

# Montmorillonite modified by unsaturated compatibilizing agents and by ionizing radiation as a potential filler in polymeric composites

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**Abstract.** For last several years we have studied modifications of montmorillonite (MMT) with different agents and the structural changes resulting from the processes. The aim of present work was focused on the preparation of polymer composites from epoxy resin and dispersed phase modified chemically and subsequently activated by irradiation. The paper presents investigations concerning intercalation of MMT by the synthesized unsaturated organophilic agents (on the basis of quaternary ammonium salts). The process was studied by: wide-angle X-ray scattering (WAXS), Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA); additionally mechanical properties of the polymer composite as well as its microscopic structure were tested. It was found that unsaturated quaternary ammonium salts can intercalate between MMT layers. The possibility of radiation-induced compatibilization between modified MMT particles and polymeric matrix was also studied. It was confirmed by electron paramagnetic resonance (EPR) spectroscopy that in the synthesized salts stable radicals are formed during irradiation, however their influence on mechanical properties of the final composite is insignificant.

**Key words:** composites • montmorillonite • unsaturated ammonium salts • radiation treatment

## Introduction

MMT – natural mineral of layered nano-structure has attracted considerable interest for the last years, due to the modification the clay might show as a nano-filler in polymer composites. Its structure constructed from silicate layers with a thickness of about 1.2 nm can be intercalated or exfoliated by several agents. Incorporation of a small amount of MMT (below 5 wt%) into some polymers, e.g. polyamides, polyolefines, epoxides and many others, can bring the significant improvement in the mechanical, thermal, fluid and gas barrier properties and fire resistance [8, 9, 15, 16].

A single-step process is possible [22] using special procedures of the direct mixing of MMT with some polymers, but in practice, before dispersion in the matrices, MMT is usually modified using organic compounds. Several types of organic substances were applied in this process [8, 17], usually of the salt type, e.g. ammonium, phosphonium, stibonium, sulfonium salts, and others. However, when quaternary ammonium salts composed usually from strongly polar compounds and having organic substituents are applied, many additional chemical processes (degradation, rearrangement, scission of polymer chains) as well as physical phenomena (migration of modifier) can occur, particularly during mixing of the modified MMT with polymeric matrix at elevated temperature, or using a reinforced polymer under extreme conditions. Some of these processes

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lead to the polymer destructions at high temperatures [9] via mechanisms dependent on the type of MMT modifiers, extent of MMT intercalation and polymer structure. The degradation was analyzed in many papers on a basis of data obtained by various experimental methods [2, 15]. The TGA, FTIR, EPR spectroscopy, and other techniques were previously applied to explain a background of degradation, but the mechanism of some processes is not clear so far, e.g. photodegradation of polymer/MMT composites [12].

In order to prepare polymer-MMT composites of improved stability, variety of methods and modifications were tested in the past [10]:

- application of selected polymers as MMT modifiers [10],
- *in-situ* polymer grafting on the modified MMT surface *via* controlled polymerization processes [21],
- using modified MMT as a filler during *in-situ* polymerization of vinyl monomers [24], unsaturated polyesters cross-linking [7], epoxy resins hardening [5]
- using ionizing radiation to improve properties of polymer/MMT nanocomposites [11, 13, 20].

Liu [10] reported that quaternary ammonium groups bounded with polymer chains as MMT modifiers do intercalate efficiently between MMT layers. In spite of strongly limited migration of the modifier, a satisfactory compatibilization between the polymer and MMT was achieved. Similar process was carried out by Viville *et al.* [21] who utilized reaction between quaternary ammonium salt containing reactive substituents, e.g. hydroxyl groups, and caprolactone monomer leading to the formation of polyester.

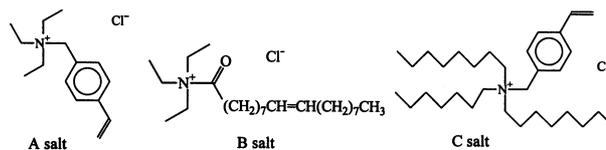
In the past many attempts have been made to modify the interaction between surfaces of the composite components, using ionizing radiation treatment, e.g. [1, 3]. The process might improve interfacial properties at molecular level, influencing macroscopic features, e.g. application of ionizing radiation for the modification of MMT reinforced polypropylene results in changes in nanocomposite structure, flammability and thermal stability of the product, depending on the absorbed dose [11–13, 20].

