Encapsulation of clay through non-aqueous dispersion polymerizations

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Encapsulation of clay through non-aqueous dispersion polymerizations

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op woensdag 31 oktober 2012 om 14.00 uur

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## 3. PREPARATION OF MICROMETER-SIZED POLYSTYRENE PARTICLES BY DISPERSION POLYMERIZATION IN POLYOLS

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General introduction.
In this chapter, we give a general overview on polymer clay nanocomposites and a general description of dispersion polymerization. The scope of the project and an outline of the thesis are presented.

1.1 Polymer clay nanocomposites

In polymer science one of the most fascinating research areas focuses on nanohybrids or nanocomposites, materials in which the components are mixed on a nanometer-length scale. The inclusion of inorganic nanoparticles in polymers enhances e.g. their mechanical properties, barrier properties and chemical resistance as compared to conventional composites. There are a number of types of nanofillers which can be defined by their dimensions (on the order of a few nanometers). In Figure 1A the nanoparticle has all three dimensions at the nanometer scale. Examples of these nanoparticles are nanocrystals, gold and other metal nanoparticles, block copolymers and spherical silica particles. If two dimensions of the nanoparticle are at the nanometer scale while the third is larger, then the particles have an elongated structure, as can be seen in Figure 1B. Nanofibers and nanotubes are examples of this group. The last type has only one dimension in the nanometer scale and they have a sheet-like structure, as shown in Figure 1C.

One of the most important sheet-like fillers used as reinforcing material is layered silicates and the reinforced polymers are referred to as polymer-clay nanocomposites (PCN). PCN are a new class of materials consisting of a nanometer-sized filler dispersed in a polymer matrix. The nanometer length scale of the filler dominates the morphology.

![Figure 1: Schematics of (A) Nanosphere, (B) Nanofiber, and (C) Sheet-like colloidal particle.](image-url)
and properties of these materials, producing better property enhancements than those obtained from conventional fillers.\(^9\)

Clay as filler has received attention in the last decades because of the low cost of the inorganic component, the relatively simple incorporation in hydrophilic and hydrophobic polymers and the fairly predictable stiffening behaviour when introduced into polymers.\(^{10-11}\) Indeed because of their high aspect ratio, clay platelets of a few nanometers thickness and several nanometers length allow a substantial enhancement in material properties when incorporated in polymer matrices.\(^{12-13}\)

In our work, attention is given to a 2-dimensional system of clay platelets which are silicate layers of nanometer thickness with a high aspect ratio, dispersed in a polymer matrix. The clay minerals are composed of a certain group of layered crystalline silicate minerals. Minerals include Vermicullite, Smectites and Micas. In this thesis we only focus on Montmorillonite (MMT), a member of the Smectite clay family. A layer of minerals of MMT is made up one central octahedral sheet sandwiched between two parallel tetrahedral sheets and thus forming a unit layer referred to as “tetrahedral-octahedral-tetrahedral” (TOT) as shown in Figure 2 with a single layer thickness of 9.6 Å. In MMT, tetrahedral layers of \([\text{SiO}_4]\) surround the octahedron layer \([\text{AlO}_5, \text{OH}]\). Isomorphous substitutions of \(\text{Si}^{4+}\) by \(\text{Al}^{3+}\) in the tetrahedral layer and \(\text{Al}^{3+}\) by \(\text{Mg}^{2+}\) in the octahedral site cause an excess of negative charges within the MMT layers. The charges are counter balanced with \(\text{Na}^+\) ions and because of its hydrophilicity, water molecules are also present between the layers. The stacking of the layers leads to a regular Van der Waals gap called gallery spacing, \(d\)-spacing or interlayer spacing.
Figure 2: Schematic representation of Montmorillonite structure, showing the two tetrahedral sheets fused to one octahedral sheet and their isomorphic substitutions.\(^6\)

Because clay is hydrophilic it is not compatible with most polymers and must be chemically modified to produce a more hydrophobic surface. This is commonly done in an aqueous system containing molecules with a long aliphatic tail (C\(_{16}\)\textasciitilde C\(_{18}\)) and quarternary ammonium cations as a head. Replacing the cations in the interlayer by the ammonium molecules leads to an increase in the interlayer distance and facilitates exfoliation.\(^{14-19}\)

Another surface functionalization route consists of using alkoxy silanes as coupling agent. The silanol group on the edge of the clay platelet reacts via a condensation reaction with the alkoxy silane.\(^{20-26}\)
1.2 Types of polymer clay nanocomposites

Polymer clay nanocomposites (PCN) are divided into three main morphologies, as can be seen in Figure 3: segregated, intercalated and exfoliated. In the exfoliated state all the clay platelets have delaminated and consist of individual platelets well dispersed in the continuous polymer matrix, whereas in the intercalated state the clay is penetrated by polymer causing a finite and regular expansion between the clay layers. In general the biggest enhancement in clay polymer nanocomposite properties is observed in the exfoliated state. This is generally regarded as the ideal morphology and its requirements have stimulated the development of many PCN routes.

In conventional composites, the clay acts as a conventional filler and forms an aggregated layered structure, immiscible with the continuous polymer matrix.

There are two main methods for the characterization of the polymer clay nanocomposites. The easiest one is X-ray diffraction (XRD) in which an increase in d-spacing of the clay can be observed. Transmission electron microscopy (TEM) is a technique to study the structure of submicrometer particles.

Transmission electron microscopy (TEM) is the most commonly used method to characterize the microstructure of the nanocomposites. Figure 3 shows TEM micrographs depicting the various morphologies of the PCN structures. In the exfoliated morphology the black lines are the individual clay platelets, uniformly dispersed. On many occasions, bending and folding of the platelets have been observed.

The microstructure of the intercalated structure shows a well-ordered multi-layer morphology consisting of alternate polymer and inorganic layers. The exfoliated morphology does not generate any diffraction signal owing to the loss of periodicity and the absence of diffraction peak is taken as a proof of the generation of exfoliated nanocomposites.

In the phase-separated morphology the filler is not at all intercalated by the polymer chains and the thick filler tactoids are present and separated from the polymer phase.
Scanning Electron Microscopy (SEM) is another powerful technique to investigate submicrometer particles. Combining SEM and TEM generally provides complete information for the morphologies of nanoparticles\(^\text{34}\).

XRD is used to quantify the amount of increase in the basal plane spacing in the clay after a surface modification as well as in the PCN. The increased basal plane spacing after the surface exchange leads to information regarding the possible alignment of the modified molecules inside the clay interlayer, whereas the presence or absence of diffraction peaks in the composites is used to assess information about the microstructure of the composites. XRD also provides information about the amount of organic matter present in the clay interlayers. However, it cannot provide information on the excess of the surface modification molecules present on the clay surface. The latter can be provided by thermogravimetric analysis. As mentioned above, the intensity of the X-ray diffraction patterns is generally taken as a measure to classify the microstructure as intercalated or exfoliated. It should be noticed that the X-ray signals are qualitative and therefore, the classification of the nanocomposite microstructure just based on intensity can be wrong. Also, the presence of diffraction signals in the diffractograms of the composite does not mean that 100\% of the microstructure is intercalated and it is quite possible to have a significant degree of exfoliation present in the composite. Similarly, the absence of diffraction signal also does not guarantee complete exfoliation, as small or randomly oriented intercalated platelets may still be present in the composite. As an example, in Figure 3, the XRD patterns are shown for the exfoliated, intercalated and segregated states.
1.3 Preparation of encapsulated clay nanocomposites

Encapsulation techniques have received considerable attention because of their function in delivery or release controlling, protection and better dispersion in a polymer matrix. Encapsulation can be used in a pharmaceutical application to control or delay the release of the encapsulated ingredient. The technique can also protect products of pharmaceutical and food industry from oxidation and moisture. Examples regarding the use for a better dispersion in polymer are encapsulation of inorganic particles for the use in coatings, inks, packaging and filler plastics.

The benefits of encapsulating inorganic particles for the use in polymers are for example: improved mechanical properties, protection of the polymer matrix from interaction with
the inorganic particles, improved barrier properties, improved thermal stability and of course better particle dispersion in the polymer matrix.

Many researchers have focused on the preparation of PCN dispersions in water using emulsion and miniemulsion polymerization. Some studies showed that clay can be successfully exfoliated under these conditions.\textsuperscript{36-40} Dispersion polymerization is one amongst other techniques used to produce a polymer dispersion. It is a simple and fast method to obtain monodisperse polymer particles of range of 1-20 \(\mu\)m, in very good yields.\textsuperscript{41} The polymerization of a monomer in a dispersion polymerization is carried out in the presence of a second polymer soluble in the reaction medium.\textsuperscript{42} Because this second polymer can act as a steric stabilizer to prevent the flocculation of growing particles it must be amphiphilic and it must contain both an anchor segment, with affinity for the final polymer particles, and a solvent soluble segment. Three types of steric stabilizers have been used: homopolymers, block and graft copolymers, and macromonomers.\textsuperscript{43} At the moment, to the best of the author’s knowledge, there are only few articles that reported on the preparation of PCN via dispersion polymerization, and only intercalated and partially exfoliated structures have been obtained.\textsuperscript{44-45}

1.4 General description of dispersion polymerization

A variety of heterogeneous polymerization systems exist of which dispersion polymerization is one of them.\textsuperscript{46-47} These systems are summarized in Table 1. Heterogeneous processes are usually two-phase systems in which the starting monomer and/or the resulting polymer are in the form of a fine dispersion in an immiscible liquid. The initiator may be soluble in the monomer or in the liquid and it may or may not be present within the polymer particles during their formation. The heterogeneous polymerization systems can be clearly distinguished on the basis of the following four criteria:

1) Initial state of the polymerization

2) Kinetics of polymerization
3) Mechanism of particle formation

4) Shape and size of the final polymer particles

**Table 1: The different types of heterogeneous polymerization methods.**

<table>
<thead>
<tr>
<th>Type</th>
<th>Typical particle radius</th>
<th>Droplet size</th>
<th>Initiator</th>
<th>Discrete phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion</td>
<td>≥ 1 μm</td>
<td>-</td>
<td>Oil-soluble</td>
<td>Initially absent, monomer-swollen polymer particles form</td>
</tr>
<tr>
<td>Emulsion</td>
<td>50-300 nm</td>
<td>1-10 μm</td>
<td>Water-soluble</td>
<td>Initially absent, monomer-swollen polymer particles form</td>
</tr>
<tr>
<td>Precipitation</td>
<td>≥ 1 μm</td>
<td>Monomer usually water soluble</td>
<td>Water-soluble</td>
<td>As in ordinary emulsion polymerization, but monomer does not swell polymer</td>
</tr>
<tr>
<td>Suspension</td>
<td>≥ 1 μm</td>
<td>1-10 μm</td>
<td>Oil-soluble</td>
<td>Monomer + formed polymer in pre-existing droplets</td>
</tr>
<tr>
<td>Micro-emulsion</td>
<td>10-30 nm</td>
<td>10 nm</td>
<td>Water-soluble</td>
<td>Monomer, co-surfactant + formed particle</td>
</tr>
<tr>
<td>Inverse emulsion</td>
<td>100-1000 nm</td>
<td>1-10 μm</td>
<td>Water-soluble</td>
<td>Monomer, water + formed polymer</td>
</tr>
<tr>
<td>Mini-emulsion</td>
<td>30-100 nm</td>
<td>30 nm</td>
<td>Water-soluble</td>
<td>Monomer, co-surfactant + formed polymer</td>
</tr>
</tbody>
</table>

Dispersion polymerization currently receives a lot of attention for the preparation of monodisperse polymer particles on a micrometer scale (1-15 μm). Compared to other heterogeneous polymerization techniques, dispersion polymerization is attractive because it forms micro-spheres in a single-step process. These particles can be used in a
wide variety of applications, such as toners, instrument calibration standards, column packing materials for chromatography and biomedical and biochemical analysis.

The particle size range is difficult to achieve with other polymerization methods in a single-step technique. Close control of the reaction conditions is essential to achieve monodispersity of the prepared microspheres. Dispersion polymerization, unlike emulsion and suspension polymerizations are found to be free from effects due to stirring speeds and reactor geometry.

Dispersion polymerization starts as a homogeneous solution polymerization reaction, but as the polymer (or oligomer) chains grow in size they eventually reach a molecular weight higher than a certain critical value and segregate from the continuous phase. Colloidally unstable precursor particles are formed and the surface is stabilized.

These precursor particles coalesce and adsorb more stabilizers from the reaction medium onto their surface until they become colloidally stable. At this point, the total number of particles in the system is fixed, and the nucleation stage ceases.

In the particle growth stage, polymerization occurs either inside the swollen nuclei or in the reaction medium depending on the partitioning of monomer between the two phases. The newly formed polymers should not form additional nuclei but should be captured by existing particles.

The key issue for preparation of uniformly sized colloidal particles is a short nucleation stage. The particle number and particle size distribution are determined during the nucleation stage. No coagulum or secondary particles should be formed during the particle growth stage. A prolonged nucleation stage usually results in a broad particle size distribution. Furthermore, the nucleation stage in dispersion polymerization is very sensitive to variations in reaction components or conditions.
1.5 Dispersion polymerization components

The typical recipe contains monomer, initiator, steric stabilizer and solvent/non-solvent.

1.5.1 Monomers

The monomer is chosen based upon its miscibility with the reaction medium (but the produced polymer should be insoluble in the medium). Styrene (ST) and methyl methacrylate (MMA) are by far the most studied systems. For instance, a great deal of work has been done on preparation of monodisperse polystyrene (PST) particles in alcohol.\textsuperscript{48-50}

By increasing the monomer concentration in a dispersion recipe the solvency of the medium will also increase, which upon its turn should reduce the rate of adsorption of the stabilizer from the medium. In the same time the molecular weight of the polymer is increased. This is because in most cases the monomer acts as a good solvent for its own polymer and higher molar mass polymer is therefore formed at higher monomer concentrations. This also leads to an increase in the rate of polymerization and therefore more nuclei will form. These are able to grow larger in dispersions with higher monomer concentration.

Therefore the solvent phase in a dispersion polymerization consists of solvent and unpolymerized monomer. This is also a major difference with emulsion polymerization: the medium in the dispersion polymerization changes with polymerization time.

1.5.2 Initiators

The initiator should be soluble in the reaction medium in order to make a homogeneous mixture in the beginning of the polymerization. An increase in the concentration of initiator leads generally to an increase in particle size in almost every case. For comparison, in the PST stabilized by polyvinyl pyrrolidone (PVP) in ethanol system, larger particles are obtained at higher initiator concentrations because lower molecular weight
polystyrene is formed making the PVP:PST more soluble in the medium and less effective as stabilizer.

