

Investigations on Microstructural and Layer Disorder Parameters of Na-Montmorillonite-Glycine Intercalation Compounds

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Abstract

Glycine-Montmorillonite (Gly-MMT) composite has been synthesized through intercalation process using Na-Montmorillonite (Na-MMT) and glycine ethylester hydrochloride. Gly-MMT was employed for the synthesis of dipeptide (Gly-Gly-MMT). Microstructural parameters such as crystallite size, r.m.s. strain ($\langle e^2 \rangle^{1/2}$) and layer disorder parameters such as variation of interlayer spacing (g) and proportion of planes affected by such defects (γ) of the samples have been calculated by X-ray line profile analysis. In comparison to Na-MMT the basal spacings (d_{001}) of Gly-MMT and Gly-Gly-MMT were reduced by 2.4Å and 1.8Å respectively. The value of d_{001} of Gly-Gly-MMT (13.3 Å) suggests the monolayer orientation of dipeptide into interlayer spaces. It is also suggested that more homogeneity in the stacking of silicate layers is attained in Gly-Gly-MMT due to the increased chain length of the dipeptide and orientation in monolayer style.

Key words : Glycine ethylester, montmorillonite, intercalation, crystallite, isomorphous, nanocomposites, microstructural.

I. Introduction

Montmorillonite is a 2:1 type of layer structure clay mineral consisting of negatively charged silica sheets separated by a van der Waals interlayer gallery containing charge-balancing counterions such as Mg^{2+} , Na^+ and Ca^{2+} etc. These interlayer cations balance the negative charges, which are generated by the isomorphous substitution of Mg^{2+} and Fe^{2+} for Al^{3+} in the octahedral sheet and Al^{3+} for Si^{4+} in tetrahedral sheet. The interesting feature of montmorillonite structure is that the interlayer cations can be replaced easily by either organic or inorganic molecules through a process called intercalation, which allows a convenient method for making new composites suitable for different applications such as catalysts¹, cosmetics², nuclear waste treatment³, etc. Moreover, by exploiting this intercalation behavior, montmorillonite is being used in preparation of different types of polymeric-clay nanocomposites and hybrid materials with better physical, mechanical and thermal properties⁴⁻⁷. It is important to note that the preparation of clay based materials and their suitability in different applications are predominantly governed by their physicochemical properties such as strength, plasticity, compressibility, swelling etc which are largely depended on the microstructure and the disorder anisotropy present in layer stacking. Thus the intercalation of different organic molecules into montmorillonite interlayers and investigation of various microstructural properties are of great importance to the users of these compounds⁸⁻¹⁰. Due to the interesting structural features of layer structured clay minerals X-ray diffraction pattern played an important role for their characterization and especially basal (001) reflection is preferred¹¹⁻¹⁴. However, this basal reflection is highly sensitive to interlayer distances, intralayer charge, interlayer cations density, and water molecules, which are present between the layers. Since the interlayer cations and intralayer charge density in not homogeneous from layer to

layer^{14,15}, a variation in the stacking of layers along c-direction is highly expected, which will affect 00l reflections, especially 001 by a greater factor. Thus the parameters, which can characterize these variations, may be important for better understanding of the different properties of pure and organomodified clay minerals. So this type of characterization of clays and organomodified clays has drawn the attention of many researchers^{9,16-20}. Polymer clay nanocomposites have been produced with an extensive array of synthetic polymers having potential applications, such as biopolymers incorporated clays found applications in drug delivery, biomedical engineering and pharmaceuticals²¹. Studies on biopolymer-clay composites such as Lysine-MMT²², lysine-, arginine- and histidine-MMT²³, Poly(L-lysine)/Na-Montmorillonite²⁴ have been reported. To the best of our knowledge incorporation of glycine α -amino acid, which is a building block in the biological systems into montmorillonite interlayers and hence synthesis of dipeptide and their microstructural and layer disorder parameters characterization has not been investigated so far. Thus in the present investigation, glycine ethylester has been intercalated into Na-montmorillonites interlayers, which further reacted with a second unit of glycine ethylester to afford a clay bound Gly-Gly dipeptide. The microstructural parameters like crystallite size (P_v , P_f), r.m.s. strain ($\langle e^2 \rangle^{1/2}$), and layer disorder parameters such as variation of interlayer spacing (g) and proportions of planes affect by such defects (γ) have been calculated from X-ray diffraction line profile analysis.