On a basis of above information, we have synthesized quaternary ammonium salts, containing the unsaturated bond in the molecule what can effectively stabilize the radical centers generated by ionizing radiation. We have expected that MMT fillers modified with species containing chemically active sites are able to initiate formation of covalent bonds with polymeric matrix during mixing processes. Therefore, the major objective of this paper has been focused on the investigation of various modification strategies of MMT. Intercalation of the synthesized salts into MMT plays a crucial role in modifying bulk properties of the composite comprising such particles.

## Experimental

### Materials

Unsaturated ammonium salts of the formulae labeled A, B and C, Scheme 1, were obtained by mixing appropriate tertiary amines (triethylamine or trioctylamine) with *p*-vinylbenzyl chloride or oleoyl chloride for



**Scheme 1.** Chemical formulae of the synthesized unsaturated compatibilizing agents.

5 days according to the procedure proposed by Viville *et al.* [21]. The chemicals were purchased from Sigma-Aldrich. In the case of A and B salts, crystalline products were recrystallized from acetone and stored in desiccator at room temperature over silica gel. C salt does not crystallize and was used as obtained.

Commercially available MMT containing above 90% of pure MMT in form of Na-salt was purchased from Riedel deHaen (RdH) and used without any additional purification or treatment. As a reference, commercially available modified MMT, type Cloisite 10 (Fluka cat. no. 11958) was applied.

Modification of MMT (RdH) was carried out using the synthesized salts according to two different procedures. The first procedure consists in preparation of the suspension comprising a salt and MMT(RdH) in a weight ratio of 4:1 in water-acetone solvent, and subsequently mechanical mixing of the components for 24 h at room temperature. In the second method, a mixture of MMT and suitable salt, both dispersed in water, was heated for 5 h at 95°C. For MMT modified with A, B and C salts, following symbols were applied: MMT(A), MMT(B) and MMT(C), respectively.

The products obtained on a basis of both procedures are filtered, dried in air, later under vacuum at 50°C and stored in desiccator over silica gel.

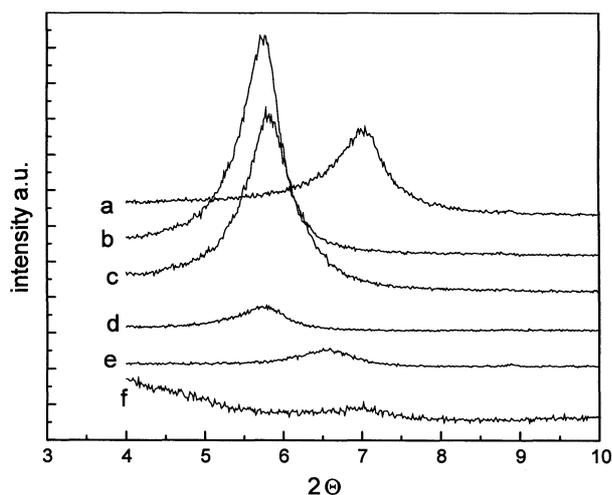
In order to assess the usefulness of the modified MMTs as fillers in polymer composites, they were dispersed in epoxy resin. At first, low molecular weight diglycidyl ether of Bisphenol A was mixed with the modified MMT in a ratio of 20:1 for 1 h at 80°C in ultrasonic water bath, up to complete homogenization. After cooling, the suspension was mixed with a hardener (triethylenetetraamine (TETA)) in the proportion of 10:1, and poured out into the aluminum mould bar of dimension 4 × 10 × 80 mm.

### Methods

The modified MMT samples were irradiated in an Elektronika 10 MeV, 10 kW electron accelerator to a dose of 56 kGy. As was estimated during preliminary EPR investigations such a dose was supposed to secure sufficient population of radicals that is a consequence of two factors: radical formation yields and kinetics of their decay.

Intercalation of the synthesized salts into MMT was evaluated using X-ray diffraction. WAXS diffractograms were obtained on D8-Advance X-ray diffractometer using graphite monochromatized Cu-K $\alpha$  radiation in the range of 2 $\theta$  from 4 deg. to 10 deg.

FTIR spectra of the samples incorporated into KBr pellets were measured on a Bruker Fourier-transform apparatus in the range of 400 cm<sup>-1</sup> – 4000 cm<sup>-1</sup>.



