Sustainable catalysts for filled and unfilled silane cross-linked polymer systems

Master's thesis in Materials Chemistry

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Abstract

Since the polymer used to make up cables is combustible and has the potential to ignite a fire, fire safety concerns about cables receive a lot of attention. This concern prompts an urgent need to address safety issues and drives the global development of flame retardant polymeric systems. Dioctyltin dilaurate (DOTL) is an organotin catalyst that is frequently used in silane cross-linking for flame retardant polymeric systems. However, DOTL is toxic and has a reprotoxic impact on humans. This study focuses on investigating robust and sustainable catalysts which can be utilized for various silane cross-linked polymeric systems to replace DOTL.

Both filled and unfilled silane cross-linked polymer systems were investigated with various types of catalysts, including four polymer systems (Polymer A, B, C, and D) and four catalysts (Catalyst 1, 2, 3, and DOTL as reference). Tapes made with various amounts of polymer base resin and catalyst masterbatch were crosslinked in ambient conditions and hot water baths. Two analytical techniques, XRF and FTIR, were used for analyzing catalyst masterbatches. Visual observation was utilized to evaluate tape surface quality. The crosslinking of different tapes was measured by hot set testing method.

The results showed that when catalyst 3 is extruded with the unfilled polymer A, highly filled polymer B and C, tapes showcased very good surface qualities and good cross-linking in ambient conditions. The catalyst also displayed good cross-linking in hot water bath for polymer A and C. Catalyst 1 and 2 cross-linked unfilled and some filled polymer systems in hot water bath and ambient conditions but the tapes had bad surface qualities.

Keywords: DOTL, Flame Retardant, Silane Cross-linking, XLPE, Sustainable Catalyst, Hot Set testing, Cables, organotin catalyst

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Contents

Abbreviations

CMB	Catalyst masterbatch
DOTL	Dioctyltin dilaurate
ED	Energy dispersive
FTIR	Fourier Transform Infrared Spectroscopy
IR	Infrared
MB	Masterbatch
Organotin	Organic tin-based
PE	Polyethylene
Reprotoxic	Toxic for reproduction
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
SVHC	Substance of Very High Concern
WD	Wavelength dispersive
wt%	Weight percentage
XLPE	Cross-linked polyethylene
XRF	X-ray fluorescence

List of Figures

List of Tables

1 Introduction

Cables are used in a wide range of industries, including construction, renewable energy, and transport. For example, cables can transmit electricity, signals, and data for power and communication systems. However, their fire hazards have caused widespread concern, especially indoor fires. The combustible or available fuel from cables is more related to polymer components that are used as insulation and sheath functions, because polymer can become a source of ignition or start a fire [1]. Polymers are not only flammable but also produce significant amounts of toxic gases during a fire, such as CO and HCl. According to the UK Fire Statistics Survey (1955-2019), gases, fumes, or toxic fumes surpassed burns as the leading cause of fire deaths [2]. Therefore, there is an urgent need to develop flame retardant polymeric materials that can be safely used in cables.

Borealis is a leading company in the field of polyolefins and base chemicals. The company produces flame retardant materials, among other things, that are designed to prevent the spread of fire along materials. The flame retardant materials at Borealis are based on silane cross-linked polyethylene (PE). Silane cross-linking is a commercial chemical cross-linking method that can improve the chemical, mechanical and thermal properties of polymers by forming chemical bonds or networks between polymer chains [3]. Mineral fillers added into polymer systems have been proven to have a flame retardant effect on polyolefin materials [4].

