

A Versatile Solvent-Free "One-Pot" Route to Polymer Nanocomposites and the in situ Formation of Calcium Phosphate/Layered Silicate Hybrid Nanoparticles

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Poly(methyl methacrylate) (PMMA), polystyrene (PS), and polyurethane (PU) nanocomposites containing well-dispersed calcium phosphate/layered silicate hybrid nanoparticles were prepared in a versatile solvent-free "one-pot" process without requiring separate steps, such as organophilic modification, purification, drying, dispersing, and compounding, typical for many conventional organoclay nanocomposites. In this "one-pot" process, alkyl ammonium phosphates were added as swelling agents to a suspension of calcium/layered silicate in styrene, methyl methacrylate, or polyols prior to polymerization. Alkyl ammonium phosphates were prepared in situ by reacting phosphoric acid with an equivalent amount of alkyl amines such as stearyl amine (SA) or the corresponding ester- and methacrylate-functionalized tertiary alkyl amines, obtained via Michael Addition of SA with methyl acrylate or ethylene 2-methacryloxyethyl acrylate. Upon contact with the calcium bentonite suspension, the cation exchange of Ca²⁺ in the silicate interlayers for alkyl ammonium cations rendered the bentonite organophilic and enabled effective swelling in the monomer accompanied by intercalation and in situ precipitation of calcium phosphates. According to energy dispersive X-ray analysis, the calcium phosphate precipitated exclusively onto the surfaces of the bentonite nanoplatelets, thus forming easy-to-disperse calcium phosphate/layered silicate hybrid nanoparticles. Incorporation of 5-15 wt% of such hybrid nanoparticles into PMMA, PS, and PU afforded improved stiffness/toughness balances of the polymer nanocomposites. Functionalized alkyl ammonium phosphate addition enabled polymer attachment to the nanoparticle surfaces. Transmission electron microscopy (TEM) analyses of PU and PU-foam nanocomposites, prepared by dispersing hybrid nanoparticles in the polyols prior to isocyanate cure, revealed the formation of fully exfoliated hybrid nanoparticles.

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1. Introduction

Since the pioneering advances by Okada et al.^[1] at Toyota, organophilic layered silicates have been used extensively in academia and industry to prepare nanocomposites.^[2–5] Low silicate content of a few weight percent can be sufficient to simultaneously improve stiffness, strength, and dimensional stability without sacrificing toughness, to enhance barrier performance and to improve thermal stability as well as halogen-free fire protection.^[2–7]

The most common layered silicates used for polymer nanocomposites are montmorillonites, to which calcium bentonites belong. Their layered structure consists of silicate nanoplatelets with dimensions of approximately 300 nm in diameter and 1 nm in thickness. Isomorphic substitution of Al³⁺ with Mg²⁺ within the layers generates negative charges that are counterbalanced by cations, i.e., Na⁺ and Ca²⁺, residing in the interlayer spacings. Since the silicates are hydrophilic and lack affinity with hydrophobic organic solvents and water-insoluble polymers, cation ion exchange reactions with organic cations, i.e., alkyl ammonium cations, are necessary in order to render the silicate surface organophilic. The resulting organophilic layered silicate is often referred to as organoclay. In most industrial processes, calcium-containing bentonites are converted into sodium bentonites by means

of cation exchange. Resulting from their improved water swelling with respect to calcium bentonites, sodium bentonites promote effective cation exchange with organic ammonium cations.^[8] Much less is known on how to exploit calcium bentonites without requiring this intermediate purification step. In fact, most conventional processes for making organoclays represent multistep processes including sodium bentonite purification, organoclay formation, washing, drying, dispersing, and compounding. An important challenge in nanocomposite development is to simplify organoclay and nanocomposite fabrication.



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Many attempts have been reported to incorporate organoclay in poly(methyl methacrylate) (PMMA), polystyrene (PS), or polyurethanes (PU), aiming at obtaining improved properties resulting from intercalation and exfoliation of organoclays. Organoclay dispersions in monomer were polymerized in bulk,^[9-15] solution,^[16-21] and also in aqueous emulsions.^[22-33] Alternatively, extrusion of polymer melts was employed successfully to prepare thermoplastic organoclay nanocomposites.^[34–36] A large number of publications have addressed the influence of the organoclay preparation processes and of the swelling agent on morphology and material properties, including investigations of enhancing exfoliation by polymerization in intergallery spacings. However, almost all approaches require syntheses of at least two steps. Usually, the organoclay is produced by exchanging the intergallery cation in aqueous solution in the presence of the organic swelling agent. The consecutive washing, drying, milling, and dispersing of the resulting organoclay represent time-consuming and relatively costly steps required prior to the polymerization. One of the few attempts to bypass two-step procedures has been conducted by Huskić et al.,^[21] reporting the solution polymerization of MMA in a dispersion of pristine montmorillonite in a mixture of ethanol, water, and varying quaternary ammonium ions. Resulting nanocomposites were determined to exhibit intercalated morphologies and enhanced thermostability. However, this one-step approach required the use of solvents and was restricted to matrix polymers soluble in the polar solvent mixture.

