

Preparation of UV Reactive Montmorillonite and Characterization of Its Nanocomposites with Poly(vinyl alcohol)

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ABSTRACT: A cation-exchanged montmorillonite clay is prepared as filler material with high dispersibility, that should act as Fe^{3+} -donor for photochemical crosslinking of PVA/ Fe^{3+} -MMT materials with filler contents of up to 50 wt % with regard to the polymer matrix. Hence, no organic photoinitiators and hazardous compounds are utilized. This material may be considered environmentally benign and could be applied in the field of food packaging or for biomedical applications. Upon UV exposure of liquid PVA/ Fe^{3+} -MMT dispersion samples, a significant change of the refractive index is determined and the absorption at 360 nm decreased. This indicates the transition of Fe^{3+} to Fe^{2+} , which initiates a radical crosslinking mechanism. A homogenous distribution and parallel orientation of the modified clay particles is revealed by SEM measurements. The solubility behavior of the PVA/ Fe^{3+} -MMT composite materials in deionized water, changes considerably due to the high filler content and UV-induced crosslinking, resulting in gel contents exceeding 90 wt %. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 665–672, 2013

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INTRODUCTION

The photochemical crosslinking of iron(III)chloride-doped poly(vinyl alcohol) (PVA/ FeCl_3) has been studied by Kuncser et al.¹ Refractive index measurements have been carried out to determine the suitability of the obtained material for waveguides, and changes in material density due to crosslinking have also been investigated.^{1–5} Possible applications of PVA/ FeCl_3 are permanent and transient data storage materials as well as basic materials for the fabrication of active and passive waveguides.³ Because of the absence of organic photoinitiators, UV curable PVA coatings may be applied in the field of food packaging or in biomedical applications.

Two different reaction mechanisms of photochemical crosslinking of iron(III)chloride-doped PVA have been suggested in the literature.

Manivannan et al.⁶ state that the mechanism of crosslinking is based on a charge transfer from excited Fe^{3+} ions to the polymer subsequent radical generation [see Figure 1(a)], while Kowalonek et al.⁷ claim that chlorine radicals are generated during irradiation of FeCl_3 and react with PVA to give macroradicals. These macroradicals subsequently recombine [see Figure 1(b)] and form crosslinks.^{6–8}

It is assumed that the photochemical crosslinking mechanism of iron(III)-doped PVA via charge transition and reduction of Fe^{3+}

to Fe^{2+} is the prevalent mechanism [as depicted in Figure 1(a)]. This lead us to the intention, that cation exchanged montmorillonite clay loaded with Fe^{3+} could be applied as a nanoscaled filler material that releases iron(III) ions and thus makes additional UV crosslinking of the PVA matrix feasible.

The smectite group mineral montmorillonite is a layered silicate with the general composition $[\text{Si}_8]^{IV}[\text{Al}_{4-x}\text{Mg}_x]^{VI}\text{O}_{20}(\text{OH})_4(\text{M}_{x/n})^{n+} \cdot \gamma\text{H}_2\text{O}$.^{9,10} Because of its special layer structure, containing two tetrahedral sheets and one octahedral sheet, negative surface charges between the clay platelets occur, that are balanced by Ca^{2+} , Mg^{2+} , or Na^+ cations. The metal cations can be easily exchanged with other metal or organic cations which could lead to an increase of the layer-to-layer distance, thus improving exfoliation or intercalation behavior.^{11,12} The principle of the exchange reaction is shown in Figure 2.

The first aim of this study was to prepare an iron(III) cation exchanged montmorillonite clay (Fe^{3+} -MMT), by mixing it with an appropriate metal salt. The cation exchange reaction was performed in accordance to Rozenson,^{13–15} McBride,¹⁶ and Gerstl.¹⁷

The second objective of this work was the preparation of UV curable PVA composite containing Fe^{3+} -MMT, with a filler content of up to 50 wt %. A major advantage of this new material

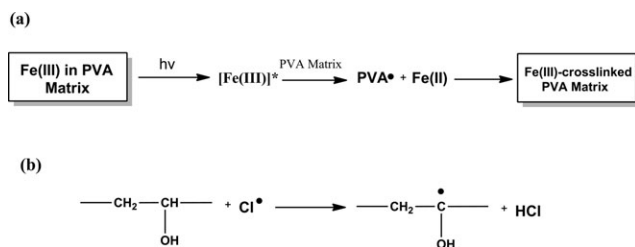


Figure 1. Reaction mechanisms for the photochemical crosslinking of iron(III)chloride-doped PVA according to Manivannan⁶ (a) and Kowalunek⁷ (b).

would be the improvement of the resistance of PVA versus water via two different ways: strong polymer-filler interactions on the one hand¹⁸ and covalent crosslinking by UV exposure on the other.^{1–4}

This novel concept will combine physical polymer-filler interactions by hydrogen bonding between PVA and the Si-OH groups of the MMT surface and covalent crosslinking of the polymer through UV-induced radical crosslinking. Hence nonhazardous photoactive species are applied and nonvolatile scission products are formed, the prepared new material should be considered as biocompatible and environmentally benign.

EXPERIMENTAL

Materials

An aqueous iron(III)chloride solution (FeCl_3 ; technical grade) with a solids content of 40 wt % was purchased from Donau-chemie (Vienna, Austria). Sodium montmorillonite clay was obtained from Southern Clay Products (Gonzales, USA) as a 10 wt % aqueous suspension.

