

Thermal evolution of PEG-based and BRIJ-based hybrid organo-inorganic materials. FT-IR studies

Elisabetta Finocchio^{a,*}, Cinzia Cristiani^b, Giovanni Dotelli^b,
Paola Gallo Stampino^b, Luca Zampori^b

^a Dipartimento di Ingegneria Civile, Chimica e Ambientale, P.le J.F. Kennedy 1, Università di Genova, 16129 Genova, Italy

^b Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

Received 15 July 2013

Received in revised form

14 December 2013

Accepted 20 December 2013

Available online 7 January 2014

1. Introduction

Polymer-modified clays, a class of hybrid organic-inorganic materials, have recently attracted industrial and academic interest due to their wide range of applications in the fields of environmental remediation, catalysis, nanofillers, biomedical application such as controlled drug release and biosensors [1–7]. Recently, the intercalation of water-soluble PEG molecules and polyethylene oxide BRIJ within the montmorillonite clay interlayers has been successfully obtained by Zampori et al. from water solution intercalation [8]. These materials and their ability to arrange organic molecules within the layers have been investigated by several techniques. In particular, XRD data and TG DTA analyses are used to demonstrate the occurrence of intercalation process, while COD measurements have been proven to be a reliable method to quantify the amount of intercalated polymer [8,9]. Issues such as the polymer conformation in the interlayer space, the interaction of the

–CH₂CH₂O– units with the matrix cations and the interlayer water molecules, the presence of polymer chains only partially hosted within the matrix layers, or interacting also with external clay surface, have been investigated by spectroscopic studies [10]. IR spectroscopy is surely a powerful tool for the understanding of the interactions between the organic moieties and the inorganic matrix at molecular level [10–12] but it can also be applied to specific studies on the thermal stability of organoclays materials, whose thermal decomposition involved different and complex mechanisms, some of them still unexploited [13–16].

In particular, Yariv and co-workers suggested the application of FT-IR spectroscopy coupled with XRD in the analysis of organic complexes (tetraalkylammonium salts) with clays materials [17–19] to better investigate the nature of decomposition of organic matter inside the interlayer of the clay mineral, from a microstructural point of view and for a better understanding of polymer thermal degradation.

In a recent paper we described the thermal characterization of PEG-modified montmorillonite using both in situ HT-XRD and FT-IR spectroscopy and evidencing the formation of a high-temperature phase as well as the complex pathway of the organic

* Corresponding author. Tel.: +39 010 3536040; fax: +39 010 3536028.

E-mail address: Elisabetta.Finocchio@unige.it (E. Finocchio).

Table 1
Preparation conditions, polymer intercalation and basal spacing of the obtained hybrid materials.

Sample	C ₀ (mM)	T (°C)	Time (min.)	Polym./clay (g/g)	M.U. (mol)	d [001] (Å)
P15-45	45	60	90	0.77	17.5	15.8
P15-90	90			1.48	34	17.0
P15-180	180			3.00	68	18.0
P40-90	90	60	90	4.24	96.5	18.0
P40-45	45	60	90	2.8	45	17.7
BR-90	90	60	90	1.17	27	17.9
BR-45	45	60	90	0.8	14	17.2
STX as received						15.1

C₀, initial concentration of polymers; M.U., intercalated monomeric units; P15, PEG 1500; P40, PEG 4000; BR, BRIJ 78.

moieties decomposition [20]. In the present work we propose a systematic investigation of the thermal evolution of PEG- and BRJI-montmorillonite composite materials, analyzing by FT-IR spectroscopy in the 70–450 °C temperature range the condensed phase species formed at increasing temperatures as well as the gaseous species. The behaviour of several IR bands in the mid-IR region towards heating has been followed and proposed as diagnostic of the matrix-polymer interaction.

2. Experimental

A standard commercial Ca-montmorillonite STx-1b (Clay Mineral Society) was used, characterized by a basal spacing of 15.1 Å.

The intercalation polymers were obtained according to the procedure reported elsewhere [8,9]. In a typical experiment a weighted amount of STx was contacted, under vigorous stirring, with a known volume of polymer solution for the fixed time. After the contacting reaction the solid was separated from the liquid by filtration. The contacting experiments were carried out at 60 °C, for 90 min in a jacketed reactor, and a cooling bubble condenser was used to prevent evaporation.

The quantification of the amount of polymer intercalated was performed via Chemical Oxygen Demand (COD) analyses (Spectrodirect Lovibond instrument) according to a standard procedure [ASTM D1252-06]. The intercalated amount was the difference between the initial and the residual polymer upon contacting reaction [8,9]. Samples will be identified in the following with a label reporting the polymer identification and the initial concentration (being temperature and reaction time constant) e.g.: P15-45/90/180 will identify the sample prepared using PEG 1500, with an initial concentration of 45 mM, at 60 °C and a reaction time of 90 min.

X-ray diffraction (XRD) measurements were carried out with a Bruker D8 Advance diffractometer (graphite monochromator, using Cu-K α radiation, step scan of 0.02°, 1 s per step). The XRD line profile analysis was performed with TOPAS P software (Bruker AXS, Karlsruhe, Germany) and the refined profiles were used for the determination of the reflection positions.

Thermal analyses measurements were performed in air with a DTA-TG SEIKO 6300 thermal analyser for all the samples, maximum heating rate of 10 °C/min in the temperature range 25–1000 °C.

FT-IR spectra of montmorillonite matrix, and the related intercalated materials have been recorded in the 4000–400 cm⁻¹ range by a Nicolet Nexus instrument flushed with dry air (100 scans, DTGS detector, OMNICTM software). Self-supporting disks of pure pressed powders (about 30 mg weight, 1 cm²) are placed in the sample holder in the cell connected to a gas manipulation apparatus described in the Supplementary data (Fig. S1). KBr windows in the cell allow recording spectra of gas phase species and organoclay samples. For thermal evolution analysis, pure powder disks of montmorillonite matrix and intercalated materials have been studied in so called “static conditions”. For instance: the IR cell is

filled with air, valves to vacuum pumps are closed and gas from organoclays reactions are collected in the IR cell at increasing temperatures. This procedure applies for all the studied samples. Condensed phase spectra are recorded by lowering the sample holder from the oven position to the IR cell kept at room temperature immediately after the heating step (i.e. sample in the oven above the cell at the reported temperatures during 5 min). Correspondingly, at each temperature the gas phase spectra are recorded while the sample is still in the oven. Analyses in the very same conditions have been also performed for the PEG 1500, PEG 4000, BRIJ powders diluted in KBr disks (1% w/w). All the spectra have been recorded in transmittance mode. The background spectrum (i.e. the empty cell) has been recorded at the beginning of the experiment, at room temperature, and all the spectra recorded following heating are referred to the same background. Thus, only a significant increase in the CO₂ signal has been confidently taken as an indication of polymer degradation.

3. Results

3.1. Thermal analysis

In Table 1 evaluation of the intercalated polymer for the different operating conditions and polymer nature are reported. The normalization of data to monomeric units, allows for the comparison among the polymers, independently from their molecular weight.

The presence of a certain amount of polymer intercalated in the clay is confirmed by the increasing of the basal spacing with respect to the pristine clay. Furthermore, intercalated polymer increases on increasing polymer concentration in solution (C₀). The intercalation process is observed also with polymers of different nature: once reaction conditions are set the amount of intercalation is related to polymer molecular weight (compare P15, P40 and BR monomeric units). Further details on preparation and characterization of such materials are fully discussed elsewhere [8–10,20].