The production rate of initiator radicals \( (d[R^*]/dt) \) in a batch process obeys:

\[
d[R^*]/dt = 2f_k d[I] = 2f_k d[I]_0 e^{-k_d t}
\]

(1)

where \( f \) is the initiator efficiency, \( [I]_0 \) is the initial concentration of the initiator, \( t \) is the polymerization time, and \( [I] \) is the concentration of the initiator at \( t \); and \( f \) and \( [I]_0 \) are constants for a specific reaction system. The rate constant of thermal decomposition \( k_d \) is a function of temperature and obeys the Arrhenius equation:

\[
k_d = A_d e^{-E_d/R T}
\]

(2)

where \( A_d \) is the frequency factor, \( E_d \) is the activation energy of decomposition, \( R \) is the gas constant, and \( T \) is the absolute temperature. At any fixed temperature, \( k_d \) is a constant and \( (d[R^*]/dt) \) decreases exponentially.

Thus, the formation rate of radicals is the highest at the beginning of the reaction but decreases sharply as the reaction continues. That is, the concentration of formed oligomers is very high in the initial stage. It is difficult to capture all free radicals and nuclei in the continuous phase unless more stable particles are formed, so the particle formation stage extends and polydisperse particles are probably produced.

One could expect an increase in particle size with increasing temperature. Because with raising the temperature, \( k_d \) will increase and therefore also \( (d[R^*]/dt) \) will increase. More oligomers are formed in the initial stage of the dispersion polymerization and therefore an increase in the particle size could be expected. Low molecular stabilizers lead to larger particles.

1.5.3 Stabilizers

In dispersion polymerization electrostatic stabilizers, common in, e.g. emulsion polymerization, are not used because of the low dielectric constant of the medium. Three types of steric stabilizers are used instead. The first type of stabilizers is
homopolymers. During dispersion polymerization a graft forms by chain transfer from the growing oligomer to the initially present homopolymer stabilizer. In this process a graft copolymer is created and this is designated as the stabilizer in the system. The second type of stabilizers is polymers with two distinct segments, e.g. block – or graft – copolymers. The stabilizing moieties should be soluble in the continuous phase and the anchor group should have a composition similar to the polymer in the particles which should be stabilized. The third group of stabilizers is macro-monomers which can copolymerize with the principal monomer to rapidly generate graft copolymer species which on their turn act as stabilizer.

Figure 4 shows structures that may be taken into account for graft copolymers prepared using monomer A (homopolymer A) and monomer B (homopolymer B) as starting monomers.51-52

Figure 4: Schematic of possible structures of graft copolymers prepared by radical polymerization.; in red, soluble chains of polymer to be grafted, and in blue, insoluble chains of graft branches. (a-e) grafted copolymers; (f-i) block copolymers.
In dispersion polymerization, increasing the stabilizer concentration\textsuperscript{53} or its molecular weight generally decreases the particle size. Higher concentrations of stabilizers will cover a larger surface area and therefore lead to smaller particles.

The molecular weight of the stabilizer is also a factor because it is linked to the hydrodynamic volume. In the case of ethanol and ST/PST higher molecular PVP leads to smaller particles. But it is a delicate balance between improved stabilization by longer PVP chains and poorer adsorption of PVP:PST chains onto the particle surface. Paine et al.\textsuperscript{54} observed that PST containing adsorbed PVP chains from the medium are better soluble in the medium because the PVP:PST ratio is greater. The greater the solubility, the larger the particle size.

1.5.4 Solvents

In many cases alcohols are used as the solvent for dispersion polymerization. Water can be added but has merely the function of fine tuning the particle size or its distribution.

In this project an exotic solvent is used: polyether polyol or polyol for short. The polyols are reaction products of an organic oxide and an initiator compound containing two or more active hydrogens. If the initiator has two active hydrogens, a diol results. The molecular weights of the polyols range from 250 to 10,000 grams per mol.

The polyol acts as a raw material for polyurethane foam. The properties of the foam are influenced by the choice of polyol type. The foams are formulated by premixing the polyol with diisocyanate and thereafter curing the mixture.

1.6 Polyols

The use of polyols is common in the polyurethane (PU) industry for foam applications and is a source of hydroxyl reactive groups to produce polyurethane. Polyurethane foam is one of the most versatile materials available with a wide range of applications such as insulation, packaging and loadbearing configurations, e.g. cushioning in a seat or armrest.
The polyol used in this work is a polymeric reaction product of an organic oxide and an initiator compound containing two or more active hydrogen atoms, i.e. glycerol, and is schematically shown in Figure 5. The active hydrogen compound in the presence of a base catalyst initiates ring opening and oxide addition occurs until the desired molecular weight is obtained. The initiator is a trifunctional initiator, in this case glycerine, and addition of ethylene oxide (EO) or propylene oxide (PO) produces growth in three directions. A triol results as schematically depicted in Figure 4. In general the properties of the final polyol depend mainly on the type of oxide or the mixtures used.

![Figure 5: Schematic representation of the reaction between glycerine and propylene oxide or ethylene oxide yielding a trifunctional polyol.](image)

It is well known that PEO interacts favourably with the surface of clay platelets.\textsuperscript{55-59} There are also some studies\textsuperscript{60-63} in which clay is incorporated in PUR by dispersing the clay directly in the polyol prior to the PUR synthesis. The formed PUR shows better thermal stability and mechanical strength compared to the PUR with unfilled polyol.

Flexible foam manufactures using polyols containing inorganic fillers (e.g. BaSO\textsubscript{4} or CaCO\textsubscript{3}) observed that fillers act as nucleating agents during the foaming process and aid cell opening at the end of the rise process. Also the hardness or load bearing properties of the filled flexible foams are improved.

As with the inorganic fillers, the organic fillers can be used as filler that are useful in making foams of higher hardness than can be obtained using the unmodified polyol alone. The method is to synthesize the polymeric filler by a free radical dispersion polymerization\textsuperscript{64} in the polyol and the preferred monomers are acrylonitrile (ACN) and styrene (ST). The resulting product after co-polymerisation is an opaque polyol, generally a white dispersion (except ACN, which are yellow dispersions). The particles in the foam can act as sites for the onset of crazing during deformation in, e.g. compression. The
Chapter 1

ST-ACN particles absorb the energy provided and effectively increase the fracture toughness of the PUR foam.

By combining the ST-ACN particles and the clay thereby creating encapsulation of the clay in ST-ACN particles foam with enhanced properties could be made.

1.7 Aim and outline of the thesis

The main objective of this project is to encapsulate clay platelets in a non-aqueous dispersion polymerization where a polyol liquid is the preferred continuous phase. The polyol with formed anisotropic clay platelets encapsulated in polymer can later be used for foam applications.

The clay material of choice is natural Montmorillonite clay platelets. The hydrophilic, exfoliated clay platelets are expected to be dispersible in a polyol medium, especially for a polyol containing a PEO segment. For better control of anticipated encapsulation of clay platelets in the polyol medium, clay platelets may be edge-modified by silanes containing polymerizable groups. The face of the clay may be additionally modified by a molecule with a quartenary ammonium group on one end and a polymerizable acrylic group on the other end. In a non-aqueous polyl medium, dispersion polymerization is well positioned for the encapsulation purpose when styrene is used as monomer.

After the dispersion polymerization, the encapsulated clay platelets will be used to prepare PU foams with desirable mechanical properties. For the preparation of PCN only a few studies have reported the use of dispersion polymerization. Supercritical carbon dioxide was used as the solvent in these studies and only partially exfoliated or intercalated morphologies were obtained.

Chapter 2 presents the study of the stability, miscibility and interaction of both natural and modified clays in different polyols in order to investigate the interaction/miscibility between unmodified and modified clay. Important parameters include, e.g. PEO segment length and the different functionalities on the platelet surface. During this research, transitions of an isotropic phase to a liquid crystalline phase were observed in
triethanol amine (TEA) and polyol. The clay-polyol and clay-TEA mixtures are later used in a dispersion polymerization.

Chapter 3 focuses on the preparation of uniform polystyrene particles of micrometer size in ethanol, TEA and TEA/ethanol mixtures as solvents. These particles will later be used in foam preparation.

Chapter 4 describes a method to obtain anisotropic encapsulated clay platelets via dispersion polymerization. First the clay platelets will be face or edge modified. Afterwards the results are given for the encapsulation of these clay platelets via a non-aqueous dispersion polymerization.

Chapter 5 is dedicated to the preparation of PUR foam with triethanol amine as polyol. Different particles are incorporated in the foam and the mechanical properties are studied.
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Chapter 1


Chapter 1
Liquid crystalline formation of Montmorillonite clay in water, triethanol amine and polyol dispersions.
Summary

It is well known that Montmorillonite (MMT) clay particles dispersed in water swells and due to their anisotropic shape and high aspect ratio (up to ~1000) these inorganic particles can form liquid-crystalline phases, e.g. imogolite in water or organophilic sepiolite clay particles in non-aqueous solvents. In a similar way we observed the transition of isotropic to liquid crystalline dispersion of MMT in triethanol amine (TEA) and polyol. The results are discussed in this chapter. Later these media and the clay dispersions are used in attempt to encapsulate clay as described in chapters 3 and 4.

All XRD data of the nascent clay dispersed in water revealed a large extent of exfoliation of the clay. The Einstein coefficient of 250 indicates that there is interaction between the particles and the media, and is consistent with the idea of exfoliation.

The behaviour of the clay in triethanol amine (TEA) is complex and not fully understood. We observed birefringence over time and flow induced birefringence. To us this indicated that some clay platelets must have exfoliated towards single platelets or stacks of a few platelets.

The Cloisite 30B is fully exfoliated in the polyol 767. The absence of a diffraction peak in the XRD pattern, an Einstein coefficient of 30 and the TEM images give rise to the idea of fully exfoliated clay samples. Substantial birefringence and flow birefringence were observed in these samples.

The MMT in polyol IP 3040 shows exfoliation in the XRD patterns till 1.5 wt%. The 2 wt% sample shows signs of intercalation and possible exfoliation. The low Einstein coefficient indicates that all clay is intercalated and no exfoliation occurred.
2.1 Introduction

Nanocomposites containing nano-sized layered silicates in a polymer matrix have attracted a great deal of attention in the last decades due to their superior mechanical, barrier and thermal properties\(^1^3\), achieved at low filler concentrations (typically 1-2 wt\%). Two types of layered silicates are found in nature: expanding clays, such as phyllosilicates, smectite and Montmorillonite (MMT) and non-expanding clays, such as talc, mica and kaolin.

MMT clay is well suited to design hybrid nanocomposites and has attracted a great deal of academic and industrial interests, especially since the development of Nylon-6-clay nanocomposite by the Toyota research group.\(^4^5\)

MMT clay is ubiquitously present in Nature and requires low cost treatment to obtain mineralogically pure clay, while the synthesis of colloidal particles, such as synthetic Gibbsite, often results in low yields (<1%) and is time consuming and expensive.

It is well known that MMT clay dispersed in water swells. This feature is widely used for various industrial applications (drilling fluids, food industry, cosmetic industry, etc.) and plays a major role in landslide triggering. Due to their anisotropic shape and high aspect ratio (diameter/thickness is about ~1000) these inorganic particles can form liquid-crystalline phases, e.g. imogolite in water or organophilic sepiolite clay particles in non-aqueous solvents. One of the earliest reports of such a liquid-crystalline phase is the observation by Langmuir in 1938, who reported a phase transition of synthetic hectorite clay in water.\(^6\)

While investigating exfoliated polyurethane (PU)/clay nanocomposites, we observed phase transitions of MMT clay present in the soft segments and in the chain extenders of the polyurethane formulation (this is not in the final PU but in the reactants before reaction). PU consists of soft segments derived from high molecular weight polyether polyls, also called polyols, and hard segments composed of diisocyanates and chain extenders, e.g. low molecular weight diol or diamines. In short, a polyl is a high molecular weight polymeric reaction product with an active hydrogen compound (in our case glycerine) as starting material. Glycerine reacts with ethylene epoxide or propylene
epoxide until the desired molecular weight is reached. Hydrophilic, exfoliated clay platelets are expected to be dispersible in a polyol medium, especially for a polyol containing a PEO segment. It is well known from the literature that poly(ethylene oxide) can interact with clay surfaces and the physical presence of the clay particles in the PEO gives it unusual properties.\textsuperscript{7-9}

The formation and control over the liquid-crystalline phase for clay is still unclear in the literature. For instance Michot et al.\textsuperscript{10} reported the occurrence of crystalline phases in liquid-crystalline aqueous nontronite clay dispersions. Leach et al.\textsuperscript{11} reported flow induced permanent birefringed samples of 5 wt% bentonite in toluene. Many studies show that poly(ethylene) oxide in water adsorbs onto clay platelets.\textsuperscript{12} In the work of Schmidt et al.\textsuperscript{13} high Mw PEO with Laponite forms gels. Other investigations also report on network like structures with a micrometer length scale. The transition of isotropic to liquid crystalline dispersions of MMT in triethanol amine and polyol are to the best of our knowledge for the first time reported here.
2.2 Experimental

2.2.1 Materials

All clay samples were purchased from Southern Clay Products and were used as received. Sodium cloisite Montmorillonite clay (Na-MMT) has a cation exchange capacity of 92.6 meq/100 g and a density of 2860 kg/m³. The four other modified Cloisite MMT clays were surface modified with molecules containing a quaternary ammonium head followed by a long aliphatic (C_{16}~C_{18}) tallow (T) or saturated/hydrogenated tallow (HT) tail. They are shown in Figure 1.

![Surface modifiers of the commercially available modified clays.](image)

Triethanol amine (TEA) (99%) was provided by Sigma-Aldrich (Zwijndrecht, Netherlands), Poly(ethylene oxide) or polyol 400 with a listed molecular weight of 400 g.mol\(^{-1}\) was provided by Dow Chemical (Terneuzen, Netherlands). Both polyol IP 3040 and polyol 767 are trifunctional PO/EO polyether polyols with molecular weight of 3040 g.mol\(^{-1}\). IP 3040 has random PO/EO (composition is 89/11) branches while polyol 767 is the block copolymer version of IP 3040 with EO units at the end of the chain. Both were provided by Dow Chemical (Terneuzen, Netherlands) and were used as received.
Figure 2: Chemical structures of triethanol amine, Polyol EP 400 with $M_w = 400 \text{ g.mol}^{-1}$, Polyol IP 3040 with random PO/EO=89/11 and molecular weight $M_w = 3000 \text{ g.mol}^{-1}$ and Polyol IP 767 with block copolymer structure of PO/EO=89/11 and molecular weight $M_w = 3000 \text{ g.mol}^{-1}$.

2.2.2 Characterization techniques

The clays were dispersed in water, TEA or polyol with a solid content of 1, 2 or 4 wt%. The dispersions were stirred at room temperature using a magnetic stirrer bar for 4 days before further analysis.