Here we report on a novel solvent-free "one-pot" process, illustrated in Scheme 1, for producing PU, PS, and PMMA nanocomposites based upon Ca-bentonites. Organophilic modification was achieved in situ by means of cation exchange of Ca²⁺ in the bentonite interlayer spacings for alkyl ammonium phosphates, prepared by neutralizing alkyl amines with the equivalent amount of phosphoric acid. Ester and methacrylate-functionalized stearyl amines were obtained by means of Michael Addition of stearyl amine with methyl acrylate or 2-methacryloxy-ethyl acrylate with exclusive reaction of the acrylate groups at



Scheme 1. Solvent-free "one-pot" process for the formation of nanocomposites containing insitu-formed calcium phosphate/layered silicate hybrid nanoparticles. a) Protonation of alkyl amines with equivalent amounts of phosphoric acid, b) cation exchange of intergallery Ca^{2+} by quaternary alkyl ammonium cations, accompanied by the simultaneous precipitation of calcium phosphate, c) swelling of organophilic calcium phosphate/layered silicate hybrid nanoparticles with monomer, and d) polymerization and in situ formation of intercalated and fully exfoliated nanocomposites.

ambient temperature.^[37] The interlayer cation exchange and insitu organophilic bentonite modification is accompanied with massive swelling in monomers and the precipitation of calcium phosphate, thus forming novel calcium phosphate/layered silicate hybrid nanoparticles in monomers such as styrene, methacrylate, and polyol prior to polymerization. This simple "one-pot" process does not require conversion of calcium bentonite into sodium bentonite and eliminates the need for extensive washing, drying, milling, and dispersion technology typical for organoclay preparation in aqueous medium.

2. Results and Discussion

2.1. PMMA and PS Nanocomposites Containing in situ Formed Calcium Phosphate/Layered Silicate Hybrid Nanoparticles

Natural Ca-bentonite was rendered organophilic by means of ion exchange using protonated stearyl amine, stearyl di(methoxycarbonylethyl) amine (SAE), or stearyl di(2-methacryloxyethyl carbonylethyl) amine (SAMA). The ester-functionalized tertiary amine (SAE) and the methacrylate-functionalized tertiary amine (SAMA) were synthesized via a Michael Addition of stearyl amine with methyl acrylate or 2-methacryloxyethyl acrylate (EGAMA) with exclusive reaction of the acrylate group at ambient temperature. This Michael Addition chemistry represents a very versatile tool to match the polarity and reactivity of bentonite organophilic modifiers with those of the monomers. The alkyl amines were protonated with the equivalent amount of phosphoric acid in MMA or styrene solution in order to produce swelling agents for calcium bentonite, respectively. Amine and acid content were equimolar to the Ca-bentonite's cation exchange capacity of 0.8 meg g^{-1} . Then Ca-bentonite was added and the cation ion

exchange of the bentonite's intergallery Ca²⁺ afforded organophilic bentonite modification accompanied by swelling and the simultaneous precipitation of calcium phosphate. Stable dispersions were formed under high shearing conditions (Ultrathurax) and polymerization was initiated at 60 °C. In order to examine the influence of calcium phosphate/layered silicate hybrid particles on morphology and mechanical properties of the composite system, the content of organoclay was varied from 5 to 15 wt%. The composites' stiffness, measured as Young's modulus, and fracture toughness, determined as critical stress intensity factor K_{1c} (mode 1) are summarized in Table 1. As reference, nonmodified PMMA and PS, prepared under identical conditions, were included. Samples are labeled FAx/polymer with FA representing the organophilic functionalization agent used in hybrid nanoparticle preparation, x representing the filler content in wt%, and polymer relating to the polymeric matrix of the nanocomposite material.