II. Materials and Methods

Na-montmorillonite (SWy-1, cation exchange capacity = 76.4 meq/100g, Clay Mineral Society, University of Missouri, Columbia) was used in the present work and intercalated using Glycine ethylester hydrochloride ($C_4H_9NO_2.HCl$). Considering the cation exchange capacity

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and the structure of Na-MMT the intercalation was carried out following the method available in the literature^{9,24,25}. Glycine-ethylester hydrochloride (0.864 g, 6.0 mmol) was taken and mixed with concentrated HCl (1 mL) and water (30 mL) in a round bottom flask and stirred vigorously at 80°C for 15 minutes. The mixture was then poured into Na-MMT dispersion (2.5 g in 100 mL H₂O) and heated at 80°C with vigorous stirring for 45 minutes. The precipitate so formed was filtered and washed repeatedly with distilled water to make it free from the chloride ion. The product was subsequently dried in air atmosphere to afford colourless powder. The synthesized compound was termed as Gly-MMT where Gly stands for glycine ethylester and MMT for montmorillonite. In case of the synthesis of Gly-Gly-MMT compound, 0.56 gm of Gly-MMT was suspended in dry dichloromethane (DCM) (10 mL) and stirred for 15 minutes in a double neck round bottle flask. In another flask, glycine ethylester hydrochloride (0.28 gm, 2.0 mmol) was suspended in DCM (5 mL) and treated with triethylamine (2.2 mmol) and mixed well. The solution of glycine ethylester was added into the suspension of Gly-MMT in three equal steps (3.0 mL each time) and stirred for 20 minutes after each addition. The product was then filtered, washed with DCM (2x10 mL) and air dried to achieve powdered material.

The X-ray diffraction (XRD) intensities of the compounds were recorded with a Philips, X'Pert PRO XRD PW 3040, X-ray diffractometer using monochromatic CuK α ($\lambda=1.542\text{\AA}$) radiation. To study the microstructural parameters, the XRD intensities were corrected for background, geometrical and Lorentz polarization factors^{19,20,26}. The value of g and γ for all the samples were calculated by adopting a single line technique and applying equations (eq.1-4) followed by Mitra and Bhattacharjee¹⁹, De and Bhattacharjee²⁰, Mandal *et al.*²⁷, Bala *et al.*¹⁶

$$g = \frac{1}{\pi d} \cot^{-1} \frac{\pi \Delta}{\beta_d}, \quad (1)$$

$$\text{and } \gamma = \frac{\beta_d}{\sin^2(\pi l . g)} \dots \dots \dots (2)$$

where β_d is the integral width of the defect profile, Δ the measure of peak shift from the centroid of the diffraction profile, and l the order of reflection^{16,27}. The values of apparent crystallite size (P_V) and r.m.s. strain ($\langle e^2 \rangle^{1/2}$) were determined from X-ray diffraction (XRD) profiles using the equations

$$W_{2\theta} = \frac{\alpha \lambda}{2\pi^2 P_V \cos \theta} + \frac{S \lambda^2}{\cos^2 \theta} \quad (3)$$

