

Studies on thermal transformation of Na–montmorillonite–glycine intercalation compounds

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Abstract Thermogravimetric (TG), differential thermal analysis (DTA) and thermal degradation kinetics, FTIR and X-ray diffraction (XRD) analysis of synthesized glycine–montmorillonite (Gly–MMT) and montmorillonite bound dipeptide (Gly–Gly–MMT) along with pure Na–MMT samples have been performed. TG analysis at the temperature range 25–250 °C showed a mass loss for pure Na–MMT, Gly–MMT and Gly–Gly–MMT of about 8.0%, 4.0% and 2.0%, respectively. DTA curves show the endothermic reaction at 136, 211 and 678 °C in pure Na–MMT whereas Gly–MMT shows the exothermic reaction at 322 and 404 °C and that of Gly–Gly–MMT at 371 °C. The activation energies of the first order thermal degradation reaction were found to be 1.64 and 9.78 kJ mol⁻¹ for Gly–MMT and Gly–Gly–MMT, respectively. FTIR analyses indicate that the intercalated compounds decomposed at the temperature more than 250 °C in Gly–MMT and at 250 °C in Gly–Gly–MMT.

Keywords Activation energy · DTA · FTIR · Glycine ethylester intercalation · Montmorillonite · TG

Introduction

Montmorillonite belongs to smectite group of clay minerals which has 2:1 type of layer structure. It consists of an octahedrally coordinated M–(O, OH)₆ sheet (O) between two tetrahedrally coordinated M–O₄ sheet (T) where M stands for Al in case of O sheet and Si for that of T sheet. The individual layers of montmorillonite is negatively charged and separated by a van der Waals interlayer gallery containing charge-balancing counterions such as Mg²⁺, Na⁺, Ca²⁺, etc. These interlayer cations balance the negative charges which are generated by the isomorphous substitution of Mg²⁺ and Fe²⁺ for Al³⁺ in the octahedral sheet and Al³⁺ for Si⁴⁺ in tetrahedral sheet [1, 2]. 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 catalysts [3, 4], cosmetics [5], nuclear waste treatment [6], 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 properties [7–15]. It is important to note that in the preparation of montmorillonite based materials and their suitability in different applications are predominantly governed by their physicochemical properties such as strength, plasticity, compressibility, pore structure etc which are highly sensitive on the thermal variation [16–19]. Thus the thermal stability of organo-modified montmorillonite have been considered an important area of investigations to many researchers such as Gao et al. [20] have investigated the trimethyloctadecyl quaternary ammonium intercalated montmorillonite, Bala et al. [21] have investigated alkylammonium intercalated

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montmorillonite, Önal and Sarikaya [22] investigated methyltributylammonium, methyltrioctylammonium and di(hydrogenatedtallow)dimethylammonium intercalation compounds, Yermiyahu et al. [23, 24] have investigated naphthylazonaphtylammonium- and naphthylammonium-montmorillonite compounds. Along with other analysis thermal transformation studies of montmorillonite organically modified with amphiphilic octadecylammonium [25], benzimidazole [26], chlorhexidine acetate [27], tributylammonium [28] have also 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 montmorillonite bound dipeptide and their thermal variation have not been investigated so far. Thus in the present investigation glycine ethylester has been intercalated into Na-montmorillonites interlayers, which is further reacted with a second unit of glycine ethylester and a clay bound Gly-Gly-MMT dipeptide has been obtained. Thermal transformation of the synthesized compounds has been investigated by thermogravimetric analysis and differential thermal analysis (DTA). Thermal degradation kinetics of the samples has also been investigated and activation energy has been calculated using Coats and Redfern method. FTIR analysis of the compounds has been performed in different temperature to confirm the thermal degradation. XRD analysis data have also been presented in support of thermal transformation of the compounds.

