtained by \textit{in-situ} intercalative polymerization of acrylamide in presence of Zn-Cr LDH was of low molecular weight than the polymer obtained outside the interlayer slabs of LDH host. In the present case the viscous average molecular weight of polymers separated from the interlayer of Zn-Cr LDH was around 9,000 whereas the same of the polymer separated from the bulk dispersion was around 141,900. Similarly, the interlayer polymer separated from the Ni-Al LDH composite was around 5,000 whereas the viscous average molecular weight of the polymer separated from the bulk dispersion was around 175,000.

The \textit{Gel Permeation Chromatography} (GPC) analysis of the extracted polyacrylamide from the external matrix of the hybrid gel comprising of acrylamide, Zn-Cr LDH and ammonium persulphate showed two peaks with two different molecular weights viz., one with number average molecular weight 48,000 and another with 6500. The same was corroborated by the two peaks obtained in the DSC pattern of the same experimental sample at 58 and 181°C respectively (Fig. 6.10).
Figure 6.10. DSC pattern of hybrid gel comprising of acrylamide and Zn-Cr LDH.

6.11a. Differential Scanning Calorimetry (DSC) analysis of the extracted polymers from the interlayer and the external matrix of the hybrid gels

The DSC characterization of the polyacrylamide derived from the interlayers of the two acrylamide derived hybrid gels showed slight shift of the glass transition temperature from 117.5 in polymer derived from Ni-Al LDH hybrid gel to 124.2°C in polymer derived from Zn-Cr LDH hybrid gel Fig.6.11a.

Figure 6.11a. The DSC patterns of polymer derived from the interlayers of the (A) Zn-Cr-acrylamide hybrid composite, (B) Ni-Al-acrylamide hybrid composite.
6.11b. Thermal analysis (TG-DTG-DTA) of the hybrid gels and the polymers extracted from the hybrid composite gels

![Thermogram of hybrid gels and polymers](image)

**Figure 6.11b.** The TG-DTA-DTG patterns of (I) Hybrid gel of Ni-Al LDH, (II) Hybrid gel of Zn-Cr LDH, (III) Polymer extracted from the hybrid gel (I) and (IV) polymer extracted from the hybrid gel (II).

The thermograms of the hybrid gels and the polymers extracted from them showed three step weight losses in three different regions from 20-100, 200-400 and 400-600°C.

6.12. The PXRD characterization of hybrid composites of PAM/LDHs

The powder XRD patterns of the composite materials revealed that the intercalation of monomers in the LDH sheets led to its *in-situ* polymerization and formation of hybrid gel in both Ni-Al LDH & Zn-Cr LDH case. Initial increase of basal spacing was seen in both the cases **Figs. 6.12** (I) and (II). However, the initial rise in the basal spacing was more pronounced in Zn-Cr-LDH case than in Ni-Al-LDH case. The
PXRD patterns of Fig. 6.12 (I) showed that in the case of acrylamide-Ni-Al LDH hybrid composite the initial value of \( d = 7.61 \text{Å} \) with basically \( \text{CO}_3^{2-} \) in the interlayer shifted to \( d = 8.02 \text{Å} \) in 6% (w/v) LDH treatment which further changed \( d = 9.22 \text{Å} \) in 8% (w/v) LDH treatment, however reverting the increasing tendency, it changed to \( d = 8.17 \text{Å} \) in the case of 10% (w/v) LDH treatment.

Similarly, in the case of acrylamide-Zn-Cr LDH hybrid composite basically with \( \text{Cl}^- \) as the interlayer species, starting from a \( d = 7.82 \text{Å} \) in untreated system it changed to \( d = 11.61 \text{Å} \) in 4% (w/v) LDH treatment. On further raising the LDH content in the hybrid composite like in the case of Ni-Al LDH there was a decrease in basal spacing to \( d = 9.39 \text{Å} \) at 8% (w/v) LDH treatment Fig. 6.12 (II). Similar behavior of increase in basal spacing followed by its decrease due to polymerization was observed earlier also [231, 346].

