THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Plasticized PVC Nanocomposites- The Effect of Montmorillonite Treatment and Processing Conditions on Material Properties

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Cover:
Exfoliation of clay mineral layers in TBC-plasticized PVC,
see page 36

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ABSTRACT

Polyvinyl chloride (PVC) is one of the world's most widely produced polymers. Its products are used in a wide range of areas such as building and construction, packaging, automotive, electrical/electronic and healthcare. PVC can easily be tailored to adapt material properties to specific applications. This is largely achieved by adding certain components to the PVC material formulation. Some of these additives are essential for PVC processing, such as heat stabilizers. Others greatly alter the material properties, like for example plasticizers that makes the material soft and flexible.

Nano-sized fillers have the advantage to remarkably improve material properties even at very low additions. Among nanoclays layered silicates have been widely studied and are known to improve mechanical properties and to add barrier properties to a material. Montmorillonite (MMT) is the most commonly used nanoclay for processing with polymers.

In this thesis the aim was to organically modify MMT to be suitable for incorporation in plasticized PVC. For this purpose novel methods for organomodification of MMT was developed in order to avoid the use of commercially available organoclays (OMMT) which are known to catalyse dehydrochlorination of PVC.

A solid-liquid state method to produce OMMTs was developed and plasticized PVC composite materials were processed. Composite materials were characterized with X-ray diffraction (XRD), mechanical testing, Scanning Electron Microscopy (SEM), gas permeability, cone calorimetry, Vicat softening temperature (VST), thermogravimetric analysis (TGA) and determination of hardness.

It was found that the addition of 10 phr sodium MMT to a tributyl citrate (TBC)-plasticized PVC significantly improved the material properties. Increased E-modulus by up to 182 %, nearly halved oxygen permeability and a significantly reduced total smoke released (TSR) by 37 % in fire testing. The whole manufacturing process of composite materials was developed to be free from solvents, prepared by dry-blending in a high-speed mixer followed by two-roll milling.

Keywords: poly(vinyl chloride), Montmorillonite, organic modification, melt processing, X-ray diffraction, barrier properties, scanning electron microscopy, mechanical properties

PREFACE

This thesis for the degree of Doctor of Philosophy reports the work carried out since April 2012 at the Department of Materials and Manufacturing Technology, Chalmers University of Technology (Gothenburg, Sweden) and RISE Bioscience and Materials (Borås, Sweden).

ACKNOWLEDGEMENTS

First of all I would like to show my deepest gratitude for all the support my three supervisors have contributed with. Main supervisor Ignacy Jakubowicz who has been an excellent support from the beginning to the very end and even offered half of his office to be occupied by me, Nazdaneh Yarahmadi from whom you can always get energy to continue struggling with all the otherwise burdensome work and Jonas Enebro who besides being the best partner in crime regarding hamburger eating always shows a never ending enthusiasm for new ideas and findings.

I would also like to thank my examiner Mikael Rigdahl for being my connection to Chalmers and always treating his PhD students with the outmost respect.

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All my colleagues at RISE and in particular Polymer Technology are acknowledged for once in a while encouraging me with pats on the back and lots of fika moments of course.

Thanks to all you others that I really intended to remember at the time for writing this, but for some inexplicable reason did not manage to stick to this paper anyway.

Of course, without all the support from my family this thesis would never exist. I have more than five years to pay back to you; I hope that we will have endless many years together…………

LIST OF APPENDED PAPERS

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I. ORGANIC MODIFICATION OF MONTMORILLONITE FOR APPLICATION IN PLASTICIZED PVC NANOCOMPOSITES
H. Petersen, I. Jakubowicz, J. Enebro and N. Yarahmadi
Applied Clay Science 107 (2015) 78–84

II. DEVELOPMENT OF NANOCOMPOSITES BASED ON ORGANO-MODIFIED MONTMORILLONITE AND PLASTICIZED PVC WITH IMPROVED BARRIER PROPERTIES
H. Petersen, I. Jakubowicz, J. Enebro and N. Yarahmadi
Journal of Applied Polymer Science, January 15, 2016, Volume 133, Issue 3

III. SOLID-STATE ORGANO-MODIFICATION OF MONTMORILLONITE FOR MANUFACTURING OF PLASTICIZED POLY(VINYL CHLORIDE) NANOCOMPOSITES
H. Petersen, I. Jakubowicz, J. Enebro and N. Yarahmadi
Journal of Vinyl and Additive Technology, accepted Oct 2017

IV. EFFECT OF MELT PROCESSING CONDITIONS ON PROPERTIES ENHANCEMENT OF PLASTICIZED PVC–MONTMORILLONITE NANOCOMPOSITES
H. Petersen, I. Jakubowicz, J. Enebro and N. Yarahmadi
Journal of Vinyl and Additive Technology, submitted Nov 2017

CONTRIBUTION TO THE APPENDED PAPERS

PAPER I

The author planned, after discussions with the reference group, and performed the experimental work such as the theoretical studies using HSPiP, the swelling experiments of MMT in various solvents and all the organic modification experiments. The author performed all the analyses, after first being supervised and trained on the equipment, except the XRD analyses which was performed by Dr. Eric Tam at Chalmers. The author was present at some of these analyses to gain understanding of the method and to discuss some results. The author compiled the results, arranged all figures and tables and took part in the writing and discussion of Paper I. The author was responsible for the submission of the paper and thus also took part in the revision of the submitted paper.

PAPER II

The author performed all the planning, after discussions with the reference group, and execution of the experiments in Paper II. The author did all the processing of plasticized PVC composite materials and also performed all the analyses except for some XRD analyses that were performed by Dr. Eric Tam at Chalmers. Other XRD analyses were performed at CBI in Borås, first under supervision from MSc Lovise C. Sjöqvist, then independently by the author at the same equipment at CBI in Borås. The author participated in the writing process of Paper II, compiled all the results into figures and tables. The author was responsible for the submission of the paper and thus also took part in the revision of the submitted paper.

PAPER III

The author planned, after discussions with the reference group, and performed the experiments in Paper III, from organic modification to processing of materials. The author did all the analyses work except for some deeper XRD studies which were performed by Dr. David Noreland at RISE in Södertälje. The author participated in the writing process of Paper III, compiled all the results into figures and tables. The author was responsible for the submission of the paper and thus also took part in the revision of the submitted paper.

PAPER IV

The author planned, after discussions with the reference group, and executed the experiments in Paper IV, except for dry-blending and two-roll milling that was performed by Arne Hallgren at INOVYN in Stenungsund in collaboration with the author. The author did all the analysis work except for the cone calorimetry which was performed by Tobias Jacobson at RISE in Borås. The author was present at this testing. The author was mainly responsible for the writing process of Paper II, compiled all the results into figures and tables. The author was responsible for the submission of the paper. Paper IV is not yet reviewed.

ABBREVIATIONS

DEHP - di-(2-ethylhexyl)phthalate
DIDP - Diisodecyl phthalate
DINP – Diisononyl phthalate
DTG – Derivative thermogravimetric analysis
HSP – Hansen Solubility Parameters
HSPiP – Hansen Solubility Parameters in Practice
IRHD - International Rubber Hardness Degree
MB – Masterbatch
MC – Micro-compounder
MMT, Mt – Montmorillonite
MMT-Na$^+$ - sodium Montmorillonite
Na$^+$-AR – as-received sodium Montmorillonite
Na$^+$-D – dried sodium Montmorillonite
NCH – Nylon Clay Hybrids
OM – Organic modifier
OMMT – Organically modified montmorillonite
phr – Parts per hundred (resin)
pHRR – peak heat release rate
PLS – Polymer layered silicate
PVC – Polyvinyl chloride
PVC-P – Plasticized Polyvinyl Chloride
PVC-U – Unplasticized Polyvinyl Chloride (Rigid Polyvinyl Chloride)
SEM – Scanning electron microscope
TBC – Tributyl citrate
TEC – Triethyl citrate
TGA – Thermogravimetric analysis
TSE – Twin-screw extruder
VCM – Vinyl Chloride Monomer
VST – Vicat softening temperature
WAXD – Wide angle X-ray diffraction
XRD – X-ray diffraction

TABLE OF CONTENTS

1 INTRODUCTION

1.1 BACKGROUND

Over the past two decades, there has been an increasing interest in the development of polymeric nanocomposites. Improved mechanical and barrier properties and higher flame retardancy have been reported in the field of polymer composites engineering [1]. Nanoclays are potentially one of the most promising nano-sized fillers with several attractive qualities, but they are also associated with some really tough challenges.

Layered silicate nanocomposites have attracted both academic and industrial attention, the latter starting with the work of Kojima et al. at the Toyota Central Research & Development Labs in Japan [2-4]. Their work on the improvement of Nylon 6 by the addition of organoclays is often considered to be pioneering work. Although the high potential of nanoclays as an additive there are to date rather few examples of commercial products, besides the use as rheological additives in coating products, drilling fluids etc. [5].

Polyvinyl chloride (PVC) is globally the third most used plastics [6]. It is appreciated for its cost-efficiency, high degree of versatility and excellent durability. To produce the many different PVC products that today are part of our daily life, various additives need to be added to the PVC resin. These are all added for specific purposes and will determine the many different properties of PVC. Plasticizers highly influence the properties of PVC and make the material soft and flexible, heat stabilizers are essential for thermal stability and other additives can improve mechanical properties, add processability or colour or be added as fillers for different purposes.

Montmorillonite (MMT) is the most commonly used nanoclay today, but due to its hydrophilic nature it needs to be organically modified to be compatible with most of the polymers of interest. This is almost always done by cation-exchange reactions with some kind of ammonium salt, often a quaternary salt; hence these OMMTs are commonly denoted as “quats” [7]. Unfortunately, these commercially available OMMTs are not suitable for incorporation in PVC. When thermally degraded these quats can act as catalysts for the dehydrochlorination of PVC [8, 9] and therefore it is of certain interest to develop alternative methods of organomodification of MMT. One feasible way could be the use of chelating agents for organic modification of MMT [10].

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1.2 AIM

The aim of this work is to organically modify montmorillonite suitable for incorporation in plasticized PVC. To avoid the use of commercially available organoclays based on quaternary ammonium salt, the use of chelating agents as organic modifiers will be examined.

Layered silicate plasticized PVC nanocomposites will be processed with optimized processing parameters to maximize the degree of exfoliation. The manufactured nanocomposite materials will be characterized with several different analysis methods to investigate the improved material properties and to perfectly understand the morphological structures.

The aim was also to evaluate long-term performance of the produced materials as well as to investigate if the barrier properties of the layered silicates can contribute to lower plasticizer migration.

2 POLYVINYL CHLORIDE (PVC)

In 1835 Liebig and Regnault reported the existence of the vinyl chloride monomer (VCM) [11]. Baumann observed in 1878 that sunlight could transform this monomer into a tough whitish material. Despite this progress it took until 1912 when the German chemist Fritz Klatte at Chemische Fabrik Griesheim-Elektron discovered the basis for PVC production. Patents for manufacturing were framed as a metal chloride catalysed process between hydrogen chloride gas and acetylene at 180°C. In the late 1920s the commercial production of PVC started in the USA with an almost immediate expansion in the early 1930s and meanwhile pilot plants for PVC production were started in Germany. When researchers at BF Goodrich and Carbide and Carbon Chemicals a few years later discovered that the addition of high-boiling-point liquids could make PVC soft and flexible, the ease of processing and the extended range of applications rapidly contributed to PVC becoming one of the world´s most used plastics.

There are some major advantages and, of course, some major limitations. In PVC´s favour, the cost effectiveness compared with other plastics is usually mentioned as one of the major advantages. Versatility of applications and durability in long-term use are two other reasons why PVC has become the number one choice in so many areas of use. Good resistance to outdoor weathering and also many different chemicals as well as certain mechanical properties can be achieved by suitable formulations.

On the other hand, the thermal stability of PVC is quite poor, leading to degradation even at rather moderate temperatures. For this reason the development of appropriate stabilizers have always been critical for PVC manufacturing and application, more about stabilizers will be discussed later on.

In a global perspective, there are today large variations in PVC manufacturing and applications, legislations and public opinion, trends and phase-out of certain additives. Therefore, this thesis will mainly focus on the European market. In 1995, European PVC resin producers signed the first European PVC Industry Charter. This dealt with voluntary emission limits for both the production of VCM and for the production of suspension PVC (S-PVC). Three years later, in 1998, a second industry charter was signed, concerning the production of emulsion PVC (E-PVC). In 2000, after some years of studies, the European Commission launched its *Green Paper* on environmental issues of PVC. Amongst many issues discussed in the Green Paper, the impact of the PVC industry in various aspects was treated, from production processes to economic importance. Of course, the extensive use of additives was another issue discussed, together with the complex management of PVC waste.

A few months before the Green Papers was launched in 2000, the voluntary commitment of the European PVC industry, Vinyl 2010, was signed and presented. The volume of the European PVC market at that time, including additives, was 8,3 million tonnes with a total value of finished PVC goods estimated to 75 billion euro [12]. In the executive summary of the *Vinyl 2010 – the Voluntary Commitment of the PVC industry* some key actions and commitments of the 10 year programme were stated [13]. Examples of those were a plan for the full replacement of lead stabilizers by 2015 (commitment of 50% reduction by 2010), the recycling of 200´000 tonnes of post-consumer PVC waste by 2010 and research and development on new recycling and recovery technologies. The Vinyl 2010 programme was reported annually and in the executive summary of the progress report of the 10th year it was concluded that the recycling goal was achieved, 260´842 tonnes of post-consumer PVC waste were recycled in 2010 [14]. Also, the reduction of lead based stabilizers reached 72% in the EU-27, well ahead of the goal of 50% set at the start of the programme.

Vinyl 2010 was renewed with another ten-year programme, the VinylPlus programme to be summed up in 2020. Some reports on today's status on PVC recycling are presented in the PVC recycling paragraph.

2.1 APPLICATIONS

Due to the versatile nature of PVC formulation there are an abundance of applications where PVC is amongst the first choices of material. Figure 1 shows examples of common PVC products, both plasticized and unplasticized (rigid) PVC.

Figure 1. Examples of PVC applications both plasticized and unplasticized. Photos INOVYN/Sissel Flo Nilsen/Tor Alvseike/Terje Knudsen.

The total demand of plastic materials (excluding some plastic fibres) in the EU (EU28 + NO/CH) was close to 50 million tonnes in 2015 [15] of which PVC accounts for 10%. By far the largest field of application for PVC is the building and construction. Profiles accounted for 28 % of the total PVC market in the EU 2014 [16] followed by pipes and fittings (22 %) and rigid film (9 %).

Water and waste water infrastructure are extremely important contributions to the social structure of a modern society. This makes great demands on the technical aspects and reliability of for example piping. PVC has excellent resistance to chemicals and compared with for example cast iron or cement pipes PVC is a light weight material which allows for longer lengths. The high stiffness of rigid PVC is suitable for piping along with its long service lifetime.

Since the 1950´s PVC has been amongst the first choices as piping material and technical innovations, such as the development of molecularly oriented PVC (PVCO) pipes, has further strengthened its market position [17]. One could also imagine that PVC pipes´ high resistance to earth movements, and even to earthquakes, could be of particular interest in the (near) future?

Extrusion is by far the most common PVC processing method, and window profiles accounts a noteworthy part of the total volume extruded PVC goods [18]. PVC window profiles are depending on good weathering resistance and high impact performance to meet market requirements.

It is often estimated that about 25% of all plastics in medical device products are made of PVC [19]. It is, not surprisingly, low cost, favourable processability, good transparency, low temperature flexibility and the wide range of applications that accounts for the popularity of PVC as the choice of material. Common medical device products are blood bags and tubing, gloves, dialysis equipment, mouthpieces and masks, oxygen delivery equipment, catheters, injection moulded parts, and device packaging [20]. These are all products made of plasticized PVC and the most commonly used plasticizer, up to now, has been the phthalic acid ester di(2-ethylhexyl) phthalate (DEHP), also known as dioctyl phthalate (DOP) [21].