Considering data here reported, it can be stated that the reaction conditions are effective to intercalate nonionic polymers in the clay, and the interlayer dimension can be modulated by polymer concentration or molecular weight. The basal expansion is strongly affected by the nature of the polymer in view of different conformations of the polymer chain or different bonding with the clay interlayer. This effect is appreciable even in the case of polymers of very close composition such as the case of PEG and BRIJ where the difference is simply due to the presence or the absence of an additional aliphatic chain.

In Fig. 1(a) and (b) DTG analysis (in air) of the different PEG-based samples is reported. Also in the case of DTG analysis the presence of intercalated polymer chains is manifest. However, as pointed out by the complexity of the thermograms, the degradation mechanisms are possibly changed: it is clear that the polymer-containing samples cannot be a simple mixture of raw clay and polymer. In fact, the decomposition of the organo-clay samples is

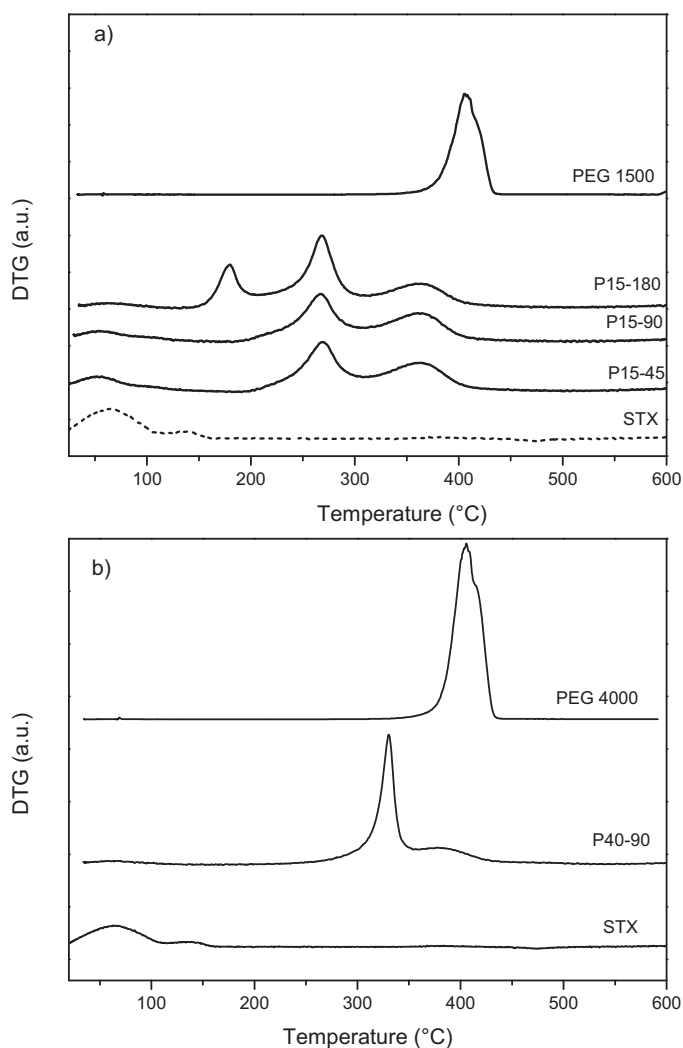


Fig. 1. DTG analysis of organoclay samples.

a complex multi-steps phenomenon largely different from those of the single raw materials. Thus, the presence of some polymer–clay interaction stronger than a simple polymer adsorption on the clay surface is active. Moreover, due to the unusually lower decomposition temperature observed for the hybrid materials, we cannot rule out some catalytic effect of the inorganic matrix itself and of its transition metal impurities on the polymer degradation. Then the behaviour of PEG and BRIJ hybrid materials towards heating has been studied “in situ”, in an IR cell connected to the gas manipulation apparatus described in Section 2. For comparison, pure montmorillonite matrix and pure PEG materials have been submitted to the same treatments and their thermal evolution is discussed below.

3.2. FT-IR spectroscopic studies: thermal evolution of reference materials

Fig. 2 shows the spectra recorded at increasing temperatures in the range 60–500 °C for pure montmorillonite powder. Bands due to hydration water, i.e. broad ν OH band in the 3700–3000 cm^{-1} range and strong deformation band at about 1645 cm^{-1} , strongly decrease in intensity, moreover, the latter band shifts downwards to 1618 cm^{-1} at 500 °C. This effect can be due to the loosening of the H-bonds between water molecules following outgassing, as reported by Majedova et al. for similar materials [21]. Finally,

following outgassing at 500 °C, three components can be detected in the OH stretching region at 3740, 3630, and 3534 cm^{-1} . The former band can confidently be assigned to silanol groups (Si–OH) exposed at the external layer surface in defect sites [22], while the broad band centred near 3630 cm^{-1} is due to Al_2OH groups within octahedral sheets of montmorillonite layers [23–26]. The low frequency band at 3534 cm^{-1} can be assigned to structural OHs of oxide and hydroxide impurities, in agreement with the composition reported for these materials [10]. The triplet of broad bands in the range 2000–1800 cm^{-1} arises from combinations and overtones of the lattice Si–O vibrations below 1300 cm^{-1} and is typical of silicate and silica-based materials. The FT-IR spectra obtained following heating of PEG 1500 and PEG 4000 polymers diluted in KBr, regardless the molecular weight, show common spectroscopic features assigned to the CH stretching and bending vibrational modes, as illustrated in Fig. 3 for PEG 1500. Following a brief heating at 60 °C, PEG spectrum shows a strong and broad band centred at 2889 cm^{-1} (ν CH₂ band), with shoulders at 2946 and 2806 cm^{-1} . Correspondingly, CH deformation modes are detected in the low frequency region of the spectra: a sharp band at 1467 cm^{-1} (asymmetric CH₂ deformation mode), a doublet at 1360 and 1343 cm^{-1} (CH₂ wagging vibrational modes), two bands at 1280 and 1242 cm^{-1} (CH₂ twisting modes). CH₂ rocking modes are also detected at 963 and 842 cm^{-1} . The triplet at 1148, 1116, 1060 cm^{-1} in the spectrum of the pure polymer is assigned to CH₂ symmetric deformation, C–O–C and C–OH stretching modes, respectively [27–29] (Fig. 3). BRIJ polymer contains a C18 saturated alkyl chain bound to –CH₂CH₂O– fragments (PEG-like), thus we expect modified spectroscopic features in the CH stretching/deformation regions. The reference spectrum of BRIJ recorded at room temperature has been discussed in Ref. [10] and not reported here. The main differences with respect to PEG spectra are detected in the high frequency region, where two sharp bands centred at 2916 and 2850 cm^{-1} are assigned to CH stretching mode of the long aliphatic CH₂ tail [10].

The thermal decomposition of PEG, investigated by FT-IR at increasing temperature shows the formation of decomposition products in the condensed phase characterized by a complex carbonyl stretching band at 1728 cm^{-1} , with a shoulder at 1754 cm^{-1} (Fig. 2). These bands appear at 175 °C and reach their maximum intensity between 200 °C and 250 °C, then decrease while the band due to CO₂ increases in the gas phase (complex band about 2350 cm^{-1} , Fig. S2 in Supplementary data).