The occurrence of settled layers of clay in the dispersions, due to a form of liquid crystal formation, was studied by a in-house made crossed polarizer. The sample is placed between two polarizers. Aligning the axes of the polarizers perpendicular to each other is called Crossed Polarization Conditions (CPC). An overview of the set-up is depicted in Figure 3. If the sample is optically isotropic, light passing through the sample will behave like light passing aside of the sample, when the analyzer is normal to the polarizer, all looks black. However, if the sample is birefringent, this is generally not the case, depending on domain size and orientation. With small birefringent domains, the result is a smooth and transparent sample. If the sample is birefringent then certain domains
Liquid crystalline formation of MMT clay in water, TEA and polyol dispersions

in the sample will light up under CPC. This provides information about possible orientation of the clay platelets in the sample.

![Figure 3: Schematic view of the polarization setup for birefringence detection. The light intensity through the analyzer depends on the angle of the transmission axis (TA) and the way the material absorbs and reflects light.](image)

Wide angle X-ray diffraction (XRD) measurements were carried out using a Rigaku diffractometer operated at 40 kV and 35 mA. The Debye-Scherrer powder diffractograms (diffractogram in short) XRD were recorded in the range of $1^\circ < 2\theta < 10^\circ$ using a step size of 0.02°/point, a scan rate of 0.24° min$^{-1}$ and employing Cu-K$_{\alpha 1}$ radiation (1.54 Å ). Samples were analysed as dry powder or in glass capillaries (diameter = 1 mm) in case of liquid samples, directly after preparation.

Rheology measurements were performed on an Anton Paar Physica MCR 301 rheometer using concentric cylinder geometry with inner/outer diameter of 22.66/28.92 mm with cone cup geometry.

Cryo-TEM microscopy was performed with a FEI Cryo-Titan, a 300 kV FEG microscope. The microscope is equipped with a GIF 2002 Gatan energy filter connected to a 2K * 2K pixel Multiscan™ CCD camera allowing both Zero Loss imaging as well as element specific imaging using the Electron Energy Loss Spectroscopy (EELS) mode and with a pre-GIF 2K * 2K US 1000™ CCD camera.
2.3 Results and discussion

2.3.1 Aqueous dispersions

The crystal structure of MMT consists of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge-shared octahedral sheet of aluminum hydroxide. Stacking the layers leads to a regular Van der Waals gap between the interlayer or gallery of the clay platelets, the so-called basal spacing (d-spacing is typically 9.6 Å for a dry sodium MMT while the platelet itself is 9.4 Å thick14).

XRD is a powerful technique to observe the extent of order in silicate structures in dispersion. In Figure 4 the XRD diffractograms of pure Na-MMT clay and the 2 and 4 wt% dispersions of Na-MMT are shown. The Na-MMT shows a diffraction peak at $2\theta = 7.3^\circ$. This corresponds to a d-spacing of 12.1 Å which can be calculated by using Bragg’s law ($d = \lambda/2 \sin \theta$). No diffraction peak is observed in the Na-MMT aqueous dispersion indicating that the clay is exfoliated; the Na-MMT dispersion in water is a good reference sample to compare with our clay dispersions in organic media.

![XRD diffractograms](image)

**Figure 4:** XRD diffractograms of Na-MMT clay and 2 and 4 wt% MMT clay in water.

The aqueous clay dispersions show long-term stability but after 1.5 months some sedimentation is visible. The sedimentation may have been caused by limited
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coaugulation or by some intercalated material. Michol et al.\textsuperscript{15} observed liquid crystalline dispersions of Montmorillonite clay in water up to 4 wt%. Upon shaking the samples, the flow induced some alignment of the clay platelets on a macroscopic length scale, causing birefringence in the sample.

The viscosity was measured for different clay concentrations in water and the viscosities were taken at shear rates of 10 and 100 s\textsuperscript{-1}. For small volume fractions (<0.05), one can characterize the viscosity by the Einstein relation\textsuperscript{16-17} which describes the viscosity of a large volume of liquid that changes due to the presence of spherical particles without interaction. At low volume fractions, Einstein’s rule states that $\eta = \eta_0(1 + K \phi)$ where $K$ represents the Einstein coefficient and is approximately 2.5 for spherical particles. Higher values indicate that there is interaction between the liquid and the particles.

Mooney developed a non-linear model in which interaction between the particles and the medium is present.\textsuperscript{18}

\[
\frac{\eta}{\eta_0} = \eta_r = e^{(a \phi)}
\]  

(1)

Connecting the Mooney model to the Einstein equation, at low $\Phi$ values, $a$ approaches the Einstein coefficient.

The result in Figure 5 shows the relation between the log of the relative viscosity and the volume fraction ($\phi_r$). It is clear that the experimental data are better described by the Mooney model. By fitting this exponential curve, an indication through the value of $a$, is obtained for the Einstein coefficient $K$. It can be said that the $K$ value is likely to be between 200 and 300 for the clay water systems, indicating that the clay is not behaving as aggregates but is exfoliated.
Figure 5: Relation between the volume fractions of clay dispersed in water and their relative viscosity. Lines are drawn according to the Mooney equation.

2.3.2 TEA-clay dispersions

Figure 6 a-e shows typical XRD patterns of the pure clay and 2 and 4 wt% dispersions. The XRD patterns of pure MMT (Figure 6a) and Cloisite 30B (Figure 6c) show the 001 reflection as a sharp intense peak at 2θ = 7.3° and 2θ = 4.7°. This corresponds to a d-spacing of 12.1 Å and 18.8 Å. All other pure clay samples show 2 peaks. The pure Cloisite 20A and Nanomer I44P have a second peak with lower intensity at a similar position as the pure MMT. We believe that these clay samples are mixtures of modified and unmodified clays. All other XRD peak data and d-spacings are listed in Table 1.

After dispersing the clay in TEA, all samples show a shift in peak position as compared to the pure clay sample, indicating intercalation by TEA. In all cases the peaks still remained, so no fully exfoliated samples were obtained in TEA.
Figure 6: XRD patterns for various pure clays and for their 2 and 4 wt% dispersions in TEA for (a) MMT, (b) Cloisite 20A, (c) Cloisite 30B, (d) Nanomer I34TCN and (e) Nanomer I44P.
Table 1: X-ray diffraction data of (a) MMT, (b) Cloisite 20A, (c) Cloisite 30B, (d) Nanomer I34TCN and (e) Nanomer I44P dispersed in TEA.

<table>
<thead>
<tr>
<th>Diffraction pattern</th>
<th>Sample name</th>
<th>2 θ (°)</th>
<th>d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>MMT</td>
<td>7.3</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>MMT_2wt%</td>
<td>5.2</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>MMT_4wt%</td>
<td>5.2</td>
<td>17.0</td>
</tr>
<tr>
<td>(b)</td>
<td>20A</td>
<td>7.2 &amp; 3.7</td>
<td>12.2 &amp; 23.9</td>
</tr>
<tr>
<td></td>
<td>20A_2wt%</td>
<td>4.7 &amp; 2.2</td>
<td>18.8 &amp; 40.2</td>
</tr>
<tr>
<td></td>
<td>20A_4wt%</td>
<td>4.7 &amp; 2.2</td>
<td>18.8 &amp; 40.2</td>
</tr>
<tr>
<td>(c)</td>
<td>30B</td>
<td>4.7</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>30B_2wt%</td>
<td>4.7 &amp; 2.3</td>
<td>18.8 &amp; 38.4</td>
</tr>
<tr>
<td></td>
<td>30B_4wt%</td>
<td>4.7 &amp; 2.3</td>
<td>18.8 &amp; 38.4</td>
</tr>
<tr>
<td>(d)</td>
<td>I34</td>
<td>4.8 &amp; 2.6</td>
<td>18.4 &amp; 34.0</td>
</tr>
<tr>
<td></td>
<td>I34_2wt%</td>
<td>4.8 &amp; 2.1</td>
<td>18.4 &amp; 42.0</td>
</tr>
<tr>
<td></td>
<td>I34_4wt%</td>
<td>4.8 &amp; 2.1</td>
<td>18.4 &amp; 42.0</td>
</tr>
<tr>
<td>(e)</td>
<td>I44</td>
<td>7.1 &amp; 3.6</td>
<td>12.5 &amp; 24.5</td>
</tr>
<tr>
<td></td>
<td>I44_2wt%</td>
<td>2.1</td>
<td>40.2</td>
</tr>
</tbody>
</table>

The Einstein coefficients were determined in a similar way as for the water clay system and are shown in Figure 7. The Einstein coefficient was between 6 and 13 and compared to the water system (250) much lower. Probably a considerable part of the clay has a lower interaction or no interaction with the TEA causing these lower Einstein values. From the XRD curve it is shown that the clay remains organized in stacks of sufficient size to give diffraction peaks in the X-ray diffractograms. So these results indicate that although no complete exfoliation occurs, the stacks of clay platelets can still organize in liquid crystals.
Liquid crystalline formation of MMT clay in water, TEA and polyol dispersions

![Relative viscosity at 100 s⁻¹](image)

Figure 7: Relation between the volume fraction of various clays dispersed in TEA and their relative viscosity measured at a shear rate of 100 s⁻¹. Lines are drawn according to the Mooney equation.

After stopping the stirring of the TEA/clay dispersions a “biphasic” mixture is formed. The mixtures show a clear separation between a denser birefringent phase at the bottom and an isotropic phase at the top. This biphasic mixture is formed within one day and remains stable for more than a year. The clay dispersions in TEA show birefringence as can be seen in Figure 8. Under CPC the Cloisite 20A dispersion shows transmission, indicating a strongly oriented layered structure. The Cloisite 30B dispersion shows less transmission compared to the Cloisite 20A dispersion and is almost transparent under CPC. The Nanomer I34TCN dispersion appears as an almost white shining solid under CPC. It appears possible that ordering of the clay platelets occurs and leads to a biphasic mixture due to liquid crystal formation.
Figure 8: Photographs of settling observed with a polarizer. At the top row, clay dispersions in TEA without polarized light and at the bottom row with polarized light. From left to right, 1 wt% Cloisite 20A, 1 wt% Cloisite 30B and 1 wt% I34TCN in TEA.

Birefringence was also studied after whirling the dispersions. We suppose that with whirling, the flow induces some macroscopic alignment of the clay platelets which leads to what is known as flow birefringence. Figure 9 shows the pictures after whirling the dispersions. With this induced flow we observed a birefringence behavior. In the case of Cloisite 20A and 30B and Nanomer I34TCN, the whirl seemed to lighten up under CPC.

Figure 9: Birefringence of various clays dispersed in TEA after whirling the samples: (a) 1 wt% and (b) 2 wt% Cloisite 20A, (c) 1 wt% and (d) 2 wt% Cloisite 30B, (e) 1 wt% and (f) 2 wt% Nanomer I34TCN and (g) 1 wt% and (h) 2 wt% Nanomer I44P in TEA.
2.3.3 Polyol-clay dispersions

In Figure 10 the diffractograms of EP 400 with different MMT clay content is shown. The clay contents are 1 and 2 wt%. A diffraction peak was observed at $2\theta = 4.8^\circ$ corresponding to the $d$-spacing 18.4 Å, so we assume most likely intercalation has taken place.

![Graph showing XRD patterns](image)

Figure 10: XRD patterns of 1 and 2 wt% of MMT clay dispersed in polyol EP 400.

Cloisite clay dispersions were prepared in EP 400 in a similar way as the MMT samples. All of them showed sedimentation after 5 months and an example of the 2 wt% sample is given in Figure 11a in which a settled layer can be observed. The settling is caused by formation of a liquid crystal. CPC showed transmission as can be seen in Figures 11b and c. Close to the air/ dispersion interface little domains of single crystals were observed.
Figure 11: (a) 2 wt% Cloisite 30B dispersed in Polyol 400 after 5 months. (b) Birefringent domains are visible at the air/dispersion interface. (c) Enlargement of the interface.

In Figure 12 the diffractograms of MMT dispersion in IP 767 with MMT clay contents varying from 0.5 wt% to 2 wt% are shown. A diffraction peak is observed at $2\theta = 4.8^\circ$ corresponding to the $d$-spacing 18.4 Å, so like the EP 400, most likely intercalation has taken place.

Figure 12: XRD patterns of 0.5, 1, 1.5 and 2 wt% of MMT clay dispersed in IP 767.
Cloisite 30B dispersed in Polyol 767 showed no signs of intercalation, as can be seen in Figure 13. This might indicate that exfoliation of the clay platelets occurred in the polyol.

![XRD patterns of pure Cloisite 30B, polyol IP 767 and 2 wt% Cloisite 30B dispersed in polyol IP 767.](image)

The birefringence was also studied for these samples. An example is shown in Figure 14. Figure 14a shows the dispersion after mixing for 4 days without polarizer. Under CPC the sample shows birefringence, as can be seen in Figure 14b. We redispersed the sample for 4 days and the sample was leaved at rest for another week and then whirled again. As can be seen in Figure 14c, the birefringence occurred less strongly as in Figure 14b. The birefringence disappeared after a few seconds indicating that temporary self-alignment of the clay platelets is the cause of birefringence while flow also induces some temporary birefringence.
Figure 14: (a) The 2 wt% Cloisite 30B in polyol 767 directly after mixing. (b) The 2 wt% Cloisite 30B in polyol 767 under CPC. (c) The 2 wt% Cloisite 30B in polyol 767 under CPC directly after whirling.

The viscosity of the polyol was 0.90 Pa.s and the dispersion had a viscosity of 1.19 Pa.s. Taking the densities of polyol and clay into account an Einstein coefficient of 30 is found, indicating that the sample is exfoliated.

In order to check the orientation of the clay platelets, Cryo-TEM images were taken from the same sample. Figure 15 a-c shows clay in polyol as hair like dark features in the images. The dark lines in these images are in the same order of magnitude as the dimensions of an individual clay platelet and the clay seems to be randomly distributed throughout the dispersion, indicating exfoliation. Only a few agglomerates can be seen in Figure 15d but most of the clay is exfoliated.
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Figure 15: (a) TEM image focused on the thickness of the clay platelets (b) a different place on the grid focused on the distribution of the clay in the dispersion (c) another place in the grid focused on a group of platelets perpendicular to the focused plane and (d) the same place but with a different focus to see the clay platelets parallel to the observed plane.

In Figure 16 the diffractograms of IP 3040 with different clay contents are shown. The clay content varied from 0.5 wt% to 2 wt%. Only a very weak peak can be found at $2\theta = 4.75^\circ$ for the 2 wt% dispersion so we assume that a combination between exfoliation and intercalation of MMT in IP 3040 takes place. An Einstein coefficient of 5 is found for this system, supporting this assumption. In a similar way as for the IP 767, we checked the possibilities of exfoliating Cloisite 30B in IP 3040. A diffraction peak is present at the position of the pure 30B clay, indicating no exfoliation but intercalation, as can be seen in Figure 17.
Figure 16: Diffraction patterns of MMT clay dispersed in IP 3040.

Figure 17: Diffraction patterns of Cloisite 30B dispersed in IP 3040.
2.4 Conclusions

All XRD data of the nascent clay dispersed in water indicate a large extent of exfoliation of the clay. The Einstein coefficient of 250 derived from the results of viscosity measurements for this system is consistent with the idea of exfoliation.