In general, two catalyst technologies are utilized in Borealis to cure silane crosslinkable materials. The first one is Ambicat™ technology, which has the advantage of fast curing in ambient conditions [5]. The active substance of this technology is based on an acid that is very sensitive to moisture. The main problem with this catalyst is its incompatibility with base chemicals due to neutralization. An alternative catalyst is dioctyltin dilaurate (DOTL). DOTL is an organotin substance where the tin atom is in the oxidation state of IV. It is compatible with both acidic and basic additives, such as color masterbatch (MB), UV stabilizer, and mineral fillers in flame retardant materials. However, it has a slower curing speed than Ambicat™ technology. Furthermore, DOTL is hazardous for human health and the environment. In 2020, the DOTL was classified as reprotoxic 1B by Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). DOTL is also in the list of the Substance of Very High Concern (SVHC). It is expected, but not confirmed, that the substance might be banned in 2027 in Europe.

Therefore, a robust and sustainable catalyst for various silane cross-linked polymeric systems needs to be figured out, which can be used in cables, filled and unfilled polymer systems, with comparable catalyzing effect to DOTL and free of organotin. Borealis has previously tested several active substances to replace DOTL in different projects. These projects showed the potential to use other active substances to replace DOTL. However, the amount of each catalyst in various polymer systems still needs to be investigated.

1.1 Aim of study

In this project, both filled and unfilled silane cross-linked polymer systems will be investigated with three types of catalysts and DOTL as a reference. The unfilled material is polymer A and the filled materials are polymer B, C and D. Catalyst 1, 2 and 3 are used to cross-link the polymer materials. The focus of the study is on the effects of the catalysts in the polymer systems, considering a good surface quality and good cross-linking degree in the hot water bath and ambient conditions. By comparing the effect of the reference catalyst, an evaluation of each catalyst will be made to show the potential to supplant the DOTL.

1.2 Limitation

Since the aim is to substitute a commercial catalyst, this project only focuses on catalysts that are compatible with the silane-based polymer systems in Borealis. Other catalysts are not considered. In this study, the catalyst masterbaches (CMB) contain limited components: a polymer resin, an antioxidant, a catalyst, a scorch retarder and an acid scavenger. Because of the time limit of the project, only the most essential components are considered. The polymer resin was used as a carrier material for the additives in the CMBs. An antioxidant was added to hinder polymer degradation by neutralizing free radicals. A scorch retarder was added to the recipe to prevent premature cross-linking. An acid scavenger was included in some of the CMBs to improve the processing in the tape extrusion. Other additives, such as colorants, were not examined in this project. This study only focuses on cross-linking speed and surface quality of tapes. No mechanical testing, ageing testing or flame retarder testing will be investigated.

2 Background

In this section, polymer systems studied in this project are introduced. The theoretical background regarding cross-linking of polymer systems is described. Moreover, different catalysts that can be used to facilitate cross-linking of polymers are presented. Furthermore, the theory behind the analytical methods used in this project are explained.

2.1 Unfilled polymer system

Polymer A is studied to evaluate how well the catalysts cross-link silane-based polymers without any fillers. The unfilled material is a commercial product manufactured by Borealis and it is used for insulation of low voltage energy cables. It is made of low-density PE copolymerized with vinyl silane. When cross-linked, the material has good thermo-oxidative stability and is suitable for both copper and aluminum conductors.

2.2 Flame retardant materials

Three different flame retardant polymers are studied in this project. These polymers are used in low voltage cable insulation. The materials are made mostly of PE which is the most produced polymer [6]. PE has excellent insulation properties. Its flexibility facilitates it to bend and insulate at the same time. The flexibility of PE is important for cable applications since it is often a requirement. However, PE is prone to thermal degradation and has a high heat of combustion. Flame retardant fillers are therefore essential when PE is used in fire resistance applications.

The flame retardant fillers help resist the fire by inhibiting at least one of the elements in the fire triangle [7], as seen in Figure 2.1. They can for example cool down the material by endothermally decomposing. Another way is to dilute the fuel in the gaseous phase by releasing inert gases during decomposition. Fillers can also form a protective layer that inhibits oxygen and heat from getting inside the material [8].