PVA was provided by the DuPont Chemical Company (Wilmington, USA) and further characterised at the Chair of Chemistry of Polymeric Materials (Leoben, Austria). The average molar mass was determined at the Institute of Chemistry at the University of Graz (Austria) by gel-permeation-chromatography using highly purified water as eluent. A value of $M_w = 130000$ g/mol and a polydispersity index of 1.32 was found. A very high

degree of saponification (>99 mol %) was confirmed by ¹H-NMR-spectroscopy using D_2O as solvent.

An aqueous PVA solution with a solids content of 5 wt % was prepared by stirring the appropriate amount of deionized water at room temperature, followed by adding the polymer thus creating a slurry. After 10 min of stirring at room temperature, the slurry was heated to a temperature of 85°C. This temperature was kept for at least 60 min until a homogenous solution was obtained.

All chemicals were used without any further purification or particular treatment.

METHODS

Preparation of Fe^{3+} -MMT

A sodium montmorillonite clay suspension was stirred and an excess of FeCl_3 solution was added, resulting in a ratio of FeCl_3 to MMT of 2 : 1 by weight. The reaction mixture was stirred for 48 h at room temperature, which is followed by filtration and leaching out of excess iron(III)chloride with deionized water. The washing process was repeated until no more iron(III) ions were detectable in the rinsing fluid by reactions with potassium thiocyanate. According to McBride et al. an additional AgNO_3 test was carried out to determine chloride anions. As no precipitate of AgCl was formed, it is concluded, that excess chloride anions are quantitatively removed by this process.¹⁶

The purified Fe^{3+} -MMT was dispersed with deionized water, to give a homogenous suspension with a total solids content of 5 wt %.

Preparation of PVA/ Fe^{3+} -MMT Dispersions

An aqueous PVA solution was stirred at room temperature with the appropriate amount of Fe^{3+} -MMT using an IKA magnetic stirring device (Staufen, Germany) for a duration of 24 h. This was followed by sonification and dispersing with an IKA Ultra-Turrax T18 high speed dispersing unit. Dispersions containing 20, 30, 40, and 50 wt % of modified (in relation to PVA) were prepared.

Preparation of Self-Supporting Thin Films of PVA/ Fe^{3+} -MMT

Thin films for SEM measurements, crosslinking studies and photolithographic patterning were prepared by the gravity settling method. A defined amount (5 g) of the PVA/ Fe^{3+} -MMT dispersion was placed into polystyrene petri dishes ($d = 85$ mm). The

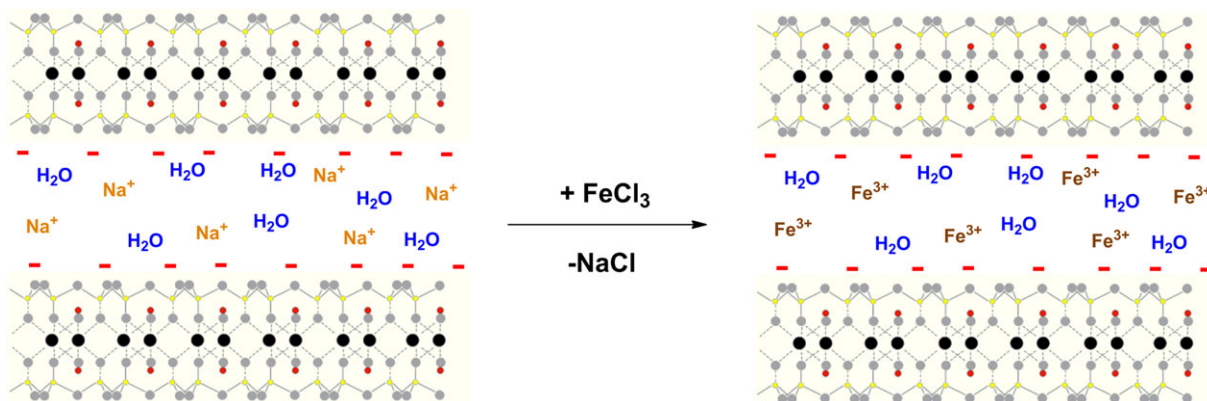


Figure 2. Principle of the cation exchange reaction that leads to Fe^{3+} -MMT. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

