# Development and Characterisation of Nanoclays from Indian Clays

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## ABSTRACT

Indian clays are known for their smecticity. One such clay sample collected from Bhuj (Gujarat) was characterised and modified by successive sedimentation processes for different time intervals. The non-plastic components of clay, viz., quartz, illite, iron oxide, *CaO*, *MgO*, and organic matter were removed in different steps, as the heavy impurities in the clay-water suspensions, settle down during sedimentation. The free iron oxide present in clay suspension was reduced by giving sodium citrate-bicarbonate-dithionite treatment and iron content was further reduced from 12–15 per cent to 5–7 per cent respectively. The organic matter was removed by sodium acetate-$H_2O_2$ treatment. The modified clay so obtained was characterised by thermal analysis, FTIR, and XRD, SEM and TEM. The cation exchange capacities of original and modified clays were determined both by methylene blue method and ammonium acetate method. The cation exchange capacity is found to enhance from 120–130 meq/100 g to 135–145 meq/100 g. Using the above procedure, 92 per cent smecticity was obtained. Organophilisation of purified clay (smectite) was carried out by intercalation with alkyl ammonium salt. The XRD analysis showed enhancement of interlamellar spacing from 1.294 nm to 2.855 nm.

**Keywords:** Indian clays, montmorillonite, intercalation, cation exchange capacity, smectite, nanoclays

## 1. INTRODUCTION

The clay minerals have layered structure and layer thickness is around 1 nm. The lateral dimension may vary to few micron or more, depending upon the particular layered silicates. Stacking of the layered silicates leads to regular van der Waal gap between the layers called interlayer or gallery. Isomorphic substitution of within the layers by metal cations generates negative charges that are counter balanced by exchange cations such as $Na^+$, $Ca^{+2}$, and $Mg^{+2}$. This type of layered silicate is characterised by a moderate surface charge known as cation exchange capacity (CEC) and it is generally expressed as meq/100 g. This charge varies and an average value is always considered.

The hydration of these inorganic exchange ions present in clays and the nature on *Si-O* groups impart a hydrophilic nature to the mineral surfaces and this property make them to adsorb water but very difficult to disperse in polymer matrices, i.e., organic compounds cannot bond with adsorption sites on the clay surfaces. As a result natural clays are ineffective sorbents for poorly water-soluble organic contaminants. However, the surface properties of these clays can be modified greatly by neutralising the anionic framework of layer silicates by using positively charged organic species such as primary aliphatic amine salts and alkyl ammonium ions[1-3].

In the modified form, the clay surface may show organophilic nature and can bond strongly

with organic compounds. Montmorillonite (MMT), a hydrated magnesium aluminium silicate belong to 2:1 layer type of clay mineral in which an octahedral alumina layer is sandwiched between two tetrahedral silicate layers (as shown in Fig. 1). The clay minerals are composed of silicate layers of 1 nm thick and 200–300 nm in the lateral dimensions. High purity montmorillonite (smectite) is one such known clay, as the ultimate properties of resultant polymer matrix composites depend on cation exchange capacity and uniform dispersion of montmorillonite in polymer matrix[4]. Aspect ratios of such silicates varies from 100 to 1000, and cation exchange capacities vary from100–150 meq/100g clay.

Bentonite is natural occuring mineral of montmorillonite (smectite). It is available in abundant in Bhuj area. Its chemical composition as well structure is not always same and varies from place to place. Therefore, a specific purification method for each bentonite needs to be developed depending upon properties of its clay and non-clay minerals.