In the range 250–300 °C, spectra of the condensed phase and spectra of the gas phase species become noticeably complex, showing several components in the 3000–2800 cm^{-1} and 1750–1100 cm^{-1} region (see Fig. 2 and Fig. S2). This effect indicates the formation of a complex mixture of decomposition products, likely low-molecular-weight fractions formed as a result of chain scission processes at the weak carbon–oxygen bonds in the PEG backbone. A more accurate assignation of the bands in this temperature range is not straightforward, however the detection of peaks in the spectral region typical of carbonyl stretching vibrational modes is in agreement with results from PEG decomposition reported by several authors and analyzed with other techniques [30,31,14]. These species have been reported to be mainly esters (acetates and formates), but also formaldehyde, methanol, acetaldehyde and ethers are formed for pyrolysis in the low temperature range, whereas higher-mass species are formed selectively only in the presence of oxygen.

Above 250 °C, CO₂ (complex band at about 2350 cm^{-1} , Fig. S2) and CO (band at 2145 cm^{-1} , Fig. S2) are the main products detected in the gas phase, due to the oxidative decomposition of organic species.

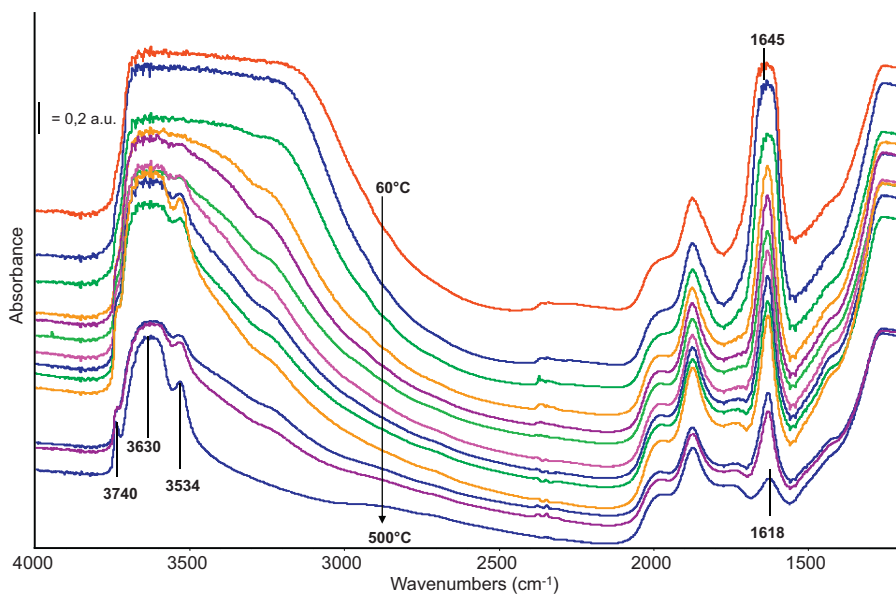


Fig. 2. FT-IR spectra of pure montmorillonite powder after heating from 60 °C to 500 °C.

In the very same conditions, the thermal decomposition of BRIJ polymer produces almost the same products (spectra not reported), pointing out the higher reactivity of the ethoxy fraction in the molecule, at least in the low temperature range. The PEG-like moiety of the polymer appears to be the main source of partial oxidation and cracking products.

3.3. FT-IR spectroscopic studies: thermal evolution of intercalated samples

In the following set of experiments, the organoclay samples have been submitted to the very same thermal treatment in situ, heating from 80 °C to 500 °C, in static conditions, using the apparatus reported in Supporting data (Fig. S1). FTIR spectra of the pure powder surfaces as well as spectra of gas phase species have been recorded at increasing temperatures (Figs. 4–9). For all the samples several common spectroscopic features can be detected

following a mild heating treatment in order to eliminate weakly (molecularly) adsorbed water. These features, discussed in the previous paragraph for pure polymers and STx matrix spectra, undergo changes in shape and position after intercalation, as summarized below.

In the spectra of sample P15–45, above the cut-off of the clay matrix, bands due to CH stretching and deformation modes of the PEG chain can be detected: two broad and quite complex bands centred at 2924 and 2881 cm^{-1} are due to CH stretching modes, whereas bands at 1460 (complex) and 1350 cm^{-1} are due to methylene deformation modes (Fig. 4). These bands correspond to the CH deformation band at 1467 cm^{-1} and to the doublet at 1360 and 1343 cm^{-1} detected in the pure PEG spectra (Fig. 2) and strongly affected by the intercalation process. On the basis of literature data, these changes in the IR spectra can be explained considering that the polymer chains extended in the interlayers of the clay in a conformation which is an intermediate form of

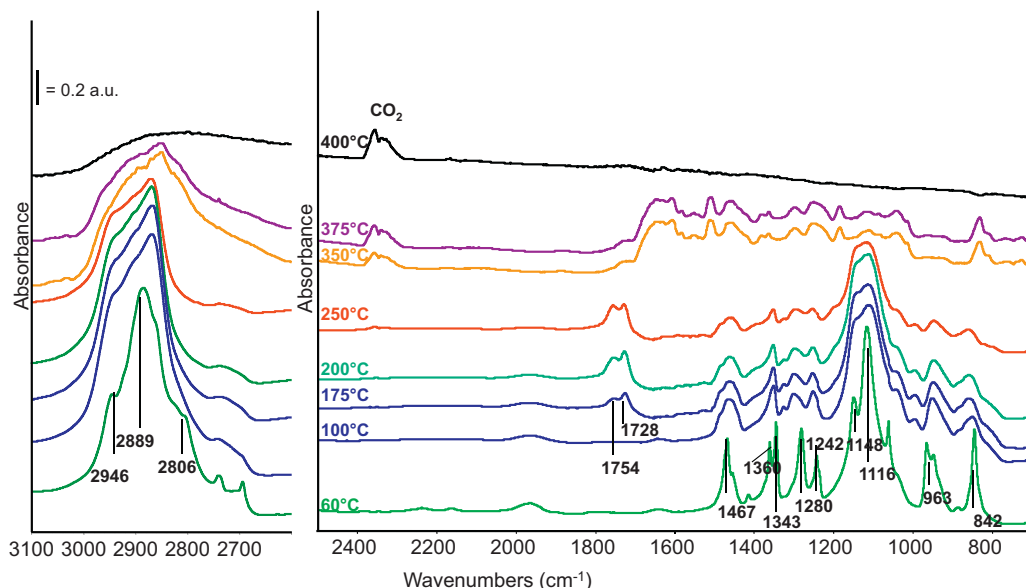


Fig. 3. FT-IR spectra of decomposition species arising from PEG 1500 in KBr heated up to 400 °C.