The decrease in basal spacing at higher LDH concentration was due to higher uptake of acrylamide molecules by the LDH layers because of the availability of larger surface area for monomers to anchor and grow. Thus, the consequent polymerization of the monomers, in the basal surface accompanied by a crumbling of the polymer chain due to conformational changes caused the decrease of basal spacing.
Figure 6.12. (I) A-Ni-Al LDH by coprecipitation method, B-F-Ni-Al LDH+2.5% (w/v) acrylamide composites at 2%, 4%, 6%, 8% & 10% (w/v) LDH loading respectively; (II) G -Zn-Cr LDH prepared by oxide hydrolysis method, H-J-Zn-Cr LDH+2.5% (w/v) acrylamide composites at 2%, 4% & 8% (w/v) LDH loading respectively.
6.13. FT-IR characterization of the hybrid gels (PAM/Ni-Al & PAM/Zn-Cr hybrid gels)

The FT-IR patterns in Fig. 6.13 revealed that in the case of Zn-Cr LDH there was no strong peak of vibration of carbonate ion in the region around 1350 cm\(^{-1}\), whereas the same was intensely present at 1359 cm\(^{-1}\) in Ni-Al LDH case. This was due to the intercalation of CO\(_3^{2-}\) originating from adsorption of atmospheric CO\(_2\) in the aqueous medium in the interlayers during synthesis of Ni-Al LDH at alkaline pH. In the patterns A and B, the peak around 1595 cm\(^{-1}\) corresponds to \(\gamma (H_2O)\) bending vibration of interlayer water molecules of LDH.

The peak at 1450 cm\(^{-1}\) in separated polyacrylamide corresponds to \(\delta (\text{-CH}_2\text{-})\), confirming the polymerisation of acrylamide [231, 346, 347]. In case of separated polyacrylamide a shoulder at \(~1400\text{ cm}^{-1}\) due to \(\gamma (\text{NH}_2)\) was observed, which in hybrid composites was observed in 1384 cm\(^{-1}\). Also, in the separated polyacrylamide the appearance of a shoulder at \(~1680\text{ cm}^{-1}\) corresponding to \(\nu (C=O)\) was seen, which shifted to around 1655 cm\(^{-1}\) in both the hybrids [346]. The peak near 1110 cm\(^{-1}\) in both the hybrid composite correspond to \(\nu_s (C-C)\) asymmetric stretching mode of polyacrylamide, which in separated polyacrylamide appeared at around 1136 cm\(^{-1}\). The probable reason for these shifts to low wave number in hybrid composites may be due to restrictions in vibrations offered by the host layers in the interlayer space, which also further confirms the acrylamide incorporation in the interlayers [347-348].
In the patterns C, D and E the peak at 1630 cm\(^{-1}\) corresponds to \(\gamma\) (C=C) arising due to the presence of some unreacted acrylamide in the system. The broad band near 3400 cm\(^{-1}\) corresponds to OH-stretching region arising due to hydroxyl group and water molecules present in the systems.

**Figure 6.13.** FT-IR patterns of A- Zn-Cr LDH, B- Ni-Al LDH, C- PAM-Zn-Cr LDH hybrid composite, D-PAM-Ni-Al LDH hybrid composite, E- PAM extracted from the composite gels.

### 6.14. Rheological measurement of the hybrid gels of polyacrylamide and LDHs

From the rheological measurements it was found that with the rise of LDH concentration against a fixed monomer concentration of 2.5 (w/v) %, the viscosity of the Ni-Al LDH-polymer hybrid composite was higher than that of Zn-Cr LDH-polymer hybrid composite. One probable reason for the same is the increased
monomer intercalation in the Zn-Cr-Cl LDH case than in Ni-Al-CO₃ LDH case resulting in poorer interlinking of monomers present outside the interlayers of Zn-Cr-Cl LDH. In the Ni-Al-CO₃ LDH case due to the presence of interlayer carbonate ion the intercalation of monomers was not prominent as in Zn-Cr-Cl LDH case (Fig. 6.14). Higher intercalation of acrylamide molecules in Zn-Cr-Cl LDH than in Ni-Al-CO₃-LDH was also shown by larger basal spacing shift in the former than in the later (Fig. 6.12). Rheological data also showed that at a 2.5% (w/v) acrylamide and 8% (w/v) LDH concentration there was a non-Newtonian type flow behaviour with a yield point indicating a closed LDH particle-particle network felicitated through encapsulation by extraneous polymer macromolecules present in the system. Such a network facilitates a strong gelation where water molecules of the dispersion medium were distributed in the interparticulate region.
Figure 6.14. Rheogram of (I) acrylamide-Ni-Al LDH hybrid gel and (II) acrylamide-Zn-Cr LDH hybrid gel.