The behaviour of the clays in TEA is complex and perhaps not fully understood. The observation of some birefringence over time and flow induced birefringence indicate that some clay platelets must have exfoliated towards single platelets or stacks of a few platelets. This feature might be convenient because efforts were made to encapsulate the individual clay layer in polystyrene with TEA as medium. The results are described in chapters 3 and 4.

The Cloisite 30B is fully exfoliated in the polyol 767. The absence of a diffraction peak in the XRD pattern, an Einstein coefficient of 30 and the TEM images give rise to the idea of fully exfoliated clay samples. Substantial birefringence and flow birefringence were observed in these samples.

The MMT samples in polyol IP 3040 show exfoliation in the XRD patterns up to 1.5 wt%. For the 2 wt% dispersion, the sample shows signs of intercalation and possible exfoliation. The low Einstein coefficient gives rise to the idea that all clay is intercalated and no exfoliation occurred.
References


Liquid crystalline formation of MMT clay in water, TEA and polyol dispersions


Preparation of micrometer-sized polystyrene particles by dispersion polymerization in polyols.
Summary

A new way to prepare polystyrene particles via dispersion polymerization in triethanolamine (TEA) and TEA/ethanol mixtures is described. Dispersion polymerization of polystyrene at 70°C in ethanol led to monodisperse particle sizes while in TEA agglomeration occurred and control over particle size formation was lost in the first hour of polymerization. By increasing the polymerization temperature to 120°C, colloidally stable polystyrene particles in TEA were obtained. Mixtures of ethanol and TEA led to stable polystyrene particles at 70°C. Probably the reduced viscosity of TEA at higher temperatures or the dilution with ethanol provides the key to the formation of stable polystyrene particles.
3.1 Introduction

Compared to other heterogeneous polymerization techniques, dispersion polymerization is attractive because it results in micrometer-sized particles in a fast single step process in very good yields. The size of the final product lies between the size of the particles produced by conventional emulsion polymerization (submicrometer particles) and suspension polymerization (50–1000 μm).

The particles obtained by dispersion polymerization can be used in a wide variety of applications, such as toners, instrument calibration standards, column packing materials for chromatography and biomedical and biochemical analysis. The 1-15 μm particle size range is difficult to achieve with other polymerization techniques in a single step process. Proper control of the reaction conditions is essential to achieve size monodispersity of the prepared particles. Dispersion polymerization is found to be less affected by stirring speed and reactor geometry as compared to emulsion and suspension polymerization.

Dispersion polymerization starts as a homogeneous solution polymerization reaction in which the polymerization proceeds in a continuous phase which is a solvent for the monomer but a non-solvent for the polymer. At elevated temperatures the initiator decomposes and generates free radicals which initiate free radical polymerization. During the nucleation stage, the polymer (or oligomer) in the continuous phase reaches a molecular weight higher than a certain critical value and segregates from the continuous phase by precipitation. Colloidally unstable particles are formed and a steric stabilizer is used to produce a colloidally stable dispersion. Without this stabilizer the polymerization would give polymer particles of uncontrolled size like in a precipitation polymerization.

These colloidally unstable particles coalesce and adsorb more stabilizer molecules from the reaction medium onto their surface until they become colloidally stable. At this point the total number of particles in the system is fixed and nucleation ceases.

The particles grow further by capturing oligomeric radicals or small nuclei from the continuous phase and polymerization occurs either in the particles or in the continuous
reaction phase depending on the partitioning of the monomer between the continuous and particle phases. The newly formed polymer chains/primary particles should not form additional nuclei but should be captured by existing particles. These processes continue until all monomers in the reaction mixture have been converted into polymer.

The key issue for preparing uniformly sized colloidal particles is a short nucleation stage. The particle number and particle size distribution are determined during the nucleation stage. A prolonged nucleation stage usually results in broad particle size distributions. No coagulum or secondary particles should be formed during the particle growth stage and afterwards.

Dispersion polymerization has been widely used for styrene\textsuperscript{5-10}, methyl methacrylate\textsuperscript{11-12} and mixtures of these monomers in polar solvents like alcohol/water mixtures. The studies focus on the effect of type and concentration of the initiator, stabilizer concentration, alcohol to water ratio and monomer dispersion ratio on particle size and particle size distribution.

In the polyurethane (PUR) industry dispersion polymerization is used to produce filled polyether polyols (abbreviated polyol). A filled polyol is a stable colloidal dispersion in which the other organic polymer particles have some stabilization to prevent floculation. These reactive polyols are then used in making foams of higher hardness than can be obtained using the unmodified polyols. The foams are used in a wide range of applications, e.g. as insulation, packaging material or for load-bearing structures such as cushioning. To the best of our knowledge, there are no reports of polystyrene particles prepared via dispersion polymerization in triethanolamine (TEA) and reactive polyols with a poly(vinylpyrrolidone) stabilizer. In this chapter the results of the preparation of PST particles using dispersion polymerization in polyols is discussed. TEA is a reaction component in polyurethane synthesis and as such it is a reactive dispersing medium.
3.2 Experimental

3.2.1. Materials

The monomer styrene (ST) was purchased from Aldrich (Zwijndrecht, Netherlands) and purified by slowly passing through a column packed with alumina after which the styrene was stored in the refrigerator until use. The initiator 2,2’-azobisisobutyronitrile (AIBN) was recrystallized from methanol. All other materials were used without further purification, including ethanol, TEA, poly(vinylpyrrolidone) (PVP K-30; \( M_W = 40,00 \) g.mol\(^{-1}\)) (Aldrich) and di-tert-amyl peroxide (DTAP).

Poly(ethylene oxide) or polyol 400 with a listed molecular weight of 400 g.mol\(^{-1}\) was provided by Dow Chemical (Terneuzen, Netherlands). Both polyol IP 3040 and polyol 767 are trifunctional PO/EO polyether polyols with molecular weight of 3040 g.mol\(^{-1}\). IP 3040 has random PO/EO (composition is 89/11) branches while polyol 767 is block copolymer with EO units at the end of the chain. Both were provided by Dow Chemical (Terneuzen, Netherlands). All polyols were used as received.

3.2.2. Polymerization

Dispersion polymerization was carried out batchwise in a 250 mL reactor with mechanical stirring at 150 rpm under argon atmosphere at 70°C (AIBN) or 120°C (DTAP).Ethanol, TEA or TEA/EtOH mixtures were charged to the reactor followed by the addition of ST (12.5 wt% based on the total amount in the recipe) and the PVP stabilizer (2.5 wt% based on the total amount in the recipe). Thereafter the initiator (2 wt% based on the ST amount) dissolved in ethanol was added at elevated temperatures and the polymerization was initiated. The polymerization lasted 12 hours. The polyol samples were made in a similar way.

During the polymerization, samples of the reaction mixture were withdrawn from the reactor to examine the conversion upon reaction time and the characteristics of the particles. The withdrawn polymerization products were washed with ethanol and
centrifuged. This procedure was repeated 3 times to remove all the non-reacted materials.

### 3.2.3. Characterization

Particle sizes and distribution were measured with a Coulter counter (LS 230). Particle morphology was observed by scanning electron microscopy (SEM) using the Phenom Desktop SEM (FEI company). SEM specimens were prepared by diluting a small sample of the polymerization product after cleaning with ethanol. After the centrifugation one drop (approximately 1-2 mL) was placed on an aluminum stub with double-coated adhesive carbon tape. After overnight drying the samples were covered with a gold layer.

Some SEM pictures were analyzed further using imaging software, (Image J v1.42q) to determine particle size and polydispersity. Two types of mean particle sizes were calculated: the number average diameter $D_n$ and the weight average diameter $D_w$. They are given by:

\[
D_n = \frac{\sum \limits_{i=1}^{n} n_i D_i}{\sum \limits_{i=1}^{n} n_i} \tag{1}
\]

\[
D_w = \frac{\sum \limits_{i=1}^{n} n_i D_i^3}{\sum \limits_{i=1}^{n} n_i D_i^2} \tag{2}
\]

where $D_i$ represents the individual particle diameter and $n_i$ is the total number of polymer particles measured. The polydispersity index $PDI$ is then given by:

\[
PDI = \frac{D_w}{D_n} \tag{3}
\]

Conversions were determined by gravimetry. A sample (1-3 g) was extracted after the onset of the polymerization with certain time intervals and was put with some flakes of hydroquinone in aluminum cups and dried at 70°C until no further weight change was detected anymore. The conversion was then calculated according to:
Preparation of polystyrene particles by dispersion polymerization in polyols

\[ X = \frac{M_2 - M_1 \cdot f_s}{M_1 \cdot f_m} \]  

(4)

where \( X \) is the monomer conversion, \( M_1 \) is the mass of the sample before drying, \( M_2 \) is the mass of the sample after drying, \( f_s \) is the weight fraction of PVP and initiator in the reactor and \( f_m \) the weight fraction of monomer in the reactor.

Rheology measurements were performed on an Anton Paar Physica MCR 301 rheometer with cone cup geometry and operating speed of 1 Hz.

3.3 Results and discussion

Because the viscosity and the properties of the solvent are controlling the solubility of the formed polymer chains and are also affecting the colloidal stability of the particles, experiments were performed in TEA/EtOH mixtures.

The effects of varying the continuous phase composition were investigated and the results of the particle size are shown in Table 1.

<table>
<thead>
<tr>
<th>Volume ratio EtOH/N(EtOH)₃</th>
<th>12/1</th>
<th>7/1</th>
<th>4/1</th>
<th>2/1</th>
<th>0.75/1</th>
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<tr>
<td>Particle size [μm]</td>
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<td>3.0</td>
<td>2.9</td>
<td>1.0-10.0</td>
</tr>
</tbody>
</table>

Figure 1 shows the conversion time history and the development of the particle size growth for the ethanol system. The conversion has the same magnitude as for results found in literature. Chen et al.¹³ describe a polystyrene system in ethanol with AIBN at 75°C. Because of the higher temperature, the initiator decomposes faster as compared to 70°C, and polymer conversions of 80% are reached after 6 hours.
The particle size is in agreement with the results predicted by Paine et al.\textsuperscript{14} Figure 3 shows a SEM picture of the polystyrene particles of the ethanol system having a particle size of 3 µm (PDI = 1.1) which is in agreement with literature.\textsuperscript{15}

![Figure 1: Conversion and size diameter of PST particles dispersed in EtOH as a function of time.](image)

After replacing the ethanol by TEA, aggregation problems occurred in the reactor. The number average molecular weight was $M_n = 80.000$ and the polydispersity (PDI) was 8.4. The experiment was repeated with a lower monomer concentration of 5 wt% based on the complete recipe and particle size was followed and measured with the Coulter LS 230 as shown in Figure 2. After 1 hour aggregates of 1.9 µm can be observed in the reactor. Control of particle stability is already lost in an early stage of polymerization as can be seen from the PDI value. A SEM picture of the TEA system after the end of the polymerization in Figure 3b shows aggregated particles.
Preparation of polystyrene particles by dispersion polymerization in polyols

Figure 2: Evolution of the particle size and polydispersity of PST particles dispersed in TEA as a function of time.

By increasing the ethanol volume fraction it is possible to obtain stable particles, as shown in Figure 3 c-f. The particle size in dispersion polymerization is related to solvency of the medium. In the case of the 12/1 ratio, the biggest particles were obtained. By increasing the triethanolamine concentration in the mixture, the particles become smaller and more polydisperse. When the ratio of the volumes of ethanol ($V_{\text{ethanol}}$) and TEA ($V_{\text{TEA}}$) approaches 0.75 again, aggregation can be observed.
Figure 3: SEM images of various particles prepared through dispersion polymerization of (a) PST particles in EtOH, (b) PST particles in TEA, and PST particles in various mixtures of ethanol and TEA: (c) $V_{\text{EtOH}}/V_{\text{TEA}} = 12/1$, (d) $V_{\text{EtOH}}/V_{\text{TEA}} = 7/1$, (e) $V_{\text{EtOH}}/V_{\text{TEA}} = 4/1$, and (f) $V_{\text{EtOH}}/V_{\text{TEA}} = 2/1$. 
To check if it is possible to obtain stable particles after the removal of alcohol, the $V_{\text{EtOH}}/V_{\text{TEA}} = 7/1$ sample was stripped from its ethanol in a Rotary evaporator. The polystyrene particles were isolated and a SEM image of the result is shown in Figure 4 (monodisperse particles of 2 µm).

![Figure 4: (a) SEM image of PST particles via dispersion polymerization in a mixture of EtOH and TEA: $V_{\text{EtOH}}/V_{\text{TEA}} = 7/1$, after alcohol removal and (b) Darkfield microscope image of the diluted TEA phase after removing the EtOH.](image)

**Effect of polymerization temperature and stirring speed on the dispersion polymerization in TEA**

Rheological measurements showed that the viscosity of TEA is approximately 3 decades higher as compared to the viscosity of ethanol at room temperature, as can be seen in Figure 5. First a trial was made by using higher shear rates to check whether stable PS particles can be obtained; aggregation was observed in the reactor at 1500 rpm. We also compared the viscosity of the TEA and TEA with 2 wt% PVP at five different temperatures as shown in Figure 6. The viscosity of TEA and 2 wt% PVP is a decade higher then ethanol at 70°C.

The viscosity of TEA at 70°C is approximately 1 decade lower than at room temperature. This led to the idea to run dispersion polymerization in TEA at temperatures higher than 70°C.
For this experiment AIBN was replaced by di-tert-amyl peroxide which has a similar half-life time at 120°C as compared to AIBN at 70°C.\textsuperscript{16} Increasing the temperature helped significantly to produce stable polystyrene particles. After polymerization no aggregates were observed in the reactor. The particle size was 0.5-0.8 $\mu$m at 150 rpm. Increasing the stirring speed to 500 rpm led to somewhat smaller particles of 0.5 $\mu$m. At 1500 rpm larger particles were found and the polydispersity of the particle size distribution also increased, implying shear induced coagulation. SEM images are given in Figure 7.

![Figure 5: Viscosity as a function of PVP concentration in ethanol, TEA, EtOH/TEA w/w=1/2 and TEA at 70°C.](image-url)
Figure 6: Viscosity of triethanol amine (TEA) and TEA with 2 wt% polyvinyl pyrrolydone at 25, 45, 70, 90 and 120°C measured with a rheometer at a shear rate of 1 s\(^{-1}\).

Figure 7: SEM images of PST particles prepared via dispersion polymerization in TEA at different conditions: (a) 70°C and 1500 rpm, (b) 120°C and 150 rpm, (c) 120°C and 500 rpm, (d) 120°C and 1500 rpm.
In order to make a polyurethane (PUR) foam with TEA, water is added to the formulation to facilitate the foaming. The foaming procedure is described in detail in Chapter 5. As such, there is no necessity to remove water for PUR preparation after the dispersion polymerization. In addition, water also helps to reduce the viscosity of the medium, similarly to the TEA/EtOH systems.