**Fig. 1.** Diffractograms of MMT samples in the range of  $2\theta = 4\text{--}10$  deg. Symbols: a – unmodified MMT; b, d – MMT modified with A salt at room temperature and at  $95^\circ\text{C}$  in water, respectively; c – MMT modified with C salt at room temperature; e – MMT modified with B salt at  $95^\circ\text{C}$  in water; f – commercially modified MMT.

EPR spectra of the irradiated samples were detected on an X-band Bruker ESP-300 spectrometer at ambient temperature.

Thermogravimetric analysis was conducted using Q500 TA Instruments apparatus at heating rate of  $10^\circ\text{C}/\text{min}$  in air atmosphere.

Flexural strength of the polymer composites filled with modified MMTs was measured according to ISO 178 using Instron 5565 universal testing machine. The cross head speed was  $1\text{ mm}/\text{min}$ . Data reported are the average of six independent measurements performed for each type of studied composite.

Scanning electron microscope (SEM) photos at different magnifications were obtained on a Jena DSM 942 (Germany).

## Results and discussion

### X-ray diffraction

The intercalation of the three synthesized quaternary ammonium salts into MMT was estimated on a basis of diffraction measurements. The data are presented in Fig. 1 and summarized in Table 1. The detected peaks correspond to the (001) plane reflection of MMT. The average basal spacing of the clay increases from

**Table 1.** Basal spacing for modified MMTs

Name of sample	Basal spacing (nm)
a unmodified montmorillonite RdH	1.25
b MMT(A) (*)	1.55
c MMT(C) (*)	1.52
d MMT(A) (**)	1.55
e MMT(B) (**)	1.34
f commercially modified montmorillonite	> 2.21

(\*) – Intercalation in water-acetone solution at ambient temperature.

(\*\*) – Intercalation in hot water solution.

1.25 nm for the original MMT to 1.52 and 1.55 nm for MMT(A) modified at ambient temperature and at  $95^\circ\text{C}$ , respectively. Similar result was obtained for MMT(C) prepared at room temperature (RT) proving that the prolongation of hydrocarbon chains in the ammonium salt substituents from 2 to 8 carbons does not change the extension of intercalation. As seen from Bragg diffraction peak, the intercalation of B salt demonstrates smaller effect as the basal distance for MMT(B) increases only till 1.35 nm. The problem of limited utility of B salt results probably from the influence of carbonyl group situated next to nitrogen atom which lower affinity of the ammonium salt to the ionic centers of MMT.

In comparison to the commercial material all results are inferior. However, even for Cloisite 10 the traces of reflection originated from non-intercalated MMT at  $2\theta = 7.05$  deg. are observed, Fig. 1, 'f'. As seen from previous studies of Garea *et al.* [5] as well as from our differential scanning calorimetry (DSC) measurements, Cloisite 10 drawback is thermal sensitivity what might limit its practical applications.

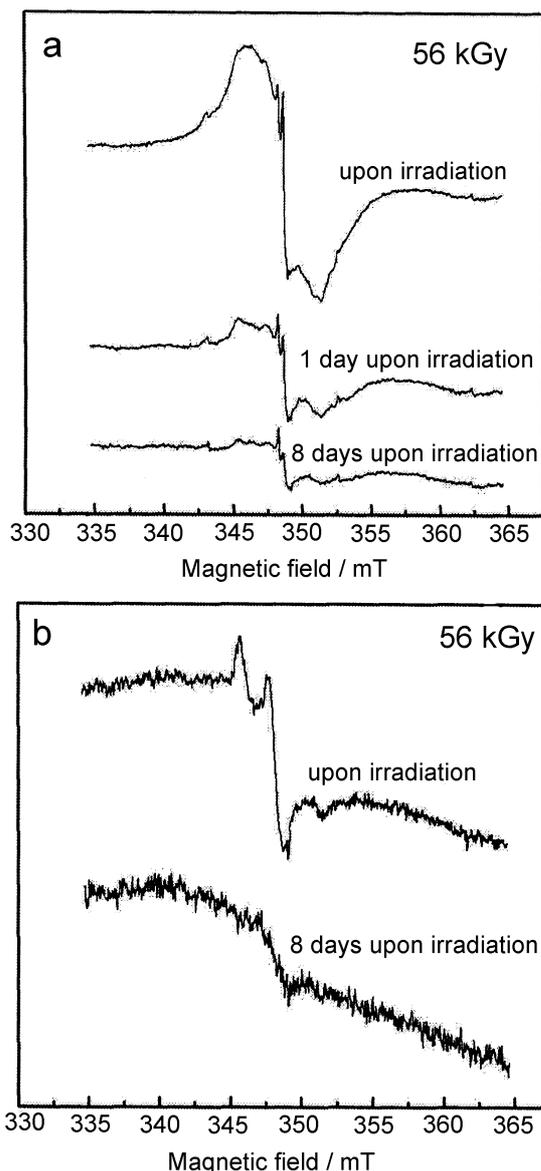
The considerable increase in the intensity of peaks corresponding to MMT modified at room temperature (Fig. 1, 'b' and 'c') resulted from growing regularity of crystalline structure, whereas significant decrease and broadening observed for the signals related to the clay modified at  $95^\circ\text{C}$  (Fig. 1, 'd' and 'e') is caused by a partial loss in ordering of the layered silicate. The later effect is supposed to facilitate distribution of the modified MMTs in polymeric matrices.