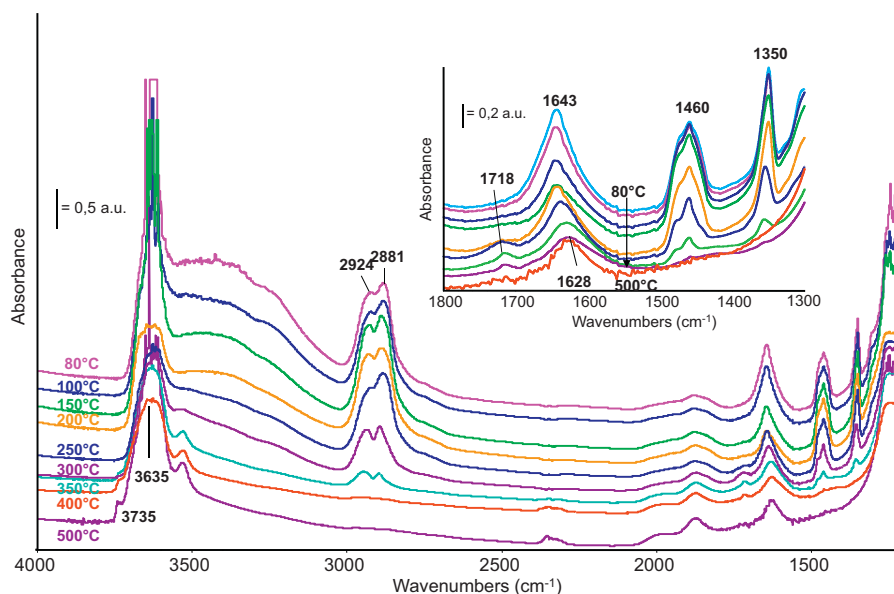


Fig. 4. FT-IR spectra of species arising from decomposition of P15-45 sample at increasing temperature. Inset: enlargement of the low frequency region.

helical and planar conformation, similar to the amorphous polymer state [10,27,28,32]. The band relative to molecular water is centred at 1643 cm^{-1} , thus at slightly lower frequency in comparison to the pure STx spectrum (Fig. 2). Moreover, this band is reduced in intensity, confirming that complexation affects water intercalated molecules, as also suggested also by the changes observed in the OH stretching region [10,20,33].

At increasing temperature bands due to CH vibrational modes are strongly reduced in intensity, as well as bands due to water. In parallel, between 200 and 250 °C, a new weak component appears at 1718 cm^{-1} , assignable to C=O stretching mode of carbonyl species due to oxidative degradation processes. The frequency of the band is consistent with the formation of aldehyde species in

the condensed phase [34]. Partial oxidation products and cracking products, from a PEG chain cleavage, start to form, as confirmed by the analysis of the gas phase spectra between 250 °C and 350 °C (Fig. 5). In the high frequency spectral region, bands at 2968 and 2862 cm^{-1} , together with a strong band at 1130 cm^{-1} , are due to ethyl ether; the band at 885 cm^{-1} is due to dioxane (showing also a component at 1132 cm^{-1} , superimposed to the ether absorption) likely formed from condensation of two glycol units. The band at 1747 cm^{-1} is assigned to CO stretching of carboxylic molecules, likely acetaldehyde in the gaseous state. Several sharp peaks in the $1650\text{--}1400\text{ cm}^{-1}$ region, overlapped with the water deformation rovibrational structure, are due to aromatic species, whose corresponding CH stretching mode can be detected as very weak

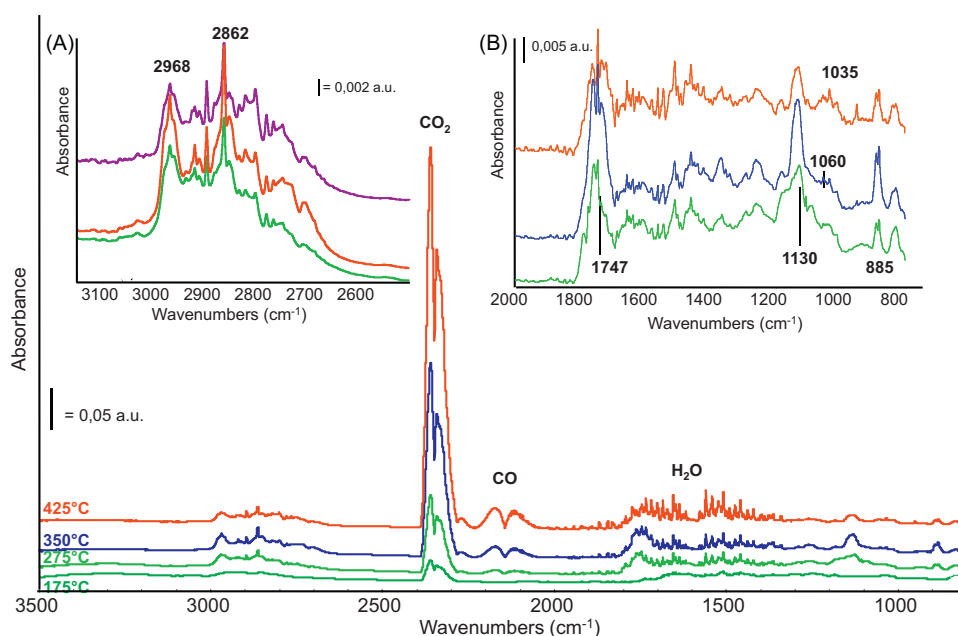


Fig. 5. FT-IR spectra of gas phase species arising from heating of the P15-45 sample. Inset A: enlargement of the CH stretching region; inset B: enlargement of the low frequency region.

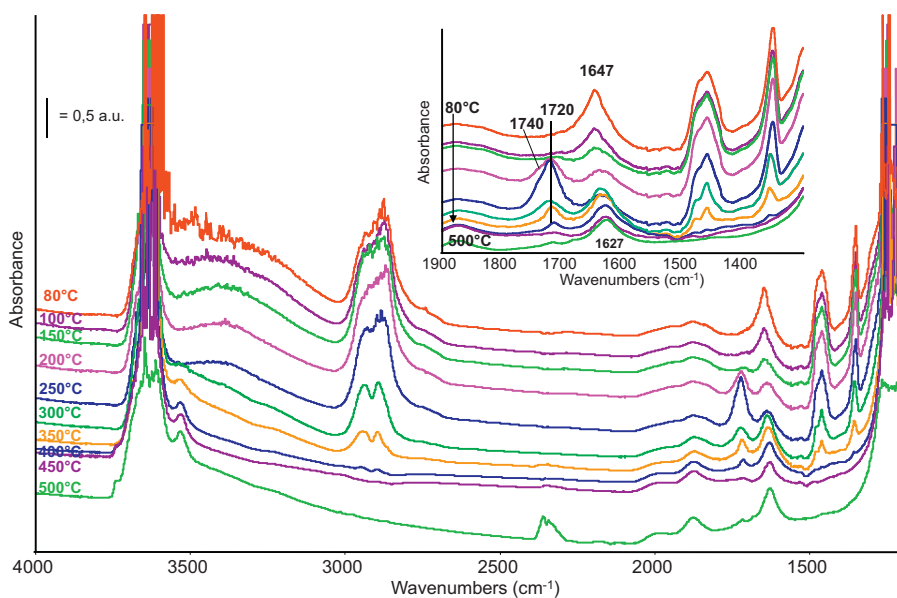


Fig. 6. FT-IR spectra of species arising from decomposition of P15–180 sample at increasing temperature. Inset: enlargement of the low frequency region.

band above 3000 cm^{-1} . The formation of aromatic compounds from organoclays thermal degradation has also been reported following thermal decomposition of alkylammonium intercalated cloisite [35].

The presence of elimination products (alkenes) is also envisaged from few sharp and weak bands below 1000 cm^{-1} (i.e. band at 949 cm^{-1} , $=\text{CH}_2$ deformation modes) and from a weak absorption above 3000 cm^{-1} . Alcohols such as methanol (C–O stretching at 1035 cm^{-1}) and ethanol (C–O stretching at 1060 cm^{-1}) can also be detected [34].