Table 1. Med	hanical pro	perties of	PMMA	and P	PS nanoc	omposites.
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Sample	Organoclay content [wt%]	Young's modulus [MPa]	$K_{1c} [MN m^{-3/2}]$		
РММА	0.0	2650 ± 20	1.52 ± 0.08		
SA5/PMMA	5.0	2800 ± 90	$\textbf{0.84} \pm \textbf{0.06}$		
SA10/PMMA	10.0	3180 ± 55	$\textbf{0.78} \pm \textbf{0.05}$		
SA15/PMMA	15.0	3250 ± 25	$\textbf{0.88} \pm \textbf{0.07}$		
SAE5/PMMA	5.0	2990 ± 60	$\textbf{0.79} \pm \textbf{0.12}$		
SAE10/PMMA	10.0	$\textbf{3220} \pm \textbf{90}$	$\textbf{0.65} \pm \textbf{0.11}$		
SAE15/PMMA	15.0	3280 ± 60	$\textbf{0.69}\pm\textbf{0.06}$		
SAMA5/PMMA	5.0	2920 ± 20	$\textbf{0.75}\pm\textbf{0.06}$		
SAMA10/PMMA	10.0	2980 ± 55	0.54 ± 0.02		
SAMA15/PMMA	15.0	3150 ± 90	$\textbf{0.57}\pm\textbf{0.06}$		
PS	0.0	3440 ± 60	1.31 ± 0.10		
SA5/PS	5.0	3510 ± 95	$\textbf{2.15} \pm \textbf{0.13}$		
SA10/PS	10.0	$\textbf{3620} \pm \textbf{95}$	1.04 ± 0.04		
SA15/PS	15.0	3820 ± 90	$\textbf{1.16} \pm \textbf{0.10}$		
SAE5/PS	5.0	3590 ± 50	$\textbf{0.80}\pm\textbf{0.05}$		
SAE10/PS	10.0	3740 ± 100	$\textbf{0.70}\pm\textbf{0.05}$		
SAE15/PS	15.0	4060 ± 120	$\textbf{0.70}\pm\textbf{0.05}$		
SAMA5/PS	5.0	3650 ± 100	$\textbf{0.60}\pm\textbf{0.10}$		
SAMA10/PS	10.0	3780 ± 100	$\textbf{0.70}\pm\textbf{0.05}$		
SAMA15/PS	15.0	4070 ± 160	$\textbf{0.50}\pm\textbf{0.05}$		

It is well known that the organoclay content has a major influence on the mechanical properties of nanocomposites.^[38] From Figure 1a it is apparent that in the case of PMMA–layered silicate nanocomposites, the Young's Modulus significantly increases with increasing filler content for all swelling agents used, while the amount of stiffening is dependent on the type of swelling agent. At a filler content of 15 wt%, the modulus is increased by about 23% in the case of SA, 24% in the case of SAE, and 19% in the case of SAMA with respect to pure PMMA.

A similar tendency can be observed for the PS–layered silicate composites. As shown in Figure 1b, the stiffness of the PS composites also increases with increasing organoclay content. At an organoclay content of 15 wt%, the stiffness was enhanced by about 11% for SA15/PS and 18% in case of both SAE15/PS and SAMA15/PS with respect to pure PS.

In Figure 2 the composites' critical stress intensity factor K_{1c} is plotted as a function of organoclay content. For the PMMA composites (Fig. 2a), no significant decrease of the stress intensity factor was obtained with increasing content of hybrid nanoparticles. All nanocomposites show a significantly lower stress factor with respect to the value of pure PMMA $(1.52 \text{ MN m}^{-3/2})$. The fracture toughness of respective PS nanocomposites are summarized in Figure 2b. In case of SAE/PS and SAMA/PS, only a very small influence of the filler content on the K_{1c} was detected. A different behavior can be observed for the SA/PS samples. The intensity stress factor of SA/PS runs through a maximum of $2.15 \text{ MN m}^{-3/2}$ for SA5/PS, representing a fracture toughness increase of 65% with respect to pure PS ($1.31 \text{ MN m}^{-3/2}$). For higher organoclay contents, the stress intensity factor decreases to $1.04 \text{ MN m}^{-3/2}$ for SA10/PS and $1.16 \text{ MN m}^{-3/2}$ for SA15/PS. SA/ PS nanocomposites offer the opportunity to obtain materials that exhibit either significantly increased toughness combined with the stiffness of pure PS at low filler contents, or increased stiffness combined with the toughness of PS when incorporating more than



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Figure 1. Young's Modulus of a) PMMA–layered silicate composites and b) PS–layered silicate composites, prepared with protonated SA (■), SAE (•), and SAMA (▲) as swelling agents.

10 wt% of calcium phosphate/layered silicate hybrid nanoparticles.