Though, India is known to have variety of clays but montmorillonite used is imported from other countries. This is very expensive and it takes time to import. Bentonite clay is natural occurring in the Bhuj, Gujarat. Therefore, it was thought to use clay from Bhuj and develop nanoclay.
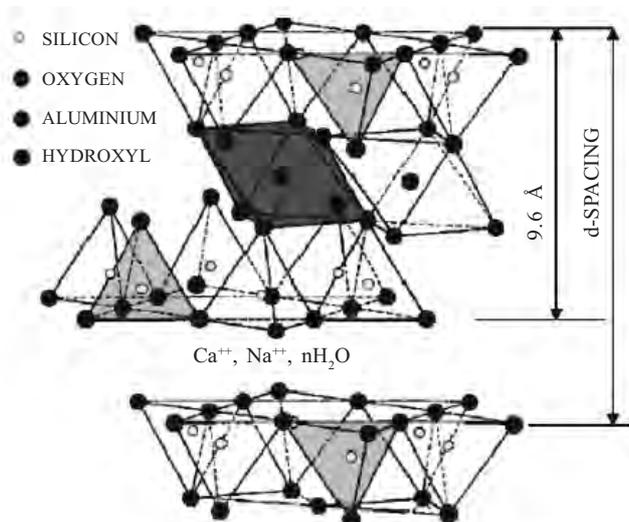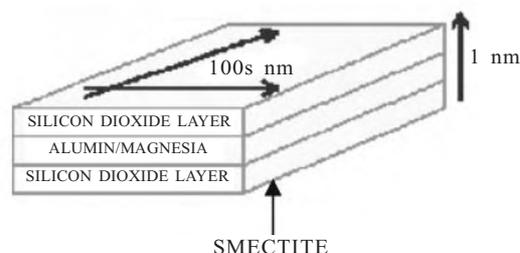
## 2. EXPERIMENTAL METHOD

### 2.1 Materials

Indian clay was collected from Bhuj areas. Trisodium citrate dihydrate, sodium bicarbonate, sodium dithionite, hydrogen peroxide (Qualigens) were used for purification of clay A. Methylene blue (Qualigens), ammonia solution and acetic acid (National Chemicals, India) were used for measurement of cation exchange capacity. Alkyl ammonium compounds (National Chemicals, India) were used to make the organophilic clays.

### 2.2 Purification of Indian Clay

The clay sample collected was reddish brown in colour. In addition to nonplastic impurities, the iron content is very high. Therefore the purification of clay was carried out and schematic diagram of purification process of Indian clay is shown in Fig. 2.

The heavy impurities like quartz; free iron etc, present in Indian raw clay was removed by dispersing clay powder in distilled water and slowly decanting the suspension. The suspension was centrifuged and settled clay was dried at 100–110 °C. The dried clay was grounded and sieved to have clay particles of < 75 μm size. This was designated as Clay A. The remaining iron oxide and organic matters present in clay structure were reduced by treatment with sodium citrate-bicarbonate- dithionite and sodium acetate- hydrogen peroxide respectively. After these treatments, the clay slurry was centrifuged, settled clay was washed with distilled water (2-3 times) and dried at 100–110 °C. Dried clay was grounded using a mortar and pestle, and sieved to collect particles with less than 75 μm fraction. The purified clay was designated as Clay A1.
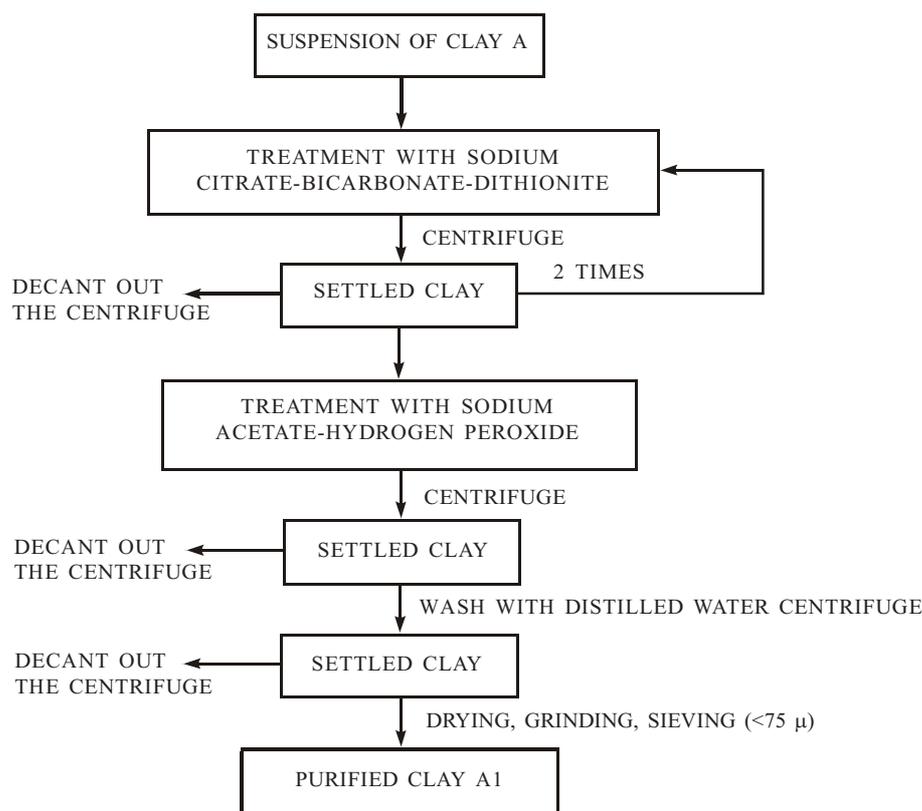