Between 300 and 350°C the carbonyl band at 1718 cm^{-1} in Fig. 4 reaches its maximum intensity, then disappears above 400°C , while CO_2 is clearly detected in the gas phase (Fig. 5) as an evidence of total oxidation of the organic polymer. The band due to water bending mode shift downwards to 1628 cm^{-1} following heating at 400 and 500°C . At 400°C , bands due to CH stretching and deformation modes of some residual organic species are still detectable at

the surface (Fig. 4), although very weak, and OH groups are partially restored (see bands at 3735 and 3635 cm^{-1}).

Increasing PEG loading (sample P15–90) leads to an increased intensity of the organic moieties main bands but the thermal behaviour is the same described above (spectra not reported), for instance: decreasing of water content in the sample, formation of carbonyl products and cleavage and oxidation of the PEG fraction to CO_x at the highest temperatures. As expected, bands due to gaseous CO_2 are stronger at the highest temperature than in the P15–45 spectra, due to the highest organic content in the starting material (spectra not reported). Finally, the spectra recorded for the thermal evolution of P15–180 sample (Fig. 6) show the carbonyl band already at 150°C , reaching its maximum at 200°C (Fig. 6, inset), then this band decreases in intensity but is still detectable at 450°C . It is worth noticing that this band is complex, showing a main maximum at 1720 cm^{-1} and a shoulder at 1740 cm^{-1} . In the high frequency region of the spectrum, very weak

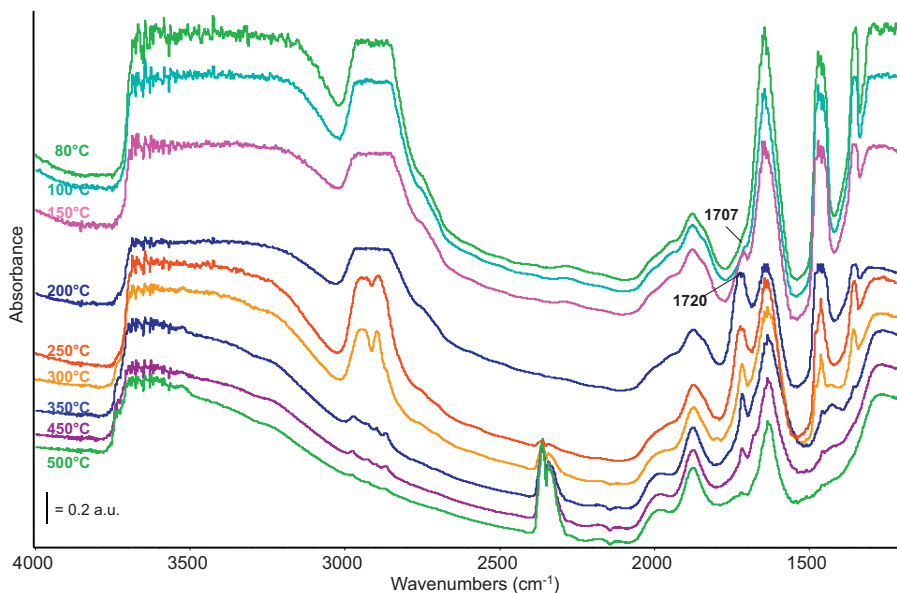


Fig. 7. FT-IR spectra of species arising from decomposition of P40–45 sample at increasing temperature.

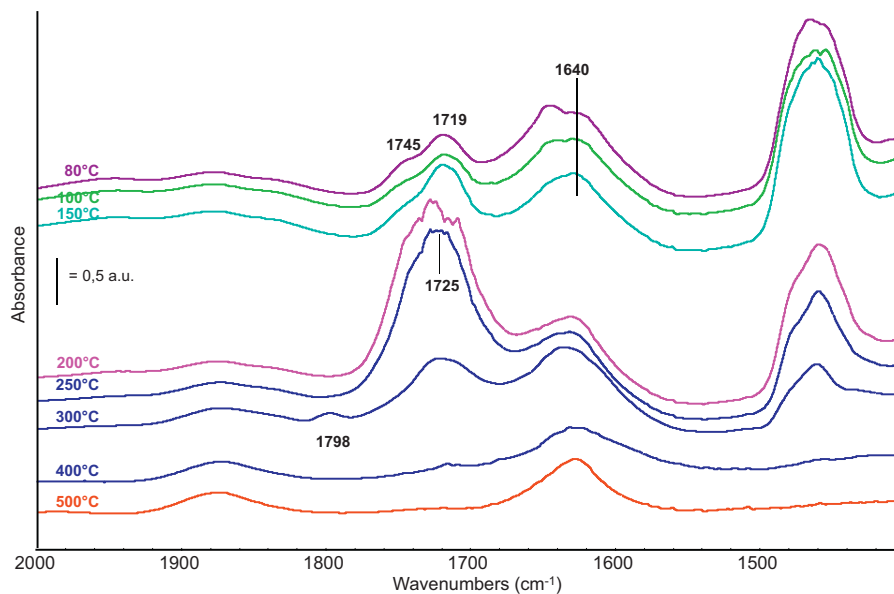


Fig. 8. FT-IR spectra of species arising from decomposition of P40-90 sample at increasing temperature. Low frequency region.

CH stretching bands are detected, due to residual organic species are detected, which can be identified as carbon-like species somehow preserved from total oxidation by the clay matrix up to 450 °C [17-19,36].

Thus an increased PEG loading leads to a low temperature step in the degradation, possibly due to a fraction of the polymer chains which are not intercalated within the clay matrix, explaining the first TG peak at 150 °C for the P15-180 sample. On the other side, comparing the spectra of thermal evolution of STx sample with thermal evolution of intercalated materials at increasing PEG content, it seems that, although reduced in intensity, the band due to hydration water is more resisting heating in the P15-180 composite materials spectra: this effect can be taken as an indication that part of interlayer water molecules are interacting with PEG chains oxygen atoms, through H-bonds.

The effect of increased PEG molecular weight on the thermal degradation of these materials has been studied in the same experimental conditions for samples P40-45 and P40-90. Spectra of the sample P40-45 are reported in Fig. 7 and can be discussed following the general indications reported above. The carbonyl band (1707 cm^{-1}) is already detected at 150 °C as a shoulder of the main, strong, water deformation band. By further increasing temperature at 250 °C, this band becomes stronger and complex, showing another maximum at 1720 cm^{-1} , then decreases in intensity but is still detectable up to 450 °C. Correspondingly, in the high frequency region, several weak absorptions can be detected below 3000 cm^{-1} , assigned to CH stretching modes of organic residual species. A broad band in the range 3800-3200 cm^{-1} is due to H-bound OHs, strongly perturbed by PEG intercalation, and peaks due to isolated OH groups cannot be restored even following PEG degradation. Interestingly, even at the highest temperatures reached in