The structure of montmorillonite consists of 2D layers formed by fusing two silica tetrahedral sheets to an edge-shared octahedral sheet of aluminium hydroxide. Stacking of the layers of clay particles is held by weak dipolar or van der Waals forces.^[39] Figure 3 shows the X-ray diffraction patterns of the unmodified clay compared with that of PMMA or PS composites with a filler content of 15 wt%. The Ca-bentonite pattern shows a d_{100} peak at $2\Theta = 5.9^{\circ}$, which corresponds to an interlayer distance of d = 1.5 nm. In all PMMA composites the 2 Θ value is shifted towards smaller angles, reflecting the increase of the interlayer distance caused by intercalation of the various swelling agents. The basal spacing of SA15/PMMA was determined to be 3.5 nm, and that of SAE15/PMMA to be 3.7 nm. In the case of SAMA15/ PMMA, a shoulder at about 5.1 nm was observed. The degree of intercalation or exfoliation is not only influenced by the type of the swelling agent, but also by the filler content. With decreasing bentonite content, an increasing interlayer spacing was observed. In Table 2, results of all wide-angle X-ray scattering (WAXS) investigations are listed. The highest interlayer distances were found for the samples SAMA/PMMA, in which the swelling agent

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Figure 2. Critical stress intensity factor of a) PMMA–layered silicate composites and b) PS–layered silicate composites, prepared with SA (\blacksquare), SAE (•) and SAMA (▲) as swelling agents.

exhibits polymerizable methacrylate moieties. In this case, intergallery spacings of up to 5.2 nm were achieved. The WAXS spectra of the PS–calcium phosphate/layered silicate composites with filler contents of 15 wt% are displayed in Figure 3b. No signals were observed in the range between 1 and 5.9° (8.8 and 1.5 nm). The WAXS spectra suggest that the silicate layers are either exfoliated in the polymer matrix or exhibit interlayer spacings higher than 8.8 nm. Samples with lower organoclay contents show similar behavior in WAXS investigations, regardless of the swelling agent used (Table 2).

The nanocomposite morphologies were examined by means of transmission electron microscopy (TEM). As shown in WAXS measurements, the best results of intercalation and of exfoliation were obtained in the case of nanocomposites with low content of bentonite using SAE or SAMA as swelling agent. Figure 4 shows nanocomposites containing 5 wt% SA-swollen bentonite in a PMMA (Fig. 4a) and a PS matrix (Fig. 4b). Fairly large silicate particles are visible. In both systems, mostly intercalated structures were obtained, although no clear reflexes can be observed in WAXS measurements of SA5/PS. In the case of SA5/PS, the composite morphology appears to show an ideal combination of matrix ligaments, single silicate layers, and



Figure 3. WAXS traces of nanocomposites containing 15.0wt% hybrid nanoparticles modified with SA, SAE, and SAMA in comparison to a) natural Ca-bentonite and PMMA nanocomposites and b) natural Ca-bentonite and PS nanocomposites.

 Table 2. Interlayer spacings of PMMA- and PS-calcium phosphate/layered

 silicate composites calculated from WAXS measurements.

Swelling agent	Organoclay content [wt%]	Organoclay d ₀₀₁ in ontent [wt%] PMMA [nm]		
SA	5.0	4.3[a]	> 8.8[b]	
SA	10.0	4.1[a]	> 8.8[b]	
SA	15.0	3.5	> 8.8[b]	
SAE	5.0	4.9[a]	> 8.8[b]	
SAE	10.0	4.3[a]	> 8.8[b]	
SAE	15.0	3.7	> 8.8[b]	
SAMA	5.0	5.2[a]	> 8.8[b]	
SAMA	10.0	5.1	> 8.8[b]	
SAMA	15.0	5.1[a]	> 8.8[b]	

[a] Reflexes cannot be assigned exactly and represent approximate values.[b] Interlayer spacings exceeding 8.8 nm cannot be detected due to overlap with the primary X-ray beam.





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Figure 4. TEM images of composites swollen in situ with protonated stearylamine: a) SA5/ PMMA and b) SA5/PS.

aggregates of intercalated layers, accounting for additional energy dissipation during fracture, which leads to the increased fracture toughness with respect to pure PS.

From Figure 5 it is obvious that composites with swelling agents, protonated SAE and SAMA, lead to more homogeneously dispersed hybrid particles. SAE swollen clay in a PMMA matrix shows large areas with anisotropically distributed fully exfoliated silicate nanoplatelets. Other silicates form an intercalated system

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responsible for the signal at 3.7 nm in WAXS measurements (Fig. 5a). In SAE5/PS (Fig. 5b), individual layers as well as stacks of two to four layers are dispersed within the matrix. Similar results were obtained for the composite SAMA5/PMMA (Fig. 5c). While WAXS traces of the sample SAMA5/PMMA indicate an intergallery spacing of about 5.1 nm, measurements showed no signals for SAE5/PS. In the case of SAMA5/PS, parallel arranged individual silicate layers are observed (Fig. 5d). With an average intergallery spacing of more than 5 nm, the 2Θ angle in WAXS investigation is too close to the primary X-ray beam to detect clear signals.