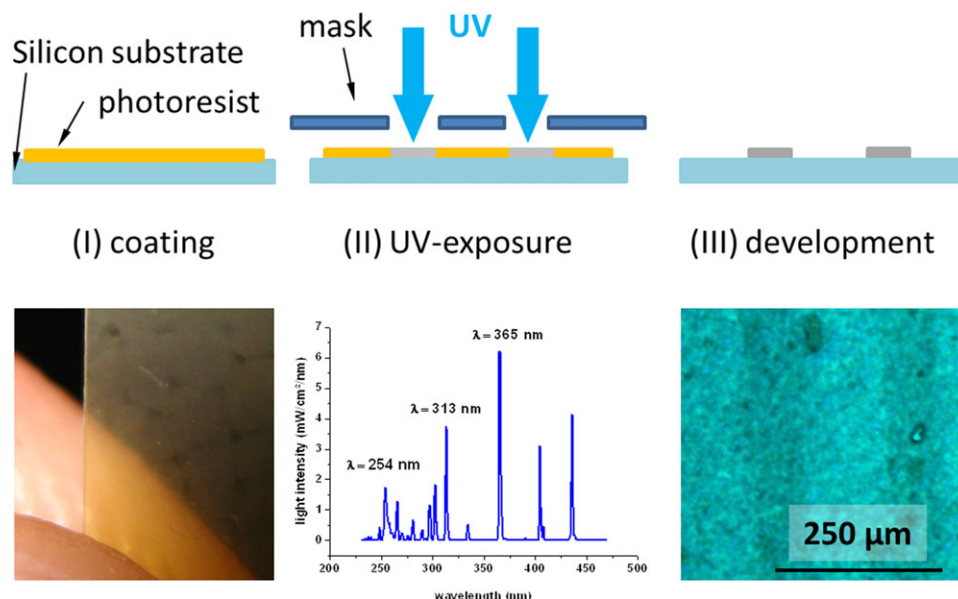


Figure 3. (I) coated substrate (bearing a hazy, yellowish PVA/Fe³⁺-MMT film); (II) UV exposure with a medium-pressure mercury-vapour lamp through a mask pattern, the non-illuminated areas remain soluble in appropriate solvents. The peaks at wavelengths of 254, 313, and 365 are relevant for cross-linking PVA/Fe³⁺-MMT composite samples; (III) development by immersion in a solvent (in this case deionized water), polarized light image of 100 μm patterns after 30 min of development. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

samples were dried under steady air flow at room temperature until constant weight was attained. The obtained samples were of yellowish color and hazy (see Figure 3.I)

UV-Irradiation Experiments

The irradiation of liquid samples was performed using an EXFO OmniCure S1000 spot curing device (Quebec, Canada), which was equipped with a flexible light guide. Light intensities of 9.25 mW cm⁻² were applied for exposure times up to 1500 s.

For UV induced crosslinking of PVA/Fe³⁺-MMT composite samples a FusionUV Light Hammer 6 (MD, USA) conveyor-belt irradiation device was applied. It is equipped with a medium-pressure mercury-vapor lamp, which generates UV light of wavelengths ranging from 225 to 450 nm (see Figure 3.II). The emission spectrum of the light source was recorded using a Solascope spectroradiometer from Solatell (Gloucestershire, UK).

The PVA/Fe³⁺-MMT thin films were exposed to UV light with an intensity of 740 mW cm⁻² for a duration of 0, 30, 60, 90, and 120 s. After irradiation the effects of UV exposure were investigated by the sol-gel technique to determine the change in solubility in deionized water.

UV-VIS Spectroscopy

UV-VIS absorption spectra were recorded using a Varian Cary 50 spectrophotometer (Santa Clara, USA) to trace changes of the optical absorption of diluted PVA/Fe³⁺-MMT dispersions during UV irradiation. A medium scanning speed was applied at a wavelength range from 250 to 650 nm and the change of the absorption at 360 nm was plotted versus the UV exposure time.

Refractometry

Refractive index changes of liquid PVA/Fe³⁺-MMT dispersion samples containing 20, 30, 40, and 50 wt % of filler material (in relation to PVA) during UV exposure with a spot curing device

were determined with an Atago NAR1T Abbe refractometer (Tokyo, Japan) using a sodium D-line light source (589 nm).

SEM/EDX Measurements

SEM and EDX measurements on Fe³⁺-MMT samples and PVA/Fe³⁺-MMT composite films were performed at the Materials Center Leoben (MCL, Austria) using a Zeiss Auriga 60 scanning electron microscope with an applied acceleration voltage of 20 kV. Energy dispersive X-ray (EDX) spectra of the modified clay material were performed to prove interlayer cation exchange of Na⁺ and Ca²⁺ cations with Fe³⁺.

To determine filler particle distribution, images of overhead views and of the cross sections of cryogenically cracked films were recorded applying a backscatter electron detector.

Swelling Behavior

Irradiated films of PVA/Fe³⁺-MMT composites were cut into 1 × 1 cm² pieces, weighed to obtain the initial sample weight (w_i) and immersed in deionized water at 23, 40, 60, and 80°C for 48 h to obtain equilibrium swelling. After this period the samples were withdrawn, dipped in chloroform to remove the water from the surface and the weight of the swollen samples (w_s) was determined. This was followed by drying of the samples under steady air flow for ~ 24 h at 60°C and the weight of the dried samples (w_d) was determined.¹⁹

The swelling ratio was calculated according to eq. (1)^{18,19}:

$$S(\%) = \frac{w_s - w_d}{w_d} * 100 \quad (1)$$

The gel content was defined according to eq. (2)¹⁹:

$$\text{Gel content}(\text{wt } \%) = \frac{w_d}{w_i} * 100 \quad (2)$$

Photolithographic Patterning

Photolithographic patterning was carried out by placing a silicon dioxide/chromium mask with 100 μm features directly onto a

$1 \times 1 \text{ cm}^2$ film samples, followed by illumination for 120 s with an intensity of 740 mW cm^{-2} , resulting in a radiation dose of 90 J cm^{-2} .

The exposed areas of the PVA/ Fe^{3+} -MMT composite films are crosslinked, thus reducing the solubility in water. The principle of the photolithographic patterning process is depicted in Figure 3.