There are of course a great number of other products made of PVC. A few examples are inflatable pools, boat fenders and garden hoses.

2.2 PVC POLYMERISATION

The molecular structure of PVC consists of three rudimentary bonds, namely the C-C, C-H and C-Cl bonds. The C-Cl bond has characteristics very close to those of an ionic bond, while the C-C bond is totally non-polar and the C-H bond only slightly polar.[22] Dipole moment is measured as the separation of charge that arises from electronegativity. It is presented with the non-SI metric unit Debye (D). The weighted dipole moment of the vinyl chloride molecule is 1,45 D which is very close to the value of the C-Cl bond, 1,56 D. These points out the importance of the C-Cl bond and its influence on the chemical properties of PVC.

2.2.1 Chlorine

Polymerization of PVC basically requires ethylene and chlorine. In the manufacturing process of caustic soda, the by-product derived is chlorine. Traditionally this was achieved in a process with a mercury cathode and a titanium anode. In this very energy intensive process a current dissolves sodium into the mercury cathode while the chlorine is released at the titanium anode. Caustic soda (NaOH) is produced when the mercury cathode/sodium reacts with water and the mercury is regenerated to the electrolytic cell. Besides consuming large amounts of energy, this process is associated with environmental issues due to the use of mercury. Today, at least in Europe, the mercury cell process is being phased out, which on the other hand requires considerable investments in alternative technologies.

At the INOVYN plant in Stenungsund, the chlorine production formerly based on the mercury cell technique is at current being replaced with a modern membrane cell plant, expected to start running in 2018. This is the most common technique in Europe to produce chlorine today. It contributed in 2016 to 66% of all chlorine produced [23] and has gained market shares in favour of the former dominating mercury process, which is consistently decreasing mostly due to its toxic character.

Put simply, an ion-selective membrane allows only sodium ions to pass. At the anode, chloride ions are oxidized to chlorine gas while hydrogen gas is produced at the cathode. Compared with the mercury cell process, the membrane cell process requires less energy and has a more favourable environmental profile.

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2 + H_2 \tag{1}$$

2.2.2 Vinyl Chlorine Monomer (VCM)

The next step is to produce the VCM. This is done by direct chlorination of the ethylene to yield 1,2-dichloroethane (Eq. 2)

$$CH_2 = CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl \tag{2}$$

1,2-dichloroethane is then cracked to give VCM (Eq. 3).

$$ClCH_2CH_2Cl \rightarrow CH_2 = CHCl \tag{3}$$

In general, vinyl chloride is a colourless, flammable gas at room temperature. VCM has a boiling point of -13,4 ^{o}C and forms explosive mixtures with air. Prior to polymerization and at transportation, VCM is pressurized and liquefied.

Studies carried out during the 1970´s revealed that prolonged exposure to VCM could cause angiosarcoma of the liver, a rare fatal cancer representing less than 1% of the primary hepatic tumours in the general population [24]. The dangers of exposure to VCM were highlighted and actions were taken to minimize the risks at PVC production plants. Since 1974 no deaths connected to exposure during PVC production have been reported.

2.2.3 PVC polymerisation

Production of PVC is made in two main processes viz. suspension or mass and emulsion polymerisation. The product is particulate in nature and comes in two main sizes depending on the process used. Since the VCM has low reactivity, PVC is polymerized via free-radical polymerization with peroxide catalysts. This is a two-step process:

$$initiator \rightarrow 2\ initiator\ radicals \tag{4}$$

The initiator, the peroxide, produces free radicals.

$$\mathit{initiator\ radical} + VCM \ \rightarrow \mathit{growing\ polymer\ radical} \tag{5}$$

The initiator radical reacts with VCM, then forming a radical which in the next propagation step grows to form PVC polymer chains:

$$\mathit{growing\ polymer\ radical} + VCM \rightarrow \mathit{growing\ polymer\ radical} \tag{6}$$

The reaction continues with the dominating head-to-tail addition of monomer to the growing polymer chain. Occasionally, a head-to-head structure is formed leading to a defect in the polymer chain. This is discussed in the degradation and stabilization chapter.

Polymerization is normally terminated at conversion rates of 80-90 % [25].

The molar mass of PVC is represented by the k-value. The k-value can be calculated from the viscosity determined with capillary viscometer according to the standard ISO 1628-2.

$$k - value = \frac{1{,}5 \log \eta_r - 1 + \sqrt{1 + \left(\frac{2}{c} + 2 + 1{,}5 \log \eta_r\right) 1{,}5 \log \eta_r}}{150 + 300c} \times 1000 \tag{7}$$

Where c is the concentration of the solution, in grams per millilitre,

$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0}$ is the ratio of the viscosities (efflux times) of the solution and solvents and

$t \ and \ t_0$ are the efflux times of the solution and solvent in seconds.

Typical applications with low k-value PVC ($k < 60$) are different foamed products while plasticized products such as cables, hoses and geo membranes often requires PVC with higher k-values ($k > 70$) [26]. The molar mass of PVC can be controlled by the choice of initiator [27]. Also, higher temperatures mean higher rates of chain transfer, thus a lower K-value. To increase the K-value, initiators with lower half-life temperatures are used. The propagation rate constant, k_p, is controlled by temperature (T) only, which is expressed by the equation:

$$k_p = 3{,}3 \times 10^6 exp\left\{-\frac{3700}{RT}\right\} \tag{8}$$

where R is the gas constant.

2.2.4 Suspension polymerization (S-PVC)

S-PVC is by far the most produced type of PVC with about 80% of the PVC market. Small monomer droplets of approximately 50-200 µm in diameter are suspended in water [6]. Since these droplets contain the monomer soluble initiator, the polymerization takes place inside them. This technique prevents excessive heat build-up from the exothermic polymerization reactions. Finally, unreacted VCM is taken care of and recycled as raw material in another batch of S-PVC polymerization. Water is also removed, usually by centrifugation followed by drying. The result is then a white powder denoted as the PVC resin.

Individual S-PVC grains are irregularly shaped and in the size of 100-150 µm in diameter [25]. These porous grains consist of primary particles, about 1 µm in diameter, which in turn are composed of about 10 nm small microdomains. The suspending agent used in the polymerization process creates a thin skin, a pericellular membrane, around the S-PVC grains.

2.2.5 Emulsion polymerization (E-PVC) and micro-suspension PVC

Emulsion PVC (E-PVC) is also known as paste PVC and accounts for approximately 10-15 % of the total PVC resin produced [25]. Certain emulsifiers are used to facilitate this particular type of process in an oxygen-free environment. The polymerization differs from the one that produces S-PVC in the way that free radicals are produced by water soluble initiators in the aqueous phase while the initiation occurs on the surface of the monomer particles. The resulting product E-PVC consists of very fine particles with sizes of 0,1-3 µm. When E-PVC is spray dried the small primary particles form agglomerates of a wide range of grain sizes.

Micro-suspension PVC is produced more like S-PVC with VCM-soluble initiators, but produces small particle (0,2-3µm [11]) with low porosity. The result is considered to consist of primary particles only, since these have the same size as the droplets in the polymerization process. Micro-suspension PVC is then often used in combination with E-PVC for plastisol or paste applications.

2.2.6 Bulk polymerization

A third type of PVC polymerization is called bulk or mass polymerization and accounts for <10 % of the world production of PVC. It is carried out without the presence of water. In the first reactor the VCM and a free-radical initiator are vigorously stirred. PVC is insoluble in its own monomer and particles absorb unreacted monomers until a conversion of 10-15 % where the viscosity becomes too high. The material is transferred to a second reactor where the polymerization continuous with a more gentle agitation until a conversion of approximately 20-40 % and the bulk PVC now appears as a dry powder. The polymerization continuous and at 70-90 % conversion the process is terminated and unreacted monomers are recovered. Bulk polymerization today is controlled by licenses originating from the developer of the first commercial process in the mid-1960´, Pechiney-St Gobain in France.

Bulk polymerization powder grains are rather similar S-PVC grains, with the exception that there is no pericellular membrane surrounding them.

2.3 PVC DEGRADATION AND STABILIZATION

85% of the produced PVC products are used in middle- and long term applications [11], especially in the building and construction area. This requires appropriate stabilization, not only during the harsh processing step, but also to secure the service life of the PVC products.

Theoretically, by studying model compounds structurally similar to the vinyl chloride molecule, PVC should theoretically be much more stable than it actually turns out to be. Unfortunately, chemical defect structures in the PVC chain reduce the stability of the polymer. Especially tertiary chlorine is considered to be one of the most detrimental threats for increased dehydrochlorination rate [27], mainly because of the often high concentration of this certain defect. These tertiary chlorine atoms are capable of initiating the dehydrochlorination of PVC at a high initial rate of decomposition [28]. This initially high rate of decomposition is slowed down when the concentration of tertiary chlorines is decreased.

Unsaturations in the form of chloroallyl groups are also considered to initiate degradation, while unsaturations at the chain ends do not affect the thermal stability. In the dehydrochlorination process, hydrogen chloride (HCl) is split off. Without the addition of suitable heat stabilizers new defects in the PVC chain are formed and the HCl elimination continuous. One or more conjugated double bonds are formed and degradation of PVC can be recognized as yellow discolouration [26]. As the length of the conjugated double bonds continues to grow the discolouration follows the characteristic sequence yellow-orange-brown-black (Fig. 2).

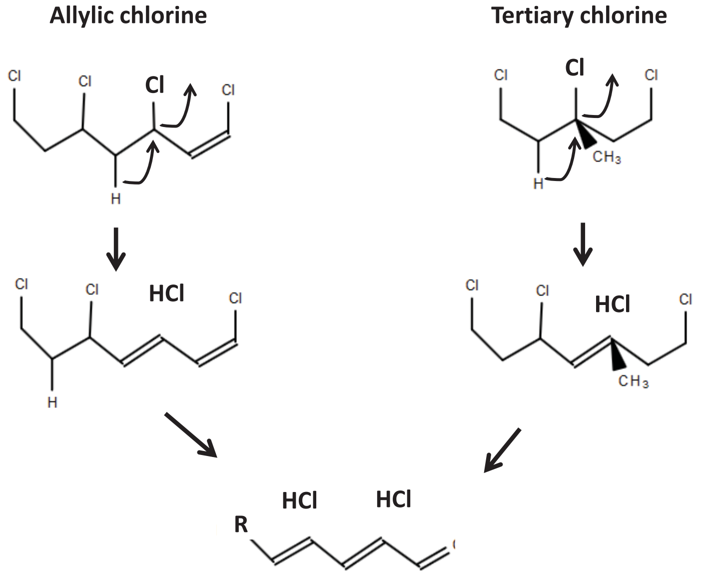


Figure 2. Labile chlorine atoms and their initiation sites of degradation.

2.4 PVC FORMULATION AND ADDITIVES

2.4.1 Dry Blend Mixing

Dry blend mixing or dry-blending is a high-speed mixing process used to prepare S-PVC formulations prior to processing. Normally, dry ingredients, such as the PVC resin, fillers and other powder additives, are added to the mixer. Then, after some mixing, the wet ingredients such as plasticizers and other liquid additives are added. The mixing speed is increased and the temperature rises primarily due to frictional heat [11]. At somewhere between 110-130^{o}C the mixing is interrupted and the dry-blend is promptly cooled to approximately 50^{o}C. The result is then a free-flowing powder even at rather high plasticizer loadings.

High intensity dry blending is carried out in vertical cylindrical bowls with propellers or knives as the mixing tools. Size and design of the equipment varies depending on the requirements of the mixing process and on the manufacturer. The laboratory high speed mixer used in this thesis is equipped with a double jacket allowing cooling water to cool the dry blend without removing it from the mixer.

For larger industrially used mixers up to perhaps a few thousand litres, the hot mix is transferred to a larger, water cooled, low speed mixer to effectively cool down the dry blend mix. These dry blends might also be filtered to ensure that unwanted particles are removed and prevented from ending up in the processing step. An example of unwanted particles in a plasticized PVC dry blend is those that for some reason were not appropriately mixed with the plasticizer. They could due to non-uniform fusion in the melt processing end up as what is in general known as fish-eyes in plasticized PVC products.

Plastisol on the other hand is based on E-PVC or microsuspension PVC resins and is defined as a suspension of PVC resin in plasticizer [29]. The PVC resins used for plastisols are non-porous and particles and agglomerates of particles are broken down to sizes varying between 1 and 20 µm during the mixing [11]. The result is a flowing liquid or a paste-like mixture, hence the denotation paste PVC. Certain additives are used in plastisols to facilitate the mixing of plastisols and the processing of PVC plastisol products. Some examples are rheology modifiers, wetting and dispersing additives for pigments and fillers, air release agents and defoamers.

Formulation of PVC dry-blends is totally dependent on what application it is intended for. Besides the fact that the right PVC resin, additives and, if so, plasticizer must be choose, the ingredients of a formulation can also interact with each other.

2.4.2 Heat stabilizers

PVC is very sensitive to heat, even at temperatures far below what is needed for the melt processing. It is reported that the energy needed for activation of heat degradation is lower than the energy needed for the generation of a PVC melt with acceptable processability.[30] There are a number of different heat stabilizers that are used to prevent the chain reaction of decomposition.

Because of the catalytic effect of HCl on the thermal degradation of PVC, the most important quality of a heat stabilizer is the ability to capture HCl. The reaction mechanisms are different depending on what type of stabilizer that is used. For stabilizer systems based on metal soaps, HCl binding can generally be described as in equation 9 [22]:

$$\begin{gathered} M(OOCR)_2 + HCl \rightarrow ClMOOCR + RCOOH \\ ClMOOCR + HCl \rightarrow MCl_2 + RCOOH \end{gathered} \tag{9}$$

where R is an aliphatic group.

In the case where a calcium/zinc stabilizer system is inserted in equation 9, the $Zn(OOCR)_2$ can be recovered by the $Ca(OOCR)_2$ according to equation 10:

$$ZnCl_2 + Ca(OOCR)_2 \rightarrow Zn(OOCR)_2 + CaCl_2 \tag{10}$$

The HCl binding ability of epoxidized compounds, such as epoxidized soya bean oils (ESO or ESBO) can be explained as showed in Fig. 3 [22].

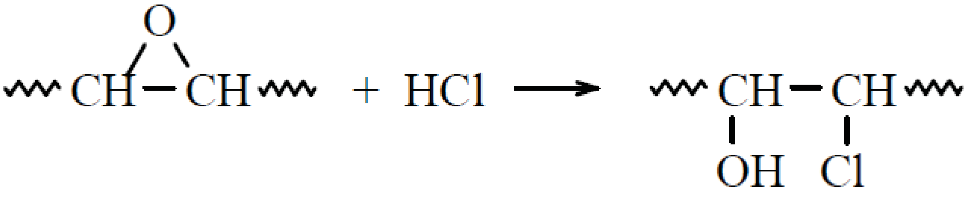


Figure 3. HCl binding of epoxidized compounds, for example ESO.

Formulation of heat stabilizer system is quite complex and producers of such additives must take several aspects into consideration.

2.4.3 Plasticizers

While stabilizers are essential for practically all PVC materials, plasticizers are the single key ingredient that has the most influence on material properties. Plasticizers transform a rigid material into a soft and flexible material. The glass transition temperature (T_g) of processed PVC is lowered when plasticizers are added. Some other characteristics of plasticized PVC are increased elongation, lower E-modulus and tensile strength, improved antistatic properties. Brittleness is decreased by plasticizers except at low additions, normally less than 10-20 phr, where a so called antiplasticizing effect occurs. One explanation presented by Robeson and Faucher [31] is that at such low concentrations the plasticizer fills the intermolecular free volume within PVC. The motion of the PVC chain is hindered and it then becomes more sensitive to impact stress.

Plasticizers also have a major influence on the processing properties of PVC. Internal lubrication is improved such that the internal friction is reduced. Also, the adhesion to metal surfaces is reduced. This is why processing of plasticized PVC normally does not require the addition lubricants.