Figure 1. Crystal structure of montmorillonite [$(Mg, Al)_2Si_4O_{10}(OH)_2$].

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                    ┌─────────────────────────┐
                    │  SUSPENSION OF CLAY A    │
                    └─────────────────────────┘
                                 │
                                 ▼
              ┌──────────────────────────────────┐
              │   TREATMENT WITH SODIUM           │◄──────┐
              │ CITRATE-BICARBONATE-DITHIONITE    │       │
              └──────────────────────────────────┘       │
                                 │     CENTRIFUGE         │
                                 │                        │
                                 ▼     2 TIMES            │
  DECANT OUT  ◄──────┌─────────────────────┐─────────────┘
  THE CENTRIFUGE     │     SETTLED CLAY     │
                     └─────────────────────┘
                                 │
                                 ▼
              ┌──────────────────────────────────┐
              │   TREATMENT WITH SODIUM           │
              │  ACETATE-HYDROGEN PEROXIDE        │
              └──────────────────────────────────┘
                                 │   CENTRIFUGE
                                 ▼
  DECANT OUT  ◄──────┌─────────────────────┐
  THE CENTRIFUGE     │     SETTLED CLAY     │
                     └─────────────────────┘
                                 │   WASH WITH DISTILLED WATER CENTRIFUGE
                                 ▼
  DECANT OUT  ◄──────┌─────────────────────┐
  THE CENTRIFUGE     │     SETTLED CLAY     │
                     └─────────────────────┘
                                 │   DRYING, GRINDING, SIEVING (<75 μ)
                                 ▼
                     ┌─────────────────────┐
                     │  PURIFIED CLAY A1    │
                     └─────────────────────┘
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**Figure 2. Schematic diagram of purification of Indian clay.**

## 2.3 Preparation of Organically-modified Clay

Organically-modified clays were prepared by cation exchange with *n*-alkyl ammonium salts. The concentration of *n*-alkyl ammonium salts varied from 1.0 to 2.5 CEC of the silicate. The mixtures of aqueous suspensions of the layered silicates and organic salts were stirred for 3 h at 70 °C. The products were washed 3–8 times with 1000 ml hot distilled water until the washing water was free of chloride ions, dried at 70 °C and grinded in an agate mortar. The organically-modified clay was designated as OClay A1.

## 2.4 Sample Characterisation

The dried Clay A and Clay A1 powders were characterised for CEC by using two different methods, e.g., ammonium acetate method and methylene blue method. The experiments have been carried out minimum ten times to ascertain the values and these are reproducible. The compositions of these clays were determined by chemical method. The TG analysis of Clay A, Clay A1, and various organo-modified clays was done with METTLER TG50, upto 900 °C with a heating rate of 20 °C/min in air. Infrared spectra of Clay A, Clay A1 and organo-modified clays were carried out using FTIR 8300 SHIMADZU. The d-spacing and hk bands were measured with CuKα radiations-*Ni* filtered (Phillips) x-ray diffractometer. The Clay A1 was given the treatment with ethylene glycol for recording x-ray patterns to characterise presence of montmorillonite. The amount of smectite present in Clay A and Clay A1 were determined by using the methylene blue method [Bureau of Indian Standards. DOS: SMDC 17 (3599) P]. The morphological structures of Clay A1 and organically-modified clay seen with SEM (Hitachi S3000N) and TEM (Phillips Tecnai 20).