After patterning the structured samples were investigated with an Olympus BX51 optical microscope. Development of patterned samples was done by immersion in deionized water for 30 min at RT, followed by drying at 40°C under steady air flow. The structures were again observed with the optical microscope and the effects of developing on the structures were compared.

To determine changes of the optical properties of the PVA/ Fe^{3+} -MMT composite films two different imaging modes were used for the investigation. Polarized light imaging was a very versatile tool to accentuate the contrast of illuminated areas and to display the patterned samples. Phase contrast imaging mode provided additional information about the changes in material density of the exposed areas, which will also result in changes of the refractive index.

RESULTS AND DISCUSSION

Preparation of Cation Exchanged Montmorillonite

EDX spectroscopy proves the successful exchange of interlayer sodium cations by iron(III) cations, which is demonstrated in Figure 4. At energies ranging from 6 to 8 keV an increase of the iron peak is observed, while the sodium and magnesium peaks around 1.5 keV are decreasing. Also a slight increase of the chloride peak is detected, which is caused by adsorbed chlorine anions.

The surface structure of a dried Fe^{3+} -MMT coating on silicon dioxide is shown in Figure 4(c). Stacks of platelets of a thickness of about 5 nm and agglomerates sizing up to 100 nm can be distinguished. These results suggest that the modification step by treatment with acidic iron(III)chloride solution leads to increased delamination of the montmorillonite clay.

UV-VIS Spectroscopy

In a first attempt, the UV-response of aqueous Fe^{3+} -MMT is observed, to demonstrate the UV activity of the prepared filler material itself. Upon irradiation the absorption at 360 nm, which can be assigned to the Fe^{3+} ions is decreasing, due to photobleaching caused by charge transition of Fe^{3+} to Fe^{2+} [see Figure 5(b)]. Control experiments on an aqueous FeCl_3 solution lead to a rapid decrease of the absorption, thus proving the photoactivity of Fe^{3+} ions [see Figure 5(a)].^{4,20}

Upon UV exposure of PVA/ Fe^{3+} -MMT dispersions the absorption of the liquid samples is decreasing, therefore suggesting that no obstruction of the photoactivity is caused by the polymer [Figure 5(c)]. The absorption at a wavelength of 360 nm decreases almost exponentially [see Figure 5(d)]. It can be assigned to the absorption of Fe^{3+} ions that are excited by UV irradiation, which is followed by reduction to Fe^{2+} , thus causing the photobleaching effect.

Refractometry

The crosslinking reactions mentioned before are affecting the material density; therefore, an increase of the refractive index

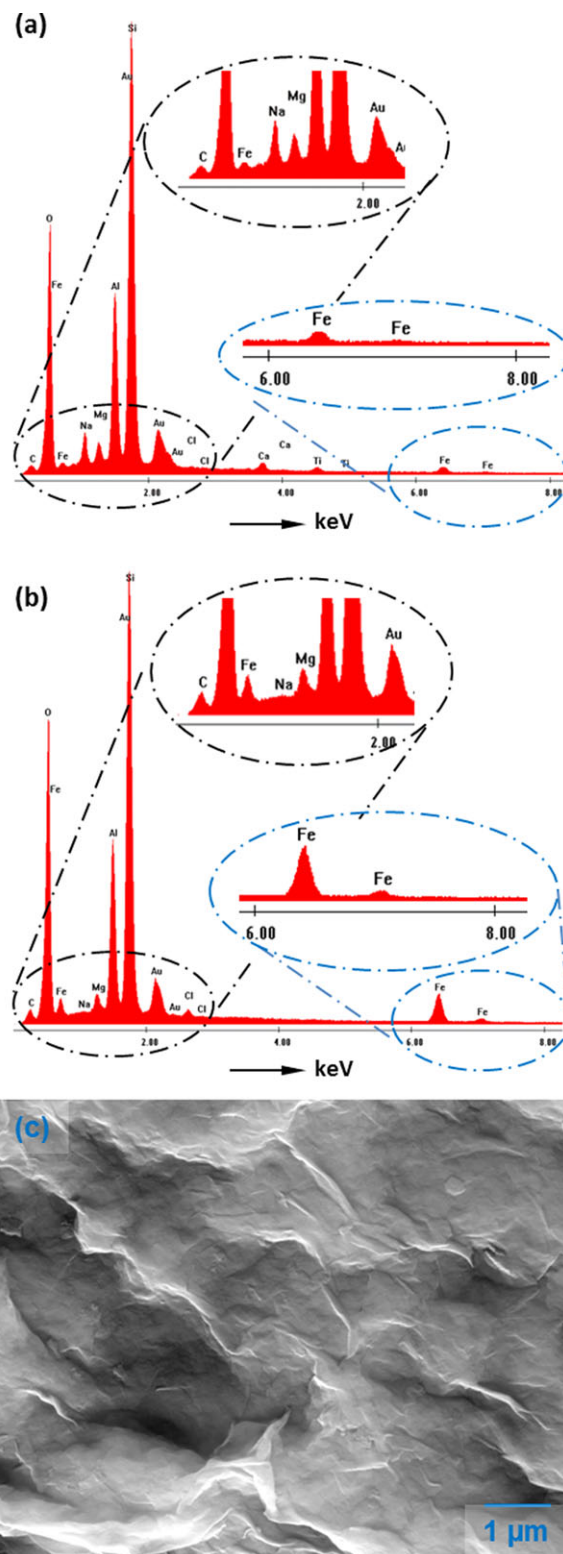


Figure 4. Energy dispersive X-ray spectra of (a) pristine sodium montmorillonite clay and (b) cation exchanged Fe^{3+} -MMT; (c) SEM micrograph of Fe^{3+} -MMT at a magnification of 10,000 recorded with backscatter electron detector. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