Experimental

Na-montmorillonite (SWy-1, cation exchange capacity = 76.4 meq/100 g, Clay Mineral Society, University of Missouri, Columbia) was used in the present work and intercalated using Glycine ethylester hydrochloride ($C_4H_9NO_2 \cdot HCl$). 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 min. The mixture was then poured into Na-MMT dispersion (2.5 g in 100 mL H_2O) and heated at 80 °C with vigorous stirring for 45 min. The precipitate so formed was filtered and washed repeatedly with distilled water to make it free from the chloride ions. 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 order to synthesis of dipeptide, 0.56 g Gly-MMT was suspended in dry dichloromethane (DCM) (10 mL) and stirred for 15 min in a double neck round bottle flask. In another flask, glycine ethylester hydrochloride (0.28 g, 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 min after each addition. After first addition the consumption of glycine ethylester was checked by thin layer chromatography (TLC) eluting with 100% ethylacetate and visualized by I_2 (chamber). The TLC monitoring showed the complete consumption of glycine ethylester of the first addition. Similarly, after second addition the TLC showed the absence of glycine ethylester but after third addition the mixture showed that a little glycine ethylester was left. The mixture was then refluxed at 40 °C for 2 h and checked by TLC, which still showed the presence of unreacted glycine ethylester, thus confirmed the completion of the reaction. The product was then filtered, washed with DCM (2×10 mL) and air dried to give powdered material and has been termed as Gly-Gly-MMT.

Thermogravimetric (TG) and DTA curves of the samples were recorded in a "LabsysTM TG-DTA 16" instrument (France), in the temperature range 25–750 °C at heating rate of 10 °C min^{-1} in argon (Ar) atmosphere. For the purpose of FTIR studies at different temperature, the respective powdered sample was divided into several portions. Each portion was then separately heated in a quartz crucible for 1 h at temperature 250 and 450 °C in an electric muffle furnace. The variation of the temperature in the furnace was within ± 5 °C around the expected temperature. On completion of heating, the samples were cooled and kept in a desiccator to avoid subsequent absorption of moisture. The FTIR measurements of room temperature and pre heated samples were performed by the pressed pellet technique using KBr and the spectra were recorded using a SIMADZU 3800 FTIR instrument having a frequency response varying from 400–4000 cm^{-1} . The XRD intensities of the compounds were recorded with a Philips, X'Pert PRO XRD PW 3040, X-ray diffractometer using monochromatic $CuK\alpha$ ($\lambda = 1.542$ Å) radiation.

Results and discussion

Figure 1 shows the X-ray diffraction profiles of Na-MMT, Gly-MMT, Gly-Gly-MMT for 001 reflection. It is observed that the peak position corresponding to 001 reflection for Na-MMT with hydrated Na^+ is shifted towards higher angle region (2θ) resulting in a decrease in basal spacing, when it is intercalated by glycine ethylester (Gly). This decrease of basal spacing confirms the exchange of hydrated Na^+ by the Gly. This agreed well with ethylenediammonium ($EDAH^{++}$) intercalation compound [29] and alkylammonium intercalation compounds [21]. The basal spacing of montmorillonite intercalation compounds mainly depends on the chain length of the intercalates and their orientation. The intercalates may arranged in different ways like monolayer, bilayer

and paraffin types. The basal spacing for alkylammonium-MMT compounds are ≈ 13.6 Å (for monolayer) and ≈ 17.7 Å (for bilayer), respectively [30–33]. In the present investigation the basal spacing of Gly-MMT and Gly-Gly-MMT are found to be 12.7 and 13.3 Å, respectively, and it was 15.1 Å for Na-MMT. The basal 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 0.6 Å 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. The similar type of results also observed when montmorillonite is intercalated with methyl ammonium [21].

Figure 2 represents TG curves of Na-MMT, Gly-MMT and Gly-Gly-MMT in the temperature range 25–750 °C. The first stage of decomposition is confined to 25–250 °C. The mass loss observed to be nearly 8%, 4.0% and 2% for pure Na-MMT, Gly-MMT and Gly-Gly-MMT, respectively. The initial mass loss for Na-MMT between 25 and 250 °C is mainly governed by the expulsion of the intercalated water molecules, which are almost free or loosely bound and coordinated to the Na⁺ ions and hydrogen bonded to the tetrahedral sheet [34, 35]. Comparatively lower mass loss for Gly-MMT and Gly-Gly-MMT in this stage indicates that the compounds are getting more organophilic in nature [36]. It also appears that in the temperature range 250–450 °C Na-MMT does not show any significant mass loss but Gly-MMT and Gly-Gly-MMT show the mass loss nearly 4%. The mass loss in this stage for Gly-MMT and Gly-Gly-MMT may be assigned to the decomposition of intercalates into the interlayer spaces of montmorillonite. The mass loss observed in the temperature range from 450 °C to onward for Na-MMT can be assigned to the dehydroxylation in the octahedral sheet of montmorillonite [34, 35]. It seems that the mass loss in this