### EPR spectroscopy

MMT modified with quaternary salts with reactive vinyl or vinylene groups might participate in the polymerization that facilitates increase in intergallery distances of layered clays [10]. Additionally, unsaturated bonds readily contribute in many radical processes, therefore, the exposition to ionizing radiation generates active centers which are supposed to localize just in these fragments of molecules [1, 4]. If such intermediates are stable enough, they can initiate formation of chemical bonds (chemical grafting) when they are contacted with polymeric matrices. EPR method allows not only to detect radicals but also to monitor their decay with time, indicating if modified MMT stabilizes radiation induced unpaired spins. Thus, the lifetime of radicals estimated by EPR spectroscopy determines their practical utility [14].

EPR spectra obtained on the MMT modified with A and C salts and subsequently irradiated with a dose of 56 kGy are shown in Fig. 2.

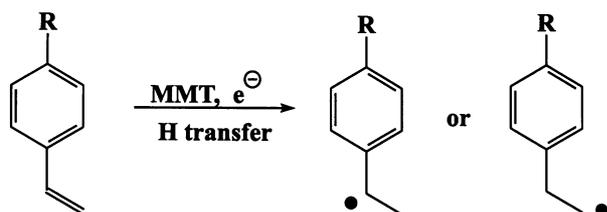
EPR signals of MMT(A) are more intensive and more stable than the spectra detected for MMT(C), however all of them decay during several days after irradiation. Sharp, small lines positioned in a distance of 10.0 mT correspond to the manganese ions that in clays might occur in traces. There is no EPR evidence for the production of peroxy radical as its characteristic anisotropic spectrum was not found. Poorly resolved hyperfine splitting typical for alkyl-type radicals (ca. 2.4 mT) reveals probably interaction between unpaired



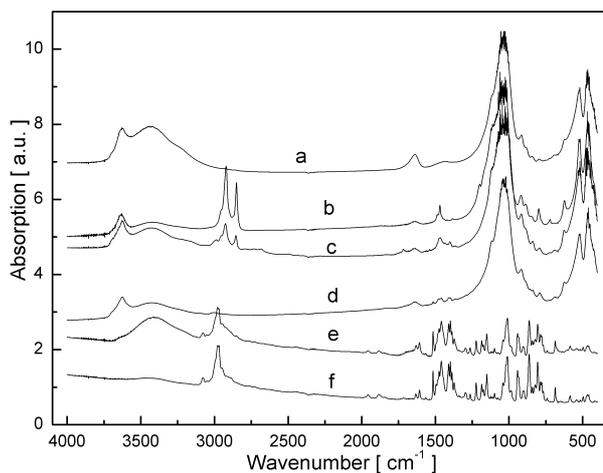
**Fig. 2.** EPR spectra of the irradiated samples: (a) – MMT(A); (b) – MMT(C), both modified at 95°C.

spins and hydrogen atoms. It seems that the observed spectrum corresponds to the product formed upon addition of a hydrogen atom, abstracted e.g. from MMT, to unsaturated bonds. Following structures of radicals are proposed (Scheme 2).