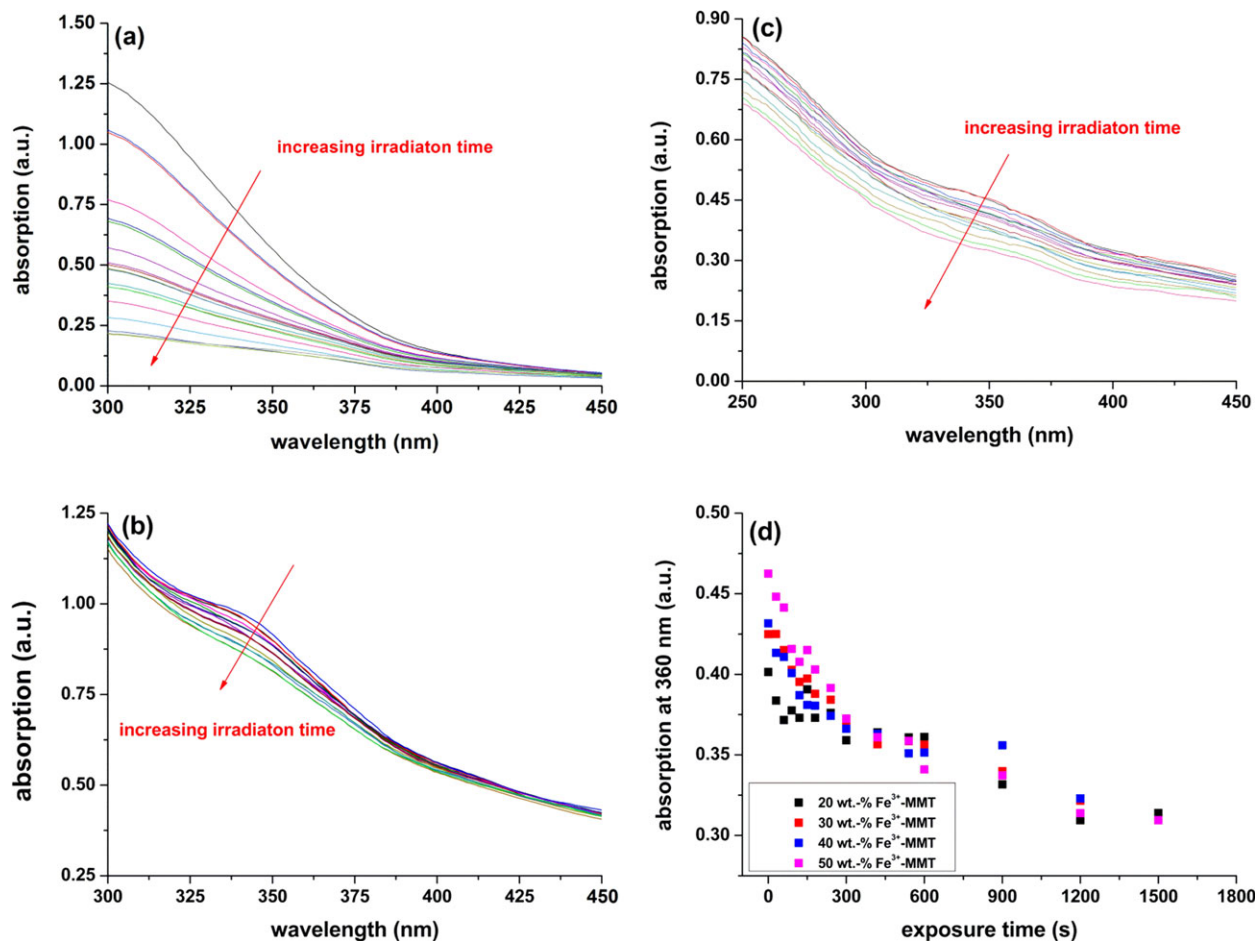


Figure 5. UV-VIS spectrum of an aqueous FeCl₃ solution (a) (1 wt %) and of an aqueous Fe³⁺-MMT suspension (b) (1 wt %); (c) UV-VIS spectrum of a PVA/Fe³⁺-MMT dispersion containing 30 wt % of MMT (with regard to PVA), and (d) Absorption at 360 nm of PVA/Fe³⁺-MMT dispersions versus exposure time using a spot curing device with an intensity of 9.25 mW cm⁻². [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

over the UV exposure time is observed (see Figure 6). Dispersions containing of 20 and 50 wt % Fe³⁺-MMT, exhibit a change of n^D of 0.029 and 0.025 respectively upon UV-exposure, while for dispersions bearing 30 and 40 wt % of filler material a change of $\Delta n^D = 0.015$ was determined. Upon an exposure time of 300 s the refractive index reaches a constant value, which indicates that the photoreaction is completed, while no correlation with the filler content is observed.