Plasticization of PVC is a rather complex process and therefore there are more than one accepted theories about the underlying mechanisms [32]. The lubricating theory asserts that plasticizers weaken the van der Waals forces between polymer-polymer and thus allow the polymer chains to move more rapidly. However, this theory cannot explain why certain plasticizers are more efficient than others, and is consequently seldom used solely to explain the plasticization mechanisms. The gel theory is based on the assumption that the rigidity arises from a three-dimensional network of certain attachments and forces along the polymer chains. The plasticizer interferes with these resin-resin interactions and thus the rigidity is reduced. The third theory deals with free volume and the theory that plasticizers increase the free volume of PVC. The glass transition temperature (T_g) is reduced, often well below room temperature, and consequently, the plasticized PVC becomes more flexible above T_g.

Plasticizers can be either monomeric or polymeric. Monomeric meaning that the plasticizer is one single molecule, normally with a molecular weight range of 300-600, while polymeric plasticizers consist of repeating units and thus have higher molecular weights. Monomeric plasticizers can be categorized either by their performing properties or by their chemical belongings. Krauskopf [33] proposed use of only 3 grades for commercial plasticizers. The first one is the general purpose (GP) plasticizers, traditionally represented by DEHP/DOP, which is highly appreciated for its properties in relation to cost. DIHP and DINP are also more or less classified as GPs. The second grade is denoted performance plasticizers (PP) and as the name indicates, these plasticizers are chosen for any particular property that can justify a higher cost. Krauskopf further divided these PPs in three subgroups. Strong solvators (SS) are specially developed for low temperature processing, low volatility (LV) has in general higher molecular weight to minimize migration in long-term applications and finally low temperature (LT) which are plasticizers designed for high flexibility and impact resistance at very low service temperatures. The third grade of plasticizers are called specialty plasticizers (SP) and covers a wide range of plasticizers with the commission to add such value to PVC formulations that justifies their cost. According to chapter 8 in Handbook of vinyl formulating [32] SPs serve an important purpose on the market represented by different benzoate plasticizers, citric acid esters, adipates, trimellitates and polyester polymeric plasticizers.

In the 90's, the plasticizer market was dominated by DEHP, but when concern arouse for the reproduction toxicity of DEHP, the use of other phthalates that were considered less toxic increased. Some of these phthalates, such as di(2-propyl heptyl) phthalate (DPHP), di-isononyl phthalate (DINP) and diisodecyl phthalate (DIDP) are the most commonly used phthalates in the EU today, whereas DEHP still dominates the global market [34].

While phthalates up to the present still dominate as general purpose plasticizers, there is a rising demand and a positive development of different specialty plasticizers.

Epoxidized soya bean oil (ESBO or ESO) is used both as a secondary plasticizer and as a heat stabilizer.

2.4.4 Fillers

The use of fillers in PVC and other polymer materials is often associated with cost reduction. However, there are plenty of fillers that are added to PVC materials for various purposes. The by far most commonly used filler for PVC, by weight, is calcium carbonate ($CaCO_3$). The annual world consumption for use in polymer applications is over ten million tonnes [35]. Natural milled $CaCO_3$ is normally found in the size range from 0,5 µm to about 100 µm, while the synthetic precipitated $CaCO_3$ often comes in nano-size, i.e. under 100 nm. $CaCO_3$ used in particularly demanding applications such as window profiles is practically always coated with an appropriate coating chemical, for example stearic acid. The amount of coating can be decisive for the quality of the manufactured products. A coating level far below optimum increases the risk of moisture uptake during storage and agglomeration during processing while too much coating will increase the risk of plate-out [26]. $CaCO_3$ coatings can when excessively used, as well as external lubricants, migrate from the polymer melt and cause build-ups in certain regions of the extrusion process [11].

2.4.5 Lubricants and processing aids

In PVC-U applications lubricants are the most important additives next to heat stabilizers. Without lubricants PVC-U processing would not even be possible [29]. As for stabilizers, lubricant packages are also designed for the specific processing conditions intended for the product that is manufactured.

There are two main classes of lubricants, external and internal. External lubricants prevent stick to the metal parts and particulate flow in the melt. Stick prevention can be controlled by two different mechanisms. The polar nature of metal soaps and organic acids gives them a high affinity to the metal surface, whereupon a lubricant film is formed at the interface between the metal and the PVC. On the other hand, low polarity esters, polyethylenes and aliphatic organic waxes are incompatible with the PVC and form a “slippery” film on the surface of the polymer. External lubricants increase particle flow by forming a friction reducing film on the surface of the resin particles. The current intensity needed for processing is reduced since the fusion is slowed down which supports powder conveying over melt conveying.

Internal lubricants are the opposite of external lubricants and are made up of low molecular compounds that are slightly polar and semicompatible with the polymer. At processing temperatures internal lubricants are compatible enough to be accepted in the polymer matrix. This reduces the van der Waals forces between polymer chains which increases the ease of movement and thus having a positive contribution to the processing properties. At room temperature the internal lubricants precipitates and becomes nonfunctional.

2.4.6 Other PVC additives

Blowing agents are additives that at certain temperatures during processing decompose to release gas in order to create a foamed material. Processing aids are added to rigid formulations to add strength to the melt and thus assist in the extrusion. These are often acrylic polymer resins (PMMA) of various molecular weights.

2.5 LEGACY ADDITIVES

The European Parliament regulation NO 1907/2006 concerns the Registration, Evaluation, Authorization and Restriction of chemicals, REACH. The "*Candidate List of substances of very high concern for Authorisation*" contains 174 substances [36] of which 18 are used in PVC [37].

One major challenge in PVC recycling is the fact that in long-term application, there might be plasticizers and/or other additives that have been phased out or are on their way to be replaced. These are called legacy additives and may be restricted by legislation. VinylPlus has initiated several studies connected to the legacy additives issue, for example migration of various heavy metal stabilizers and the phthalate plasticizer DEHP from recycled PVC.

2.5.1 Phthalate plasticizers

There are some phthalate plasticizers that are classified according to CLP ((EC) No 1272/2008). The most recognized one is the DEHP plasticizer which is classified as category 1B for reproductive toxicity. This means that the use of it is restricted by authorisation, particular regulation are valid for medical devices containing DEHP. For the latest directions one could visit https://echa.europa.eu.

2.5.2 Chlorinated paraffins

There are three groups of chlorinated paraffins, short-chain (SCCP) with carbon chain lengths between 10 and 13, medium-chained with carbon chain lengths between 14 and 17 and long-chained chlorinated paraffins (LCCP) with chain lengths of 18 and more [38]. Chlorinated paraffins have been used as secondary plasticizers, but their contribution to an increased chlorine content in a material also adds flame retardant properties[26]. Adding a plasticizer to PVC normally decreases the flame resistance, while then chlorinated paraffins can be added to reduce this effect. The major drawbacks of chlorinated paraffins are their ability to further weaken the thermal stability of PVC and they are also in different grades being considered as toxic [39]. From 1994 to 2010 the use of chlorinated paraffins decreased with about 80% in Sweden to approximately 400 tonnes annually. Only about 2% of this consumption is SCCPs [40].

2.5.3 Various heat stabilizers based on heavy metals

An example of a heavy metal that is restricted by the EU Commission Regulation 494/2011 is cadmium. Until they are being reviewed 31 December 2017, the limits for cadmium originating from recyclates are 100 ppm for use in polymers and up to 1000 ppm in specified rigid PVC applications [41].

2.6 PVC RECYCLING

In the Progress Report 2017 from VinylPlus, the number one challenge is defined as "Controlled-loop management". This implies for example to annually recycle 800 kilotons of PVC by 2020, unfortunately the goal to include the recycling of 100 kilotons of difficult-to-recycle PVC materials was withdrawn due to the lack of working technologies. The challenges defined in the report are directly associated with goals in the resolution "Transforming our world: the 2030 Agenda for Sustainable Development" presented by United Nations General Assembly in October 2015 [42].

It is reported that the total amount of recycled PVC in 2016, within the Vinyl 2020 and VinylPlus frameworks, almost reached 600 kilotons, which is a six times increase over the past ten years[41]. Window profiles and related products have been the dominating group of recycled products followed by cables. Recovinyl, an organization to facilitate the recycling of PVC from waste stream to manufacturing of new product, was the main contributor to the total amount of recycled PVC in Europe 2016. Fortunately enough, the amount of recycled flexible applications is rising, this group includes roofing and waterproof membranes, flooring and coated fabrics.

There are a number of on-going projects focusing on recycling of PVC within the VinylPlus programme. One example is the RecoMed project, which aims to collect and recycle non-contaminated PVC from, at present, nine attending hospitals in the UK. There are current plans to extend the number of external participants and also to include veterinary clinics and university training facilities. In 2016 the collected amount of PVC products, such as IV solution bags and oxygen masks and tubings was 1394 kg.

The VinyLoop plant in Ferrara, Italy has a capacity to process 10000 tonnes/year (2010) of waste PVC into recycled [43]. However, the plant does not make the most of its capacity and in 2016 the amount of recycled PVC was 3777 tonnes, a decline of 16,2 % compared with the previous year. The PVC to be recycled is dissolved in a closed system and undesired ingredients such as textile, metal and rubber. With the implementation of the Vinyloop extension named Texyloop, the capacity of recyclable waste PVC was extended to include tarpaulins and other fibre containing products. The R-PVC is used to produce for example garden hoses, geomembranes, different foils and shoe soles. In 2016 VinyLoop Ferrara (together with Stena Recycling AB (Gothenburg, Sweden) and Plastic Planet srl (Cittadella, Italy)) was granted a time limited REACH authorization to industrially process recycled

PVC containing DEHP to produce plasticized R-PVC products. Applications that are exempt from this authorization are for example toys and childcare articles, textiles and clothing to be used at skin-contact and certain cosmetics and food contact materials.

3 POLYMER PROCESSING

3.1 PRINCIPLES OF PVC PROCESSING

With melt processing the PVC grains are transformed from individual particles to a continuous solid material. This counts for all rigid formulations and to some extent plasticized recipes. The process is called fusion, or gelation, and is of vital importance for the material properties [44]. Two mechanisms for PVC fusion, differentiated from each other by the level of shear, were proposed by Allsopp [45]. At very high shear rates, such as in Brabender rheometers and Banbury rheometers, PVC grains are broken down into primary particles and fused together. On the other hand, at very low shear rates such as compression moulding, a much higher temperature is needed to achieve gelation.

The most common melt processing technique for rigid PVC is extrusion and together with for example two-roll milling these represent the second mechanism for PVC fusion. The CDFE mechanism describes how the PVC grains initially are compacted (C) and densified (D) to become less porous whereupon they under rising heat and pressure undergo intragranular fusion (F) which causes elongation (E) in the flow direction [25]. Supplementary theories regarding crystallization have been added to the original CDFE mechanism [46]. The primary particles accommodate the crystals of which some will melt under normal processing temperatures, typically 170^{o}C to 210^{o}C, whereas others will remain unmelted. Under and after cooling a secondary crystallinity is formed which links the polymer network together and gives PVC its characteristic material properties. The CDFE mechanism was initially developed for rigid PVC, but has been confirmed to be applicable to plasticized PVC as well [47].

3.2 EXTRUSION

Extrusion basically means that some kind of material is pushed through an opening or a die. This counts for toothpaste as well as heavy duty aluminium profiles.

There are many different extrusion processing techniques and equipment for polymer processing. In this thesis we used a twin-screw extruder (Fig. 4) to process different PVC material compositions. Twin-screw extrusion is particularly well suited for handling and processing of powder compounds [48]. Pipes and profiles extrusion can well be processed directly from the dry blend while for example calendering usually requires an additional step where the dry blend is compounded into pellets or similar [49].

PVC, especially unplasticized PVC, is a relatively difficult material to process. That is why the versatility of multi-screw extruders suits PVC manufacturing well [17]. The flexibility in the design of the equipment and screws allows for processing at lower temperatures, compared with single screw extruders, which makes it possible to better control the dimensions and quality of the extrudate.

Figure 4. Brabender TSE 20/40 at RISE Borås, here with the barrel opened.

Twin-screw extruder can be either co-rotating or counter-rotating, the former can operate at higher screw speeds due to a narrower distribution of the shear forces while the latter in general is limited to processing at lower screw speeds.

3.3 TWO-ROLL MILLING

Two-roll mills are suitable equipment for plasticized PVC due to the potentials for variation of processing parameters. Besides temperature it is also possible to vary roll speed and to adjust the gap between the rolls. These can both have a positive effect on the shear rate and if the equipment is capable of running with asymmetric speed the level of shear can be even further increased. The design of two-roll mills facilitates cleaning and allows for fast and accurate consecutive processing of different formulations with low risk for contamination.

4 POLYMER NANOCOMPOSITES

Nanocomposites belong to a class of materials that involves structures with at least one dimension at the nanometer scale, defined as less than 100 nm.

4.1 CLAY MINERALS

Montmorillonite (MMT) is the main clay mineral constituents of the clay Bentonite [50]. It belongs to the Smectite group and possesses a 2:1 layered structure (Fig. 5). One single octahedral aluminium layer is located between two tetrahedral layers of silicon, giving the chemical formula of $[(Al_{1,67}Mg_{0,33})Si_4O_{10}(OH)_2]Na_{0,33} \cdot nH_2O$. This is the nominal formula and depends on the source of the clay [51].

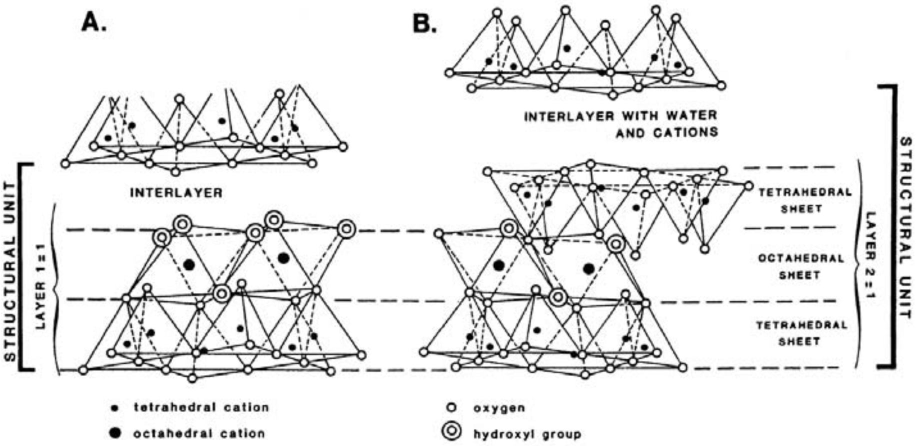


Figure 5. An example of a 1:1 layered structure (A) and the montmorillonite 2:1 layered structure (B) [51].

The layer thickness of a 2:1 phyllosilicate is around 1 nm and the lateral dimensions vary depending on the type of clay mineral. MMT is often presented to have an aspect ratio of a few hundred meaning that the length of a single layer normally is 200-600 nm. A permanent negative charge on the surface of the clay mineral layers is due to isomorphous substitution of for example Al^{3+} replaced by Mg^{2+}. This is compensated for by alkali and alkaline earth cations present in the interlayer space except for a minor part that is found on the edges of the layers. The negative charge is defined as the mean layer charge density and is generally represented by the unit mequiv/100g [52].

As an example, a particle of Cloisite Na^+, which is a natural MMT with mostly sodium cations present in the interlayer space, has a typical dry particle size of <25 µm according to available data sheets. Such a particle consists of a large number of stacks of clay mineral layers. Each stack is then composed of up to 1000 single layers, held together by rather week electrostatic and van der Waals forces [53]. The cations are easily hydrated and the stacks then swell and finally disperse into individual layers. This property of layered silicates is known as exfoliation and drastically increases the specific surface area of MMT to 700-800 m^2/g [54]. It is thus easy to realize why nano-sized fillers can have such a dramatic influence on material properties even at very low loadings.