In two mixtures some TEA was replaced with 10 wt% and 15 wt% water and a batch polymerization with ST was prepared similarly to the EtOH dispersion. The mixture containing 15 wt% water is close to the upper limit because adding more water to the TEA system leads to a hazy solution.

Figure 8 a-f shows the result after dispersion polymerization. In the case of the 10 wt% water mixture, a bimodal mixture forms. The bigger population has a particle size of about 4 μm and the smaller population has a polydisperse particle size ranging from 450 nm up to about 1 μm. Adding more water to the system led to bigger particles in the bigger population. The smaller particle population shows a particle size distribution ranging from 100 nm to 2 μm.

Figure 8: SEM images of PST particles prepared via dispersion polymerization in (a-c) 10 wt% water and 90 wt% TEA and (d-f) 15 wt% water and 85 wt% TEA.
In a similar experiment an attempt was made to obtain uniformed sized particles in water/TEA 10/90 by using a pump to feed within 10 hours the monomer with initiator to the reactor during polymerization. A somewhat similar result was found as the single batch polymerization. The sample prepared via the feeding procedure exhibited a much broader size distribution, as shown in Figure 9, since a bigger and smaller particle population disappeared compared to the previous experiment.

![Figure 9: SEM images of PST particles prepared via dispersion polymerization in 10 wt% water and 90 wt% TEA. The monomer/initiator mixture was fed to the reactor within 10 hours.](image)

From these experiments it appeared that adding water did not lead to particles with a monodisperse size or small particle size distribution. The water changes the polarity and the solubility too much compared to the TEA/EtOH system.

As mentioned before polyol can be used in the formation of PUR. The polyols can be “filled” with polymers to produce a white viscous fluid for the production of foam and aid in the process, e.g. by improving cell-openness. The same recipe was used as for the EtOH dispersions and the polyol 400 behaved in a similar way as TEA at 70°C, leading to aggregation.
Chapter 3

The polymerization at 120°C gave a stable end product with a PST content of 12.5 wt% at room temperature. The result is shown in the SEM image in Figure 10. The dispersion had a particle size of approximately 500 nm.

Figure 10: SEM image of PST particles prepared via dispersion polymerization in EP 400 diol at 120°C.

Changing the solvent to IP 3040 also led to stable dispersions and the result is shown in Figure 8. The particles size was again approximately 500 nm.

Figure 11: SEM images of PST particles prepared via dispersion polymerization in IP 3040 polyol at 120 °C.
3.4 Conclusions

Micrometer-sized polystyrene microspheres were successfully prepared via dispersion polymerization in ethanol with AIBN as initiator. Dispersion polymerization of styrene in TEA led to agglomeration of particles and control over particle size formation is lost in the first hour of polymerization. Increasing the stirring speed at 70°C to 1500 rpm did not lead to stable dispersions. However, by increasing the polymerization temperature to 120°C, stable dispersions of polystyrene particles in TEA were obtained. Also diluting TEA with ethanol and thus also reducing the viscosity of the dispersion medium resulted in a stable dispersion. Diluting with water has an opposite effect and led to particles with a broad particle size distribution. This type of dispersion polymerization is to the best of our knowledge new and can be used in foam preparation as will be shown in chapter 5.
References


Encapsulation of clay in a non-aqueous dispersion polymerization.
Summary

A way to prepare encapsulated clay via dispersion polymerization in ethanol (EtOH) is described. First the clay is modified by covalent edge modification of OH groups using silane or electrostatic interaction on the face of the clay platelet. We used TMC-10 and poly(ethylene glycol) methacrylate (PEGMA) for the face modification. An increase in the $d$-spacing of the clay indicated that the clay was intercalated with the face modifier. Afterwards the modified clay platelets are used in a dispersion polymerization to obtain encapsulated clay in polystyrene. Intercalated and exfoliated clay structures were obtained in the polymer nanocomposites and were found to be thermally more stable than the polystyrene (PST) particles. Encapsulation of clay in triethanol amine (TEA) and polyol was challenging and not as successful as the encapsulation in EtOH.
4.1 Introduction

Clay is a widely investigated material for the production of polymer clay nanocomposites (PCN). We have chosen for the synthesis of PCN because it is easily available, considered environment-friendly and relatively cheap. Because of the hydrophilic nature of clay, they are easily miscible with hydrophilic polymers such as polyethylene oxide and poly(vinyl alcohol). To make the clay compatible with hydrophobic polymers such as polystyrene, it is necessary to make the clay more hydrophobic. One way to achieve this is by exchanging the cations present in the clay layers of Montmorillonite (MMT) with the cationic surfactants such as quaternary alkylammonium salts.

After reporting the clay structure by Pauling\(^1\) it became known that the edges of the clay contain hydroxyl groups from the silanol or aluminol groups. A second approach to make the clay more hydrophobic is to treat the edge groups as conventional Si-OH groups and modify them by direct grafting reactions with silanols or titanates.

The encapsulation of clays by dispersion polymerization or any other free radical polymerization appears to be very challenging. Zhao and Samulsk\(^2\) prepared poly(methyl methacrylate) (PMMA) nanocomposites in supercritical carbon dioxide (CO\(_2\)) with clays having fluorinated surfactants. Exfoliated structures were obtained. In another study\(^3\), they used aminopropyl terminated poly(dimethylsiloxane) as clay modifier and nanocomposites were prepared in CO\(_2\) with MMA and styrene (ST). In the case of PMMA, exfoliated clay platelets were found in the composite. For the polystyrene (PST) however, a nanocomposite with a partially exfoliated structure was found. It was demonstrated that the obtained morphology depends on the clay concentrations.

Greesh et al.\(^4\) prepared polystyrene/silanated MMT nanocomposites by dispersion polymerization in ethanol/water and studied their morphology. Their small angle x-ray scattering measurements and transmission electron microscope images indicated the presence of fully exfoliated clay platelets in PST at a low clay concentration while intercalated structures were found at higher clay concentrations. Lanchis et al.\(^5\) synthesized polystyrene latexes by surfactant-free emulsion polymerizations in the
presence of Montmorillonite clay modified by grafting alkoxy silanes and they observed exfoliated clay in snowman like particles. Voorn et al.\textsuperscript{6} used MMT modified with methacryloxy silanol derivatives and obtained encapsulated clay via surfactant-free emulsion polymerization of MMA.

In this chapter two different approaches were reported to modify clay and subsequently encapsulate the clay platelets. Figure 1 gives a schematic representation of the approaches.

First the results of the surface modified clay platelets are described. Subsequently, the non-aqueous dispersion polymerization in the presence of face or edge modified clay is described.
Encapsulation of clay in a non-aqueous dispersion polymerization

Figure 1: Modification scheme of clay platelets by covalent edge modification of OH groups using silane or electrostatic interaction on the face of the clay platelet. Subsequently, the modified platelets are used in a dispersion polymerization to obtain encapsulated particles.
4.2 Experimental

4.2.1. Materials

All clay samples were bought at Southern Clay products. Styrene (ST, 99%, Aldrich) was purified by slowly passing over an inhibitor removing column (hydroquinone remover, Aldrich) after which the styrene was stored in the refrigerator until use. The initiator 2,2′-azobisisobutyronitrile (AIBN, Wako Chemicals GmbH) was recrystallized from methanol (Biosolve, AR grade). Methacryloyl chloride, tetrahydrofuran (THF, Biosolve, AR grade), ethanol (Biosolve, AR grade), poly(vinylpyrroldione) (PVP k-30; $M_w = 40,000$ g.mol$^{-1}$, Aldrich), triethanol amine (TEA) (99%, Aldrich), 1-bromo-11-undecanol (Aldrich), triethylamine (Aldrich), sodium carbonate (Aldrich), chloroform (Biosolve, AR grade), magnesium sulfate (Aldrich), 11-bromoundecyl methacrylate (Aldrich), diethyl ether (Biosolve, AR grade), toluene (Biosolve, AR grade) and trialkoxy silane 3-methacryloyloxypropyltrimethixysilane (TMPS, 98%, ABCR), di-tert-amyl peroxide (DTAP) (Aldrich) were used as received. The polyol IP 3040 was provided by DOW Chemical.

4.2.2 Synthesis of TMC-10

TMC-10 was prepared according to Yoshinaga et al. and is schematically shown in Figure 2.

![Figure 2: Synthesis of TMC-10.](image)

In short the synthesis is as follows: in an ice bath, 4.8 g methacryloyl chloride in 80 mL dry THF in a nitrogen atmosphere was added dropwise to a mixture of 8 g 1-bromo-11-undecanol and 3.4 mL triethylamine. The mixture was then stirred at room temperature overnight.
Encapsulation of clay in a non-aqueous dispersion polymerization

Washing with aqueous Na₂CO₃ solution (5%) and extraction with chloroform, drying over MgSO₄, and evaporation of the solvent gave an oily product of 10-bromoundecyl methacrylate. The product was dissolved in acetone, the solution was filtered, and was then provided with quaternary ammonia groups using trimethylamine/H₂O 50:50 solution, which was added drop wise. After evaporation of the solvent, the crude product was dissolved in chloroform and filtered to remove the diammonium salt. Precipitation with diethyl ether and drying under reduced pressure gave a white solid.

4.2.3 Modification of clay

4.2.3.1 Surface modification of clay platelets

A typical procedure for the dispersion of clay in water was to disperse 10 g MMT in 1000 mL demi-water and treated with a rotor-stator system (Ultra Turrax®) at 2000 rpm for 30 minutes. The mixture was then stirred for 10 days at room temperature by magnetic stirring.

An amount of 200 mL aqueous clay platelet dispersion was treated with 200 mg TMC-10, and the mixture was stirred for 7 days. After this the mixture was centrifuged (2x10 min, 15000 rpm), water was removed and the clay was redispersed twice in water/EtOH (1:1 v/v) to remove the excess of TMC-10. The dispersion was centrifuged again using the same settings; the solid was collected and redispersed in EtOH. The solid content was determined. Dry samples for analysis were prepared by drying the sample for 12 hours at 40°C in a vacuum oven.

4.2.3.2 Covalent modification of clay platelets

The sodium Montmorillonite was dried at 120°C for 12 hours. A Vibracell VC 750 tip sonicator operating at 40% of its maximum power using a frequency of 20 kHz for 30 minutes was used to disperse 1 g of the clay in toluene and 1.5 meq of the MPS was added at the constant feed of 0.1 mL.min⁻¹ using a Harvard Apparatus 11 plus syringe
pump. The mixture was stirred for 4 days at ambient temperature and afterwards the modified clay platelets were collected with a Büchner funnel and washed twice with 300 mL toluene to remove the excess of MPS.

### 4.2.4 Dispersion polymerization

The dispersion polymerization reaction was performed in a 250 mL reactor equipped with a mechanical stirrer operating at 300 rpm under argon atmosphere at 70°C or 120°C. In a typical procedure the clay was dispersed in the medium together with 2.5 wt% PVP and the mixture was vigorously stirred with an Ultra Turrax®. After charging the reactor with the mixture, the reactor was heated to 70°C or 120°C and purged with an argon flow. The monomer phase was prepared by dissolving 1 wt% AIBN in styrene monomer (12.5 g). The mixture was then purged with argon for 20 minutes. A Harvard Apparatus 11 plus syringe pump with a flow rate of 0.5 mL.h⁻¹, was used to feed the monomer/initiator mixture to the reactor. During the polymerization, samples of the reaction mixture were withdrawn from the reactor to determine the conversion time history and the characteristics of the particles. The withdrawn polymerization products were rinsed with ethanol and centrifuged. This procedure was repeated 3 times to remove all the non-reacted species.

### 4.2.5 Characterization

Surface tension measurements of the pure TMC-10 and PEGMA solutions and the supernatant after addition of clay were determined at room temperature using a DataPhysics DCAT automated tensiometer, which employs the Wilhelmy plate method.

Thermogravimetric analysis (TGA) was performed using a high resolution TA-Q500 instrument operating under a nitrogen flow of 50 mL.min⁻¹. The sample was heated from room temperature to 700°C at a heating rate of 10°C.min⁻¹.

Wide angle X-ray diffraction (XRD) measurements were carried out using a Rigaku diffractometer operated at 40 kV and 35 mA. The XRD spectra were recorded in the
Encapsulation of clay in a non-aqueous dispersion polymerization

range of $1° < 2\theta < 10°$ using a step size of $0.02°/\text{point}$, a scan rate of $0.24° \text{ min}^{-1}$ and employing Cu-K$_{\alpha_1}$ radiation (1.54 Å). Samples were analysed as dry powder or in glass capillaries (diameter = 1 mm) in case of liquid samples, directly after preparation.

Particle morphologies were studied by using the FEI Quanta 3D FEG Scanning Electron Microscope (SEM). Before scanning, the SEM samples were mounted onto aluminium stubs and coated with gold.

A vitrification robot (FEI Vitrobot Mark III) equipped with a humidity- and temperature-controlled glove box was used to prepare the Cryo-Transmission Electron Microscope (Cryo-TEM) samples. Cryo-TEM grids, R2/2 Quantifoil Au Jena grids, were purchased from Quantifoil Micro Tools GmbH and before the vitrification procedure they were surface plasma treated using a Cressington 208 carbon coater. 3 μL of the reaction solution was taken from the sample vial and applied to the Au grid inside the vitrobot chamber, at 100 % humidity and 20°C. Subsequently, the grid was blotted for 2 seconds with filter paper and plunge-frozen in melting ethane at liquid nitrogen temperature. The samples were then kept in liquid nitrogen and loaded into the Cryo-TEM. Cryo-TEM microscopy was performed with a TU/e CryoTitan (FEI). The microscope is equipped with a GIF 2002 Gatan energy filter connected to a 2K * 2K pixel Multiscan™ CCD camera, allowing both Zero Loss imaging as well as element specific imaging using the Electron Energy Loss Spectroscopy (EELS) mode, with a pre-GIF 2K * 2K US 1000™ CCD camera.
4.3 Results and discussion

4.3.1 Attempts to encapsulate surface modified clay

Pre-treatment of the natural clay platelets with cationic molecules for face modification or covalent bonded edge modification was necessary to make the platelets hydrophobic and reactive. The used molecules have specific moieties that are needed to enhance the compatibility or reactivity during the polymerization processes. In the following section the modification and subsequent dispersion polymerization are described.

4.3.1.1. Synthesis of TMC-10

The reaction with trimethylamine and the successive purification steps, after synthesis of TMC-10, was checked with $^1$H-NMR (CDCl$_3$) and is shown in Figure 3. TMC-10 is responsible for several peaks in $^1$H-NMR (CDCl$_3$) spectrum: $\delta$ 1.33 (m, 14H), 1.68 (m, 2H), 1.78 (m, 2H), 1.95 (s, 3H), 3.47 (s, 9H), 3.57 (t, 2H), 4.14 (t, 2H), 5.55 (d, 2H), 6.10 (d, 2H) ppm.