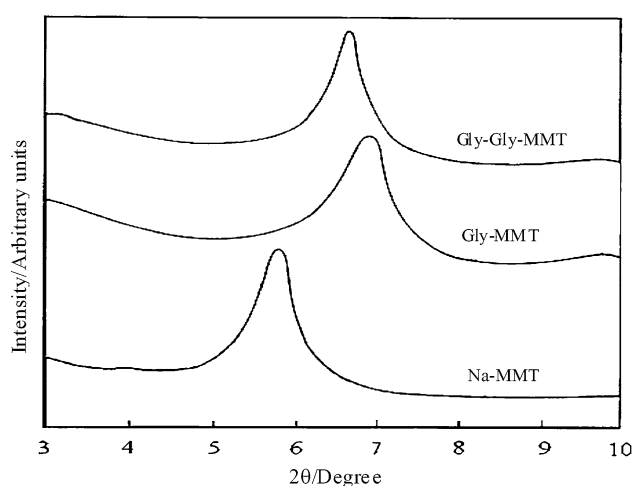


Fig. 1 X-ray diffraction profiles for the 001 reflection of Na-MMT, Gly-MMT and Gly-Gly-MMT

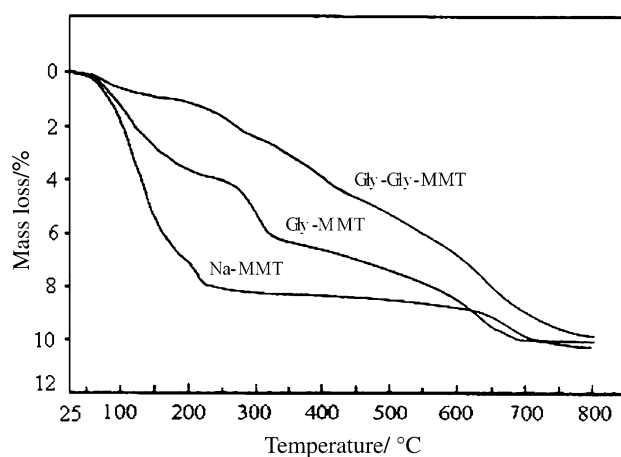


Fig. 2 Thermogravimetric analysis (TG) curves of Na-MMT, Gly-MMT and Gly-Gly-MMT

stage for Gly-MMT and Gly-Gly-MMT is associated both to the dehydroxylation of octahedral sheet and also the decomposition of residual intercalates. It is interesting to note that both in first stage and second stage, the mass loss observed up to a certain temperature follows the relation Na-MMT > Gly-MMT > Gly-Gly-MMT. This type of relation in the first stage may be attributed to the fact that glycine ethylester intercalated into the interlayer spaces with an ion exchange reaction to hydrated Na⁺ ions which expulse the considerable amount of water molecules from the interlayer spaces thus Gly-MMT shows lower mass loss with compare to pure Na-MMT. Again, the mass loss for Gly-Gly-MMT in this stage may be explained as the another glycine ethylester molecules interacts with the previously intercalated molecule which increase the size of intercalates and be responsible for the removal of more water molecules from the interlayer gallery which is supported by the increase of d(001) value in X-ray diffraction data.

Figure 3 shows the DTA curves of pure Na-MMT, Gly-MMT and Gly-Gly-MMT. It is observed that Na-MMT shows two peaks corresponding to endothermic reactions at 136 and 211 °C where their onset point is 83 and 186 °C, respectively. These two peaks may be assigned to expulsion of interlayer free water molecules and hydrogen bonded and co-ordinated water molecules [24, 34, 37]. Interestingly, Gly-MMT and Gly-Gly-MMT do not show any endothermic reactions in this temperature indicating the interlayer free and loosely bonded water molecules and coordinated water molecules have been expelled to a great extent and the composites become organophilic which has been supported by the variation of d(100) values in XRD analysis of Na-MMT, Gly-MMT and Gly-Gly-MMT and thermogravimetric analysis. It is also observed that Gly-MMT shows two consecutive exothermic peaks one at 322 °C (onset at 304 °C) and another at 404 °C (onset at