Detected radicals are reactive intermediates able to initiate chemical processes between fillers and surrounding substances. Such a phenomenon introduces compatibility between the dispersed phase and matrix due to radiation-induced grafting of particles onto macromolecules.



**Scheme 2.** Proposed structure of radical formed upon addition of a hydrogen atom to an unsaturated compatibilizing agent.



**Fig. 3.** FTIR spectra: a – unmodified MMT; b – commercially modified MMT from Fluka; c – MMT(A); d – MMT(B); e – B salt; f – A salt.

C salt was excluded from further studies as the population of radicals generated by radiation seemed to be insufficient to play a substantial role in chemical bond formation (see signal to noise ratio, Fig. 2b).

### Infrared spectroscopy

FTIR spectra might confirm adsorption and intercalation of salts into the MMT structure. In Fig. 3, 'a' the absorption bands of MMT at near 3630, 3440, and 1630  $\text{cm}^{-1}$  are attributed to O–H stretching vibrations of water, at 1090 and 1040  $\text{cm}^{-1}$  to Si–O stretching vibrations, and 800  $\text{cm}^{-1}$  bands to Al–O stretching vibrations [2, 5, 23].

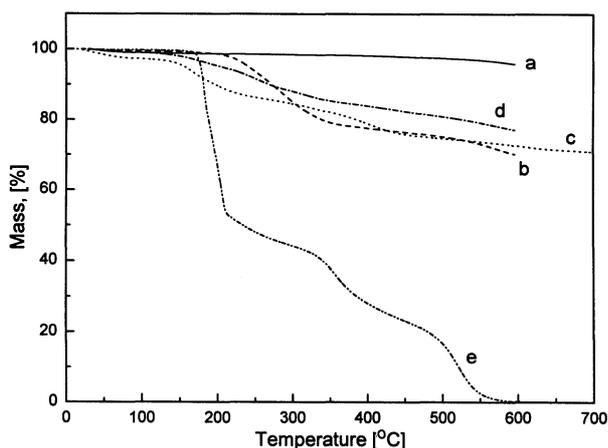
Comparison of the signals measured for salts before and after intercalation into MMT makes possible to identify bands of the salts in the modified MMT spectra.

Characteristic peaks in the range of 2950–2990  $\text{cm}^{-1}$  assigned to aliphatic C–H vibration of the methylene group – bonds stretching [2] are observed for A and B salts as well as for modified MMTs, however for MMT(B) their intensities are very low. In modified MMT the additional band at 2850  $\text{cm}^{-1}$  is growing, probably due to interaction of the salts with MMT. In these ranges unmodified MMT does not absorb, thus identification of the bands is unambiguous. Observed in Fig. 3, 'e' and 'f' peaks between 1100 and 1400  $\text{cm}^{-1}$  result probably from C–C and aromatic C=C stretching of the bonds present in the substituents of quaternary ammonium salts [2].

The correlation between FTIR bands and diffraction measurements is apparent: low intensity of B salt peaks in modified MMT rises from insignificant intercalation reflected by a small shift in basal spacing measured by WAXS method.

### TGA analysis

The results of thermogravimetric analysis are shown in Figs. 4a and 4b. While pure clay remains stable till 600°C, the intercalated MMT starts to decompose at much lower temperatures. MMT(A) is stable till 220°C and above this temperature one step decomposition extended over 100 days is observed, as a consequence



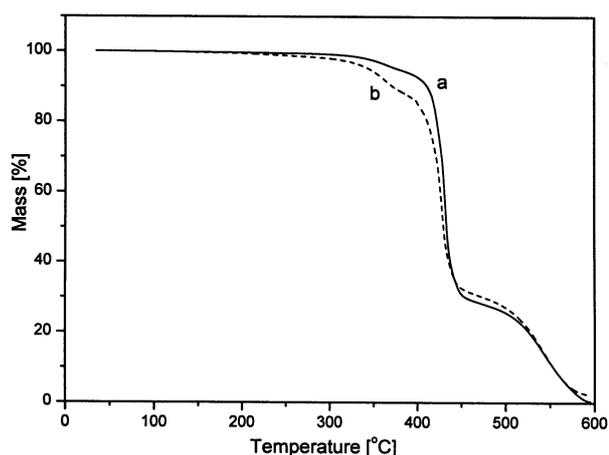
**Fig. 4a.** TGA measurements: a – MMT; b – MMT modified with A salt; c – MMT modified with B salt, (all modified at 95°C); d – commercially modified MMT; e – A salt.

of A salt decay, Fig. 4a. However, destruction of A salt unaccompanied by MMT proceeds during three stages and begins at temperature about 20°C lower. Considerable differences in the thermal decomposition between A ammonium salt and MMT(A) do result from chemical stabilization of A molecules inside MMT galleries.