The exchange of Ca²⁺ ions by organophilic ammonium phosphates was accompanied by precipitation of calcium phosphates, such as

CaHPO₄ or Ca₃(PO₄)₂. To localize the salts, energy dispersive X-ray (EDX) line-scan measurements were conducted (Fig. 6). The silicon signal clearly shows the distribution of silicate as function of the distance from the origin. Peaks of calcium and phosphorus are located exclusively in the same positions as silicon. The results confirm the formation of calcium phosphate/layered silicate hybrid nanoparticles by precipitation of CaHPO₄ and Ca₃(PO₄) at the interfaces of the silicate nanoplatelets.



Figure 5. TEM images of nanocomposites swollen in situ with protonated tertiary amines: a–b) intercalated and exfoliated silicate layers in SAE5/PMMA (a) and in SAE5/PS (b); c–d) higher intergallery spacings and exfoliated layers in SAMA5/PMMA (c) and SAMA5/PS (d).

2.2. PU and PU-Foam Nanocomposites Containing Calcium Phosphate/Layered Silicate Hybrid Nanoparticles via in situ Swelling

Polyurethane composites were prepared using a trihydroxy-terminated oligo(propylene oxide) (Desmophen PU-IK-01) as monomer, in which stearyl amine was protonated by phosphoric acid. Amine and acid content were equimolar to the Ca-bentonites cation exchange capacity of 0.8 meq g^{-1} . Addition of 4 wt% of Ca-bentonite resulted in the exchange of stearyl ammonium ions with the bentonite's intergallery Ca²⁺ ions and simultaneous precipitation of calcium phosphate. Consecutive high shear treatment leads to a uniform dispersion of calcium phosphate/layered silicate nanoparticles in the polyol (PU-SA-bent). This dispersion was crosslinked by the addition of the methylene diphenyl diisocyanate (Baymidur-KL-3-5002) without any further purification. Morphology investigations revealed a homogeneous distribution of swollen inorganic hybrid particles in the PU matrix. Particle sizes were determined to be in the range of 20-1500 nm in the case of PU-SA-bent, while the particle diameters of nonswollen calcium bentonite in sample PUbent were determined to be more than $10 \,\mu m$ (Fig. 7a). Intercalated structures with an average





Figure 6. EDX line-scan of SAE10/PMMA: a) scanning vector and b) element distribution as a function of position, showing Ca-phosphates to be located in close proximity of silicate layers.



Figure 7. TEM images of PU composite materials: a) untreated primary bentonite particles (dark) in bulk PU matrix (bright) in PU-bent, b) homogenously distributed hybrid particle fragments showing intercalated silicate layers after swelling in situ with stearyl amine and phosphoric acid (PU-SA-bent), and c–d) PU foam containing exfoliated and intercalated silicate layers compatibilized by swelling in situ with polyols featuring protonated amine moieties (PU-f-H₃PO₄-bent). Ca-bentonite content is 4 wt% in all composite materials.

interlayer distance of 2.8 nm were observed in the case of PU-SA-bent (Fig. 7b). One can assume that the incorporation of the quaternary ammonium ions in the silicate layers led to massive swelling and intercalation of the primary particles of the Ca-bentonite. In the case of PU-bent, the major part of the inorganic filler settled at the bottom of the mold due to the ineffective dispersion of the large primary particles.

Tensile tests were carried out in order to investigate the mechanical properties of the PU-composites. The results are displayed in Table 3. In comparison to the unfilled polyurethane (PU-pure), the modulus of the filled samples increased by about 210% in the case of PU-bent and 160% in the case of PU-SA-bent. Polymer composites filled with inorganic materials often show increased stiffness compared to the corresponding matrix materials. This stiffening effect is commonly aligned with a decrease in toughness.^[7] For elastomeric materials, toughness can be described with the elongation at break. While the elongation at break in PU-bent was in the order of magnitude of the unfilled sample, it was significantly enhanced by about 160% for PU-SA-bent. The extraordinary effect of the swelling procedure on composite materials' toughness may be explained with the different morphologies observed. Within PU-composites with natural Ca-bentonite, few large silicates agglomerates are divided by broad matrix ligaments. The fracture behavior of the unfilled matrix material dominates the composites overall performance, which is reflected in a comparable elongation at break. Better dispersion of the filler within the PU matrix, along with enhanced interaction



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Table 3. Mechanical properties of PU-pure, PU-bent, and PU-SA-bent.