4.2 ORGANIC MODIFICATION OF MONTMORILLONITE

Because of its hydrophilic nature, MMT needs to be organically modified prior to processing with most of the commonly used thermoplastics. Generally, this is achieved with an ion-exchange reaction. The interlayer cations are replaced by a cationic surfactant with the intention to lower the surface energy of the clay mineral layers and to improve the wetting characteristics, which is increased compatibility, with the polymer matrix. In this way the interlayer distance is increased due to the bulky organic tails of the ammonium ions which is often characterized with different X-ray diffraction (XRD) techniques [52].

One of the major goals within this thesis was to organically modify MMT without the use of quats. The idea of using chelating agents (Fig. 6) have been presented by Jakubowicz et al [10]. Sarier and Onder [55] intercalated polyethylene glycol molecules of various molecular weights into sodium MMT.

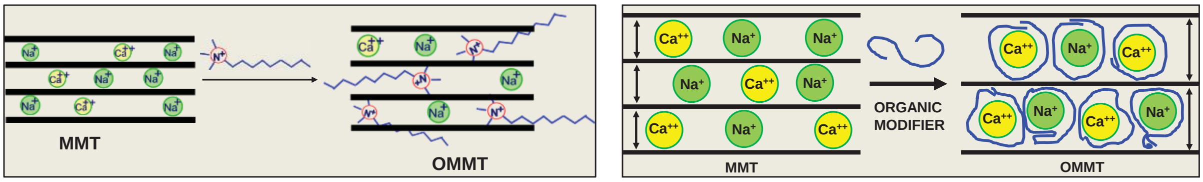


Figure 6. Principles of organic modification by (left) ion-exchange and (right) chelation.

4.3 LAYERED SILICATE NANOCOMPOSITES

Kojima et al [2-4] at the Toyota Central Research & Development Labs in Japan are often considered to be industrial pioneers in the use of layered silicates as filler in polymeric nanocomposites. They used ε-caprolactam to intercalate the natural montmorillonite after which the ε-caprolactam was polymerized to poly-caprolactam, also known as nylon-6 or polyamide 6, in a one-pot reaction also including phosphoric acid and 6-aminocaproic acid. At 23°C the tensile strength and the E-modulus for this nylon-6 nanocomposite was increased with 49% and 103% respectively at an inorganic loading of 4,1 wt% compared with a nylon-6 without the addition of MMT. At 120°C the same improvements were measured to be 30% and 253% respectively. The heat distortion temperature (HDT) was increased from 65°C for neat nylon-6 to 160°C for the nanocomposite material. MMT has ever since then been the number one choice for manufacturing of layered silicate nanocomposites.

There have been lots of reports on attempts to produce layered silicate PVC nanocomposites with the use of commercially available OMMTs, most of them based on different quaternary ammonium salts. Wan et al processed PVC composite materials with low plasticizer content, only 5 phr (DOP), and compared different material properties with the addition of either natural sodium MMT or a quat-modified OMMT[56]. TEM analysis showed that the dispersion and exfoliation was much better with OMMT compared with natural MMT. On the other hand, composites containing OMMT was found to discolour even during processing while natural MMT did not discolour the material. Still, composites containing OMMT showed a 20°C higher onset of thermal degradation compared with neat PVC and PVC with MMT, in TGA-analyses. While OMMT caused discolouration during processing, it still had a positive effect on the thermal stability according to TGA-analyses.

The most industrial applicable method of layered silicate nanocomposite preparation would be melt processing and is the choice of technique in this thesis. Organically modified MMT is directly mixed with PVC prior to or at fusion. Shear forces are needed to split OMMT particles into stacks of clay mineral layers. The polymer chain then needs to intercalate into the interlayer space of MMT stacks (Fig. 7). The driving force is the enthalpy contribution from the polymer-organoclay interaction [57]. At the best, the layers are exfoliated in a combined diffusion and shear process and the degree of dispersion is also governed by the mean residence time in the mixing process [58].

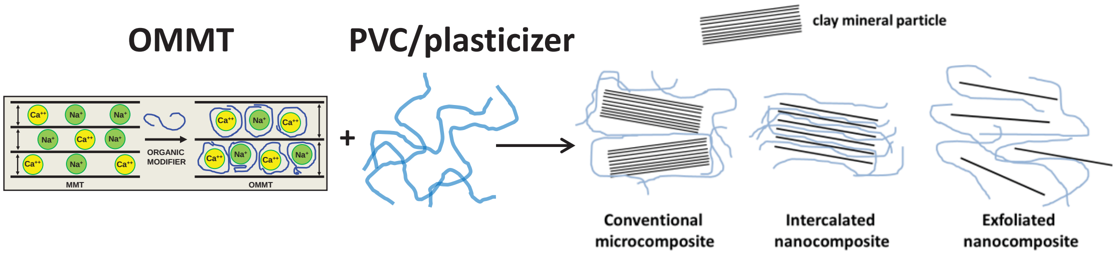


Figure 7. Melt processing of plasticized PVC/layered silicate nanocomposites.

4.4 OTHER NANOCOMPOSITES

There are many other examples of nanocomposites with various nanosized fillers developed for certain purposes. One example is carbon nanotubes (CNTs) that can exist either as single walled CNTs (SWCNT) or as multi walled CNTs (MWCNT) [44]. CNTs have a very high aspect ratio with regard to length-to-diameter, typically in a wide range from a few hundred to several thousands. CNTs are primarily appreciated for their contribution to the mechanical and electrical properties of nanocomposites. While carbon fibres normally have an E-modulus in the order of 750 GPa, CNTs are reported to have about twice as high modulus and Treacy et al even reported values for individual nanotubes exceeding 4 TPa [59]. There are numerous papers investigating influence of the electrical properties with the addition of CNTs, even those regarding PVC/CNT [60, 61].

Nanosilica has been used to improve mechanical properties of PVC [62], expandable graphite was used as flame retardant [63] and graphene oxide (GO) improved thermal stability and mechanical properties in GO/PVC nanocomposite films [64].

5 HANSENS SOLUBILITY PARAMETERS (HSP)

Hildebrand had been studying solubility theories for some decades when he and Scott in 1950 first published the term "solubility parameter" [65]. The Hildebrand solubility parameter, δ, is defined as the square root of the cohesive energy density:

$$\delta = (\frac{E}{V})^{\frac{1}{2}} \tag{11}$$

V is the molar volume of the pure solvent and E is the energy of vaporization.

In 1967 Charles Hansen presented his thesis that developed the term solubility parameter to include all types of physical bonds that are broken during evaporation[66]. These are the nonpolar bonding, polar bonding and hydrogen bonding. Basically, the Hildrebrand solubility parameter was divided into three, atomic nonpolar interactions (δ_D), dipolar interactions (δ_P) and hydrogen bonding interactions (δ_H):

$$(\delta_t)^2 = (\delta_D)^2 + (\delta_P)^2 + (\delta_H)^2 \tag{12}$$

These are now known as Hansen solubility parameters (HSP) and act in the three-dimensional Hansen space. Since then there are many papers using HSP for various purposes.

Krauskopf [67] used HSP to predict plasticizer solvency of PVC and found it to provide a quantitative measure of the interactive forces between a plasticizer and PVC. It was also concluded that lubricants could be placed further away from PVC in the three dimensional Hansen space, than well-known PVC plasticizers. Some papers present solubility experiments when there are no known HSP accessible, Batista et al [68] determined HSP for different potential bio-fuels.

Charles M. Hansen himself has published a number of papers proposing different applications for the HSP theory. In 2002 [69] he presented a paper on how to predict environmental stress cracking (ESC) in polymers. ESC is considered to be one of the major causes for plastic failures, 25% has been proposed as the number of ESC failures [70]. As ESC is a complex of problems and not always easy to foresee, a robust concept to predict ESC over time would be of great significance. Hansen has also presented how to use HSP to predict the physical behaviour of different additives in polymers [71].

Ho and Glinka [72] used HSP to analyse the dispersion and exfoliation of an organoclay, based on MMT and dimethyl dihydrogenated tallow (di-tallow) quaternary ammonium, in various solvents. They found correlations between the HSP of the solvents and the behaviour of the OMMT in the same solvents.

In this thesis HSP theory was used in paper I to predict the compatibility between different OMs and the PVC/plasticizer matrix. It was also performed studies on the swelling of different types of natural MMT in various solvents. These results were compared with the HSP of the different solvents.

All calculations and predictions using HSP can be facilitated by the use of the software called Hansen Solubility Parameters in Practice (HSPiP). It contains an extensive set of solubility data for both solvents and polymers. These solubility parameters can be obtained either by solubility experiments or by theoretically based calculations.

6 EXPERIMENTAL METHODS

6.1 X-RAY DIFFRACTION TECHNIQUES (XRD)

XRD is one of the most commonly used techniques to thoroughly investigate the crystalline quality of different nanostructures. It is more or less always used to characterize clay minerals, before and after organic modification, to determine the interlayer d-spacing which means the distance between the basal layers of the MMT clay. A shift to lower theta-angles means that the distance between the crystal planes has been increased. XRD is often used in combination with other analysis, for example TEM and SEM. The absence of distinct peaks for a layered silicate nancomposite within the range of interest for OMMTs is often interpreted as full exfoliation while there in fact are many more parameters to take into consideration. A limited orientation of the crystal planes as well as the concentration of the OMMT can affect the intensity together with the knowledge that XRD is rather sensitive to surface roughness.

In this thesis XRD analyses were performed in all four papers, Paper I-IV. Depending on the accessibility, different instruments at different departments at Chalmers, KTH and RISE were used. In general, the 2-theta angles from 2-12 were analysed except for the deeper study at very low angles performed in Paper III.

6.2 SCANNING ELECTRON MICROSCOPY (SEM)

It is important to understand the structure and morphology of layered silicate nanocomposites as well as the pure OMMTs. In many studies transmission electron microscopy (TEM) is used in combination with XRD, but in this study we focused on the use of HR-SEM. This was mainly due to the simple sample preparation of SEM specimens compared with TEM specimens. Although the SEM specimens were cryogenically fractured in liquid nitrogen and the sputter coated with a thin (10-15 nm) layer of gold-palladium, this sample preparation is still much less time and labour consuming than in the case of TEM sample preparation. Also, we have the high-resolution SEM-instrument readily available in-house at RISE in Borås, an asset not to be underestimated. SEM analyses were performed with a Zeiss Supra 40VP field emission scanning electron microscope (FE-SEM). The instrument is equipped with a high-efficiency in-lens detector and all SEM characterization was performed in high vacuum. SEM plays an important role in the determination of the morphology down to a few nanometers in resolution and was used in Paper II-IV.

6.3 MECHANICAL TESTING

Plastic materials in different applications are often expected to be “tough” or “strong” or “flexible” or several other properties that are connected to the mechanical properties of the polymer. In this thesis the mechanical properties were examined in Paper II-IV. Tensile test specimens of type 5A with a thickness of 1mm were tested according to the ISO 527-2 standard on a Zwick Z 1.0 universal testing machine equipped with a long-stroke extensometer. A preload of 2 N was applied and up to 2 % strain the test speed was 1 mm/min, after that the test speed was 50 mm/min. The equipment is located at RISE in Borås.

6.4 THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA is a simple and well-tried method to measure the weight change against time or temperature [73]. The atmosphere is controlled and can be adapted to the purpose of the analysis. TGA can be used to control the thermal stability of any compound. In this thesis a quantitative and qualitative method to examine the chelating effect of the OM in OMMTs was evaluated in Paper I-III. All TGA analyses were carried out at RISE in Borås on A Mettler Toledo TGA/DSC 1 STARe System thermogravimetric analyzer.

6.5 GAS PERMEABILITY

Due to the geometry of the MMT´s primary particles and the fact that they are impermeable, gas permeability can be highly affected by the addition of layered silicates to a material. The key is to achieve as high degree of exfoliation as possible. The tests of gas permeability in Paper II and IV in this thesis were carried out on a Lyssy L100-5000 manometric gas permeability tester according to the ISO 15105-1:2009 method (*Plastics – Film and sheeting – Determination of gas-transmission rate – Part 1: Differential-pressure methods*).

6.6 FLAME RETARDANCY

Nanocomposites are often prepared with the intention to improve the flame retardancy of the material. There are several test methods, but three of them are more frequently used [74]. The UL94 test methods are used to determine various flammability ratings, either vertical burn or horizontal burn. Specimens are exposed to a defined flame under a specified time and the burning time and dripping are used to classify the material. The limiting oxygen index (LOI) is a standardized test method to measure a materials resistance to ignition. The test specimen is vertically placed in a glass tube with an atmosphere of controlled proportions of oxygen and nitrogen. A small flame at the bottom of the glass tube is used to ignite the specimen at the lowest oxygen concentration that will just about support combustion.

These two test methods are rather cost-efficient and provide a few but useful parameters for fundamental understanding of plastic materials flame retardant qualities in certain applications. Cone calorimetry on the other hand produces a broad range of various results that can even be used for modelling of large scale fires [75]. A horizontal sample is exposed to an irradiance source with a specified heat flux and the first parameter that is measured is the time to ignition (t_{ig}). Several other results are based on the principles of oxygen consumption during combustion [76]. The heat release rate (HRR) is measured as a function of time and is often considered to be the single most important parameter to predict fire hazard [77]. HRR is the driving force of a fire with the peak HRR (pHRR) indicating a critical situation in a fire where the heat threatens to ignite surrounding materials and further spread the fire. The smoke development from a material upon fire can be quantified either by the specific extinction area (SEA) or by the total smoke released (TSR).

Cone calorimetry tests in Paper IV were performed at RISE in Borås according to ISO 5660 with a heat flux of 35 kW/m^2. Each material was represented by two specimens with the dimensions 100x100x3 mm.

6.7 OTHERS

Some other analysis methods were also used for characterization of the plasticized PVC composites. Vicat softening temperature (VST) was used in Paper II and IV and indicates at what temperature a plastic material softens and loses certain material properties. The tests were carried out using a CEAST HV3 HDT Vicat thermomechanical tester. Method A50 with a force of 10 N and a heating rate of 50 K/h was used according to ISO 306:2013 method (Plastics – Thermoplastic materials – Determination of Vicat softening temperature (VST)).

Hardness testing was used as a complement to the testing of mechanical properties. Hardness was used in Paper II and IV and performed with a Bareiss Digitest hardness tester equipped with an IRHD M (microtest) measuring unit.

Although it will be realized in the results and discussion section that plasticizer migration tests were not performed, migration is still a very important parameter to be examined in future works.

7 RESULTS AND DISCUSSION

This section highlights and discusses interesting and important findings. For the sake of simplicity, since INEOS during this thesis have become INOVYN and SP today is known as RISE, the current names (November 2017) are used in the following section independent of when the actual work was carried out.

7.1 ORGANIC MODIFICATION OF MONTMORILLONITE

Yarahmadi et al [10] prepared OMMTs using some different chelating agents as the OMs. These organic compounds were chosen as substitutes to "quats" and were intercalated into the interlayer space of MMT to decrease the electrostatic forces between the clay mineral layers and to improve the compatibility against PVC. Organic modification was carried out in either water or in ethanol under vigorous stirring. The OMMTs were used to produce PVC-U composite materials. In this thesis the ideas of chelating agents were adopted to produce plasticized PVC composite materials.

It is well known that natural MMT is easily hydrated with noticeable swelling of the clay mineral. Water molecules form a number of pseudo-layers depending on for example the water content. A monolayer typically gives a d-spacing of 1,18 to 1,24 nm [78] which is close to the d-spacing of 1,16 nm reported for as-received Cloisite® Na^+ (Na^+-AR) in paper I-IV. Na^+-AR contains mostly sodium cations and has moisture content of approximately 5% by weight measured with TGA. In Paper I two other types of natural MMT was evaluated, Nanomer® Mt-PGV containing a mixture of monovalent and polyvalent cations while Cloisite®Ca^{++} contains mostly calcium cations.