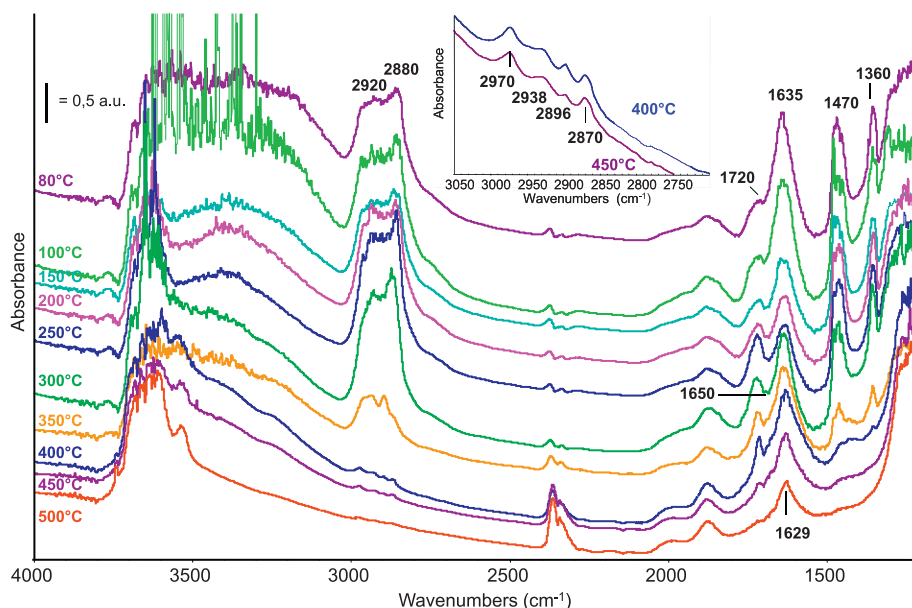


Fig. 9. FT-IR spectra of species arising from decomposition of BR-90 sample at increasing temperature. Inset: enlargement of the CH stretching region.

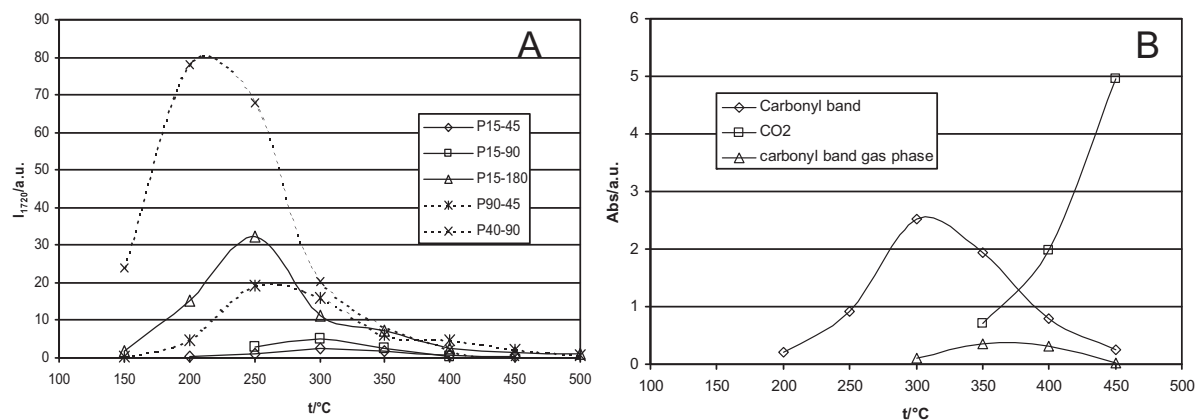


Fig. 10. (A) Intensity of the carbonyl 1720 cm^{-1} band at increasing temperature (a.u.), (B) evolution of carbonyl species and CO_2 for P15-45 sample.

this experiment, several weak bands in the region $3000\text{--}2800\text{ cm}^{-1}$ are clearly detectable, due to CH stretching vibrational modes of residual organic material stable up to $450\text{ }^\circ\text{C}$. This can actually explain the persistent perturbation of OHs in the matrix.

In the gas phase spectra, similar to those reported in Fig. 5, bands due to volatile organic species are also detected, reaching a maximum overall intensity at $350\text{ }^\circ\text{C}$ (Fig. S3 in Supporting data). These bands can be assigned mainly to oxygenate species such as ethers and cyclic ethers, i.e. dioxane, as reported for the P15 samples. Also carbonyl species can be detected in the gas phase (PQR band around 1750 cm^{-1}). The formation of such species in this series of samples is a further confirmation of PEG chain fragmentation. At lower temperatures unsaturated molecules (alkenes) can be detected in the gas phase, due to elimination processes. CO can be detected, as well as CO_2 , starting from $300\text{ }^\circ\text{C}$ and increasing at increasing temperatures.

In the spectra of thermal evolution of the sample P40-90 the carbonyl band is strong and complex (Fig. 8). At least two components can be detected at 1719 and 1745 cm^{-1} , as we reported for the thermal evolution of pure PEG polymer. Correspondingly, also the water deformation band at about 1640 cm^{-1} shows a shoulder at higher frequencies. Therefore these observations can be interpreted as an indication that a fraction of the polymer is only weakly interacting with the matrix surface, following an oxidation path more similar to the pure PEG oxidation.

Previous studies using P40-90 powder diluted in KBr, submitted to the same thermal treatment, pointed out that after heating above $250\text{ }^\circ\text{C}$ skeletal spectra were characterized by a slight broadening of the bands due to Si-O and Al-O vibrational modes, indicating a loss in the crystalline order consistent with some modifications in the clay matrix [20].

Fig. 9 shows spectra of surface species arising from the thermal evolution of sample BR-90, whose features will be discussed in the following paragraphs, whereas the spectra of the BR-45 sample are reported in Supplementary information (Fig. S4) and not further discussed, showing features completely consistent with those of sample BR-90. In the high frequency spectral region, BR-90 spectra (Fig. 9), show strong and ill defined bands with maxima centred roughly at 2920 cm^{-1} and 2880 cm^{-1} , due to CH stretching modes of CH_2 groups of the long alkyl chain. These bands are only slightly affected by intercalation in comparison with reference BRJI spectra [10]. Also the complex and very strong band at about 1470 cm^{-1} , due to CH_2 deformation mode, is completely consistent with the frequency reported in the pure BRJI spectrum. Moreover, in the spectrum of the organoclay we noticed the same merging of the two deformation bands at 1360 and 1345 cm^{-1} resulting in a single broad band centred below 1360 cm^{-1} , also reported for PEG-based materials as a further evidence of the increased disordered

conformation assumed by the organic chains within the montmorillonite structure.

Water deformation vibrational mode appears centred at about 1635 cm^{-1} after mild heating at $80\text{ }^\circ\text{C}$. The carbonyl band at 1720 cm^{-1} appears already at the same temperature and quickly becomes the main band of the spectrum up to $250\text{ }^\circ\text{C}$. Further heating leads to a decrease in the intensity of this band which becomes sharper. At the same time few weak absorptions appear in the range $1450\text{--}1300\text{ cm}^{-1}$, due to CH deformation modes (Fig. 9). As in the case of the PEG based materials, there is a clear evidence of partial oxidation products, and fragmentation of the polymer chains. Moreover, at $350\text{ }^\circ\text{C}$ a broad shoulder appears between $1680\text{--}1650\text{ cm}^{-1}$, whose frequency is consistent with the presence of unsaturated compounds, likely alkenes and this effect suggests the elimination reaction to occur, possibly from the long alkyl chain. This is the only difference detected by FTIR spectra in comparison with PEG based materials, which implies that the thermal degradation follows the same main path we observed in the case of P15 and P40 samples (Figs. 4-8). Thus, there is no clear evidence of the degradation path for the alkyl tail, other than oxidation to CO and CO_2 . Possibly the alkyl chain undergoes oxidation only at high temperatures, leading mainly to CO_x formation.