![NMR spectrum of TMC-10](image)

Figure 3: $^1$H-NMR spectrum of TMC-10.
4.3.1.2 Modification of clay

To check the possibility of using TMC-10 as a surfactant, the critical micelle concentration (CMC) was determined in water by measuring the surface tension of the solutions. Figure 4 shows the surface tension plotted against TMC-10 concentration and the threshold concentration at which micellization begins is known as the CMC. The CMC of TMC-10 in water is 0.47 g/l. To put this number in perspective, the CMC of sodium dodecyl sulphate in water is 2.33 g/l.

![Graph showing variation of surface tension with increasing TMC-10 concentration in water](image)

**Figure 4: Variation of surface tension with increasing TMC-10 concentration in water measured with the Wilhelmy plate method.**

*Note the change in behaviour at the CMC (=0.47 g/l).*

In order to check the adsorption of the modifier on the clay, surface tension measurements were performed on PEGMA and TMC-10 solutions. After 1 wt% MMT was added to the samples and sonicated for half an hour, the mixture was centrifuged and the supernatant was collected and measured again in the surface tensiometer. The results are collected in Figure 5, in which both samples of TMC-10 and PEGMA show an increase in surface tension of the supernatant indicating that adsorption of the surfactant on the clay platelet surface occurred. In the case of TMC-10 all surfactant is
adsorbed on the clay surface at a concentration of 0.01 wt% since the supernatant has the value of pure water 72 mN/m.

![Figure 5: Surface tensions, measured with the Whilhelmy plate method, of: a) PEGMA solutions in water and b) TMC-10 solutions in water before and after the addition of clay.](image)

TGA was used to gain quantitative insight into the extent to which surface modification took place. Figure 6 shows the thermograms before and after the exchange of the TMC-10 and PEGMA molecules onto the clay. The weight loss between 20°C and 100°C corresponds to the removal of water coordinated with Na⁺ from the interlayer. The difference between the weight loss of the unmodified and modified clay confirmed the presence of TMC-10 and PEGMA on the clay. The amount of TMC-10 and PEGMA on the clay surface was calculated using equation (1) which was taken from Herrera et al., using the weight loss between 200°C and 600°C. In this equation, \( M \) is the molecular weight of the adsorbed surfactant on the clay and \( W_{200-600} \) is the weight loss between 200°C and 600°C. The results are shown in Table 1 indicating that the clay contains adsorbed PEGMA and TMC-10.

\[
\text{adsorbed amount (mequiv.*/ g⁻¹) } = 10^3 \frac{(W_{200-600})}{(100-W_{200-600})M} \tag{1}
\]
Encapsulation of clay in a non-aqueous dispersion polymerization

Figure 6: TGA thermograms of (a) Na-MMT clay and MMT modified with different PEGMA concentrations and b) Na-MMT clay and MMT modified with different TMC-10 concentrations.

Table 1: Weight loss and adsorbed surfactant on clay.

<table>
<thead>
<tr>
<th>Name</th>
<th>Weight loss 200-600 °C (%)</th>
<th>adsorbed amount (mequiv. *g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MMT</td>
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<td></td>
</tr>
<tr>
<td>MMT 0.125 wt% PEGMA</td>
<td>9.74</td>
<td>0.21</td>
</tr>
<tr>
<td>MMT 0.25 wt% PEGMA</td>
<td>13.28</td>
<td>0.29</td>
</tr>
<tr>
<td>MMT 0.5 wt% PEGMA</td>
<td>18.52</td>
<td>0.43</td>
</tr>
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<td>MMT 1 wt% PEGMA</td>
<td>21.40</td>
<td>0.52</td>
</tr>
<tr>
<td>MMT 0.03 wt% TMC-10</td>
<td>9.11</td>
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<tr>
<td>MMT 0.07 wt% TMC-10</td>
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<td>0.55</td>
</tr>
<tr>
<td>MMT 0.11 wt% TMC-10</td>
<td>19.11</td>
<td>0.79</td>
</tr>
</tbody>
</table>

The changes in interlayer distance (d-spacing) after adsorption were determined using XRD measurements. Figure 7 shows an increase of basal spacings for PEGMA and TMC-10 modified clay which is 18 and 14 Å compared to the nascent clay. These data indicate that PEGMA and TMC-10 are located at the surface of the clay platelets.
4.3.1.3 Dispersion polymerization in the presence of the surface modified clay

In chapter 3 we showed that pure polystyrene particles could be prepared in ethanol with a diameter of 2.3 µm and showed a uniform size distribution. Adding 1 wt% MMT resulted in a broader particle size distribution, 500 nm – 2 µm, as can be seen in Figure 8. Yang et al.\(^\text{10}\) prepared PST colloid particles armoured by clay layers in suspension and observed that the layers had a similar effect on the particle size and distribution. Greesh et al. claim that the nucleation is disturbed by the presence of clay, leading to a broader particle size distribution. In our case the clay is present between and on top of the particles as can be seen in Figure 8. There is no proof of armored surface morphology and the particles appear to be smooth.
Encapsulation of clay in a non-aqueous dispersion polymerization

Adding 1 wt% of Cloisite 30B to the dispersion leads to a similar result as adding nascent MMT clay, as can be seen in Figure 9. A similar broad particle size distribution is observed (500 nm – 2 µm) and clay is found between the particles.

Several attempts were made to try to encapsulate nascent MMT clay in TEA. An example is shown in Figure 10. The particle size distribution is broad and ranges from 550 to 1000 nm. Some aggregated features and anisotropic particles can be seen in the SEM images.
Figure 10: SEM images of PST particles prepared via dispersion polymerization in TEA at 120°C containing 1 wt% MMT.

Similar attempts were made with hydrophobic clay. Figure 11a shows the PST particles containing 1 wt% Cloisite 30B and Figure 11b the PST particles containing I34 TCN in TEA after dispersion polymerization at 120°C. Similar results compared to the nascent MMT clay are found. A similar broad particle size range was found as in the case of the nascent clay.

Figure 11: SEM images of PST particles prepared via dispersion polymerization in TEA at 120°C containing (a) 1 wt% Cloisite 30B and (b) I34 TCN.
When using the IP 3040 and nascent MMT we obtained aggregated spherical like particles as can be seen in Figure 12. Aggregated structures were obtained ranging from 500 nm to several micrometers.

![SEM images of PST particles prepared via dispersion polymerization in IP 3040 at 120°C containing 1 wt% MMT.](image)

**Figure 12**: SEM images of PST particles prepared via dispersion polymerization in IP 3040 at 120°C containing 1 wt% MMT.
After changing to a more hydrophobic clay like Cloisite 30B and Nanomer I34TCN we obtained structures similar to the MMT in IP 3040 and bigger particles or aggregates as shown in Figure 13.

Figure 13: SEM images of PST particles prepared via dispersion polymerization in IP 3040 at 120°C containing (a-b) 1 wt% Cloisite 30B and (c-d) 1 wt% Nanomer I34TCN.
After trying to encapsulate clay in polyol or TEA we decided to take a step back and look at the EtOH dispersion polymerization in combination with the PEGMA and TMC-10 modified clay. With the addition of 1 wt% of PEGMA or TMC-10 modified clay to the dispersion polymerization in ethanol, a broader particle size distribution is obtained and the particle size is approximately 1.5 µm as shown in Figure 14.

![SEM images of PST particles prepared via dispersion polymerization in ethanol containing (a-c) 1 wt% MMT modified with PEGMA and (d-f) 1 wt% MMT modified with TMC-10.](image)

The presence of the modified MMT in the polymer matrix was supported by TGA analysis. TGA of the composite showed a residue bigger than the pure PST indicating that clay is present in the polymeric phase, as can be seen in Figure 15. The onset of degradation shifts approximately with 10°C from 350°C for pure polystyrene particles to 360°C for the composites. First, a derivative of the weight loss curve can identify the point where weight loss is most abundant and this shows a similar shift of 10 degrees. The addition of surface modified clay leads to an improvement in thermal stability of the composite.
Figure 15: TGA thermograms of polystyrene (PST), polystyrene particles with PEGMA modified clay (PST-PEGMA) and polystyrene particles with TMC-10 modified clay (PST-TMC-10).

The changes in interlayer distance ($d$-spacing) of the MMT in PCN were measured with XRD. The XRD spectra are shown in Figure 16. Both $d$-spacings of the PCN show an increase in interlayer distance compared to the modified clay in Figure 7 suggesting that the clay is in the polymer phase intercalated and possibly exfoliated.

Figure 16: XRD patterns of polystyrene (PST), polystyrene particles with PEGMA modified clay (PST-PEGMA) and polystyrene particles with TMC-10 modified clay (PST-TMC-10).
Encapsulation of clay in a non-aqueous dispersion polymerization

We used Bright Field Conventional Transmission Electron Microscopy (BF-CTEM) and Dark Field Scanning Transmission Electron Microscopy (DF-STEM) to study the morphology of the particles obtained via dispersion. In the DF-STEM mode, the contrast between the phases is created by their differences in density and to a certain extent their crystallinity.\textsuperscript{11} An example is given for the PST dispersion in Figure 17b.

![Figure 17: (a) BF-CTEM image and (b) DF-STEM image of the polystyrene dispersion prepared in ethanol.](image1)

In the case of the 1 wt% TMC-10 and PST we observed interesting morphologies under BF-CTEM conditions as can be seen in Figure 18; a non-spherical particle can be seen with an aggregate attached to it to what we believe is clay.

![Figure 18: BF-CTEM images of PST particles with TMC-10 modified clay.](image2)
Using the DF-STEM mode we observe clay between the particles, as can be seen in Figure 19b as the light area between the particles and as the dark lines between the particles in Figure 19c.

![Figure 19: Dark Field Scanning Transmission Electron Microscopy images of the PST particles with TMC-10 modified clay in the same area as in Figure 18.](image)

To be sure that the clay is in between the particles the TEM stage was tilted and images were taken at three different angles. Figure 20 a-c shows that the clay, appearing as the light area between the particles in the images, always remains visible in between the two particles. Therefore the clay particles are encapsulated by the PST. Figure 20 d-f shows that the clay, appearing as the dark line between the particles in the images is partially sticking out and is also in between the two PST particles.
Encapsulation of clay in a non-aqueous dispersion polymerization

Figure 20: Dark Field Scanning Transmission Electron Microscope images of the PST particles with TMC-10 modified clay at three different tilted angles.

For the particles shown in Figure 20 a-c, tilted images were taken and a volume reconstruction of the particle was made with a computer. The result is presented in Figure 21a. The top of the particle is rough and cut off; this is due to the limitation of the computer capacity and also because of the relative big size of the PST particles making the DF-STEM mode work on its upper limitation and causing this surface in the reconstruction. The volume reconstruction is made upon a tomography of a set of images. The polymeric matrix is removed after reconstruction, as shown in Figure 21 b-c. After removal of the polymeric matrix the clay particle remains, as can be seen in Figure 21d. Figure 21e shows the particle with the partial polymeric matrix at the background from an underneath view. The tomography cannot be used as a quantitative technique but only to reveal the location of the clay platelets. So the apparent two particles are believed to consist of one clay platelet or multiple platelets; only the thicker part of this platelet is taken into account for the reconstruction. The thinner
parts have not enough contrast compared to the rest of the polymer matrix or appear transparent in the images. This is an extra validation that the clay is encapsulated.

Figure 21: ADF-STEM tomography volume reconstruction showing the clay particle between the PST particles with TMC-10 modified clay.
The TGA data in combination with the TEM images seem to suggest that some clay may be in the interior of the PST particles. Therefore we took from a one week settled dispersion the top layer for a TEM sample. By doing so only the particles smaller than ~500 nm would be taken and in this way the electron beam in the TEM can pass the particle. The particles appear as transparent features instead of black features found for the big particles. In this way the interior of the PST particle could be studied.

The TEM images in Figure 22b shows perhaps some clay in the interior of the PST particles. The result is unconvincing since the TEM experiment was challenging and only one such particle was found. The majority of the particles were simply too big for studying the interior of the particle. What was obvious from the TEM images was that in the entire sample no free clay or clay aggregates were found.

Figure 22: TEM images of the top layer of a settled PST particles with TMC-10 modified clay dispersion. In this way the interior of the PST particle can be studied.

An experiment with a ten times lower PVP concentration was performed to check if the clay was really inside the polymer particles. The idea was that by reducing the PVP stabilizer concentration by 10-time and keeping the clay concentration constant, the clay is forced to the boundary of the polymer particle and medium to act as a pickering stabilizer. The Pickering stabilization is named after S.U. Pickering, who described the phenomenon in 1907 in which an emulsion was stabilized with solid particles.12
Chapter 4

The PST dispersion is stabilized by solid particles, in this case the clay that acts as Pickering stabilizer and adsorbs onto the interface between the two phases.

The dispersion polymerization was performed exactly in the same way as before. In this way armored particles were obtained as shown in Figure 23, similar to the armored particles reported before.\textsuperscript{13} The particle distribution was broad and ranged from several μm up to 30 μm. Also some aggregates were found. This may be an indirect proof that in the system with normal PVP concentration the clay is actually inside the particles.

![Figure 23: SEM images showing the PST armored particles prepared via a Pickering dispersion in ethanol at low PVP concentration with 1 wt% TMC-10 modified clay.](image-url)
4.3.2 Attempts to encapsulate covalent modified clay

This part describes the results obtained with edge modified clay. The MPTMS is grafted on the edges of the clay platelets.

4.3.2.1 Edge modification of clay

Figure 24 shows the thermogram before and after the covalent modification on the edge of the clay. The value of pure clay corresponds with the one of literature.\(^{14}\) Again the weight loss between 200 and 600°C is taken as a measure for the amount of MPTMS grafted on the clay. By using equation (1) this corresponds to 0.18 mequiv.g\(^{-1}\) of grafted MPTMS on clay.

To check whether the MPTMS is actually grafted on the side of the MMT and not physisorbed on the clay facial surface area, an XRD measurement was made. Figure 25 shows that diffraction peak of the MMT-MPTMS is not shifted as compared to the peak from MMT, indicating that the \(d\)-spacing of the MMT-MPTMS is not increased and this is evidence that the MPTMS is grafted on the edge of the clay platelets and not physisorbed on the clay surface.

![TGA thermograms of nascent MMT and MMT grafted with MPTMS (MMT-MPTMS).](image-url)
4.3.2.2 Dispersion polymerization in the presence of the surface modified clay

Adding 1 wt% of MMT surface modified with MPTMS (MMT-MPTMS) to the dispersion polymerization recipe leads to similar result as nascent MMT clay as can be seen in Figure 26a. A broad particle size distribution results (500 nm – 2 µm), and some clay platelets appear to be in between PST particles. The MMT-MPTMS leads to various morphologies, as shown in Figure 26. In this case we observed non-spherical particles and dumbbell shaped particles. The result was difficult to reproduce and peanut shaped morphologies were found after one half hour.
Encapsulation of clay in a non-aqueous dispersion polymerization

Figure 26: SEM images of PST particles containing MMT-MPTMS modified clay after (A-C) 24 hours, (D-F) 4 hours and (G-I) 30 minutes.