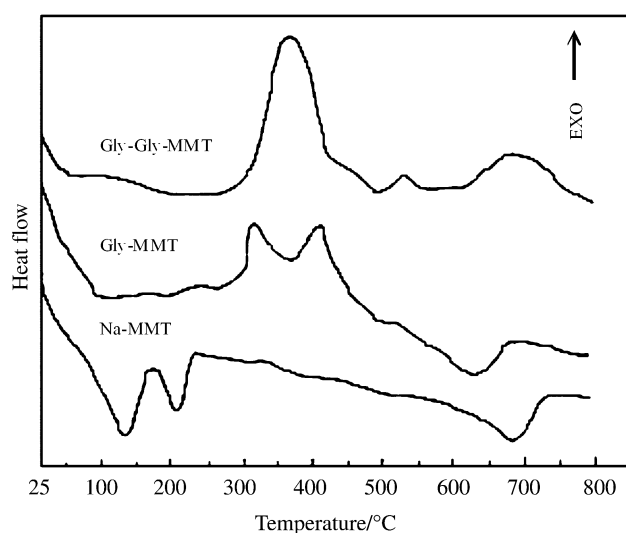


Fig. 3 Differential thermal analysis (DTA) curves of Na-MMT, Gly-MMT and Gly-Gly-MMT

402 °C) whereas Gly-Gly-MMT compound shows one strong exothermic peak at 371 °C (onset at 250 °C). Presence of exothermic peaks in this temperature range may be responsible for the oxidation of hydrogen component of organic compound present in the interlayer galleries of montmorillonite. These observations are in agreement with the reported results for other organomodified-montmorillonite [24, 38, 39]. In the present investigation, the first exothermic peak in Gly-MMT is expected due to the breaking of secondary bond that may form between the carboxyl oxygen of glycine moiety and metal present inside the Na-MMT. The ester hydrolysis released ethanol by the attack of existing water remaining inside Gly-MMT. This ethanol will burn at around 400 °C to produce CO₂ and H₂O which is also an exothermic reaction and shows a second peak at 404 °C in Gly-MMT. The possible decomposition route for this compound has been depicted in Fig. 4. In case of Gly-MMT, the possibility of formation of secondary bond between the carboxyl oxygen of glycine moiety and metal ions present in the montmorillonite sheet may be due to the reason that intercalated glycine occupied into the hexagonal holes present in the tetrahedral sheets get a closer environment with metal ions which facilitate the bond formation. But this type of secondary bond may not be suitable in case of Gly-Gly-MMT due to the longer distances between the intercalated organic species and metal ions present in the montmorillonite sheet which is supported by XRD analysis. Possibly, due to these reasons Gly-MMT shows two exothermic peaks whereas Gly-Gly-MMT shows single peak.

Assuming the degradation of organic species into montmorillonite interlayers follows approximately the first order reaction such as solid (1) → solid (2) + gas, the

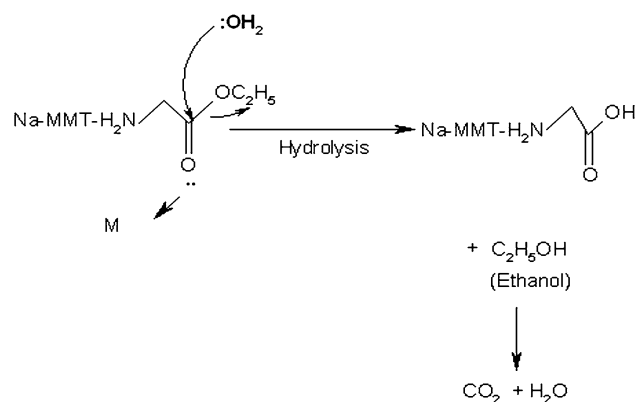


Fig. 4 Possible route of decomposition of glycine ethylester into MMT

activation energies were calculated following the Coats and Redfern equation as follows [22, 40];

$$\ln\left\{\frac{-\ln(1-\alpha)}{T^2}\right\} = -\frac{E}{RT} + \ln\left[\frac{AR}{\beta E}(1-2RT/E)\right]$$

where α is the mass fraction of the degradation calculated from thermogravimetric data, T is the temperature (K), R is the universal gas constant, A is the frequency factor and $\beta = dT/dt$ 10 Ks⁻¹ is the heating rate. The second term in this equation is nearly constant [22]. The Coats-Redfern straight lines for the degradation of the organic species into the montmorillonite interlayers are given in Fig. 5. The activation energies of degradation for Gly-MMT and Gly-Gly-MMT were calculated from the slopes of straight lines and found to be 1.64 and 9.78 kJ mol⁻¹, respectively. The greater activation energy of Gly-Gly-MMT compound possibly due to the longer chain length of intercalates and greater separation of the montmorillonite sheets with compare to Gly-MMT compound. Similar type of results were observed for methyltributylammonium smectite, methyltrioctylammonium smectite and di(hydrogenatedtallow)dimethylammonium smectite [22].