6.15. Conventional vertical jar test with the prepared hybrid gels

The particle-particle interaction made the hybrid gels quite stable and kept the coloured LDH particles suspended for several weeks. Fig. 6.15 shows the photographs of conventional jar tests of such stable dispersions of 8% (w/v) Zn-Cr-Cl and Ni-Al-CO$_3$ LDH-2.5% (w/v) acrylamide after sonication. These organic-inorganic hybrid dispersions were found to be stable even after thirty weeks.

Figure 6.15. Conventional vertical jar test of the prepared hybrid gels.
6.16. Dip-coating of the hybrid gels over solid ceramic preforms

The stable PAM/LDH hybrid dispersions were dip-coated upon solid ceramic preforms to see their ability to form thin films by Layer-by-Layer (LBL) assembling. In the Fig. 6.16, the photographs of such hybrid gels dip-coated over cut out segments of macro-porous tubular α-alumina are shown. The coated thin films were found to be free from any cracks.

![Figure 6.16](image)

**Figure 6.16.** Close-up view of dip-coating (A) Zn-Cr LDH-acrylamide and (B) Ni-Al LDH-acrylamide hybrid gels over macroporous α-alumina surface.

6.17. Physical characterization of hybrid gels and their derived coats over solid ceramic preforms by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

The SEM results revealed that the Ni-Al-LDH on sonication did not break out of their coagulative nature and remained as aggregated small flocs of around 20 μm
dimension (Fig. 6.17.A), while on treatment with acrylamide combined with ultrasonication they got distributed in the body of the gel with reduction of number of flocs as well as their size reduced to around 1 to 2 μm (Fig. 6.17.B). Similarly, in case of Zn-Cr-Cl LDH also the sonicated products before acrylamide treatment formed flocs of around 20μm dimension (Fig. 6.17.C). Similar to Ni-Al case the flocs disaggregated on acrylamide treatment combined with sonication and formed a cloudy dispersion of inorganic phase in the polymer matrix (Fig. 6.17.D). The SEM images of the coats formed by the hybrid gels of acrylamide and LDHs (Ni-Al & Zn-Cr) over solid ceramic preforms (α-alumina in this case) showed thin crack free coats on drying (Fig. 6.17 E & F).
Figure 6.17. The SEM images of (A) Ni-Al LDH prepared by coprecipitation method (B) acrylamide-Ni-Al LDH hybrid composite, (C) Zn-Cr LDH prepared by oxide hydrolysis (D) acrylamide-Zn-Cr LDH hybrid composite (E) coat of acrylamide-Ni-Al hybrid composite over α-alumina preform and (F) coat of acrylamide-Zn-Cr hybrid composite over α-alumina preform

The TEM image of 8% (w/v) LDH treated with 2.5% (w/v) acrylamide after sonication and drying under slow drying condition in a continuous flow of dry air with 35% relative humidity showed total exfoliation of the individual layers to hexagonal nano-sheets (Fig. 6.17. G & H).
Figure 6.17. The TEM images of (G) polyacrylamide-Ni-Al LDH composite (H) polyacrylamide-Zn-Cr LDH composite.

6.18. Physical characterization of the hybrid gels by XPS

As XPS is an important surface sensitive analytical technique useful for the identification as well as characterization of the chemical environment around the elements present in the system it gave several valuable information. Fig. 6.18 showed the high resolution narrow scans of Ni and Al in Ni-Al LDH acrylamide and Zn and Cr in Zn-Cr LDH acrylamide composite. As can be seen, the observed binding energy peaks at 854 and 871 eV are characteristic of Ni in 2+ oxidation state and in the oxide form, which can be attributed to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ transitions, respectively. The binding energy peak at 74.5 eV for Al 2p is due to Al$^{3+}$ in the oxide form. From (Fig. 6.18c) it can be inferred that Zn is in 2+ oxidation state with characteristic binding energy peaks at 1021 and 1044 eV due to Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ transitions, respectively. On the other hand in the both component LDH and hybrid composite Cr
exists in two different oxidation states namely, 3+ and 6+ (Fig. 6.18d) with characteristic peaks at 577.8 eV (Cr 2p₃/₂) and 586.9 eV (Cr 2p₁/₂) and 580.0 eV (Cr 2p₃/₂) and 588.7 eV (Cr 2p₁/₂) respectively. This is because the excess Cr³⁺ supplied during hydrolysis of ZnO got oxidized to Cr⁶⁺. Similar reports of oxidation of Cr³⁺ to Cr⁶⁺ over oxide surface in acidic pH are also there [349, 350].

**Figure 6.18.** XPS patterns of (a & b) Ni-Al LDH-acrylamide (c & d) Zn-Cr LDH-acrylamide hybrid gels.