Sample	Young's modulus [MPa]	Elongation at break [%]
PU-pure	0.7 ± 0.2	140 ± 25
PU-bent[a]	1.5 ± 0.2	145 ± 10
PU-SA-bent	1.1 ± 0.2	220 ± 20

[a] Bentonite precipitated during polymerization process.

strength due to compatibilization, intercalation, and exfoliation allows additional mechanisms of energy dissipation to become efficient in PU-SA-bent nanocomposites. The specific changes in the fracture mechanism that lead to increased toughness were not further investigated in this work, but it is well known from the literature that nanocomposites, especially when featuring intercalated silicate layers, facilitate energy dissipation in the form of local plastic deformation, crack pinning, and crack deflection.^[40]

PU-foam composites containing calcium phosphate/layered silicate hybrid nanoparticles were prepared using an aminefunctionalized polyether polyol derived from ethylene diamine and propylene oxide (Lupranol 3402). The tetrafunctional polyol contains two tertiary amine groups. The polyol was dissolved in water and amine groups were partially protonated upon addition of phosphoric acid. The cation exchange process took place in the reactive solution by adding Ca-bentonite. After water was removed, a PU-foam was prepared upon crosslinking with methylene diphenyl diisocyanate (PU-f-H₃PO₄-bent). Morphological investigations by scanning electron microscopy (SEM) and TEM revealed pore sizes in the range of 100 µm. Single silicate layers as well as particles with diameters up to 300 nm were homogeneously distributed in the PU matrix, indicating that the untreated bentonite particles (with diameters of several micrometers) were exfoliated during the swelling process. The accumulation of the hydrophilic inorganic filler at the interface air/polymer, typical for some conventional PU nanocomposite foams, was not observed, most likely due to the very high wettability of the polyol. Exfoliated as well as intercalated structures with an average interlayer distance of 1.9 nm were found (Fig. 7c,d).

3. Conclusions

A versatile "one-pot" process for the formation of nanocomposites containing calcium phosphate/bentonite hybrid nanoparticles was developed. Amine functionalization, protonation with phosphoric acid, cation exchange with calcium bentonite, intercalation, exfoliation, and polymerization were performed in bulk monomers such as styrene, methyl methacrylate, and polyols without requiring solvents. Moreover, extensive purification associated with conventional organoclay preparation and special milling and dispersing processes were eliminated. Various primary and tertiary amines proved to be very effective swelling agents for calcium bentonite when the amines were protonated with phosphoric acid in monomer solution. Methacrylatefunctionalized amines prepared in situ via Michael Addition of stearyl amine with 2-methacryloxyethyl acrylate and protonated with phosphoric acid produced methacrylate-functionalized organoclay by means of cation exchange. Such methacrylate-



functionalized bentonites are highly reactive and can copolymerize in free radical polymerization. Such organoclays are difficult to handle in conventional multistep nanofiller preparations with drying temperatures at which polymerization of the methacrylate groups and crosslinking of the nanoparticles can occur. Moreover, methacrylate-functional bentonites can copolymerize and account for the effective attachment of styrene and acrylic polymers to the nanoparticle surfaces. Such attachment was also achieved for polyurethanes when protonated amine-functionalized polyether polyols were used as monomer components. During the cation exchange of calcium cations for alkyl ammonium ions, the in situ organophilic modification of bentonite was accompanied by swelling and precipitation of calcium phosphates exclusively on the bentonite nanoplatelet interfaces. The resulting novel calcium phosphate/layered silicate nanoparticles were effectively dispersed in the monomer and afforded good adhesion between nanoparticles and polymer matrix. Moreover, this "one-pot" process enabled effective intergallery polymerization and attachment of polymer chains, which accounted for excellent nanoparticle dispersions, nanoparticle adhesion, and energy dissipation at the crack tip. In conclusion, the one-pot process represents a very versatile method for the preparation of nanocomposites and for upgrading and diversifying thermoplastics, engineering plastics, thermosets, elastomers, adhesives, and coatings. Toughness/stiffness balances of polymers such as styrenics, acrylics, and polyurethanes can be improved significantly. Synergisms appear feasible when hybrid nanoparticles are dispersed in multiphase polymers such as rubber-toughened styrenics and fiber-reinforced polymers. Alkyl ammonium phosphate-functionalized polyols together with calcium bentonites represent attractive intermediates for the preparation of polyurethane nanocomposite and nanoparticle-armored polyurethane foams.

This solvent-free "one-pot" process with its "functionalized nanoparticle tool box" can be exploited for many formulated systems based upon bulk polymerization of monomers such as styrene, acrylics, isocyanates, and also other thermoset resins.