There are some practical issues related to the use of water as the solvent in the organic modification processes of MMT. The ability of MMT suspensions to form self-standing films after evaporation of water has been highlighted in literature. Quite contrary to what is normally desired for OMMTs for the use in melt processing of layered silicate nanocomposites, Bennadji-Gridi et al [79] took advantage of the self-assemble ability of MMT upon drying. A clay mineral with approximately 65% MMT was dispersed in water with the addition of a sodium salt. Textured film was then produced when water was evaporated. The bending strength of these MMT-films were analysed to be 120 MPa which can be compared with the bending strength of 190 MPa obtained for natural nacre. The major limiting factor for these MMT-films is the formation of cracks during the drying process. Walley et al [80] produced similar films of self-assembled clay to evaluate the possibilities to prepare preforms for ordered layered nanocomposites.

While water is an excellent solvent for swelling of MMT, it is a quite poor solvent for most of the organic substances intended for modification of MMT. An organic solvent like tetrahydrofuran (THF) is an excellent organic solvent for the OMs, but not very efficient for swelling of MMT. In the search for a practicable way to use water as the solvent, several different techniques and combinations of these were investigated. Freeze drying of a water/MMT/OM suspension produced an extremely fluffy material with low bulk density. SEM analyses of freeze dried OMMTs in Fig. 8b showed very thin agglomerates with a high aspect ratio. Unfortunately, the thickness was still in the micrometer scale and the morphology was very compact compared with the small porous sodium MMT particle seen in Fig. 8a. A compact structure of highly oriented clay mineral layers is without doubt unfavourable for the degree of exfoliation.

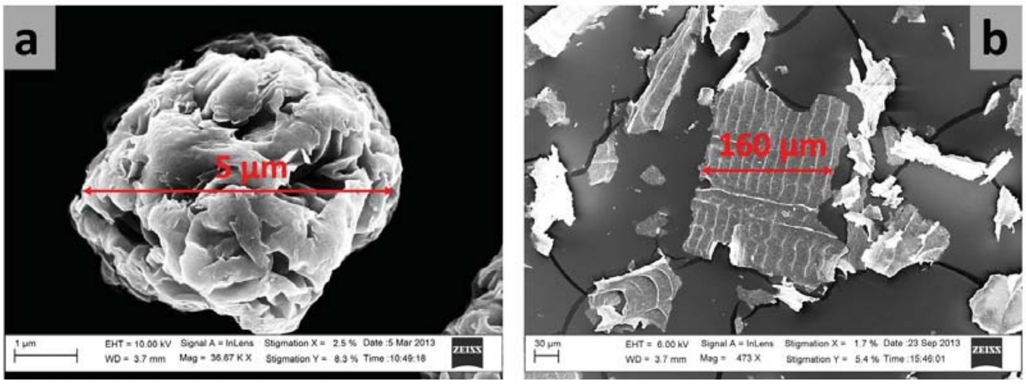
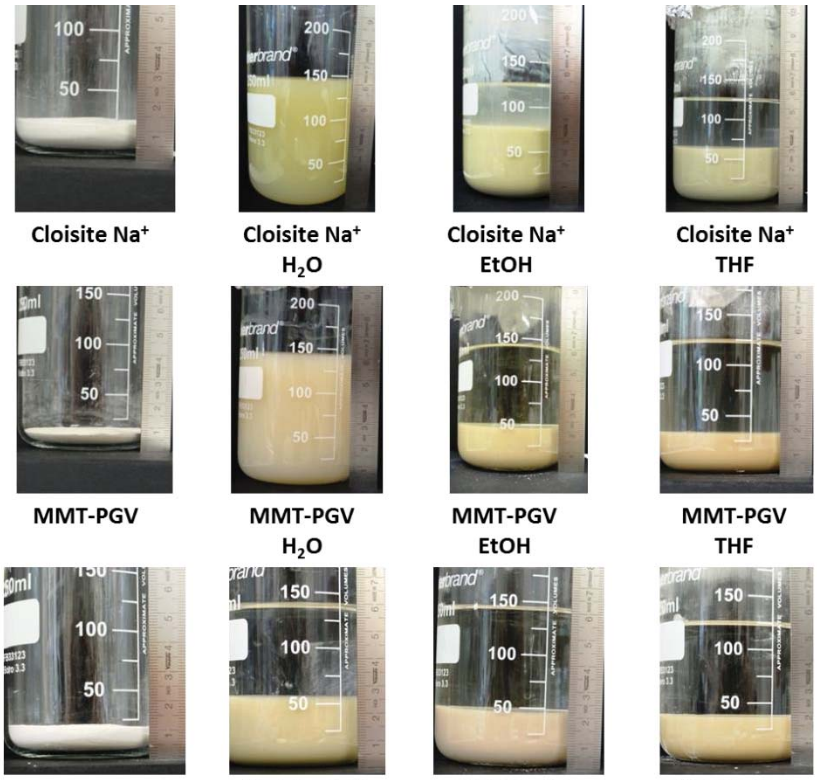


Figure 8. SEM images of (a) a small porous particle of natural sodium MMT and (b) thin agglomerates from freeze drying experiments.

Another technique that was investigated to facilitate the use of water for organic modification was cryogenic ball milling using a Retsch Mixer Mill MM 400. The grinding jars containing the sample material and stainless steel balls were immersed in liquid nitrogen prior to the mixing and milling process. Some different settings such as time and vibrational frequency of milling were tried and the OMMT particle size was perhaps to some extent reduced. On the other side was the compact morphology of the OMMT particles preserved regardless of how small particles the milling produced. This was interpreted as clear evidence that melt processing of this OMMT with plasticized PVC at best would result in a micro-composite material.

Spray-drying was never tested and evaluated as the drying process for water suspensions of OMMT and could possibly have been a suitable method. Still, if the issues with the compact morphology cannot be solved, an even smaller particle size will not alone guarantee a higher degree of exfoliation.

An alternative way to organically modify MMT with chelating agents without the use of water is to select other suitable organic solvents. In the process of this selection the swelling of MMT in some different organic solvents was investigated in Paper I. The different MMTs were swelled in various solvent using an Ultra-Turrax® T50 dispersing instrument. After being dispersed for a defined time, the clay-solvent suspensions were left to settle for 1 hour. The results are shown in Fig. 9 and it is evident that Cloisite Na^+ is the most convenient to swell regardless of the solvent. Quite interestingly, the Cloisite Ca^{++} did not swell completely even in water. Because of its better swelling properties Cloisite Na$^+$ was chosen as the preferred clay mineral to work with in Paper II-IV.


Cloisite Na$^+$

Cloisite Na$^+$ H_2O

Cloisite Na$^+$ EtOH

Cloisite Na$^+$ THF

MMT-PGV

MMT-PGV H_2O

MMT-PGV EtOH

MMT-PGV THF

Cloisite Ca^{++}

Cloisite Ca^{++} H_2O

Cloisite Ca^{++} EtOH

Cloisite Ca^{++} THF

Figure 9. Swelling experiment of different types of montmorillonite in various solvents.

In paper I different OMMTs were successfully produced. One combination of clay mineral and OM is shown in Fig. 10, namely the MMT-Na$^+$/TBC OMMT. This OMMT was readily produced and the choice of solvent did not affect the interlayer distance of OMMTs to any appreciable extent. Amongst all the OMMTs prepared in the screening for suitable combinations, the OMMT based on MMT-Na$^+$ and TBC was selected for further evaluation in melt processing with plasticized PVC.

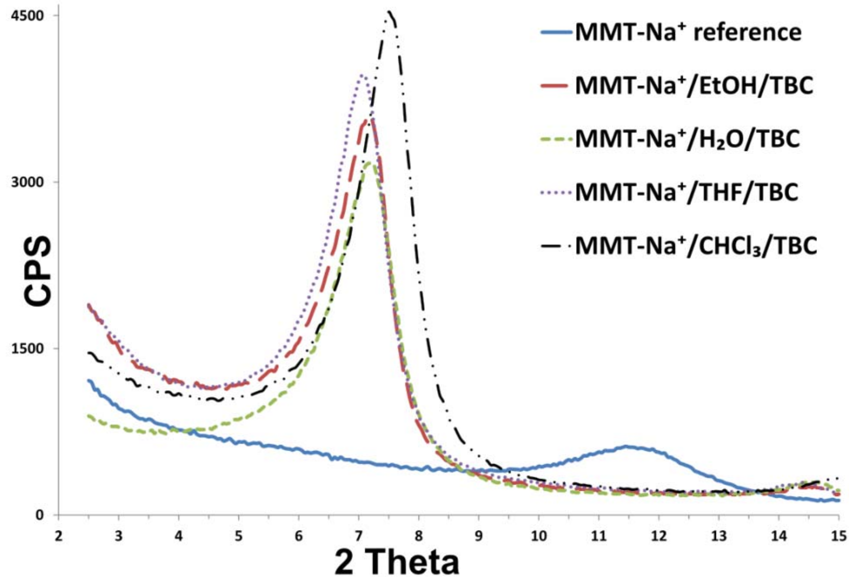


Figure 10. XRD analysis of OMMTs based on MMT-Na+ and TBC modified in various solvents.

7.2 HANSENS SOLUBILITY PARAMETERS

HSP analyses played an important role in the choice of suitable OMs in Paper I. In Fig. 11A the compatibility of different plasticizers and possible OMs can be seen. The green dot with the green sphere around belongs to the solubility parameters of the chosen PVC quality. Inside this frame the compatibility or solubility between the polymer and the solvent or organic compound is considered to be “good”. Outside the sphere “good” changes to “bad”. In Fig. 11B the solubility of TEC and TBC in various solvents is visualized. TBC was chosen amongst many other candidates as the first choice of OM to be deeper evaluated. The criteria involved commercial availability, chelating properties, thermal stability and compatibility with PVC.

Quite interestingly the results from the swelling experiments of MMT in different solvents correspond well with the results from HSP analyses in Fig. 11B. The further away from water a solvent is located in the HSP space the less swelling of the MMT was achieved, illustrated by the arrow in Fig. 11B. There are no solubility parameters available for natural MMT, but one could imagine that they would be close to water due to the unlimited swelling.

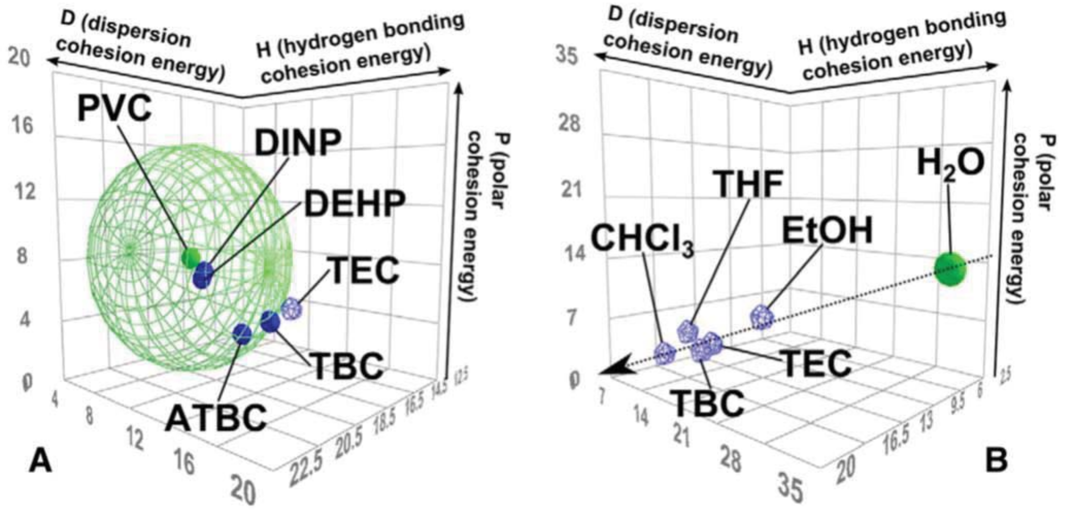


Figure 11. Graphic results obtained with HSPiP, displaying compatibility between PVC and different plasticizers (A) and solubility of TBC and TEC in various solvents (B).

7.3 FIRST ATTEMPT OF PROCESSING OMMTS WITH PLASTICIZED PVC

After the successful preparation of OMMTs in Paper I, these results were used to process OMMTs with plasticized PVC in Paper II. Two different solvents, water and THF, were used to produce OMMTs based on MMT-Na$^+$ and TBC. As can be seen in Fig. 12 the morphology of OMMTs is highly dependent on the choice of solvent. In Paper II the idea was to investigate how this morphologically extremes would affect the dispersion and degree of exfoliation in melt processing.

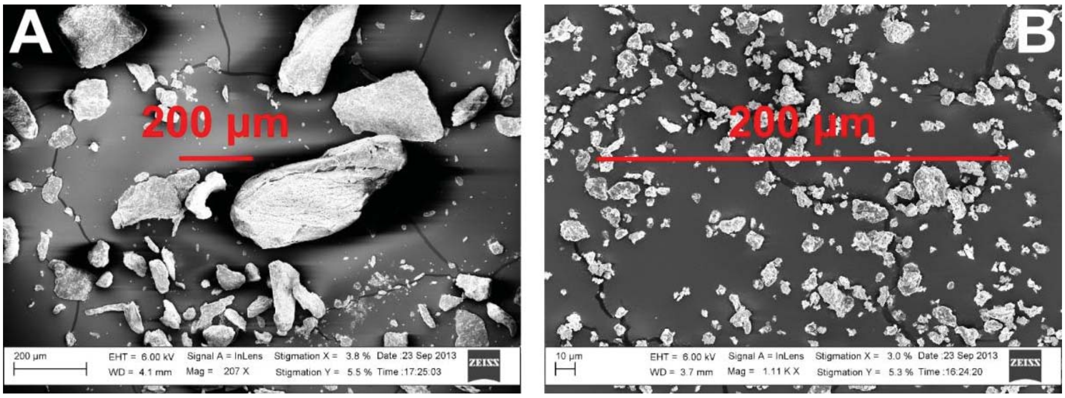


Figure 12. Representative SEM images showing the size distribution of dried and ground OMMTs: (A) MMT-Na$^+$/TBC/H_2O and (B) MMT-Na$^+$/TBC/THF. The difference in magnification is highlighted by the length of the scale bar.

Dry-blends of DINP-plasticized PVC were prepared at INOVYN in Stenungsund. OMMTs (MMT-Na$^+$ modified with TBC) were added as ground powders to the dry-blends. A master batch (MB) process was used to produce plasticized PVC with the addition of OMMT. The content of MMT based on the inorganic weight was 20 phr in the MB and 5 phr in the final composite formulation. The MB was processed on the twin-screw extruder at RISE in Borås and pelletized to suitable size. The screw configuration included several kneading elements, in each case directly followed by a back-conveying element, see Fig. 13. This has been shown to increase the shearing forces and to extend the residence time in favour of dispersion and exfoliation of OMMT [81]. Materials with the final formulations were processed on a two-roll mill at INOVYN in Stenungsund. Plates for characterization purposes were manufactured in a hydraulic laboratory press at RISE in Borås.

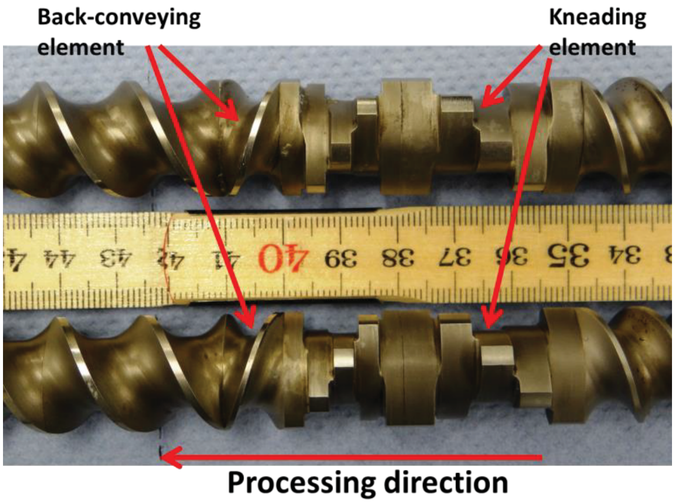


Figure 13. Screw configuration with kneading and back-conveying elements.