## 3. RESULTS AND DISCUSSION

The iron is present both as divalent and trivalent cations and it is believed that the presence of iron hinders the exchange of organic cation as well as expansion of d-spacing upon organophilisation. Therefore

the amount of iron was reduced both in Clay A and Clay A1. Clay A was treated to remove excess iron, which is present as cations between the clay platelets. The amount of iron was reduced to 5–7 per cent from 12–15 per cent. The characteristic properties of Clay A and Clay A1 are given in Table 1. Upon treatment of Clay A for removal of iron impurities, the CEC increased to 135–145 meq/100 g from 120–130 meq/100 g. This proves the above fact that upon removal of iron from clay, the total cation exchange capacity of clay increases.



Figure 3. TG curve of washed and dried purified clay (Clay A1).

**Table 1. Properties of clay**

| Properties | Original clay Clay A | Purified clay Clay A1 |
|---|---|---|
| Colour | Reddish | Offwhite |
| p$H$ | 9-10 | 9-10 |
| *CEC (meq/100 g clay)* | | |
| Ammonium acetate method | 95-105 | 105-115 |
| Methylene blue method | 120-130 | 135-145 |
| Density (g/cc) | 2.0 | 2.58 |
| *Chemical compostion* | | |
| per cent $SiO_2$ | 48-50 | 50-55 |
| per cent $Al_2O_3$ | 15-18 | 17-20 |
| per cent $Fe_2O_3/FeO$ | 12-15 | 5-8 |
| per cent MMT | 98.63 | 92.26 |



Figure 4. TG curve of organically modified clay.

This result is also supported by the TGA analysis of organoclay from Clay A and Clay A1. The TG analysis of Clay A1 after being submitted to above treatment indicated a mass loss of 1.2 per cent up to 200 °C, due to dehydration and a mass loss of 6 per cent from 200 °C to 800 °C, which can be attributed to dehydroxylation (Fig. 3).

The differential thermal curve of organo-modified clay (OClay A1) shows three peaks (Fig. 4), viz., (a) the free water region in the temperature below 200 °C; (b) the region where organic substances evolve in the temperature range 200–500°C; and (c) the structural water in the temperature range 500–800 °C.

The TG curves for MMT organically-modified with different concentrations of the alkyl ammonium[5,6] salt is shown in Fig. 5. The comparison of thermograms of Clay A1 (a) with that of organically modified clay reveals the removal of incorporated organic
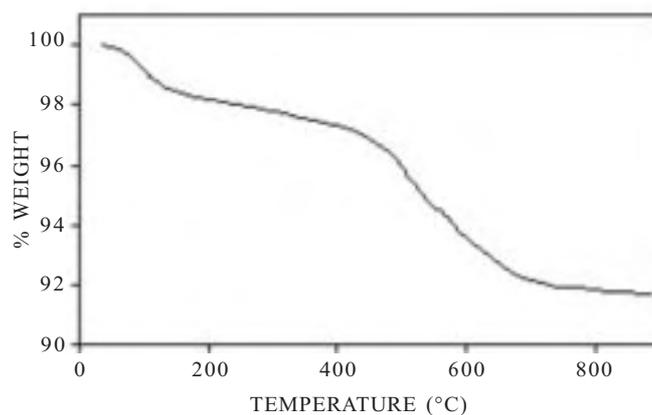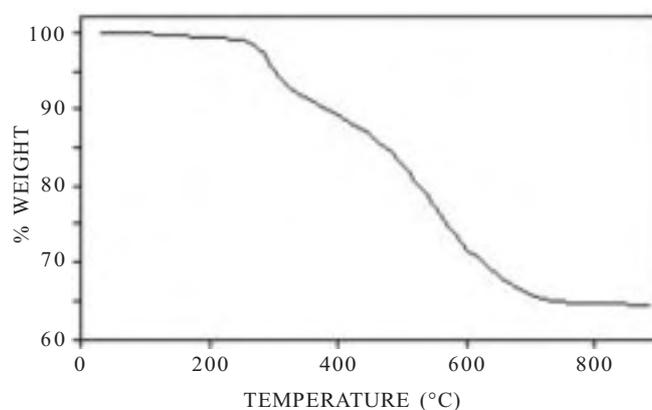
compounds. The loss is more in curve (c), because of high salt concentration 1.5 CEC of clay, which is optimum amount of alkyl ammonium salt adsorption between intergalleries of clay.