The changes in interlayer distance (d-spacing) of the MMT-MPTMS in PCN were measured with XRD and are shown in Figure 27. No diffraction peak is visible, suggesting that the clay is in the polymer phase and exfoliated.
Figure 27: XRD patterns of polystyrene (PST) and polystyrene particles with MMT-MPTMS modified clay (PST-MMT-MPTMS).

The TGA thermogram of the MMT-MPTMS PCN does not show a significant increase in the onset of degradation nor a shift in thermal stability compared to the pure PST as can be seen in Figure 28. The residue shows that clay is present in the PCN.

Figure 28: TGA thermograms of polystyrene (PST) and polystyrene particles with MMT-MPTMS modified clay (PST-MMT-MPTMS).
DF-STEM mode was used to study the morphology of the obtained dispersion. Figure 29 shows an image where the clay, as bright lines, is present in between polystyrene particles. The particles have smooth surfaces. The clay is encapsulated in the polystyrene.

Figure 29: DF-STEM image of polystyrene particles with MMT-MPTMS modified clay (PST-MMT-MPTMS).

Encapsulation of nascent and hydrophobic clays in the polyol IP 3040 and TEA seemed challenging and less successful. Aggregated structures were obtained in these media.
4.4 Conclusions

The MMT clay was successfully modified with TMC-10 and PEGMA as can be seen in the surface tension measurements. The increase in the $d$-spacing of the clay indicated that the clay was face-modified. PST particles with face-modified clay was successfully encapsulated with a dispersion polymerization in a non-aqueous medium. The particle size ranged from 500 nm – 2 µm and was broader than the distribution of pure PST particles. Intercalated and exfoliated structures were obtained and both synthesized face-modified PCN were found to be thermally more stable than the PST.

In the case of edge modified clay different morphologies were found for the same recipes. The dumbbell shaped particles resembled the morphologies found with the face modified clay, therefore showing the possible encapsulation of clay in a non-aqueous dispersion. TGA and XRD results indicate that the clay is present in the PST phase and is fully exfoliated.
References

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Polyurethane/clay nanocomposite foams.
Summary

Now that clay containing polymer dispersions in polyols can be obtained the next step is to use these dispersions in polyurethane formation. In this chapter some preliminary experiments are shown using different dispersions. Polyurethane foams with clay were prepared by adding clay containing TEA and polymeric methylene diphenyl diisocyanate (MDI). It was found that reproducing the properties of the foams, even without particles, seemed already very challenging. Therefore this chapter might be seen as a first attempt to prepare foams with encapsulated particles but no sound conclusions can be drawn yet. After adding the clay or polymeric particles to the recipe, scanning electron microscopy (SEM) images revealed a disrupted foam structure. By using dynamical mechanical thermal analysis (DMTA) an attempt was made to investigate the storage modulus of the foam. A decrease was found after the incorporation of clay or polymer particles.
5.1 Introduction

The development of materials modified with nanofillers is the basis for producing many sophisticated products. The first works with polymer nanocomposites were carried out in the 1980s by researchers from Toyota.\(^1\) This resulted in intensive research on these materials and the application of different matrixes like polyamide\(^2\), polyester\(^3\), polyethylene oxide\(^4\) and polystyrene.\(^5\)

Polymer nanocomposites obtained for a polyurethane matrix with an adequate nanofiller offer a change to produce materials where the properties of polyurethanes (PUR) can improve. PUR can be tailored to meet certain demands for the use in various applications such as coatings, adhesives, fibers, thermoplastic elastomers and foams.

A way to tailor PUR foam is to add a polyol which contains dispersed styrene-acrylonitrile copolymer particles. These particles aid in the control of foam hardness and processing. The first commercial filled polyol was based on the use of acrylonitrile as the sole monomer.\(^6\) As the filled polyol continue to evolve and to be used in other areas, such as flexible foam, deficiencies were found. One such deficiency was the discoloration in the foams and this led to the development of styrene-acrylonitrile copolymer polyol dispersions.\(^7\) It is believed that the presence of these particles in the foams introduces a heterogeneous morphology that creates sites for localized stress concentration.\(^8\) The particles act as sites for the onset of crazing during large deformation in, e.g. compression. The SAN particles absorb the energy provided and effectively increase the fracture toughness of the PUR foam.

PUR also has some other disadvantages, such as low thermal stability and low mechanical strength. To overcome these disadvantages, a great deal of effort has been devoted to the development of nanostructured PUR/Montmorillonite (MMT) composites in recent years.\(^9-11\)

MMT is natural belonging to the smectite 2:1 phyllosilicates and its crystal structure is made of two layers of silica tetrahedral fused together between an octahedral sheet of aluminum or magnesium hydroxide. These silicates self-organize to form stacks with a regular van der Waals gap between the galleries. The presence of ionic bonds (Al\(^{3+}\)
replaced by Mg$^{2+}$ generates negative charges that are balanced with cations like Na$^+$ and the ability to form hydrogen bonds with water make MMT hydrophilic and incompatible with organic polymers. The properties improvement upon organoclay addition is related to the morphological structure and the dispersion of the organoclay particles in the polymer. For this reason, in order to achieve an optimal dispersion of the silicates in the polymer, it is of prime importance to modify the MMT with various organic molecules/cations.

There are a few studies in the literature regarding the use of nanoclay for the preparation of PUR foam. For instance Wilkinsons et al.$^{12}$ used unmodified MMT in water as blowing agent for the formation of flexible PUR foams and studied the kinetics of this system. Up to 10 wt% of MMT clay was added to the polymer and they reported faster creaming time (the time required for the bubbles within the reaction to grow to a size where the mixture turns opaque) and increased rate of CO$_2$ generation after addition of MMT clay to their system.

Widya et al.$^{13}$ added 1 wt% Cloisite 30B into rigid PUR foam and this resulted in reduced cell size compared to the neat PUR. The mechanical properties of the various foams (the polyol content was varied) showed in general reductions in compression strength and compression modulus. They reported difficulties of mixing at higher clay loadings. Mondal et al.$^{14}$ prepared rigid PUR foams with 5 wt% MMT and Cloisite 30B and found an increase in storage modulus of 25% for both clay types at 35°C compared to the neat PUR. Upon addition of the clay the foam cell size decreases. They reported the hydrolytic resistance of the foams and concluded that the addition of clay increases the overall mechanical properties; however, the cell windows are weakened.

A very promising study is the one from Cao et al.$^{15}$ who studied the preparation of PUR foams with 5 wt% modified clay (Cloisite 30B). They used two trifunctional polyols ($M_w$ is 540 and 300 g.mol$^{-1}$) in the preparation of PUR. The higher molecular weight polyol produced rigid foam with a 650% increase in compressive strength and a 780 % higher modulus as compared to their neat PUR foam. The PUR foam prepared with the low molecular weight polyol and 5 wt% clay showed a reduction in compressive strength of 7% and a reduction in the modulus of 39% compared to their neat PUR.
The objective of this chapter is to present the effect on PUR by introducing nascent and modified clay or polymer hybrid particles to the foam and to combine clay in polystyrene particles for the use in PUR foam.

5.2 Experimental

5.2.1. Materials

Nascent Montmorillonite and modified with a quaternary ammonium salt, Cloisite 30B (30B) and Cloisite I34 (I34) were obtained from Southern Clay Products. The clays were dried before use for 24 hours at 100°C in a vacuum oven. The triethanol amine (TEA) was dried at 40°C in a vacuum oven. The polymeric MDI (pMDI) M220, Huntsman with $M_w = 400$ g.mol$^{-1}$, was used as received. A poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO) of $M_w = 1800$ g.mol$^{-1}$ was used as chain extender. Surfactant TEGOSTAB B1048, silicone based surfactant (Evonik), and pentane (Aldrich) were used as received.

5.2.2. Polyurethane foam preparation

The foam was produced using a lab-scale batch process shown schematically in Figure 1. 2.5 wt% of clay was dispersed in TEA by means of an Ultra Turrax® (5000 rpm). The mixture was then transferred to an aluminum cup and the surfactant and chain extender were added. In case of polymeric particles a loading of 10 wt% polymer particles was used based upon TEA. Particles were removed from the ethanol phase by centrifugation at 1000 rpm for 10 minutes. The EtOH phase was slowly replaced with no more than 2 washing steps with TEA and centrifugation steps.

Afterwards the polymeric MDI was added as quickly as possible to the cup and the mixture was stirred for 6 seconds with an overhead stirrer equipped with a propeller mixer. After 6 seconds the foaming started and the solidified foam was annealed at 120°C for 4 hours to complete the reaction. A typical formulation can be seen in Table 1.
Figure 1: Lab-scale batch foaming procedure. A 200 mL aluminum cup was used for mixing. The components were added while stirring. The mixture was poured into another aluminum cup for foaming.

Table 1: Foam formulations.

<table>
<thead>
<tr>
<th></th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA</td>
<td>50</td>
</tr>
<tr>
<td>EO-b-PO-b-EO</td>
<td>25</td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
</tr>
<tr>
<td>Surfactant</td>
<td>1</td>
</tr>
<tr>
<td>pMDI</td>
<td>185.6</td>
</tr>
<tr>
<td>Pentane</td>
<td>13.5</td>
</tr>
</tbody>
</table>

After curing a table drill equipped with a hole saw of 4 cm was used to extract disc-shaped test specimens from the sample for further analysis.
5.2.3. Characterization

Wide angle X-ray diffraction (XRD) measurements were carried out using a Rigaku diffractometer operated at 40 kV and 35 mA. The XRD spectra were recorded in the range of $1^\circ < 2\theta < 10^\circ$ using a step size of $0.02^\circ$/point, a scan rate of $0.24^\circ\text{ min}^{-1}$ and employing Cu-K$_{\alpha1}$ radiation (1.54 Å ). Samples were analyzed as dry powders directly after preparation.

Thermogravimetric analysis (TGA) was performed using a high resolution TA-Q500 instrument operating under a nitrogen flow of 50 mL.min$^{-1}$. The sample was heated from room temperature to 700°C at a heating rate of 10°C.min$^{-1}$.

Particle morphologies were studied by using the FEI Quanta 3D FEG. Before scanning the SEM samples were mounted onto aluminum stubs and coated with gold.

A DMA Q800 (TA instruments) was used for the visualization of the temperature dependant mechanical properties and the determination of the glass transition temperatures ($T_g$). The measurements were done in compression mode with amplitude of 15 μm at a frequency of 10 Hz and were simultaneously heated from 0 to 180°C at a rate of 10°C/min. The $T_g$ was set to be the temperature at the maximum of the peak of the tangent $\delta$ curve. DMA was also used for the acquisition of the elastic modulus, defined here as the slope of the stress vs. strain curve in the linear region.
5.3 Results and discussion

5.3.1. Morphology of the foam with Scanning Electron Microscopy (SEM)

Upon preparing PUR from nanofilled TEA with polymeric MDI, a nanofilled PUR was obtained. The cellular morphology of the freeze-fractured foams is shown in Figure 2 a-g. The neat PUR exhibits a structure with hexagonal and polygonal faces and an average cell size of approximately 1.2 mm.

Adding 2.5 wt% of clay to the PUR foam causes the cell of the foams to disrupt and to close partially. Less stable cells are formed since the number of asymmetric polygonal faces increases. Also the cell size decreases, as in the case of the foam containing Cloisite 30B to 0.4 mm. Areas also appear in which a lower degree of interconnection between the cells can be seen in these foams as compared to the neat foam.

It is well known that H-bonding formation among PUR groups greatly contributes to the strength and modulus of the PUR. Reaction can take place between the –OH group of the clay and the –NCO groups. The clay may interfere with the PUR bond formation causing a negative effect on the properties of the clay filled PUR foams resulting in this type of cell structures.

Similar asymmetric cell structures can be found in the foams that are filled with polystyrene particles (average pore size of 0.6 mm) and polystyrene hybrid particles like the encapsulated clay (0.9 mm) and armored particles (0.8 mm).

The involvement of clays or PST particles in the PUR reaction affects the network structure and the formation of PUR.
Figure 2: SEM images of various foams: (A) non-filled (reference), and foams containing (B) MMT clay, (C) I34 clay, (D) Cloisite 30B, (E) PST particles, (F) Encapsulated clay particles and (G) Armored clay PST particles.
5.3.2. Wide angle X-ray diffraction (XRD)

Figure 3 gives the XRD diagrams of the prepared foams. The foams with the clay do not show any diffraction peak indicating that the clay might be exfoliated in the foams. The foams with polystyrene hybrid particles also do not show any sign of clay intercalation.

Figure 3: XRD patterns of the reference foam and foams containing nascent Montmorillonite (MMT), Cloisite 30B, Nanomer I34, encapsulated clay particles and armored clay PST particles.
5.3.3. Dynamic mechanical thermal analysis (DMTA)

DMTA is a technique used to detect thermo-mechanical transitions/relaxations in materials. Transitions occur in amorphous or semi-crystalline polymeric materials when the energy threshold for certain molecular motions is exceeded. Increasing the temperature causes an increase in mobility in the material because of the softening of the material. This process usually manifests itself as a drop in the storage modulus (E’), a peak in the loss modulus (E’’) and a peak in tan δ. The dynamic mechanical thermal analysis of the mechanical properties enables the estimation of the glass transition temperatures of the polyurethane foams with and without clay and polymer composite particles as filler. Other transitions due to small-scale motions, local relaxations, kink motions, rotations of terminal groups and other motions can also be detected as peaks in the loss modulus and tan δ.

By using DMTA meaningful changes were registered for the storage modulus as shown in Figure 4.
The storage modulus at -50°C for the reference foam was almost twice as high as compared to the clay filled foam. The modified clay has a bigger effect on the modulus than the nascent MMT clay. Probably the mechanical properties are influenced by the cell structure of the PUR foams. The cell structure of the neat PUR showed the most symmetric and continuous cell structure and gives probably therefore the highest storage modulus.
Addition of the modified clay did not produce an increase of storage modulus. This sample demonstrates the significant interaction between the polyurethane phase and clay; the addition of clay causes an increase of 20 degrees in the maximum of the tan δ peak, as shown in Table 2, but with a drastic decrease of the storage modulus.

Addition of polystyrene particles or peanut shaped particles does not give an increase in tan δ. The storage modulus also decreases in this situation. The foam with the armored particles seems promising because it has a higher value for the storage modulus compared to the clay and polystyrene filled foam. However, the value is still lower than the neat PUR foam. The peak maximum of the tan δ has a significant increase of 100°C compared to the reference foam.

The DMTA data suggest that two aspects determine the final properties of the foam; firstly the size, shape and nature of the particles and secondly the affiliation between the particles and foam components during and after the foam formation. It is known that clay can act as a bubble nucleating agent\textsuperscript{16} or as a cell opener\textsuperscript{17-19} in the foam process, and can cause bubble growth and coalescence.