Because of photoinduced crosslinking reactions, changes in material density occur, which causes an increase of the refractive index for PVA/Fe³⁺-MMT dispersion samples, while contrary to this results n^D is decreasing for PVA/FeCl₃ systems due to photobleaching caused by charge transition.^{4,20}

Subsequently to the optical characterization of dispersion behavior, self-supporting thin films are prepared of the aqueous PVA/Fe³⁺-MMT dispersions.

SEM Measurements

Scanning electron microscopy of self-supporting PVA/Fe³⁺-MMT composite films reveals, that the modified clay particles are embedded in the matrix with perpendicular orientation to

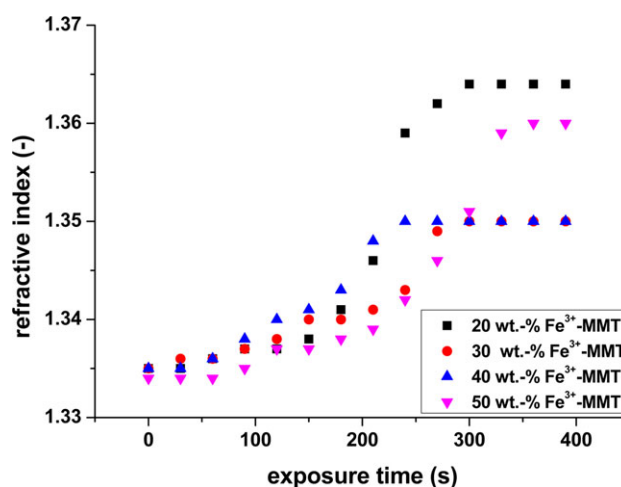


Figure 6. Refractive index of liquid PVA/Fe³⁺-MMT samples versus exposure time upon irradiation with a spot curing device. A pristine liquid PVA solution (5 wt %) exhibits a refractive index $n^D = 1.330$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