The IR spectra of MMT and corresponding organo-modified clay are shown in Fig. 6. The common feature in these spectra is the appearance of bands frequency near to 3622 cm$^{-1}$, 1627 cm$^{-1}$ due to $-OH$ (Free), $-OH$ (bending) vibration, respectively[7-9]. The infrared spectrum of the unmodified clays shows two peaks which corresponds to *Si-O* stretching (969 cm$^{-1}$) and interlayer deformation (1633 cm$^{-1}$) vibrations. The *Al-Al-OH* stretching frequency was observed at 3620 cm$^{-1}$ while the bending frequency was 915 cm$^{-1}$. These can be considered as characteristic of dioctahedryl smectite[10-11].

The spectra of the organophilic MMT shows the presence of new common bands at about 2848 cm$^{-1}$
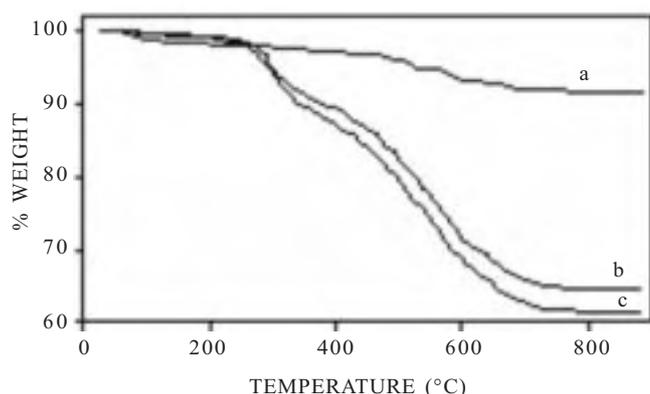
**Figure 5. TG curve of: (a) Clay A1, (b) and (c) organically–modified Clay A1 with salt concentration, i.e., 1.0 CEC of clay and 1.5 CEC of clay, respectively.**
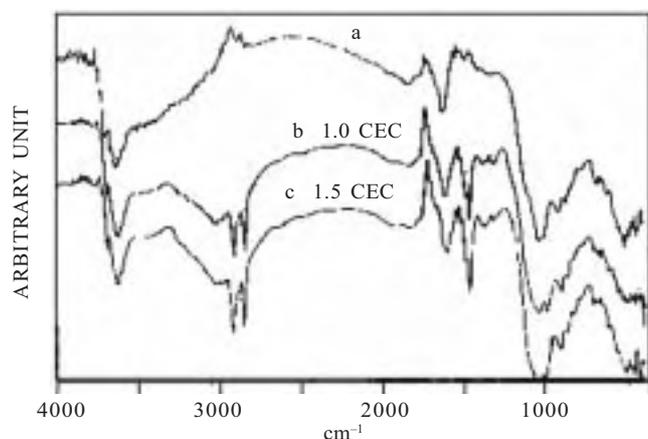


**Figure 6. FTIR spectra of: (a) Clay A1, and (b) and (c) organically-modified Clay A1, with salt concentration as shown.**

and 1469 cm^{-1} which correspond to the symmetrical $-CH_3$ stretching absorption band and $-CH_2-$ scissor vibration band respectively[12]. The weak band near to 3260 cm^{-1}, is due $NH_4^+$ stretching vibration of

intercalated primary aliphatic ammonium. The presence of $--CH_3$, $-CH_2-$ and $NH_4^+$ transmission bands in organophilic MMT confirms the alkyl ammonium intercalation in the interlayer spaces of MMT and the systematic decrease in intensity of $-OH$ (free) band shows that the organophilic MMTs become more and more organophilic with increasing concentration of organic compounds.

The XRD pattern of Clay A1 (Fig. 7) shows the characteristic peaks of montmorillonite, indicating that there is no structural decomposition during purification. The XRD patterns of Clay A, Clay A1 and glycolated clay are shown in Figs 8(a), 8(b) and 8(c). The XRD peaks of Clay A1 shows that curve (b) coincides with peaks of Clay A, curve (a) indicates the retention of layered structure of clay and increase in the intensity of individual peaks indicates removal of bulky cations ($Fe^{+3}$, $Fe^{+2}$, $Ca^{+2}$) with small size cations ($Na^+$) as the basal spacing decreases from 1.379 nm (Clay A) to 1.294 nm (Clay A1) as shown in Fig. 8 (curves a and b). The glycolation shifts the d (001) basal spacing of Clay A1 sample from 1.294 nm to 1.745 nm, d (002) from 0.629 nm to 0.865 nm and d (003) from 0.452 nm to 0.568 nm as shown in Fig. 8 curve c. It is the characteristic property of smectites.