MMT(B) is more thermally sensitive than MMT(A) and decomposes gradually in two ranges of temperatures: 150–220°C and 300–400°C. The effect originates probably from much lower thermal resistance of aliphatic substituent in quaternary ammonium salts in comparison with aromatic ones. A similar process was confirmed for commercially modified MMT that gradually loses weight with rising temperature in multistage decomposition.

The comparable results were obtained by Cervantes-Uc *et al.* [2] for series of the Cloisites which onset decomposition temperatures were situated in the range of 160–212°C. On a basis of TGA-FTIR measurements the authors suggested that low temperature decomposition is related to the release of water and aliphatic chains showing bands in the 2990–2800 wavenumber range. We identified the same signal characterizing MMT modified with synthesized salts. The evolved hydrocarbon compounds are formed presumably due to the Hofmann processes or nucleophilic substitution reactions [2, 8, 18]. According to papers cited above, the decomposition at higher temperatures causes the release of alkenes, aldehydes, amines, aromatics, etc.

Figure 4b shows that incorporation of irradiated MMT(A) into epoxy resin decreases thermal stability. The same relationship was determined for non-irradiated fillers. Similar effect was also confirmed by Gu *et al.* for composite Cloisite – epoxy resin [6]. It seems



**Fig. 4b.** TGA measurements: a – epoxy resin; b – composite constructed from epoxy resin and irradiated MMT(A) (ratio of components – 20:1).

that in the presence of montmorillonite particles, the resin curing is less efficient; therefore density of cross-linking decreases. Moreover, intercalated composites have lower thermal stability than exfoliated ones [18] thus TGA plot measured for MMT(A) is shifted towards lower temperatures in comparison with MMT thermograph.

#### Mechanical properties

In order to investigate the functionality of the fabricated MMT particles in polymeric composites, they were introduced into common epoxide. Flexural strength and deflection of epoxy resin and its composites comprising MMT modified with A or B salts are reported in Table 2. The mechanical properties are slightly improved for the resin filled with MMT intercalated with A salt and depleted when B salt is incorporated into MMT, as corresponding flexural strength measured for composites containing MMT(A) and MMT(B) rises and falls respectively, in comparison to unfilled resin. For the composite comprising MMT(A), deflection increases simultaneously with the enhanced flexural strength. In order to follow the effect of radiation treatment of the studied fillers on the composite features, MMT(B) was irradiated with a dose of 56 kGy and introduced into epoxide matrix, (Table 2). It seems that for applied dose, the influence of radical centers induced by ionizing radiation is statistically insignificant as flexural strength changes from 91 to 93 MPa for non-irradiated and irradiated particles, respectively.