Mechanical testing and gas permeability analysis was chosen as adequate characterization methods because the features of a successful dispersion of OMMT in plasticized PVC would, at least, be a higher E-modulus and lower gas permeability. The outcome was however quite contrary to the expected with a lower E-modulus and increased gas permeability compared with a material without the addition of OMMT. On a closer examination of the formulations of all the different materials, it could be noticed that the addition of 5 phr of MMT also brought 2,5 phr of TBC as the OM. At the same time the SEM analyses showed an evident presence of OMMT agglomerates and only very few small particles that could be identified as exfoliated layers or tactoids. The interpretation so far was that the OMMT had collapsed and was present as micro-sized particles while the higher gas permeability and decreased E-modulus could unequivocally be explained by the extra addition of 2,5 phr TBC.

Experiments were performed where 2,5 phr TBC was added to a DINP-plasticized PVC and it could be concluded that this rather small contribution of extra plasticizer had a significant effect on the mechanical properties and oxygen permeability. The effects were in the same magnitude as with the results from testing of the above extruded/roll-milled materials. Thus, it is of vital importance to appropriately formulate dry-blends, particularly in the case of comparative testing.

To investigate why the OMMT seemed to have collapsed, TBC-modified MMT was dispersed in DINP with the aid of an Ultra Turrax T25 high-performance dispersing instrument at 180°C and 23°C, for 5 min. The temperature and time was chosen in order to as far as possible simulate the melt processing conditions. In addition, OMMTs with different proportions of MMT and TBC were prepared to investigate how the concentration of OM in the OMMTs affects the interlayer spacing. Samples were analysed with XRD, OMMT that were dispersed in DINP were also analysed prior to the dispersion. The results are shown in Fig. 14 and it can be seen that OMMT with the proportion of 2 parts of MMT and 1 part of TBC (2:1) exhibits the same interlayer distance as the OMMT with the composition of 4:1. If the OM content is lowered to a proportion of 8:1 the interlayer distance is decreased. This could be interpreted as a rearrangement of chelating OM molecules in the interlayer space due to the deficiency of the TBC. From this perspective it can be concluded from Fig. 14 that dispersion of the OMMT in DINP at room temperature did not affect the interlayer distance. On the other hand, when dispersion was performed at 180°C the XRD results showed that the interlayer distance was decreased to the same level as the 8:1 OMMT. This clearly indicates that, at melt processing conditions, the TBC can be extracted from the OMMT since the chelating effect of TBC is not strong enough and consequently the OMMT collapses. The overall result is poor dispersion and an almost total lack of exfoliation.

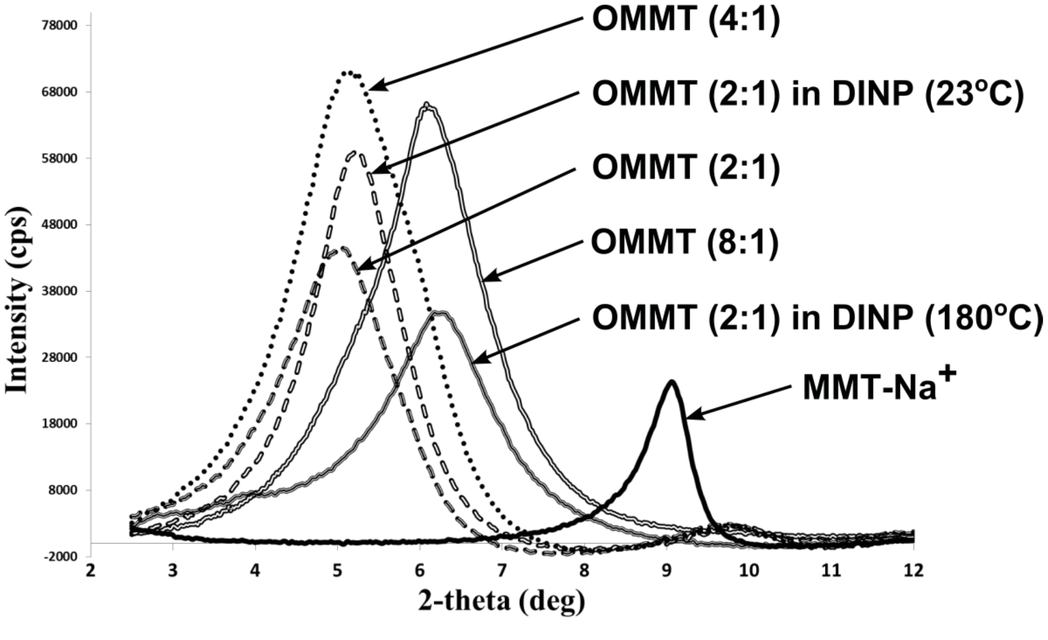


Figure 14. XRD pattern of OMMTs with various concentrations of OM and of OMMTs dispersed in DINP.

7.4 NEW FORMULATION CONCEPT

To overcome the issues with extraction of the OM into the plasticizer/PVC matrix a new concept was introduced in Paper II. The idea of using the plasticizer as the OM was proposed at the start of this thesis, but since DINP was part of the original formulation and did not present sufficient chelating properties, alternatives had to be put forward. To prove the concept of layered silicates as nano-fillers for plasticized PVC, a material with TBC acting both as the OM and as the primary plasticizer was produced. In this way the risk for extraction of OM into a different plasticizer could be eliminated. As a control, a material DINP-plasticized PVC with the addition of natural unmodified MMT-Na^+ was produced. All materials were processed via MB using a DSM Xplore microcompounder which have proved to be a helpful equipment for time-efficient and easy production of different material compositions [82].

The results showed that it is possible to produce a TBC-plasticized PVC composite material with improved material properties with the addition of OMMT based on TBC and MMT-Na^+. With the addition of 10 phr MMT the E-modulus was increased for both materials. Oxygen permeability, highly affected by the degree of exfoliation of impermeable clay mineral layers, was decreased with 22 % for the TBC-plasticized material with OMMT while the DINP-plasticized PVC with the same amount of unmodified MMT-Na^+ showed no change in gas permeability. Figure 15 shows SEM images of the TBC-plasticized PVC with the addition of 10 phr OMMT based on TBC and MMT-Na^+. It can be seen at low magnification (a) that good dispersion was achieved and at higher magnification (b) it is obvious that a noticeable high amount of exfoliated layers or tactoids are present.

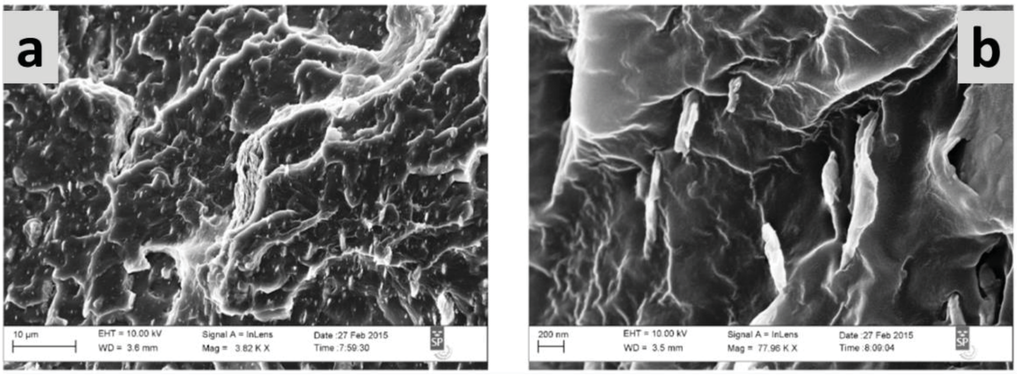


Figure 15. TBC-plasticized PVC with the addition of 10 phr OMMT based on TBC and MMT-Na^+.

7.5 CHELATING PROPERTIES OF ORGANIC MODIFIERS

Thermogravimetric analysis have been proposed as a method to analyse quats-modified OMMTs not only with regards to thermal stability, but also to determine the amount of surfactant intercalating the MMT [83]. Yarahmadi et al adapted this theory on the use of chelating agents as OMs, where the loss of the OM occurred in two mass loss steps [10]. In Paper I this was observed for MMT-Na^+ and MMT-Ca^{++} modified with TBC in water or THF as shown in Fig. 16. The DTG curves show that mass loss of TBC in the OMMTs occurs in two steps for both types of clay minerals while mass loss of pure TBC occurs in one single step only. For MMT-Na^+ one of these steps occurs at a higher temperature than mass loss of pure TBC, while for MMT-Ca^{++} both OM mass loss steps occur at lower temperatures than mass loss of pure OM. The presence of two mass loss steps for OM is interpreted as one step being desorption of OM molecules from clay mineral surfaces and the mass loss step at the higher temperature representing the chelating effect of the intercalated OM molecules. Thus, the higher mass loss temperature in MMT-Na$^+$ OMMT is interpreted as a stronger chelating effect than in MMT-Ca^{++} OMMT.

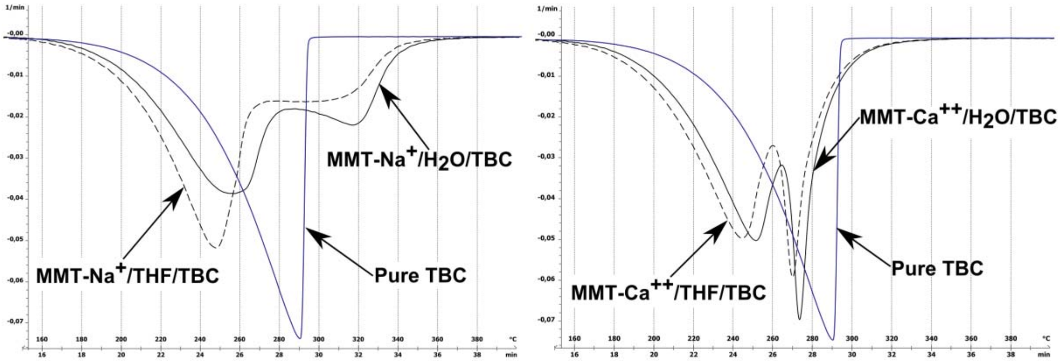


Figure 16. DTG curves of MMT-Na$^+$ and MMT-Ca^{++} modified with TBC using water and THF as solvents.

In Paper II this theory was applied on OMMTs with varying concentrations of OM. In table 1 it can be seen that at the proportion of MMT-Na$^+$:OM of 2:1 there are two mass loss steps attributed to the mass loss of OM. For the 4:1 sample there is still two OM mass loss steps, only that now when the total amount of OM is lower the first OM mass loss step is reduced. For the 8:1 OMMT there is only one OM mass loss step occurring at the higher temperature, even though this temperature is gradually decreasing with decreasing OM concentration. This indicates that there are no excess OM molecules in the 8:1 sample, rather a deficiency of chelating TBC molecules since the interlayer distance for this sample showed to be lower than for the 4:1 sample. It can also be seen in table 1 that the moisture pickup is higher for the OMMT with the lowest OM concentration (see mass loss Step 1, in table 1), indicating that this OMMT is slightly more hydrophilic due to the deficiency of OM molecules.

Table 1. TGA measurements of MMT-Na$^+$ and OMMTs with various concentrations of OM.

	Step 1		Step 2		Step 3	
Material	Temp (°C)	Mass loss (%)	Temp (°C)	Mass loss (%)	Temp (°C)	Mass loss (%)
MMT-Na$^{+a,b}$	<100	0.7	–	–	–	–
OMMT (2 : 1)^{a,c}	<100	1.0	~ 250	21.1	~ 320	11.3
OMMT (4 : 1)^{a,c}	<100	1.7	~ 240	7.7	~ 310	11.7
OMMT (8 : 1)^{a,c}	<100	3.4	–	–	~ 280	10.4
TBC	–	–	~ 290	100	–	–

[a] MMT-Na$^+$ was dried in a vacuum oven at 70°C for 68 h before modification.
[b] Unconditioned.
[c] Conditioned at 23°C and 50% RH for 72 h.

In Paper III OMMTs based on Na$^+$-AR and DINP or TBC were analysed with TGA. Figure 17a shows that the OMMT based on DINP and Na$^+$-AR has only one OM mass loss step, possibly with a much undefined shoulder, occurring at a lower temperature than the mass loss step of the pure DINP. For the OMMT based on Na$^+$-AR and TBC in Fig. 17b there are two distinct OM mass loss steps. One of them occurs at a higher temperature than the pure TBC mass loss temperature and the other one occurs at a lower temperature. The results in Fig. 17 are interpreted as the chelating effect of TBC molecules being stronger than the chelating effect, if there is any, of the DINP molecules.

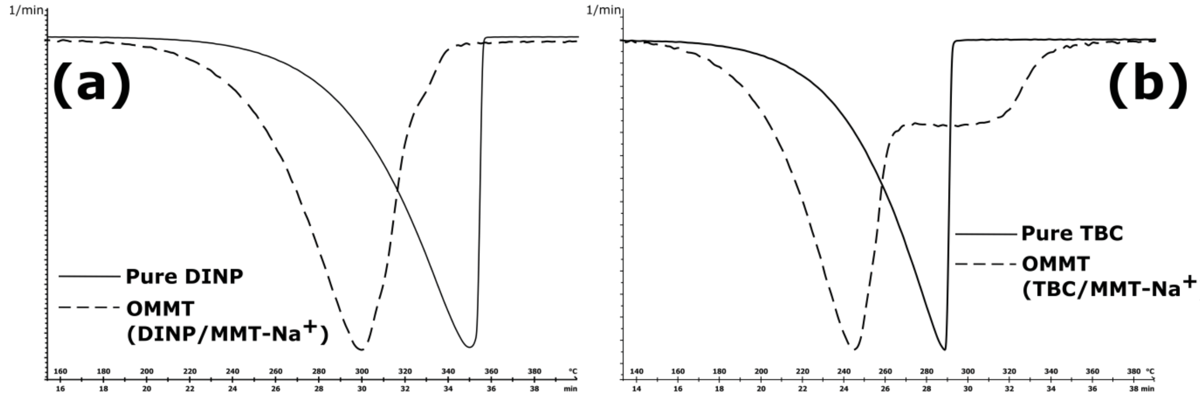


Figure 17. DTG curves of (a) OMMT (DINP/Na$^+$-AR, heat-treat) vs pure DINP and (b) OMMT (TBC/Na$^+$-AR, heat-treat) vs pure TBC.

7.6 SOLID-LIQUID STATE ORGANOMODIFICATION

Already in Paper I it was found that the choice of solvent in the modification process of OMMTs did not significantly affect the XRD results. In Paper III a process free from solvents was developed to produce OMMTs. MMT-Na$^+$ was mixed in an IKA A10 Basic laboratory mixer with the OM being either TBC or DINP. MMT-Na$^+$ was used in two forms, either as-received (Na$^+$-AR) with a moisture content of approximately 5 % and a interlayer distance of 1,16 nm or dried in an oven (Na$^+$-D) with a moisture content of about 0,7 % and the interlayer distance being 0,98 nm. Finally, the mixed OMMTs were analysed either directly after the mixing or after being heat-treated in an oven at 65°C for 20 h (“heat-treat”).

XRD analyses shown in Fig. 18 reveals that MMT-Na$^+$ can easily be intercalated by TBC without the use of process involving a solvent. The results of the interlayer distance of about 1,8 nm correspond to the results found in Paper I where various solvents were used in the organomodification process. A peak at 0,9 nm, which is rather small in proportion to the peak at about 1,8 nm, is interpreted to correspond to very dry MMT-Na$^+$ that has not been intercalated by TBC molecules. Interestingly, TBC/Na$^+$-D shows a very low intensity peak at about 1,8 nm which becomes significantly more distinguishing after heat-treatment. It has deliberately been avoided to draw extensive quantitative conclusions from the XRD patterns regarding intercalation of MMT-Na$^+$.