The diffractogram of these organically modified OClay A1, shown in Fig. 8 (curve d) and Fig. 8 (curve e), organically-modified clay was prepared from octadecyl ammonium chloride and Clay A1 registered an increase in the d-spacing of the original Clay A, from 1.294 nm to 2.855 nm. The maximum increase was detected for samples submitted to
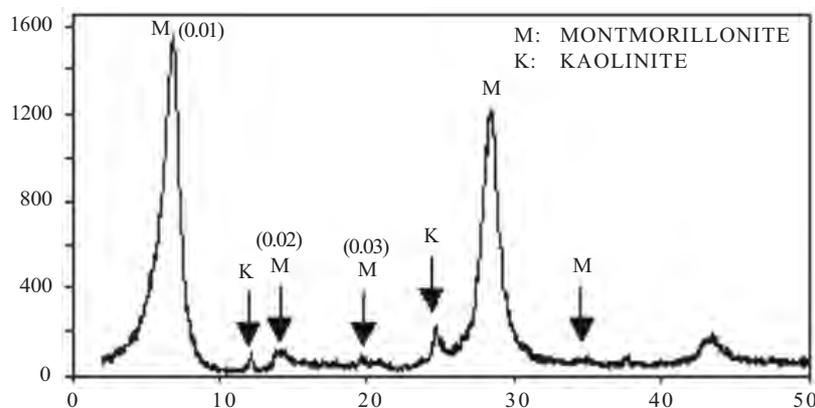


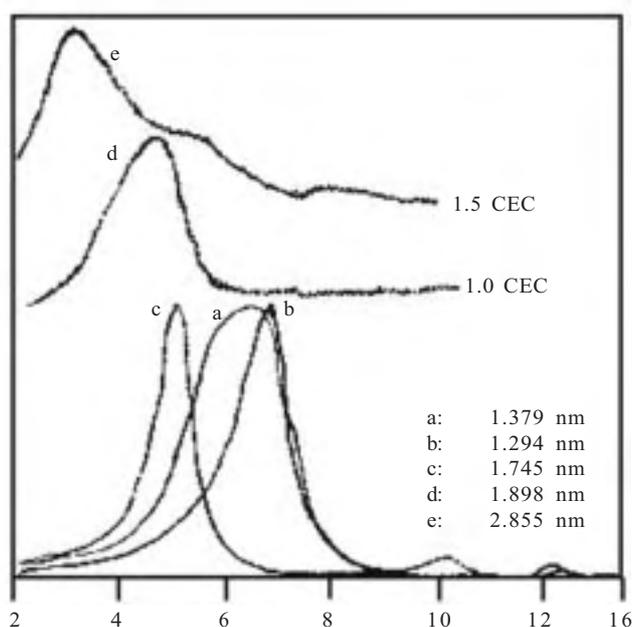**Figure 7. X-ray diffractogram of purified clay (Clay A1).**

**Figure 8. X-ray diffractogram of: (a) clay as such (Clay A), (b) purified clay (Clay A1), (c) glycol-solvated Clay A1, and (d) and (e) organically-modified Clay A1 (OClay A1) with salt concentration of 1.0 CEC of clay and 1.5 CEC of clay, respectively.**

higher salt concentration i.e. 1.5 CEC of smectite. The shift of the XRD peak from 1.294 nm to 2.855 nm can be attributed to re-orientation of the long organic salt chain between MMT layers[15]. The modification process occurred in such a way that the alkyl ammonium ions were adsorbed in the interlamellar space of the clays. The adsorption was through an exchange reaction between the inorganic cations on the clay and the alkyl ammonium ions in the solution. The TG curves shown in Fig. 5 also supports these results[13-14].