From 350 to $500\text{ }^\circ\text{C}$, the careful analysis of the spectra reveals several weak absorptions at 2970 , 2938 , 2896 and 2870 cm^{-1} , assigned to CH stretching vibrations of $-\text{CH}_2-$ and $-\text{CH}_3$ groups (Fig. 9, inset). All these components become weaker but even more defined at $400\text{ }^\circ\text{C}$ and do not disappear completely after heating at $500\text{ }^\circ\text{C}$. Intercalated organic species, characterized by CH bonds, are thus resistant decomposition at high temperature as proposed by Yariv et al. [17-19].

4. Discussion

From the data reported above, the thermal evolution of montmorillonite-intercalated organoclays can be studied by FT-IR spectroscopy in situ conditions, focusing on several diagnostic bands in the mid-IR region.

4.1. Carbonyl bands at $1720\text{--}1750\text{ cm}^{-1}$

Products of partial oxidation characterized by bands in the region $1750\text{--}1700\text{ cm}^{-1}$ form over both PEG-based and BRJI-based samples in the temperature range $150\text{--}350\text{ }^\circ\text{C}$. These bands characterize carbonyl compounds, likely aldehydes species, formed in the condensed phase and can be considered as the evidence of the first step of the oxidative degradation. Increased PEG loading in the organoclay allows the detection of this band at lower temperatures (Fig. 10), for instance the spectrum of P15-180 sample shows

Table 2
Wavenumber of water deformation vibrational mode.

Sample	$\delta\text{H}_2\text{O}$ at 80 °C (cm^{-1})	$\delta\text{H}_2\text{O}$ at 450 °C (cm^{-1})
P15-45	1643	1627
P15-90	1644	1627
P15-180	1647	1627
P40-45	1644	1633
P40-90	1644, 1630 sh	1628
BR-45	1640 complex	1630 complex
BR-90	1636	1629
STx (in air)	1650-1610 complex	1624
STx (in vacuum)	1628	1622

this band already at 200 °C and this effect is in agreement with the hypothesis that some PEG chains are intercalated within the clay matrix and resent of a protection against oxidation, whereas increasing PEG loading leads to the deposition of the polymer also at the surface or border sites, more reactive towards degradation phenomena [17–19,36]. For the same reason, the intensity of this band also increases at increasing PEG content, keeping constant the temperature (Fig. 10A) pointing out an increased amount of oxidation products at increasing PEG content.

On the other side, the frequency of this band is almost the same for all the samples analyzed, thus suggesting that a same oxidation species is mainly formed. As for the shape of the band, it is quite sharp in the P15 intercalated samples spectra, while is complex (two components) in the pure PEG spectra (see for instance Fig. 3): possibly the inorganic matrix catalytic activity affects the thermal degradation allowing the preferential formation of some oxidation products.

Spectra of P15–180 and P40–90 samples also evidenced the complexity of the carbonyl band, showing a shoulder at higher frequencies. As discussed above, increasing polymer loadings and polymer molecular weight could allow the deposition of PEG at the outer surface of this material, leading to the oxidation which follows a reaction pathway similar to that of the pure polymer, indicating that a fraction of the polymer is not affected by the matrix effect, this fraction extending possibly out of the interlayer space.

If we compare the intensity of the band plotted versus the temperature, as reported in Fig. 10, with the TG analyses in Fig. 1, we can notice that for the P15 series, this band reaches its maximum at 300 °C in the condensed phase (Fig. 10B), than appears in the gas phase accounting for the weight loss detected by TG, when also CO_2 is forming (in correspondence of the high temperature decomposition peak).

In sum, the comparison of the reported data allows us to explain the three different TG peaks detected in the PEG series as due to the thermal decomposition of the polymer scarcely interacting with the clay matrix (i.e. at the external surface), polymer interacting with active sites of the matrix (i.e. acidic OH groups, edges and corner coordinatively unsaturated sites) and finally polymers chain within the interlayer spaces, decomposing at the highest temperatures due to the protection effect of the clay galleries towards thermal decomposition.

4.2. Water deformation band

The frequency of the water deformation mode shifts downwards at increasing temperature for all the intercalated samples (Table 2): indeed water molecules in the heated organoclays are less hydrogen bound than those in the fully hydrate system [37].

By comparing data in Table 2, it is also possible to notice a small increase of the frequency at increasing PEG loadings, this shift being slightly lower for the P40 samples spectra. Possibly, the highest number of ethoxy groups units corresponding to the

increased molecular weight of the polymer allows a more effective interaction with water molecules through H-bonding [38]. In particular, for the sample P40–90, the band due to water deformation is clearly split at low temperature and the component at high frequencies disappears first. The comparison with the same band for the pure montmorillonite support shows that at high temperature, when the polymer is almost completely decomposed, the water molecules are characterized by IR deformation band falling almost at the same frequencies observed for reference STx material.

The analysis of water deformation band for the BRIJ-based materials appears to be more difficult, due to the complexity of this absorption which broadly falls at frequency slightly lower than in the PEG based materials. In this case, the less hydrophilic nature of the polymer should explain a decreasing of H-bonds interactions. Following heating there is a further decrease in the frequency as previously reported.

The relative intensity of water deformation band decreases at increasing temperatures, as well as the broad band due to OH stretching modes in the 3800–3500 cm^{-1} range. This is due, as expected, to the progressive dehydroxylation of the samples, occurring already below 200 °C. By comparing the thermal evolution of pure montmorillonite sample with thermal evolution of intercalated materials, it seems that, although reduced in intensity, the band due to hydration water is more resisting to heating in the composite materials spectra: possibly part of interlayer water molecules are interacting with PEG chains oxygen, through H-bonds. Moreover, the relative intensity of the band due to water deformation mode decreases in the sample having the highest PEG loading, a further indication of the competition of PEG with water (likely hydration water in the cations coordination sphere).

Finally, bands due to OH stretching mode, characterizing the different hydroxy groups at the montmorillonite surface, are at least partially restored at high temperature, in parallel with the decomposition of the organic molecules. Only samples P40–45 and BR-45 behave differently and no free OH groups can be detected after organic chains decomposition.

4.3. CH stretching region

In our experiments, even at the highest temperatures, several weak absorption in the region 3000–2800 cm^{-1} are detectable, due to CH stretching vibrational modes of residual organic material. This can be taken as an evidence of the coke formation characterized by a high CH content, whose further oxidation is hindered by the effect of the clay matrix. Yariv et al. also proposed to study the high frequency region of the spectrum (i.e. CH stretching vibrational modes) in order to follow the thermal behaviour of the adsorbed species, namely tetraalkylammonium montmorillonites [17–19]. The detection of several decomposition organic products in the clay matrix and in the gas phase accounts for the complexity of the intercalated polymer degradation revealed by TG analyses.

Spectra of gas phase species, recorded in situ at increasing temperatures confirmed the formation of partial oxidation products together with light cracking products, as a further indication of the complexity of the thermal decomposition of organoclays. CO_2 and CO are formed at the highest temperatures. Correspondingly, in the low frequency range of the spectra, bands due to CC and CO stretching mode characterize the formation of alcohols, ethers and a mixture of light alkanes and alkenes. In particular we had evidence of C2 fragments formations, which are detected in the gas phase as dioxane (sharp bands at 1258, 1132, 883 cm^{-1}) and ethyl ether.