4. Experimental

Materials: Ca-bentonite EXM 918, which represents a natural montmorillonite, was supplied by Süd-Chemie, Moosburg, Germany. The negative charge of the silicate layers is compensated by Ca²⁺ ions in the interlayer galleries. The cation exchange capacity (CEC) was 0.8 meg g⁻ The interlayer spacing calculated from WAXS was 1.47 nm. Methyl methacrylate and styrene (Fluka, Germany) were distilled under reduced pressure and stored over a 3 Å molecular sieve. The following commercial products were used as received: Ethoquad C12 (Akzo-Nobel, Germany); Lupranol 3402, Lupranat M50, and Accelerator NL64-10P (BASF, Germany); Desmophen PU21-IK-01 and Baymidur KL-3-5002 (Bayer, Germany); stearyl amine (SA), triethyl amine, and 2-hydroxyethyl methacrylate (Aldrich, Germany); 2,2'-azoisobutyronitrile (AIBN), methyl acrylate and acryloyl chloride (Fluka, Germany); phosphoric acid 85% (Merck, Germany); [2-(methacryloy-l-oxy)-ethyl]trimethyl ammoniumchloride (MOETACl; Röhm, Germany); and 2,2'-azobis-(isobutyl amidine hydrochloride) (AIBA; WAKO, Germany).

Synthesis of Swelling Agent, Stearyl Di(methoxycarbonylethyl) Amine (SAE): Methyl acrylate (29.20 g, 0.340 mol) was dissolved in a toluene/ methanol mixture (150 mL, 16/10). To the resulting solution, stearyl amine (45.75 g, 0.170 mol), dissolved in a toluene/methanol mixture (500 mL, 16/ 10), was added at 0-5 °C under stirring within 3 h. After completion of the

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Scheme 2. Structure of SAE.

addition, the mixture was allowed to react for a further 24 h at room temperature. Then the solvent was evaporated and the product (see Scheme 2) was dried under vacuum. Yields of up to 93% were obtained.

¹H-NMR (300 MHz, CDCl₃): δ = 3.69 (22), 2.88 (19), 2.60 (20), 2.53 (18), 1.50–1.26 (2-17), 0.88 (1); ¹³C-NMR (75.4 MHz, CDCl₃): δ = 174.6 (21), 55.2 (18), 52.9 (22), 51.1 (19), 35.8 (20), 24.0–33.9 (2–17), 15.4 (1).

Synthesis of Swelling Agent, Stearyl Di(2-methacryloxyethyl carbonylethyl) Amine (SAMA): 2-Methacryloxyethyl acrylate (EGAMA) was prepared according to a synthesis reported by Luchtenberg and Ritter [41]. In short, acryloyl chloride was slowly added to a solution of 2-hydroxyethyl methacrylate and triethyl amine in toluene at 0–5 °C. After completion of the reaction, precipitated triethyl ammonium chloride was removed by filtration and the solvent was evaporated. The resulting product was isolated by fractional vacuum distillation. Yields of up to 83% were obtained.

EGAMA (50.40 g, 0.273 mol) was dissolved in a toluene/methanol mixture (180 mL, 16/10). To the resulting solution, stearyl amine (36.77 g, 0.137 mol), dissolved in a toluene/methanol mixture (600 mL, 16/10), were added at 0–5 °C under stirring within 2 h. After completing the addition, the mixture was allowed to react for a further 24 h at room temperature. The solvent was evaporated, and the product (see Scheme 3) was dried under vacuum. Yields of up to 94% were obtained.

¹H-NMR (300 MHz, CDCl₃): $\delta = 6.07$ (27b), 5.53 (27a), 4.27 (22, 23), 2.71 (19), 2.39 (18, 20), 1.89 (26), 1.20–1.24 (2–17), 0.82 (1); ¹³C-NMR (75.4 MHz, CDCl₃): $\delta = 174.0$ (21), 169.2 (24), 137.8 (25), 127.7 (27), 64.2 (23), 63.8 (22), 55.6 (18), 51.0 (19), 34.0 (20), 24.5–31.5 (2–17), 20.1 (26), 15.9 (1).



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Preparation of PMMA- and Polystyrene-Calcium Phosphate/Layered Silicate Nanocomposites: PMMAand PS-calcium phosphate/layered silicate nanocomposites with various swelling agents (SA, SAE, SAMA) and various organoclay contents (5, 10, 15 wt%) were prepared according to Table 4. Phosphoric acid (equimolar to amine content) was dissolved in MMA or styrene. The respective swelling agent (SA, SAE or SAMA) and Ca-bentonite were added. The mixture was stirred for 10 min using a magnetic stirrer and then dispersed using an Ultrathurax (10 min, 18 000 rpm). AIBN, dissolved in MMA or styrene, was added. The mixture was degassed and polymerized between two glass plates for 48 h at 60 °C in a water bath.