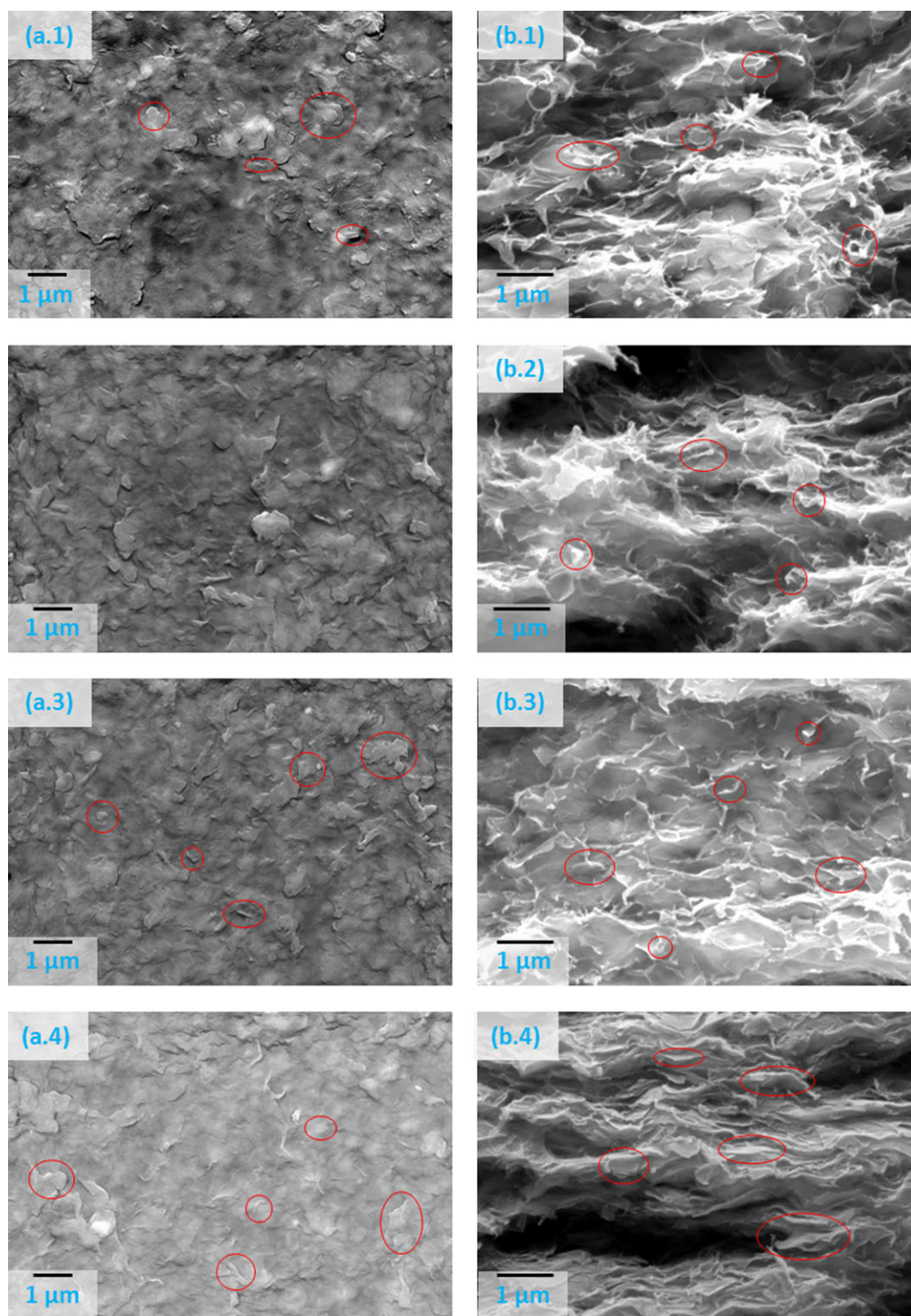


Figure 7. SEM micrographs of PVA/Fe³⁺-MMT composite films (a) top view (b) cross section; numbers 1 to 4 indicate the Fe³⁺-MMT content of the films in relation to the dry matter, which is for (1): 20 wt %; (2): 30 wt %; (3): 40 wt %, and (4): 50 wt %. The marked areas indicate delaminated montmorillonite platelets and should act as a guide for the eye. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the cross section (see Figure 7b.1-4). The size of the filler particles is ranging from 150 to 15 nm and a homogenous distribution over the sample thickness is determined.

In the top view of the samples platelet-like structures are observed, while only few particles are oriented perpendicular to the surface (see Figure 7a.1-4). Because of the delamination and

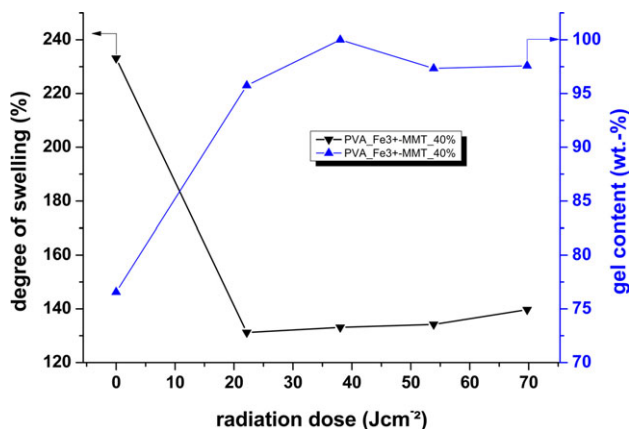


Figure 8. Swelling behavior of self-supporting PVA/Fe³⁺-MMT films (30 wt % Fe³⁺-MMT) in dependence of the UV radiation dose; degree of swelling and gel content. Detailed results are listed in Table I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

parallel orientation of the clay particles it is assumed, that very strong interactions between the PVA matrix and the filler particle surface occur.

Swelling Behavior

Because of the good intercalation of the filler particles gel contents ranging between 65 and 75 wt % are obtained without UV-exposure. Samples containing 50 wt % of modified clay particles are almost insoluble in deionized water. Subsequent UV irradiation leads to a strong increase of the gel content up to 98 wt % for composite samples containing of 30 to 50 wt % Fe³⁺-MMT (compare Figure 8 and Table I).

The swelling behavior of PVA changes significantly due to the presence of the cation exchanged montmorillonite clay. UV exposure leads to a decrease of the degree of swelling from 250% down to 120%, which indicates that additional crosslinks are formed (see Figure 8). This is caused by the light induced crosslinking mechanism of PVA/Fe³⁺ systems.

The high gel content and the low degree of swelling of PVA/Fe³⁺-MMT composite films are both caused by the high disper-

Table I. Swelling Behavior of PVA/Fe³⁺-MMT Composite Films in Dependence of the UV Irradiation Dose

Sample	Degree of swelling (%) UV-exposure		Gel content (wt %) UV-exposure	
	0 J cm ⁻²	70 J cm ⁻²	0 J cm ⁻²	70 J cm ⁻²
20 wt % Fe ³⁺ -MMT	247	193	68	94
30 wt % Fe ³⁺ -MMT	234	193	75	99
40 wt % Fe ³⁺ -MMT	233	140	77	98
50 wt % Fe ³⁺ -MMT	205	184	93	91

sibility of the filler particles that leads to increased polymer-filler interactions. Additional UV irradiation leads to formation of covalent crosslinks which reduces the swelling of self-supporting composite films in deionized water significantly (see Figure 8 and Table 1).

Photolithographic Patterning

Because of the improved swelling upon UV irradiation, the preparation of patterned thin films was investigated. The photolithographic patterning resulted in a change of color upon UV-exposure, which has already been characterized by UV-VIS spectroscopy.

The illumination of PVA/Fe³⁺-MMT composite films through a quartz/chromium mask with 100 μm features shows excellent pattern contrast, which is depicted in Figure 9(a) for a composite film containing 20 wt % clay particles. The nonilluminated areas are colored, while a photobleaching effect is observed after UV exposure. The loss of color is caused by the change of oxidation state of Fe³⁺ to Fe²⁺.