The SEM micrograph of purified clay is shown in Fig 9(a). The layered structure of clay can be seen distinctively showing the retention of characteristic properties of clay after giving the chemical treatment. Fig. 9(b) shows the SEM micrograph of organically-modified clay. The layered structures as seen in micrograph is no more continuous and the scattered platelets show an increase in 'd', the interplaner distance.
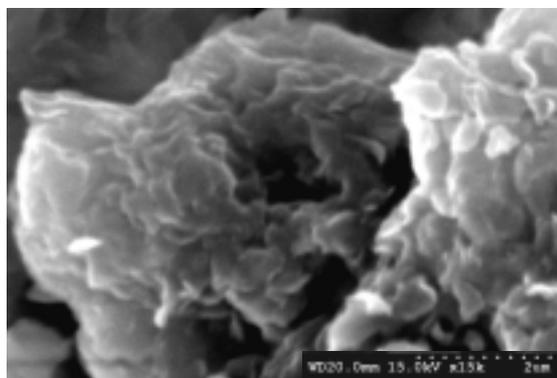
The TEM micrograph of purified Clay A1 is shown in Fig. 10. It shows the laminated clay layers and the average thickness of pristine layers varies from 1.2 nm to 1.5 nm, a characteristic property of nanoclay. These micrographs show the formation of nanoclays. The TEM images also supports the XRD results, as d-spacing measured by two methods are same and the value between two platelets is 1.25 nm by both the methods.

## 4. CONCLUSIONS

The natural occurring clay in Bhuj (Gujarat) was washed, cleaned and modified. It was characterised for cation exchange capacity and smecticity. The experimental data described indicate that on submitting the Clay A to the chemical treatment, result in enhancement in the cation exchange capacity of clay from 120–130 meq/100g to 135–145 meq/100 g and the smecticity (MMT) from 89.63 per cent to 92.26 per cent. A maximum of 56.55 gm of the salt could be incorporated to 100 g of clay and it resulted in an average basal distance of 2.855 nm. Also the TEM results indicate the pristine layers thickness lies between 1.2 nm to 1.5 nm.
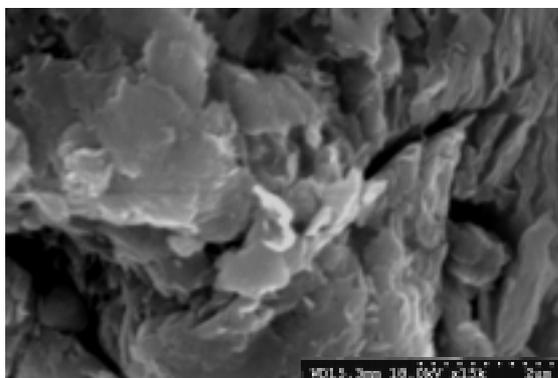


**Figure 9. SEM micrograph of: (a) purified clay and (b) organically-modified clay.**
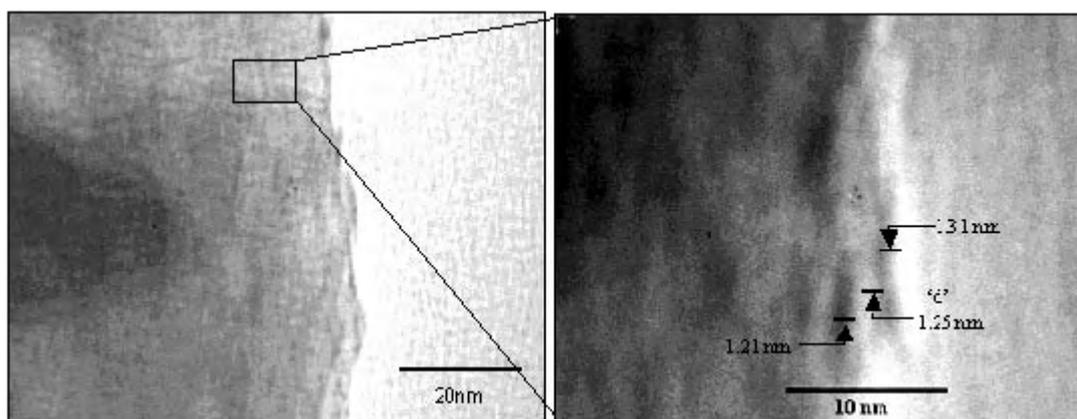
**Figure 10. TEM micrograph of purified Clay A1 at high-resolution.**

These results indicate that it is possible to modify the Indian clays (available in Bhuj, Gujarat) by using *n*-alkyl ammonium salts in to nanoclays.

## ACKNOWLEDGEMENTS

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