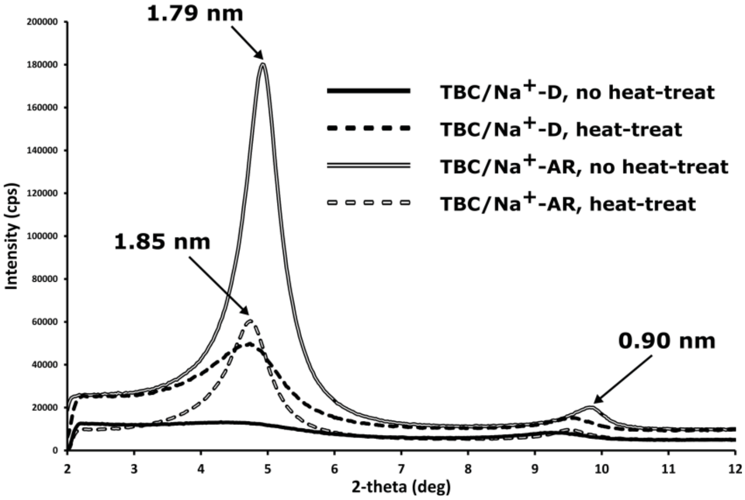


Figure 18. XRD of mechanically mixed OMMTs of MMT-Na$^+$ and TBC.

If the same solid-liquid state modification experiment is performed with DINP as the OM, the results are much more diversified. In Fig. 19a it can be seen that there is a peak at 1,21 nm for the DINP/Na$^+$-AR (no heat-treat) sample derived from the moisture of as-received MMT-Na$^+$. When heat-treated or for the OMMTs containing Na$^+$-D, this peak is shifted to higher 2-theta angle indicating lower moisture content, yet there are evidently still parts of the clay mineral that are not intercalated by DINP. There is a peak at about 1,6 nm that is only present in OMMTs based on the as-received MMT-Na$^+$. At very low 2-theta angles additional analyses were performed and are presented in Fig. 19b. These indicate that the intercalation of MMT-Na$^+$ by DINP molecules is favoured by the initially higher moisture content and a subsequent heat-treatment.

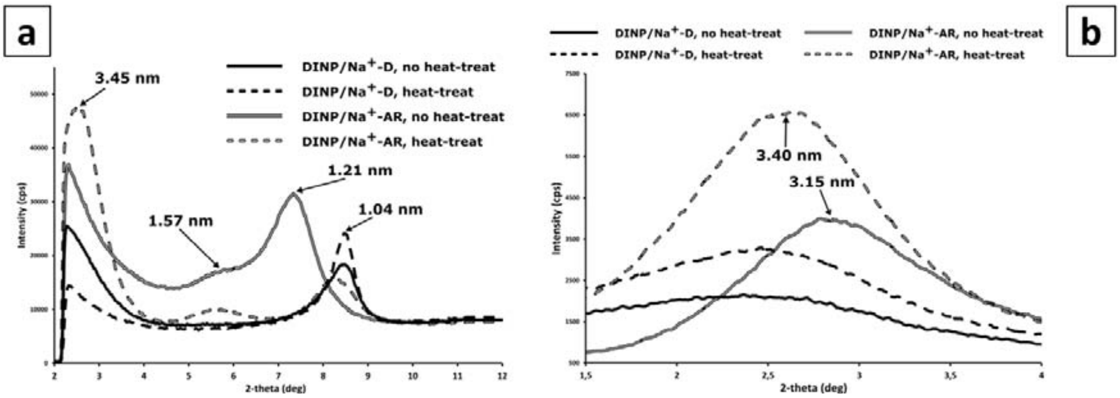


Figure 19. XRD of mechanically mixed OMMTs of MMT-Na$^+$ and DINP at (a) 2-theta angles above 2 and (b) at very low 2-theta angles.

Plasticized PVC composite materials were produced in a MB process using the micro-compounder. MMT-Na$^+$-AR was mixed with either DINP or TBC followed by heat-treatment to produce OMMTs. At a final concentration of 10 phr MMT, mechanical testing showed that the E-modulus was increased by 76 % for the TBC-plasticized composite with OMMT based on TBC/Na^+-AR (heat-treat) and a 51 % increase of E-modulus for the DINP-plasticized composite with OMMT based on DINP/Na^+-AR (heat-treat). At the same time the elongation at break was decreased with 11 % and 31 % respectively. SEM analyses showed good dispersion with a significant degree of exfoliation or tactoids without the obvious possibility to distinguish between these two composite materials.

The perhaps most striking results were those from the XRD analyses. In Fig. 20a it can be seen that TBC-plasticized composites show XRD patterns very similar to those of the OMMTs, one distinct peak corresponding to an interlayer distance just below 1,8 nm and one peak at 0,9 nm, indicating the intercalation of TBC molecules and dry MMT-Na^+ respectively. Together with SEM images, this is interpreted as the existence of tactoids intercalated by TBC only.

Looking at the XRD results for the DINP-plasticized composites in Fig. 20b, a totally new peak appears at about 1,32 nm. So far, this peak did not have any natural connection to neither moisture nor the DINP plasticizer. At very low 2-theta angles there seems to be a peak for some of the composite materials, but additional analyses would be necessary to draw any conclusions at these very low angles. The 1,32 nm peak on the other hand was further investigated as being an unexpected intercalation.

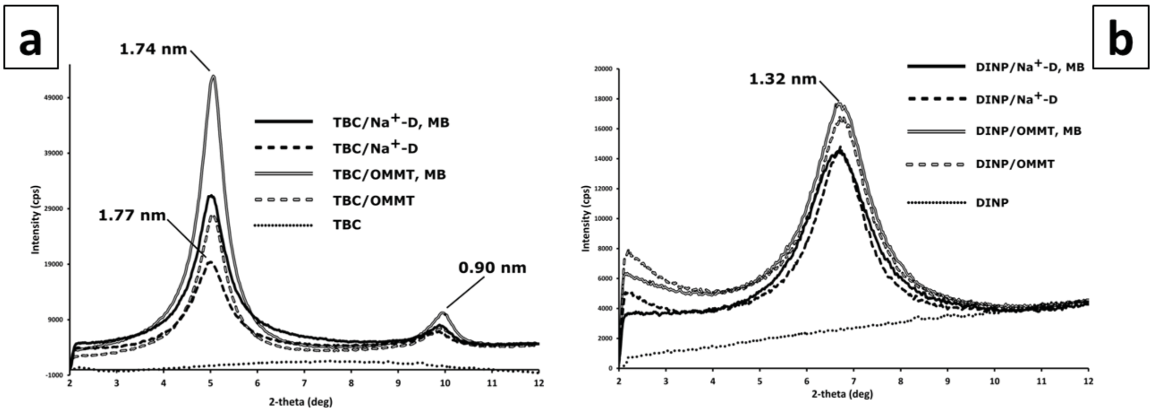


Figure 20. XRD patterns of PVC composite materials with TBC and MMT-Na^+ (a) and PVC composite materials with DINP and MMT-Na^+ (b).

7.7 UNEXPECTED INTERCALATION

One main effort in this thesis has been to intercalate MMT with carefully selected organic compounds, but what if there is unexpected, or even undesired, intercalation during for example melt processing? The peaks at 1,32 nm in figure 13b from work carried out in Paper III are definitely suspected to belong to this category, needing further examinations. The only component in the material formulations that has not been the subject of organic modification with MMT-Na^+ is the liquid mixed metal Ba-Zn stabilizer. The content of this heat stabilizer formulation is not known in detail; however these compounds are known to contain carboxylate components according to some of the market leading manufacturers. Therefore, the work of Singla et al [84] supported the Ba-Zn stabilizer case since they reported that a natural MMT intercalated by a Zn-stearate showed an interlayer distance of 1,39 nm.

Some additional experiments were performed to as far as possible prove the origin of the 1,32 nm peak. An OMMT based on the liquid Ba-Zn stabilizer and Na$^+$-AR only was produced with subsequent heat-treatment following the same procedure as for OMMTs produced by the solid-liquid modification process in Paper III. Also, DINP-plasticized composite materials with the addition of Na$^+$-D was produced; one material containing the liquid Ba-Zn stabilizer and one material without.

Figure 21 presents the results from the Ba-Zn stabilizer study. It can be seen that the OMMT based on the liquid Ba-Zn stabilizer and Na$^+$-AR showed as distinct peak at 1,34 nm, very close to the peak at 1,32 nm seen in Fig. 20b. When a formulation of DINP-plasticized PVC and Na$^+$-D was processed the XRD analysis shows a peak at 0,99 nm corresponding to the peak of pure Na$^+$-D. If the liquid Ba-Zn stabilizer is added to this formulation, the peak at 0,99 nm is shifted to 1,28 nm. This is interpreted as an intercalation of any molecule from the liquid Ba-Zn stabilizer, probably some carboxylate component, into the Na$^+$-D. The overall conclusion for the DINP-plasticized PVC composites is that the materials contain agglomerates and tactoids of MMT-Na$^+$ intercalated by the liquid Ba-Zn stabilizer only.

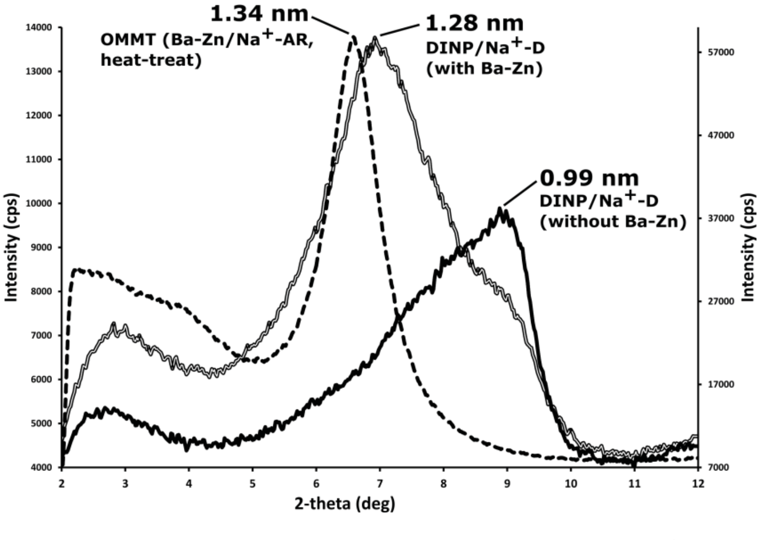


Figure 21. The somewhat unexpected intercalation of the liquid mixed metal Ba-Zn stabilizer into MMT-Na$^+$.

7.8 IMPROVED PREPARATION AND PROCESSING

Finally, in Paper IV all the findings in the preceding three papers were gathered to produce the best possible plasticized PVC nanocomposites. The aim was to investigate two different preparations of MMT-Na$^+$, namely the Na$^+$-AR added as a powder component to the dry-blend and the Na$^+$-AR pre-dispersed in the plasticizer (Na$^+$-PD) and added to the dry-blend as a liquid component. Furthermore, different processing parameters were used and as a control sample, besides the materials without the addition of MMT-Na^+, a material with the addition of $CaCO_3$ was used to compare the two different fillers. TBC and DINP were used both as the plasticizers and the OMs.

In Paper IV an industrial approach was applied on the whole work starting with the dry-blend preparation. The different dry-blends were prepared in a high-speed mixer at INOVYN in Stenungsund. All plasticized PVC materials were melt processed on a two-roll mill in a one-step process, meaning that the final content of MMT, 10 phr, was added to the dry-blends.

Several different analysis methods were applied on the produced materials to characterize them as far as possible. All results can be found in detail in Paper IV, but some of them will be highlighted here in this paragraph. The addition of 10 phr Na^+-AR to TBC-plasticized PVC increased the E-modulus with 106 % to 182 % depending on the processing parameters. At the same time the elongation at break was remained almost unchanged. The addition of 10 phr $CaCO_3$ did not have any significant effect on the mechanical properties.

Gas permeability is always of great interest for layered silicate nanocomposites. Reduced gas permeability indicates that there must be a certain degree of exfoliation. In Paper IV the oxygen permeability was at the best reported to be almost halved by the addition of 10 phr Na^+-AR to TBC-plasticized PVC. Again, the addition of 10 phr $CaCO_3$ only reduced oxygen permeability by a few percent.

The SEM images in Fig. 22 show a very good dispersion of the Na^+-AR particles (a) and a high content of small particles (b) being either individual clay mineral layers or tactoids. It is most likely a combination of all the findings in Paper I-III that form the basis of the successful results in Paper IV, all from the high-speed mixing of the dry-blends via a carefully developed formulation of the materials to the suitable melt processing with the two-roll mill.

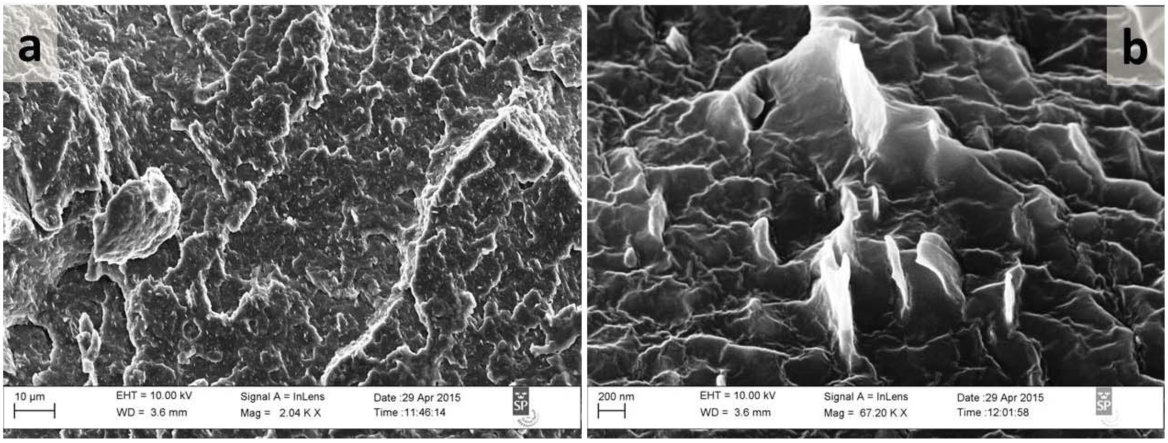


Figure 22. Representative SEM images showing the dispersion and exfoliation of MMT-Na^+ in TBC-plasticized PVC: at low magnification (a) and at high magnification (b).

7.9 CONE CALORIMETRY

Development of new flame retardants is of interest for a wide variety of plastic materials, including plasticized PVC. There are rather few examples of papers that present results of the flame retardancy of layered silicates in plasticized PVC. Most probably because the fact that rigid PVC is inherently fire resistant, but also due to frequently reported difficulties to process layered silicate PVC nanocomposites with maintained thermal stability.

Liang et al [85] prepared two different organically modified MMTs (OMMT) based on sodium montmorillonite (Na-MMT) and either a thermally stable rigid-rod aromatic amine modifier or 1-hexadecylamine. According to the authors, dioctyl phthalate (DOP) was used as the plasticizer, but the amount was not specified in the article. A glass transition temperature of 54,6^{o}C for the PVC material without OMMT indicates that the amount of DOP must be very low. XRD and TEM analyses pointed out the rigid-rod based OMMT to have the best exfoliation and nanocomposites with a loading of 3 wt% of this nanofiller exhibited an almost halved PHRR, from 237,6 kW/m^2 to 122,6 kW/m^2, and a reduction of the mean SEA by 13 %, from 740,2 m^2/kg to 643 m^2/kg.

Beyer [86] prepared plasticized PVC composite materials with 35 phr di-isodecyl phthalate (DIDP) and different OMMTs. Interestingly, composites with the OMMT based on MMT and a quaternary tributyltetradecyl-phosphonium cation had the lowest thermal stability and did not even survive the processing conditions. The cone calorimetry results showed a reduction of the peak HRR and lower smoke production while the time to ignition was unchanged.