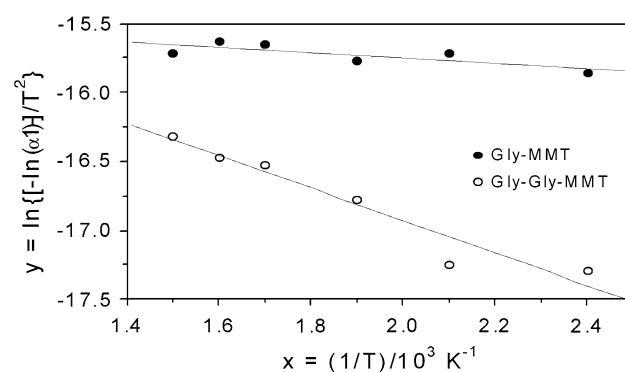


Fig. 5 The Coats and Redfern straight lines for degradation of interlayer organic species in the temperature range 150–400 °C

The FTIR spectra of Na-MMT, Gly-MMT and Gly-Gly-MMT at 25 (room temperature), 250 and 450 °C have been shown in Figs. 6, 7 and 8, respectively. The common feature in IR (at room temperature) for Na-MMT, Gly-MMT and Gly-Gly-MMT is the presence of band at about 1035 cm^{-1} due to Si-O-Si stretching vibration and the bands at about 3618 , 3421 and 1645 cm^{-1} are because of OH (free), OH (hydrogen bond) and OH (bending) vibrations, respectively [41, 42]. It is observed from the present investigation that the intensity of the bands due to OH (free), OH (hydrogen bond) and OH (bending) decreased with respect to the intensity of Si-O-Si band in case of Gly-MMT and Gly-Gly-MMT (Fig. 6), indicating that the water molecules from the interlayer spaces were removed

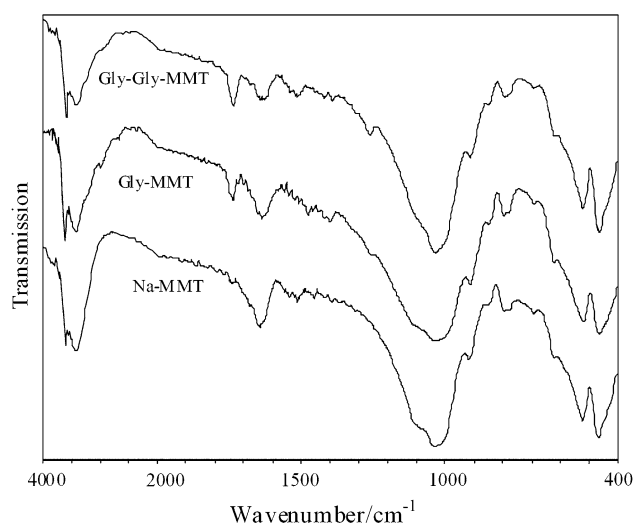


Fig. 6 FTIR spectra of Na-MMT, Gly-MMT and Gly-Gly-MMT at 25 °C (room temperature)