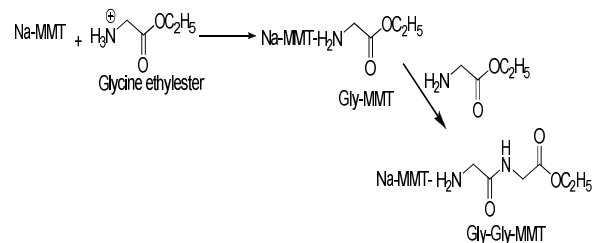
$$\text{and } \frac{1}{P_V} = \frac{1}{P_F} + \frac{\beta_d}{d}, \quad (4)$$

where $S = (\langle e^2 \rangle - \beta_d^2/\pi^2)/d^2$

where $W_{2\theta}$ is the variance of the profile and α is the angular range over which the intensity distribution is appreciable, $\langle e^2 \rangle$ is the mean square strain, λ is the wavelength of the X-ray, θ is Bragg angle, d is the interplanar spacing, and P_V is the apparent crystallite size. Thus if the graphs of $W_{2\theta}$ against α are plotted, a straight-line graph should be obtained and from its slopes and intercepts P_V and $\langle e^2 \rangle$ can be calculated^{16,27}. The values of the true crystallite size (P_F) have been evaluated following Warren and Averbach's method of Fourier analysis²⁸.

III. Results and Discussion

Scheme 1 represents the possible reaction mechanism taking place in the synthesis of Gly-MMT and Gly-Gly-MMT. The formation of dipeptide into the interlayer galleries of montmorillonite has been justified by thermogravimetric analysis (TGA), differential thermal analysis (DTA) and Fourier transform infrared (FTIR) analysis of the samples presented elsewhere²⁹. Figure 1 shows the X-ray diffraction profiles of Na-MMT, Gly-MMT, Gly-Gly-MMT for 001 reflection, which has been used to calculate P_V , P_F , $\langle e^2 \rangle^{1/2}$, g and γ . The values of P_V and $\langle e^2 \rangle^{1/2}$ were calculated from the intercept of the abscissa and the slope of the variance ($W_{2\theta}$) – range (α) plots (Figure2)^{16,27}. The linear relationship in the variance-range plot establishes the correctness of the background corrections. Different microstructural and layer disorder parameters for Na-MMT, Gly-MMT and Gly-Gly-MMT are presented in Table 1.



Scheme 1. Synthesis of Gly-MMT and Gly-Gly-MMT.

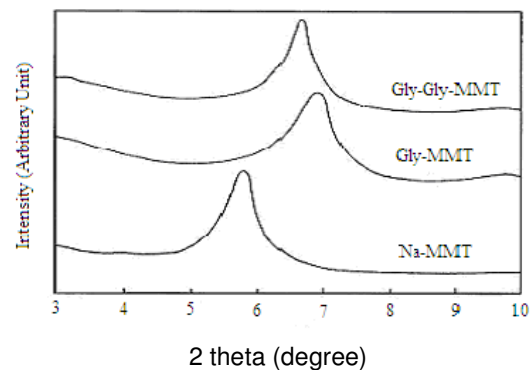


Fig. 1. X-ray diffraction profiles for the 001 reflection of Na-MMT, Gly-MMT and Gly-Gly-MMT

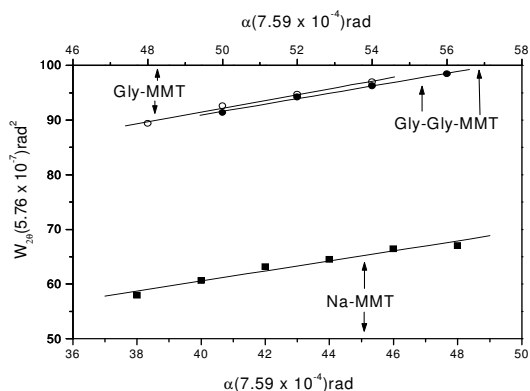


Fig.2. Variance (W_{20}) – range (α) plots for the 001 reflection of Na-MMT, Gly-MMT and Gly-Gly-MMT.