In Paper IV cone calorimetry was used to investigate the flame retarding properties of the addition of 10 phr MMT-Na$^+$. Two test samples were tested for each material and the results in Fig. 23 show one representative sample for each material. First, the time to ignition was not affected in either way. Then, it can be seen that the peak HRR is reduced with an average of almost 20 % for both the TBC-plasticized PVC composite and the DINP-plasticized PVC composite. The time to peak HRR is in general delayed by the addition of MMT-Na$^+$ which can be decisive for life-saving efforts in case of a fire. Particularly gratifying to plasticized PVC was the change in total smoke released with the addition of 10 phr Na$^+$-AR. TSR was reduced by 37 % for the TBC-plasticized PVC composite and by 22 % for the DINP-plasticized PVC composite.

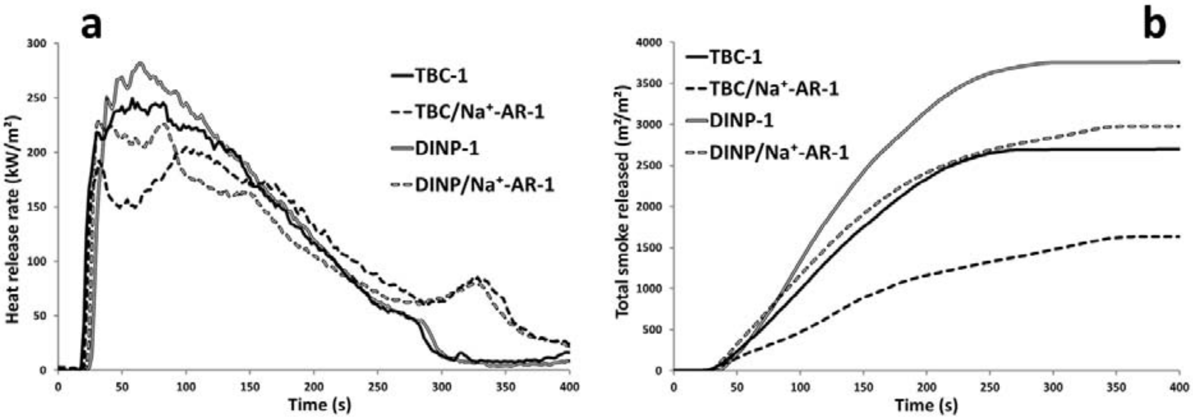


Figure 23. Result from cone calorimetry; heat release rates (a) and total smoke released (b).

8 CONCLUSIONS

In Paper I it was shown that there are several aspects to take into consideration for organic modification of MMT. Different types of MMT behave differently and the choice can most certainly influence organic modification and processing as well as nanocomposite formation. The choice of solvent in an organic modification process did not have a significant effect on the d-spacing of the OMMTs according to the XRD analyses. This conclusion formed the basis of the solid-liquid state organomodification method developed in Paper III and IV. The morphology of the OMMTs was highly affected by the choice of solvent. Organic modification in water resulted in a hard-to-grind material with a very compact morphology which was very difficult to exfoliate. It would be necessary to develop a drying method that can preserve the porous structure of the unmodified MMT if any water based process will be used. Organic modification in other organic solvents such as THF did not generate these morphological issues.

Hansen Solubility Parameters (HSP) has the necessary qualities to be an aid in material formulation and in the development of new additives. This has to date been frequently presented and in Paper I a correlation between experimental swelling of MMT in various solvents and HSP was found. It was shown that the further away from water in the Hansen space a solvent is the less swelling of the clay was achieved. HSP was also used to verify the compatibility qualities between OM candidates and PVC.

The importance of total control of the formulation and careful selection of all ingredients has been highlighted more than once in this thesis. In Paper II the unexpected results were more or less a consequence of the formulation. The negative effect on mechanical properties and gas permeability was due to the extra addition of 2,5 phr TBC in the samples where MMT was added. At the same time it was shown by the decrease of the d-spacing that the OMMT collapsed when TBC abandoned the OMMT in favour for the DINP/PVC matrix. This phenomenon was in the same paper shown to be possible to circumvent by using the plasticizer also as the OM for MMT. This resulted in 33 % higher E-modulus and a 22 % reduction of the oxygen permeability by the addition of 10 phr OMMT (based on MMT-Na^+ and TBC) to a TBC-plasticized PVC. The corresponding results for using DINP as plasticizer and OM were 45 % higher E-modulus, but no change in gas permeability indicating a less pronounced exfoliation of clay mineral layers.

There was also some unexpected intercalation discovered in Paper III. A peak at about 1,32 nm in the XRD patterns for DINP-plasticized PVC composites was shown to originate from the intercalation of the liquid Ba-Zn stabiliser into the MMT-Na^+ galleries. The influence on the thermal stability of the plasticized PVC materials of this finding was not investigated within the scope of this thesis, but could be worth taking into consideration at future formulation of layered silicate nanocomposites.

In Paper III it was shown that the organic modification of MMT could be performed without the use of solvents. However, the moisture content seems to have an influence on the results. The best results were found when an as-received MMT-Na^+ with a moisture content of about 5 % and a d-spacing of 1,16 nm was modified with the OM and subsequently heat-treated at 65°C for 20 hours. If instead a dried MMT-Na^+ with a moisture content of 0,7 % and a d-spacing of 0,98 nm was used the XRD patterns showed less distinct peaks with lower intensities for the OM intercalation in proportion to the peak for the non-intercalated MMT.

The findings in Paper III resulted in the experimental set-up in Paper IV. In this paper the whole process from formulation via dry-blending to processing of plasticized PVC composite materials can be considered as industrial applicable. It was shown in this paper that as-received MMT-Na^+ added to TBC plasticized PVC and then processed on a two-roll mill resulted in the composite material with several improved properties. With the addition of 10 phr MMT-Na^+ the E-modulus was nearly tripled without affecting the elongation at break. Oxygen permeability was almost halved and the softening temperature VST was increased by up to nearly 11°C. For comparison, a material with the addition of 10 phr $CaCO_3$ showed only 4 % higher E-modulus and 4 % lower oxygen permeability along with a 3,9°C higher VST. When instead 10 phr as-received MMT-Na^+ was added to a DINP-plasticized PVC the improvement of material properties was significant but throughout considerably lower.

MMT has the potential to be an important filler with regard to flame retardancy. It is of particular interest to evaluate the potential for synergistic effects in combinations with other flame retardants. A lower pHRR and a longer time to achieve this critical point is absolutely worth striving for and in Paper IV the pHRR for plasticized PVC composites was 19 % lower than for the material without the addition of 10 phr MMT. Worth mentioning is that there is a chance that the results can be further improved if the formation of the char layer can be controlled [87]. The effect of MMT as a smoke suppressant with a 37 % lower total smoke released in Paper IV is a gratifying result for applications where low smoke evolution is required.

Finally, the results of this work indicate that the complete dispersion and exfoliation of MMT have not been achieved and consequently there is still potential to substantially improve the properties of such PVC nanocomposites.

9 SUGGESTIONS FOR FUTURE WORK

There are some points of suggestions for future work with strong affiliation to this doctoral thesis:

9.1 THERMAL STABILITY STUDIES

This point of future work suggestion has been dedicated a whole paragraph, mostly because some of the work was performed within this thesis.

The main goal with this thesis was not only to manufacture plasticized PVC nanocomposites with all the improved material properties that have been reported so far, but also to evaluate the long-term behaviour of these novel materials. At the end of Paper IV the intention was to carry out some kind of migration test on the different plasticized PVC materials. Unfortunately, quite promptly it was discovered that the thermal stability of the TBC-plasticized PVC materials in Paper IV had questionable thermal stability. Owing to this finding the migration studies was interrupted. In Fig. 24 the thermal stability at 90°C is compared between DINP-plasticized PVC and TBC-plasticized PVC, both of them containing 4 phr of a liquid Ba-Zn stabilizer. It is quite obvious that the thermal stability of the latter is rather insufficient. These samples were weighed and after 10 days of thermal ageing the DINP-plasticized PVC had lost 2,5 wt% while the TBC-plasticized PVC had lost close to 20 wt%. It should be noted that the initial formulation contained about 28 wt% plasticizer.

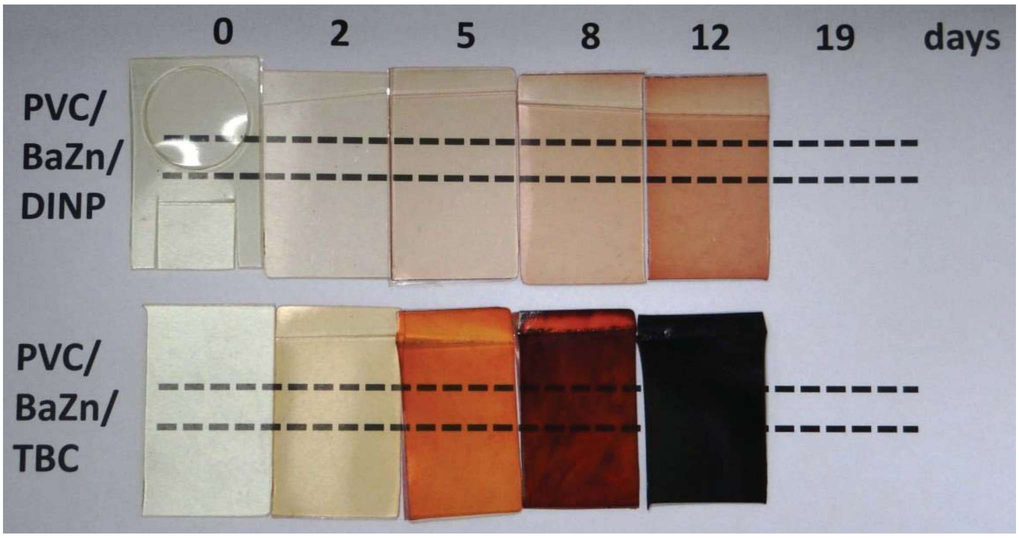


Figure 24. Thermal stability study of DINP-plasticized PVC and TBC-plasticized PVC at 90°C, both materials with 4 phr liquid Ba-Zn heat stabilizer.

It was investigated if there could be found any other type of heat stabilizer more suitable for the use in TBC-plasticized PVC materials including composites containing 10 phr MMT-Na^+. The results from this study are shown in Fig. 25. The sample designated "Ref" contained 4 phr liquid Ba-Zn stabilizer and was processed without the addition of MMT-Na^+. All other samples contained 10 phr Na^+-AR and besides that various heat stabilizers in amount recommended by the supplier (the upper limit of the recommendations); “A” contained 4 phr Ba-Zn stabilizer, “H” contained 2,5 phr Ca-Zn stabilizer, “I” contained 4 phr of Organic Based Stabilizer (OBS) and “K” contained 2,5 phr Ca-Zn stabilizer together with 2,5 phr ESO co-stabilizer. It can be seen in figure 14 that the addition of 10 phr MMT-Na^+ to TBC-plasticized PVC with 4 phr Ba-Zn stabilizer affects the thermal stability in a negative way. In fact, all other heat stabilizers except the Ba-Zn would be a better choice in this case. Judging from this study only, the OBS stabilizer seems to outlive all the others. One drawback with the OBS stabilizer that was observed during processing and evaluation was the reduction of the transparency.

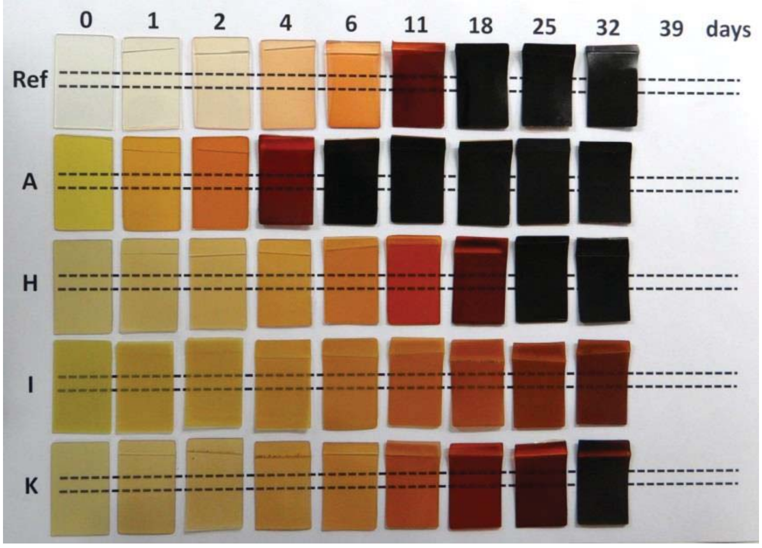


Figure 25. Thermal stability study at 90°C with different thermal stabilizers in TBC-plasticized PVC composite materials (Ref is without the addition of 10 phr Na^+-AR);4 phr Ba-Zn (Ref,), 4 phr Ba-Zn (A), 2,5 phr Ca-Zn (H), 4 phr OBS (I) and 2,5 phr Ca-Zn+2,5 ESO (K)

The results in Fig. 26 were confirmed by the dynamic heat stability test performed in a Werner Mathis oven. The temperature was 190°C and the dwell time 20 min after which the samples were automatically evacuated from the oven at a speed of 10 mm/min. The results are shown in figure 19 and it can be observed that the sample containing 10 phr MMT-Na^+ and 4 phr Ba-Zn stabilizer (corresponding to sample A in Fig. 25) did not survive the 20 min dwell time. The test was repeated for this sample with shorter dwell time and its thermal stability could be established to 12 min. Again, the sample containing the OBS stabilizer was discoloured, but did not turn black within the limitations of this test.

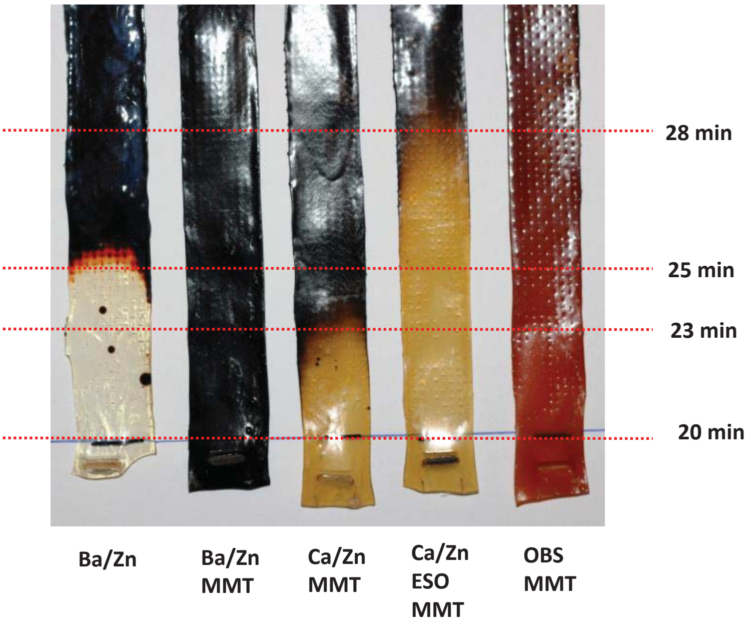


Figure 26. Dynamic heat stability test of different stabilizers at 190^{o}C in Werner Mathis oven.

These results can hopefully contribute to the selection and evaluation of the most suitable stabilizer (package) to be used in layered silicate plasticized PVC nanocomposites.

9.2 OTHER SUGGESTIONS FOR FUTURE WORK

- Find a plasticizer with chelating properties, but with more beneficial thermal stability than TBC. In this way the processing parameters can be even further optimized to maximize the exfoliation of clay mineral layers.
- Evaluate synergistic effects from the combination of MMT and conventional or novel flame retardants. Flame retardants act in different phases and most often the synergistic effects can be superior to the individual flame retardant’s qualities.
- Further involve the use of HSPiP in the selection and development of additives for use in PVC applications. HSPiP can be a time-saving aid in this work.
- When sufficient thermal stability has been achieved there are some long-term properties of interest, such as the plasticizer migration. It is of particular interest to evaluate if the barrier properties of the produced materials can contribute to lower plasticizer migration.

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