5. Conclusions

Thermal degradation of PEG based and BRIJ intercalated montmorillonite is a multi step process, as pointed out by TG DTA

analysis, and in situ FT-IR spectroscopy allows a good insight in the process mechanisms. Results indicate that PEG fragmentation through the cleavage of the C–O bond seems to be the main reaction step, leading to the formation of short chain carbonyl adsorbed species (such as acetaldehyde), alcohols (ethanol and methanol) and, to a lesser extent, esters species, characterized by the frequency of the carbonyl band. The carbonyl stretching IR band pointed out the formation of partial oxidation products in the condensed phase as first step of the thermal degradation.

The position and intensity of the water deformation band evidences the interaction of PEG hydrophilic fraction with montmorillonite hydration water. Extensive dehydration of the composite materials occurs in the low temperature range, but hydration water is still detectable at high temperature as a further indication of the interaction with organic moieties through H-bonds.

Increasing polymer loadings, as well as increasing polymer molecular weight leads to lower temperature of formation of the first oxidation products. No clear indication of the effect of the chemical nature for the intercalated polymers can be obtained. BRIT thermal decomposition seems to be mainly driven by the PEG-like moiety chemistry.

CH stretching bands detected at 450–500 °C for the P40–45, P40–90 and P15–180 samples indicated the formation of residual organic compounds resisting oxidation, possibly char species preserved from further oxidation by the interlayer galleries.

Acknowledgement

Master's Degree student Irene Baccini is gratefully acknowledged for her help in the experimental work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

References

- [1] T.S. Anirudhan, M. Ramachandran, *Appl. Clay Sci.* 35 (2007) 276–281.
- [2] F.A. Bergaya, *Microp. Mesop. Mater.* 107 (2008) 141–148.
- [3] F.A. Bergaya, B.K.G. Theng, G. Lagaly, *Handbook of Clay Science*, first ed., Elsevier, Amsterdam, 2006.

- [4] K. Campbell, D.Q.M. Craig, T. McNally, *Int. J. Pharm.* 363 (2008) 126–131.
- [5] E. Ruiz-Hitzky, M. Darder, P. Aranda, *J. Mater. Chem.* 15 (2005) 3650–3662.
- [6] F. Leroux, C. Taviot-Guého, *J. Mater. Chem.* 15 (2005) 3638–3642.
- [7] E. Ruiz-Hitzky, M. Darder, P. Aranda, K. Ariga, *Adv. Mater.* 21 (2009) 1–14.
- [8] L. Zampori, P. Gallo Stampino, C. Cristiani, G. Dotelli, P. Cazzola, *Appl. Clay Sci.* 48 (2010) 97–102.
- [9] L. Zampori, P. Gallo Stampino, C. Cristiani, G. Dotelli, P. Cazzola, *Appl. Clay Sci.* 50 (2010) 266–270.
- [10] E. Finocchio, I. Baccini, C. Cristiani, G. Dotelli, P. Gallo Stampino, L. Zampori, *J. Phys. Chem. A* 115 (2011) 7484–7493.
- [11] J. Madejova, *Vib. Spectrosc.* 31 (2003) 1–10.
- [12] J. Madejová, L. Jankovic, M. Pentrák, P. Komadel, *Vib. Spectrosc.* 57 (2011) 8–14.
- [13] W. Xie, G. Zongming, K. Liu, W.P. Pan, R. Vaia, D. Hunter, A. Singh, *Thermochim. Acta* 367–368 (2001) 339–350.
- [14] B. Chen, J.R.G. Evans, S. Holding, *J. Appl. Polym. Sci.* 94 (2004) 548–552.
- [15] B. Tyagi, C.D. Chudasama, R.V. Jasra, *Spectrochim. Acta A* 64 (2006) 273–278.
- [16] F. Bellocci, G. Camino, A. Frache, A. Sarra, *Polym. Degrad. Stab.* 92 (2007) 425–436.
- [17] S. Yariv, I. Lapidés, *J. Therm. Anal. Cal.* 80 (2005) 11–26.
- [18] S. Yariv, *Appl. Clay Sci.* 24 (2004) 225–236.
- [19] S. Yariv, *Thermochim. Acta* 274 (1996) 1–35.
- [20] L. Zampori, G. Dotelli, P. Gallo Stampino, C. Cristiani, F. Zorzi, E. Finocchio, *Appl. Clay Sci.* 59–60 (2012) 140–147.
- [21] J. Madejova, M. Pentrák, H. Palkova, P. Komadel, *Vib. Spectrosc.* 49 (2009) 211–218.
- [22] U. Flessner, D.J. Jones, J. Rozière, J. Zajac, L. Storaro, M. Lenarda, M. Pavan, A. Jiménez-López, E. Rodríguez-Castellón, M. Trombetta, G. Busca, *J. Mol. Catal. A: Chem.* 168 (2001) 247–256.
- [23] J.T. Klopogge, E. Mahmutagic, R.L. Frost, *J. Colloid Interface Sci.* 296 (2006) 640–646.
- [24] J. Madejova, H. Palkova, P. Komadel, *Vib. Spectrosc.* 40 (2006) 80–88.
- [25] J. Madejova, P. Komadel, *Clay Clay Miner.* 5 (2001) 410–432.
- [26] J.D. Russel, A.R. Fraser, in: M.J. Wilson (Ed.), *Infrared Methods Clay Mineralogy: Spectroscopic and Chemical Determinative methods*, Chapman and Hall, London, 1994, pp. 11–67.
- [27] P. Aranda, E. Ruiz-Hitzky, *Chem. Mater.* 4 (1992) 1395–1403.
- [28] Y. Deng, J.B. Dixon, G.N. White, *Colloid Polym. Sci.* 284 (2006) 347–356.
- [29] M. Rozenberg, A. Loewenschuss, Y. Marcus, *Spectrochim. Acta A* 54 (1998) 1819–1826.
- [30] Y. Kitahara, S. Takahashi, T. Fujii, *Chemosphere* 88 (2012) 663–669.
- [31] S. Han, C. Kim, D. Kwon, *Polymer* 38 (1997) 317–323.
- [32] J. Billingham, C. Breen, J. Yarwood, *Vib. Spectrosc.* 14 (1997) 19–34.
- [33] R.L. Frost, Q. Zhoua, H. Hea, Y. Xi, *Spectrochim. Acta A* 69 (2008) 239–244.
- [34] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, *The Handbook of Raman and Infrared Characteristic Frequencies of Organic Molecules*, Academic Press, Boston, USA, 1994.
- [35] J.M. Cervantes-Uc, J.V. Cauich-Rodriguez, H. Vazquez-Torres, L.F. Garfias-Mesias, D.R. Paul, *Thermochim. Acta* 457 (2007) 92–102.
- [36] B. Bellocci, G. Camino, A. Frache, A. Sarra, *Polym. Degrad. Stab.* 92 (2007) 425–436.
- [37] J. Madejova, M. Janek, P. Komadel, H.-J. Herbert, H.C. Moog, *Appl. Clay Sci.* 20 (2002) 255–271.
- [38] F.O. Libnau, O.M. Kvalheim, A.A. Christy, J. Toft, *Vib. Spectrosc.* 7 (1994) 243–254.