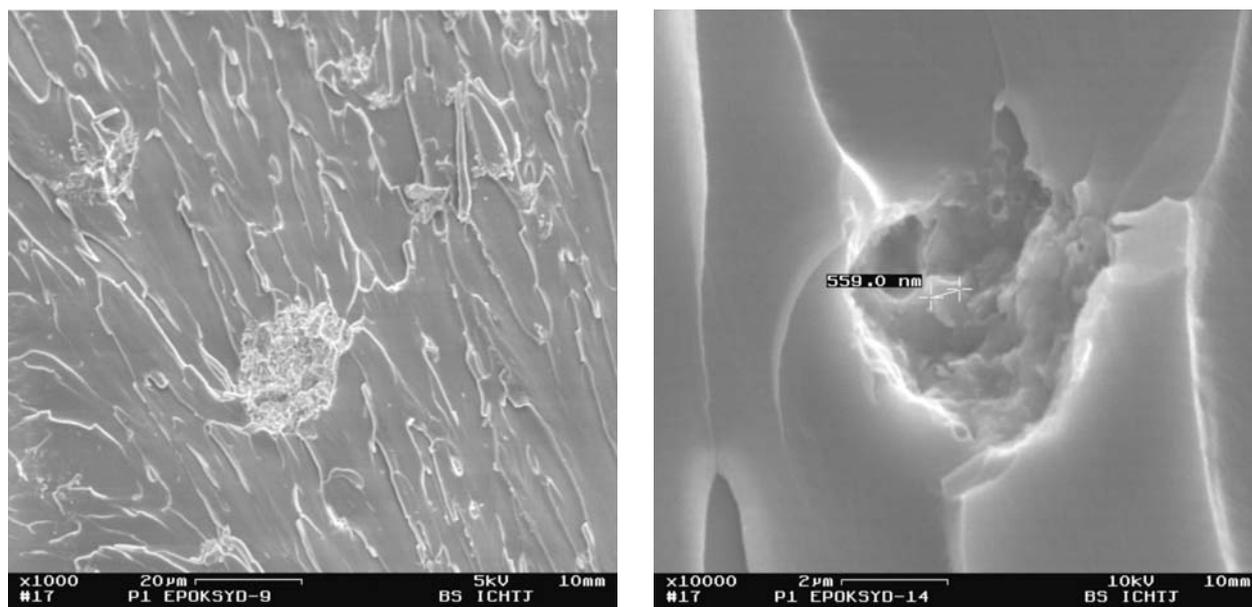
The determined effects are unambiguous and on a basis of the obtained results it is difficult to conclude if the polymer chains of epoxy resin are intercalated

**Table 2.** Flexural properties of epoxy resins composites

Name of sample	Flexural strength** (MPa)	Deflection (%)
Epoxy resin	102	3.1 ± 1.0
Epoxy resin filled with MMT(A)	106	3.7 ± 0.7
Epoxy resin filled with MMT(B)	91	3.1 ± 0.5
Epoxy resin filled with MMT(B)*	93	3.1 ± 0.4

\* The sample was irradiated with a dose 56 of kGy.

\*\* Average of six measurements, a margin of error ± 10% (confidence interval).



**Fig. 5.** SEM pictures of cracked composite constructed from epoxy resin and MMT(A) (modification at 95°C) at different magnification; selected fragments containing dispersed phase.

into a crystallographically regular structure of MMT, preserving multilayers morphology or are exfoliated and uniformly dispersed in the epoxy matrices. Observed deterioration of mechanical properties of the composites proves that interfacial interaction between components is insufficient to reinforce epoxy resin. The same phenomenon was found earlier for Cloisite/polypropylene system [19].

### SEM photos

In order to follow nature of the composites, SEM photos of fractures of the epoxy resin filled with MMT(A) at different magnifications were taken and analyzed, Fig. 5. The photos reveal that the clay mineral is not delaminated in the composite as the single MMT particles are still noticeable. The character of the interface zone between continuous and dispersed phases seems to indicate that surface of the filler is affected by polymer and intercalated with macromolecule chains. Thus, the particles have a special layered microscale structure in outer zone showing tendency towards separation. Taking into account that synthesized salts increase the basal distances of layered MMT only to limited extend, the method of particle incorporation of into the polymeric matrix has to be improved in order to reach exfoliation, e.g. by the increase of shearing forces during stirring.

### Summary

1. We synthesized three types of quaternary ammonium salts containing unsaturated bonds, designed for the modification of MMT. As was confirmed by EPR spectroscopy, such a type of compatibilizing agents stabilizes radiation induced radicals which, if used as fillers, might initiate chemical bonds between dispersed phase and polymeric matrix.

2. As it was confirmed by WAXS measurements as well as FTIR and TGA assays, the synthesized ammonium salts intercalate into MMT layers; the effect does not depend on the applied method of modification (at room temperature and at 95°C).
3. On a basis of EPR measurements we suggest that the mechanism of the radiation induced processes in the MMT modified with ammonium salts, consists in the transfer of hydrogen atoms from MMT to the unsaturated bonds and subsequently formation of alkyl-type radicals.
4. The composites constructed from MMT modified with A salt and epoxide matrix achieved mechanical properties superior to the initial epoxy resin, although the distributed particles do not belong to the nanoscale. The increase in thermal stability of A ammonium salt intercalated into MMT reveals interaction between both components.
5. Radical centers generated in the fillers by ionizing radiation improve neither thermal nor mechanical properties of the composite. The studies revealed that the disadvantages resulting from the reduction of cross-linking density of the composite by MMT particles prevail over the benefits arising from radiation induced grafting.

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