Also during foam formation the PUR molecules can be grafted onto the clay surface through the reaction between the –NCO groups and the –OH groups on the clay. Cao et al. reported that clay may interfere with the H-bond formation in PUR. It is well known that H-bond formation among urethane groups greatly contributes to the strength and modulus of PUR. The interference by the clay could cause negative properties and change the network structure of PUR.

By encapsulating the clay, the negative contribution of the clay of PUR formation is removed and the encapsulated clay does not influence the thermal properties of the foam. In case of the armored particles, the clay is still nearby the particle surface and can be present during foam formation. This arrangement causes the armored particles to have an influence on the thermal properties of the PUR foam.
Table 2: Storage modulus at different temperatures, maximum peaks of the tan δ (T) curves and elastic modulus of various PUR foams.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage modulus (MPa)</th>
<th>$T_{\text{max}}$ (tan δ) (°C)</th>
<th>Elastic modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-50°C</td>
<td>0°C</td>
<td>30°C</td>
</tr>
<tr>
<td>Reference</td>
<td>6.6</td>
<td>6.1</td>
<td>5.6</td>
</tr>
<tr>
<td>MMT</td>
<td>2.9</td>
<td>2.7</td>
<td>2.4</td>
</tr>
<tr>
<td>Nanomer I34</td>
<td>2.1</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Cloisite 30B</td>
<td>1.4</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>PST</td>
<td>2.9</td>
<td>2.7</td>
<td>2.5</td>
</tr>
<tr>
<td>Encapsulated clay</td>
<td>2.5</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Armored clay PST particles</td>
<td>4.7</td>
<td>4.2</td>
<td>3.6</td>
</tr>
</tbody>
</table>

A complex modulus can also be determined by performing a compression test on the foams and the results are shown in Figure 5. The beginning of the slope was used to determine the elastic modulus and the results are shown in Table 2.
Figure 5: Stress strain curves of the compression test for (a) PUR foam and foams containing polystyrene, encapsulated clay, and armored polystyrene clay particles and for (b) PUR foam, foams containing MMT, Cloisite 30B and Nanomer I34 clay, measured at room temperature.
5.3.3. Thermogravimetric analysis (TGA)

TGA is one of the most important methods to study polymer nanocomposites. The results of these measurements indicate the influence of the nanofiller on the thermal properties of the polymer. Nevertheless even for commercial nanocomposites it is possible to find results of studies that indicate the absence of thermal improvement for modified polymer. Figure 6 shows the first weight loss during thermal degradation of the neat PUR due to the degradation of the matrix as a consequence of the relatively low thermal stability of the urethane groups whereas the second weight loss has been associated to the soft segment.

A shift of about 60°C between the MMT containing foam and the PUR foam can be noticed which indicates a considerable improvement of thermal stability. The derivative shows a peak at 210°C for the pure PUR. The foams with clay have this as well but it is a shoulder towards a middle transitions. The clay increases the thermal stability in the foam.

According to the analysis of the results obtained for the hybrid system, lower amounts of clay show a clear improvement of the thermal parameters. The analysis of the maxima on the derivative curve of % mass conservation as a function of temperature indicates distinct increase of thermal stability for the foam with armored particles.

An improvement of thermal stability is found for all the system. It is also worth noticing that the improvement in thermal stability is visible in the DMTA experiments. The foam with armored clay showed no plastic deformation after being heated to 250°C. Only a slight yellowing occurred.
Figure 6: (a) % mass conservation and derivative dependence on temperature for PUR foam and the foam containing MMT, Cloisite 30B and Nanomer I34TCN. (b) % mass conservation and derivative dependence on temperature for the derivative of the TGA curve for PUR foam and the foam with PST, encapsulated and armored particles.
5.4 Conclusions

Polyurethane with clay was prepared by adding clay containing TEA and polymeric MDI. The XRD showed exfoliation and no proof of intercalation of the clay. The addition of 2.5 wt% MMT, Nanomer I34TCN and Cloisite 30B has direct consequences on the PUR network. The freeze-fractured samples show a disrupt foam structure which is also sometimes partially closed. There is a lower degree of interconnection between the cells observed in these foams. An increase in less stable cells is observed and the number of asymmetric polygonal faces increases. Also the cell size decreases as in the case of the foam containing Cloisite 30B to 0.4 mm. Also areas appear in which a lower degree of interconnection between the cells can be seen in these foams as compared to the neat foam. The same principle is true for the foams with PST, encapsulated and armored particles.

The study of the mechanical strength shows a clear decrease of the storage modulus after the incorporation of clay or polymeric particles. This is related to the change in PUR network.

Adding clay has also an effect on the $T_g$ of the polymer network. This effect is less/not present when the clay is added in the foam incorporated in polymeric particles. When clay is directly added to the foam formulation it can interfere with H-bond formation in PUR and this cause changes in the network structure in the PUR foam. The encapsulated clay removes this contribution because it does not influence the thermal properties of the foam. If the clay is still accessible during the foam formation, as is the case in the arrangement of the armored particle, an influence on the thermal properties of the PUR foam is observed.

Due to the addition of clay, an increased effect on the thermal stability of the foam is found. A shift of about 60°C between the MMT foam and the PUR foam can be noticed which indicates an improvement of thermal strength.
References


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Chapter 5


Conclusion and Outlook

In this thesis the encapsulation of Montmorillonite (MMT) clay in a polyol as the preferred continuous phase and subsequently as one of the reagents for producing polyurethane (PUR) foams was studied. From the research several issues arose that might need further investigations. We would like to point out these open issues which can perhaps be subject of future research.

Significant research has been made towards the use of environmental friendly solvents for polymerization such as supercritical carbon dioxide or ionic liquids. In a recent paper by A.G. West et al.\textsuperscript{1}, it is claimed that the use of polyethylene glycol can be considered as environmental friendly. They show the use of polyethylene glycol as solvent for controlled radical polymerizations, the reversible addition fragmentation (RAFT) process (for PMMA in this particular case). The polyol used in this thesis might also be considered environmental friendly if one is allowed to elaborate along this way.

In the thesis from Syed Imran Ali\textsuperscript{2} an anionic RAFT copolymer is adsorbed on the surface of synthetic Gibbsite clay. These particles were then used in a MMA emulsion polymerization under starved feed conditions, thereby creating anisotropic flat latex particles. Later, nascent MMT was encapsulated by a similar approach.

This might be the right direction to create flat encapsulated clay particles in a polyol, if the RAFT agent can be tuned to the right conditions. It should have the right interaction for the colloidal stability and be oppositely charged for successful adsorption on the clay surface.

The scope and emphasis during this PhD project was on the preparation of encapsulated clay particles. But in a preliminary study also the next step was studied; polyurethane foams with clay were prepared by adding clay containing triethanol amine (TEA) and polymeric methylene diphenyl diisocyanate (MDI) together. It was found that reproducing the properties of the foams, even without particles, was already very challenging. Therefore chapter 5 might be seen as a first attempt to prepare foams with encapsulated particles but no sound conclusions can be drawn yet. It might be
premature to make conclusive remarks because of the lack of data. More work could be done on varying the content of the clay or PST particles in the foam or the distribution of the particles in the foam. It is known that DOW Chemical uses polystyrene-acrylonitrile particles (generally the particles used are micrometer sized) in polyol for the foam process and this is a proven technique.

These particles act as formation points or nucleation centres for the gaseous phase in the foam process. The nucleation free energy is reduced by the nucleation agents that are added to obtain foam cells with a controlled structure and uniform distribution. Amongst them the organic nucleation agents are the most commonly used. Compared to conventional micrometer-sized filler particles used in the foaming processes, nanoparticles could offer unique advantages for enhanced nucleation.

The extremely large surface area of nano-clay particles provides much more intimate contact between the particles, polymer matrix and gas. Probably exfoliated nanocomposites will yield a much higher nucleation rate than the intercalated nanocomposites and higher effective particle concentrations can be obtained with the exfoliated clay at a low clay concentration. Both could lead to improved nucleation efficiency.

Lee et al.\(^3\) showed that using the right polyol in combination with clay is the key to success in terms of improving the mechanical properties. They produced foam with a polyol with an equivalent weight of 180 (polyol 180). Two types of clay were used, namely nascent MMT and an organtin complex adsorbed on the surface of the clay. A substantial increase in both compressive strength and modulus were observed. This demonstrated high reinforcement by nanoparticles.
For the rigid foam system (as used in this research) the presence of clay nanoparticle interfered with the network structure in the matrix and led to reduced mechanical properties as shown in Figure 1b. So the right combination of clay and polyol could lead to reinforcement of the foam and improved properties.

Nanoclay has also been used to improve the thermal insulation and aging properties of PUR foam. This could be beneficial for the production of microcellular foams. Microcellular foams have been considered as a lightweight and high strength material for structural applications.

Mass production of polymer nanocomposite and nanocomposite foams depends on reliable and affordable preparation methods. The bottleneck for the transfer of technology from laboratory to industry might be the cost of the process. There must be preferably a single step and robust techniques to prepare exfoliated nanocomposites in large quantity at low cost. For foam products various desirable cell morphologies must be possible through the successful control of nucleation and growth of bubbles. The pathway as laid out in this thesis is definitely promising.
References

In nanotechnology one very interesting theme is to combine different types of materials by inclusion of nanoparticles in polymer particles thereby enhancing for example mechanical properties, barrier properties and chemical resistance of the resulting films or foams. Several types of nanofillers exist of which an important naturally occurring one is Montmorillonite (MMT) clay. MMT has a high aspect ratio and can be made hydrophobic by chemical modification. The MMT is expected to be dispersible in a polyol. In case the inorganic filler (either encapsulated to as it is) is present in one of the components of the polyurethane formation an elegant route towards hybrid polyurethanes can be envisioned.

By using polyols in combination with inorganic fillers (e.g. clay, BaSO₄ or CaCO₃) in polyurethane foam manufacturing, cell-openness and the hardness or load bearing properties of the flexible foam are improved. It is observed that the inorganic fillers act as nucleating agents during the foaming process. By introducing the particles in the foam, a heterogeneous morphology is created and the particles can act as sites for localized stress concentration. The particle absorbs the fracture energy and therefore increases the toughness of the foam. Instead of inorganic fillers, organic fillers can be used in a similar way. The preferred method at Dow Chemical is to synthesize the polymeric material in-situ, by a free radical dispersion polymerization in a liquid polyether polyol medium. At the moment it is most common to use styrene-acrylonitrile copolymer polyol dispersions.

The goal of this thesis is to encapsulate Montmorillonite (MMT) clay in polymer using the polyol as the preferred continuous phase and subsequently as one of the reagents for producing polyurethane foams. The first step in the research was to explore the possibilities of exfoliating nascent and modified MMT in polyol liquids. Exfoliation is needed before any encapsulation can be attempted and is described in chapter 2. We found that dispersing the MMT in various polyols leads to birefringence due to formation of liquid crystals. The behaviour of the MMT in triethanol amine (TEA)
appeared to be complex and maybe not fully understood. But the observation of birefringence over time and flow induced birefringence indicates that some platelets have exfoliated towards single platelets or stacks of a few platelets. From the rheological and X-ray diffraction (XRD) data and observations in the transmission electron microscope we found that Cloisite 30B exfoliates in polyol 767. The nascent clay gave broad diffraction peaks in the polyol 767 and IP 3040, giving rise to the idea that the clay is intercalated.

Subsequently we started exploring our envisaged encapsulation technique; dispersion polymerization in the presence of clay. The results are presented in chapter 3. We started with clay free recipes in order to explore the possibilities of free radical dispersion polymerization in polyols and in ethanol. Monodisperse polystyrene particles of 2 µm in diameter were obtained in ethanol at 70°C. Dispersion polymerizations at 70°C in TEA and the polyols led to agglomeration and in the first hour control over particle formation was lost. Experiments with higher stirring rates did not result in stable dispersions. By increasing the polymerization temperature to 120°C, colloidally stable polystyrene particles in TEA were obtained. Mixtures of ethanol and TEA led to stable polystyrene particles at 70°C. We believe that the reduced viscosity (by the dilution with ethanol or by increasing the temperature) provides the key to the formation of stable polystyrene particles. By using 120°C stable dispersions of polystyrene in polyols are formed.

Subsequently we attempted to encapsulate the clay in polyol as a polymerization medium, as shown in chapter 4. First attempts to encapsulate nascent clay in the polyols led to aggregation. We modified the faces of the clay platelets by using electrostatic interaction (ion exchange) or the side of the clay platelet by a covalent bond between the hydroxyl group of the clay and a silane. The increase in d-spacing of the clay indicated that the clay was modified with TMC-10. The clay containing polymer particle sizes ranged from 500 nm- 2 µm and was broader than that of pure polystyrene particles. Thermogravimetric analysis (TGA) indicated that these particles were thermally more stable than the pure polystyrene particles.
In case of the edge modified clay different morphologies were found for the same recipes. The dumbbell shaped particles resembled the morphologies found with the face modified clay. TGA and XRD results indicate that the clay is present in the polystyrene phase and is fully exfoliated.

Now that clay containing polymer dispersions in polyols can be obtained the next step is to use these dispersions in polyurethane formation. In chapter 5 some preliminary experiments are shown using different dispersions. Polyurethane foams with clay were prepared by adding clay containing TEA and polymeric methylene diphenyl diisocyanate (MDI). It was found that reproducing the properties of the foams, even without particles, seemed already very challenging. Therefore chapter 5 might be seen as a first attempt to prepare foams with encapsulated particles but no sound conclusions can be drawn yet. After adding the clay or polymeric particles to the recipe, scanning electron microscopy (SEM) images revealed a disrupted foam structure. By using dynamical mechanical thermal analysis (DMTA) an attempt was made to investigate the storage modulus of the foam. A decrease was found after the incorporation of clay or polymer particles.

Also the $T_g$ of the foam changed due to the addition of clay. This effect was less when the clay is added in the foam incorporated in polymeric particles. If the clay is still accessible during the foam formation, as in the case of arrangement of the armoured particles, an influence on the thermal properties of the PUR foam is observed. From this exercise in producing particle containing foams it is concluded that lab scale foam production is very difficult to reproduce. With some caution however we can see that the presence of (clay containing) particles does affect the properties of the foams and that the accessibility of the clay for the reagents might be an important factor.
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Curriculum Vitae

Mark Berix was born December 19th 1980 in Limbricht, the Netherlands. He completed his secondary education at “Bouwens van der Boijecollege” in Panningen. Shortly after, he started a bachelor program in chemical engineering at Fontys in Eindhoven. In 2004 he graduated and started a master program in Material Sciences at the Eindhoven University of Technology. In January 2008 he started a PhD project on encapsulation of clay through non-aqueous dispersion polymerization in the Laboratory of Polymer Technology and Synthesis and Laboratory of Materials and Interface Chemistry at the Eindhoven University of Technology, under the supervision of prof. Alex van Herk, prof. Bert de With and dr. Marshall Ming. The most important results are presented in this dissertation.