Table. 1. Microstructural and layer disorder parameters of Na-MMT, Gly-MMT and Gly-Gly-MMT

Parameters	Na-MMT	Gly-MMT	Gly-Gly-MMT
Interplaner spacing, d_{001} (Å)	15.12	12.72	13.27
Crystallite size, P_V (Å)	108	83	89
Crystallite size, P_F (Å)	127	102	110
Variation in interlayer spacing, g	0.442	0.447	0.417
Proportion of planes affected, γ	0.081	0.088	0.058
r.m.s. strain, $\langle e^2 \rangle^{1/2} \times 10^2$	4.7	3.5	3.8

spacing found in Gly-Gly-MMT is very close to that of monolayer compounds but the basal spacing found in Gly-MMT compound is nearly 0.6Å less than that of Gly-Gly compound which may be due to the occupation of the Gly in the hexagonal holes present in the tetrahedral sheets or to kinks to the monolayer chains. The similar type of results also observed when montmorillonite is intercalated with methyl ammonium⁹. Interestingly, the increase of basal spacing in Gly-Gly-MMT compared to Gly-MMT justified that further addition of glycine ethylester to Gly-MMT produced dipeptide which increased length of the intercalate and it was large enough not to occupy the hexagonal holes.

The values of the crystallite size obtained in the present investigation are 108Å, 83Å and 89Å for Na-MMT, Gly-MMT and Gly-Gly-MMT respectively (Table 1.). It was observed that crystallite size decreased for Gly-MMT than that for pure Na-MMT. However, the crystallite size of Gly-Gly-MMT was slightly bigger than that of Gly-MMT. The lower value of crystallite size in case of Gly-MMT with respect to Na-MMT can be attributed to the fact that Gly is being intercalated in the interlayer spaces of Na-MMT by substituting hydrated Na^+ ions. The similar type of result is also observed when hydrated Na^+ ions are substituted with methyl ammonium from montmorillonite interlayers⁹. It has been reported that when longer chain alkylammonium is intercalated, the crystallite size increases than that for the

intercalated compound having shorter chain length⁹. In the present investigation, it appears that the little increase of crystallite size in the case of Gly-Gly-MMT with respect to Gly-MMT is due to the formation of dipeptide of Gly which increases chain length of the intercalates. It is further observed that Na-MMT is associated relatively with greater $\langle e^2 \rangle^{1/2}$ values and is possibly related to the layer charge, interlayer cations distribution and the water molecules being present in the interlayer space. The relative decrease in $\langle e^2 \rangle^{1/2}$ in Gly-Gly-MMT and Gly-MMT is more likely to be due to the lesser amount of adsorbed water in the interlayer space¹⁶. It was observed that the variability change in interlayer spacing (g) and fractions of the planes affected by such variations (γ) were lower for Gly-Gly-MMT and little higher for Gly-MMT than that for pure Na-MMT. It seems that the distribution, chain length and orientation of interlayer organic species are responsible for the observed variation in the value of g and γ ^{13,14}. In the present investigation the variation in the value of g can be attributed to the fact that intercalates are oriented in a random way in Gly-MMT with the possibility of occupation in the hexagonal holes present in montmorillonite layers which may happens due to its shorter chain length and possibly be responsible for higher value compared to that for Gly-Gly-MMT where the chain length of the intercalates increased and oriented in monolayer style. The values of g obtained

for Gly-Gly-MMT also indicated that stacking of silicate sheets are more homogeneous here than in pure Na-MMT and Gly-MMT and the value of γ suggests that orientational asymmetry decreases in this compound.

IV. Conclusion

Gly-MMT shows relatively lower value in crystallite in comparison to that of pure Na-MMT but Gly-Gly-MMT shows little increase in crystallite size confirming the formation of dipeptide. More homogeneity in the stacking of silicate layers is achieved in Gly-Gly-MMT compound. The lower values in r.m.s strain of Gly-MMT and Gly-Gly-MMT may be correlated to the organophilic nature of the compound.

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