Also the material density of the composite films is affected by UV-exposure and crosslinking reactions, which cannot only be determined by an increase of the refractive index *n^D*, but also

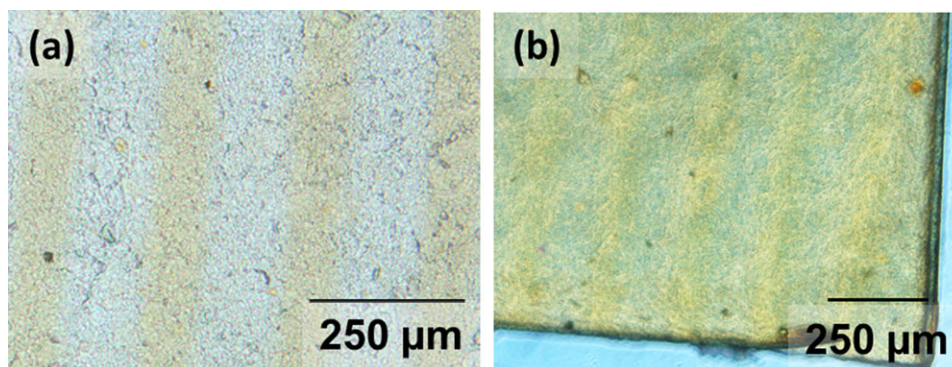


Figure 9. Self-supporting PVA/Fe³⁺-MMT composite films after irradiation through a 100 μm pattern and development in deionized water for 30 min at RT. (a) 20 wt % of Fe³⁺-MMT; optical micrograph in polarized light mode; (b) 50 wt % Fe³⁺-MMT; optical micrograph in phase contrast imaging mode. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

by phase contrast imaging as depicted in Figure 9(b) for a sample containing 50 wt % after immersion in deionized water.

CONCLUSIONS

Poly(vinyl alcohol)/Fe³⁺-MMT dispersions with Fe³⁺-MMT contents up to 50 wt % in relation to the solid matter, were prepared using high speed dispersion tools. The distribution of the modified filler particles appeared to be homogenous with almost parallel orientation over the cross-section of the samples and a high dispersibility was observed. This leads to high gel contents that can be further increased by UV-irradiation up to 90 wt %. Patterned illumination using a silicon dioxide/chromium mask gives excellent contrast behavior after development with deionized water and a photobleaching effect was observed, which would make irradiation of thick substrates feasible. Phase contrast imaging revealed patterned changes in material density of the exposed substrates.

PVA/Fe³⁺-MMT nanocomposite systems are of potential interest as environmentally benign coating materials, due to the application of nonhazardous and irritant compounds. Hence all excess modification reagents are leached out of the filler material and the photoactive species is bound onto the clay surface, no migration of the reactive species onto the surface will occur. This provides a great advantage compared with the application of common coating materials intended food packaging or biomedical applications. Because of the strong polymer-filler interactions and additional crosslinking caused by illumination with UV-light, the coating material will be water resistant, though development was performed in deionized water.

Further studies concerning the barrier properties of the obtained materials with regard to organic compounds and the influence of different humidity levels are in progress.

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REFERENCES

- Kuncser, V.; Avramescu, A.; Filoti, G.; Rotaru, P.; Podgorsek, R.; Biebricher, M.; Franke, H. *J. Alloys Compounds* **1997**, *256*, 269.
- Obreja, P.; Cristea, D.; Budianu, E.; Rebigan, R.; Kuncser, V.; Bulinski, M.; Filoti, G. *Prog. Solid State Chem.* **2006**, *34*, 103.
- Bulinski, M.; Iova, I.; Belea, A.; Kuncser, V.; Filoti, G. *J. Mater. Sci. Lett.* **2000**, *19*, 27.
- Kuncser, V.; Filoti, G.; Avramescu, A.; Podgorsek, R.; Biebricher, M.; Franke, H. *J. Alloys Compounds* **1997**, *257*, 285.
- Filoti, G.; Kuncser, V.; Franke, H.; Kardinahl, T.; Manivannan, G. *J. Radioanalytical Nuclear Chem.* **1995**, *190*, 315.
- Manivannan, G.; Nikolov, O.; Kardinahl, T.; Keune, W.; Franke, H.; Changkakoti, R.; Lessard, R.A. *SPIE Proc.* **1994**, 98.
- Kowalonek, J.; Kaczmarek, H.; Bajer, D. *Macromol. Symp* **2010**, *295*, 114.
- Changkakoti, R. *Opt. Eng* **1993**, *32*, 2240.
- Chassin, P. *Bull. Groupe franc. Argiles* **1969**, 71.
- Effenberger, F.; Schweizer, M.; Mohamed, W.S. *J. Appl. Polym. Sci.* **2009**, *112*, 1572.
- Wang, J.; Merino, J.; Aranda, P.; Galvan, J.-C.; Ruiz-Hitzky, E. *J. Mater. Chem* **1999**, *9*, 161.
- Pavlidou, S.; Papaspyrides, C. D. *Prog. Polym. Sci.* **2008**, *33*, 1119.
- Rozenon, I. *Clays Clay Minerals* **1976**, *24*, 271.
- Rozenon, I. *Clays Clay Minerals* **1976**, *24*, 283.
- Rozenon, I. *Clays Clay Minerals* **1978**, *26*, 88.
- McBride, M. B. *Clays Clay Minerals* **1975**, *23*, 103.
- Gerstl, Z. *Clays Clay Minerals* **1980**, *28*, 335.
- Paranhos, C. M.; Soares, B. G.; Oliveira, R. N.; Pessan, L. A. *Macromol. Mater. Eng.* **2007**, *292*, 620.
- Nam, S. Y.; Nho, Y. C.; Hong, S. H.; Chae, G. T.; Jang, H. S.; Suh, T. S.; Ahn, W. S.; Ryu, K. E.; Chun, H. J. *Macromol. Res.* **2004**, *12*, 219.
- Schauberger, J. G.; Riess, G.; Kern, W. *J. Appl. Polym. Sci.* submitted Nov. **2012**.