Preparation of Polyurethane-Calcium Phosphate/ Layered Silicate Nanocomposites: A mixture of trihydroxy-terminated oligo (propylene oxide) with a number average molar mass of 3800 g mol^{-1} (192 g, Desmophen PU-IK-01), stearyl amine (1.36 g), phosphoric acid (0.58 g), and Ca-bentonite (6.36 g) was dispersed using an Ultrathurax (IKA) at 18 000 rpm for 10 min. Amine and acid content were equimolar to the Ca-bentonites cation exchange capacity of 0.8 meg g^{-1} . Traces of water were removed at 100 $^\circ\text{C}$ and 3 mbar using a Molteni Planimax high shear mixer. After cooling to room temperature, the mixture was blended together with diisocyanato diphenyl methane isomers (17.6 g, 55 wt% 2,4isomer and 45 wt% 4,4'-isomer, isocyanate functionality: 2.0, Baymidur KL-3-5002). After stirring for 3 min at room temperature and 3 mbar to remove air bubbles, the mixture was poured into a mold (200 mm \times 200 mm \times 4 mm). Curing was performed at 80 °C for 24 h in a vented oven (PU-SAbent). For comparison, the pure matrix material (PU-pure) and a sample without organophilic compatibilization (PU-bent) were prepared.

For preparing polyurethane foams, a tetrafunctional polyether polyol derived from ethylene diamine and propylene oxide with an average molar mass of 480 g mol⁻¹ (18.8 g, Lupranol 3402) were diluted in distilled water (50 mL) and H₃PO₄ (85%, 1.01 g, 0.8 meq perg Ca-bentonite). Cabentonite EXM 918 (2.44 g) was added to the resulting mixture. After dispersion with an Ultrathurax (IKA) for 10 min at 18 000 rpm, the water was removed at 110 °C and 7 mbar using a Molteni Planimax high shear mixer. Tegostab B 8443 (0.4 g), *N*,*N*-dimethyl benzylamine (0.4 g, NL64-10P), 4,4'-diisocyanato diphenylmethane (30 g, functionality: 2.9, Lupranat M50) and distilled water (0.5 g) were added. The obtained PU-foam (Pu-f-H₃PO₄-bent) was stored at room temperature. For comparison, a sample without phosphoric acid was prepared (Pu-f-bent).



Scheme 3. Preparation of SAMA via Michael Addition.



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Table 4. Recipes for the preparation of nanocomposites of PMMA and PS containing calcium phosphate/layered silicate hybrid nanoparticles.

Chemicals		Sample, X=filler content [wt%]								
	SA X/PMMA or PS		SAE X/PMMA or PS		SAMA X/PMMA or PS			PMMA or PS		
	5	10	15	5	10	15	5	10	15	
MMA or Styrene [g]	285	270	255	285	270	255	285	270	255	270
H ₃ PO ₄ [g] [a]	1.14	2.27	3.41	1.02	2.04	3.07	0.92	1.83	2.75	3.41
SA [g]	2.66	5.30	7.98	_	_	_	-	_	_	-
SAE [g]	_	-	_	3.92	7.83	11.75	-	_	_	-
SAMA [g]	_	-	-	_	_	_	5.07	10.15	15.22	-
Ca-bentonite [g] [b]	12.34	24.68	37.02	11.08	22.17	33.25	9.93	19.85	29.87	-
AIBN _{MMA} [g] [c]	0.57	0.54	0.51	0.57	0.54	0.51	0.57	0.54	0.55	0.54
AIBN _{PS} [g] [d]	2.28	2.16	2.04	2.28	2.16	2.04	2.28	2.16	2.04	2.16

[a] $n_{acid}:n_{amine} = 1$. [b] CEC: 0.8 meq g⁻¹. [c] 0.2 wt% based on MMA. [d] 0.8 wt% based on styrene.

NMR: ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ using a Bruker ARX 300 spectrometer operating at 300 and 75.4 MHz, respectively.

Mechanical Testing: Test specimens were milled using a Mutronic Diadrive 2000 milling machine. Tensile tests were conducted using a Zwick tensiometer Z005 (ISO/DP527). The critical stress intensity factor K_{1c} was determined by measuring the maximal force at break of compact tension specimens on a modified Zwick tensile testing machine (Zwick 1340) equipped with a peak voltmeter (ERMA, Type U 568.01-FHI). The notch root was sharpened with a razor blade. Tensile loading (mode 1) was carried out with a deformation speed of 2 mm min⁻¹ [42]. Specimens were dried at 60 °C overnight prior to mechanical testing at room temperature.

WAXS: The interlayer distance of the layered silicates was studied by means of WAXS using a Siemens D5000 apparatus with Cu K_{α} radiation ($\lambda = 0.154$ nm).

TEM: Morphology was examined by TEM. For TEM measurements, ultrathin sections were prepared with an Ultracut E ultramicrotome (Reichert & Jung, Germany) equipped with a diamond knife. TEM measurements as well as EDX analysis were carried out on a LEO 912 Omega with an acceleration voltage of 120 keV.

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