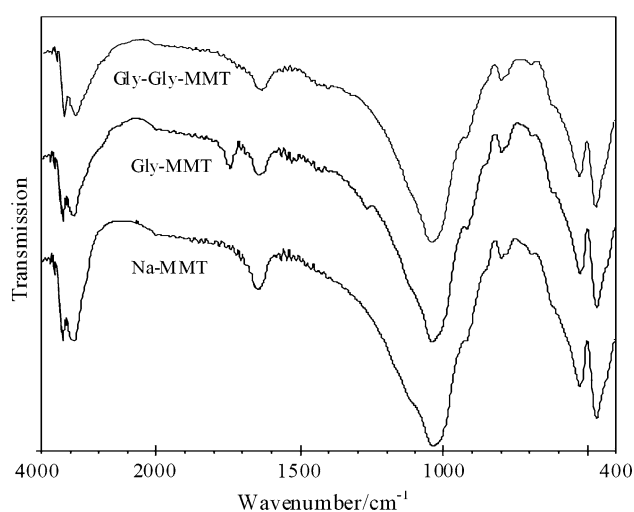


Fig. 7 FTIR spectra of Na-MMT, Gly-MMT and Gly-Gly-MMT at 250 °C

and the samples become organophilic in nature which is supported by our TG analysis. Here, both Gly-MMT and Gly-Gly-MMT show the presence of two new bands at around 3236 and 1739 cm^{-1} which can be assigned to NH_3^+ (protonated- NH_2) and C=O stretching vibrations, respectively [42–44]. The presence of these two bands conform the intercalation of glycine ethylester in the interlayer sheets of Na-MMT. It is interesting to note that the intensity of OH stretching (hydrogen bonded) band (at 3419 cm^{-1}) in Gly-MMT and Gly-Gly-MMT becomes lower with compare to OH (free) band which is just the opposite in pure Na-MMT. These observations infer that hydrated Na^+ ions are replaced through an ion exchange reaction. It is interesting to note in the FTIR spectra of the samples heated at 250 °C (Fig. 7) that Gly-MMT compound showed the bands for OH (free), OH (hydrogen bond), NH_3^+ and C=O stretching vibrations but these bands (NH_3^+ and C=O stretching vibrations) are absent in Gly-Gly-MMT. It appears from IR analysis that Gly-MMT compound does not decomposed up to 250 °C but Gly-Gly-MMT compound decomposes at this temperature. With combination of DTA analysis it can be infer that in case of decomposition of interlayer species onset temperature plays an important role. It can be mention that Gly-Gly-MMT showed exothermic peak whose onset temperature was about 250 °C. It seems that the decomposition started at this temperature and by getting sufficient time (1 h) the decomposition completes in Gly-Gly-MMT but in case of Gly-MMT compound the onset temperature is about 304 °C which possibly be responsible not to decompose at 250 °C which justify the presence of bands due to organic species in FTIR of this compound. The higher temperature required for the decomposition of

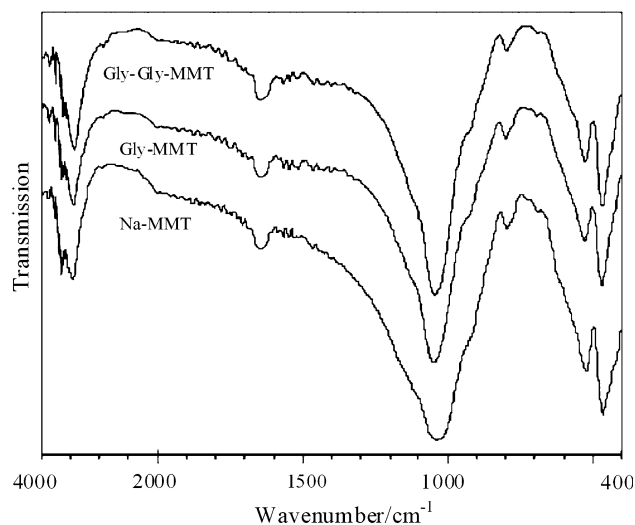


Fig. 8 FTIR spectra of Na-MMT, Gly-MMT and Gly-Gly-MMT at 450 °C

organic species in Gly–MMT may be due to the hindrance in the clay sheets and force between them [20] which are supposed to be greater in Gly–MMT with compare to Gly–Gly–MMT that was supported by DTA and XRD analysis. It is observed from Fig. 8 that all the bands responsible for organic species are absent both in Gly–MMT and Gly–Gly–MMT and the spectra are almost similar with that of pure Na–MMT. This indicates that organic compounds are decomposed after sample is heated to 450 °C.

Conclusions

Glycine ethylester intercalated into montmorillonite interlayers decomposed at two steps showing exothermic reaction at 322 and 404 °C. When dipeptide is formed into the interlayer galleries of montmorillonite the intercalates decomposed in single step with exothermic reaction at 371 °C. FTIR analyses indicate that the onset temperature of the exothermic reaction together with heating time plays an important role in decomposition of organic species but this requires further investigations. In the present investigation range, it is observed that dipeptide decomposed at 250 °C with 1 h heating but simply intercalated glycine ethylester need more temperature from that of dipeptide to decompose. The activation energy of the decomposition of the Gly–MMT and Gly–Gly–MMT were observed to be 1.64 and 9.78 kJ mol⁻¹, respectively.

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