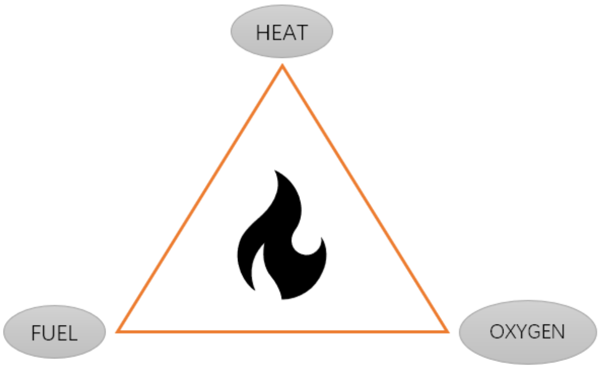


Figure 2.1: The fire triangle. It illustrates the three elements a fire needs to ignite: fuel, oxygen and heat.

2.2.1 Filled polymer systems

Polymer B, C and D are the three filled flame retardant materials studied in this project. The materials are halogen free and silane-based polymer materials designed for low voltage cables. Polymer D is a commercial product manufactured by Borealis while the other polymers are not commercial products yet. All three materials are silane-based PE copolymerized with different numbers of polar polymers. Polymer B and C are more polar than polymer D. Since the materials are used in flame retardant applications, different flame retardant fillers are added to the materials to improve their fire-resistant properties. Polymer B and C are highly filled with filler I and II respectively while polymer D is low filled with filler III. Furthermore, the fillers can absorb water.

2.3 Cross-linking of polyethylene

Cross-linkable polyethylene (XLPE) has been the most common material used for cable insulation for several decades [9]. XLPE is obtained by introducing cross-linking into PE chains. Compared with commercial thermoplastic PE polymers, XLPE is a thermoset material and has higher resistance to chemicals and advantages in long-term thermal stability. The reason is that the cross-linking network introduced into polymer chains restricts the chain movement due to strong covalent bonds and is thus favorable for the material to keep its shape at high temperatures [10]. XLPE can be obtained mainly by three methods, peroxide cross-linking, irradiation cross-linking, and silane cross-linking [9][11].

2.3.1 Peroxide

Peroxide cross-linking is a radical polymerization process and the most common one among the three methods [9]. Organic peroxides are used as initiators to start cross-linking reactions. Upon heating, peroxide decomposes into reactive oxygen radicals. Then those peroxide radicals attract one hydrogen atom from the polymer chain and change the PE molecule into polymer radicals. Subsequently, cross-linking forms between polymer chains through a combination of polymer radicals. In addition, it should be noted that the organic peroxide added in this process is highly sensitive to heat and shock, and strongly reactive with reducing agents and heavy metals. This means that the transportation, handling, and storage of organic peroxide need to follow strict regulations to decrease the risks [9][12].

2.3.2 Irradiation

Irradiation cross-linking is a physical method and does not involve adding any chemicals [12]. Generally, PE chains are ionized by high-energy beams, normally electron beams or gamma beams. Those beams influence polymer chains in two ways, chain scission and cross-linking. In the chain scission process, polymer molecules lose various atoms and form radicals. In the cross-linking process, those polymer radicals produced from the scission step connect with each other by forming new bonds. These two processes are competitive with each other, and the dominant one is influenced by the environment. This radiation method is suitable for PE film or thin materials since beams can penetrate a limited depth.

2.3.3 Silane cross-linking

In this method, silane compounds are used as coupling agents to bind PE backbones together [12]. The silane compounds consist of two parts, a central silicon (Si) atom and side groups (vinyl or alkoxy). This coupling agent can be directly grafted onto PE chains during extrusion or copolymerized with PE base resin in a high-pressure reactor [13]. The silane cross-linking consists of two reactions, hydrolysis and condensation [14]. Copolymerized silane cross-linking is shown as an example in Figure 2.2. In hydrolysis reaction, methoxy groups react with water and yield silanol groups [15]. Water plays an important role in the hydrolysis step and that is why this method is also called silane moisture curing method. Then in the second reaction, with the help of catalyst, silanol groups undergo condensation reactions and release water molecules at the same time. Thus, cross-link networks form among polymer chains.

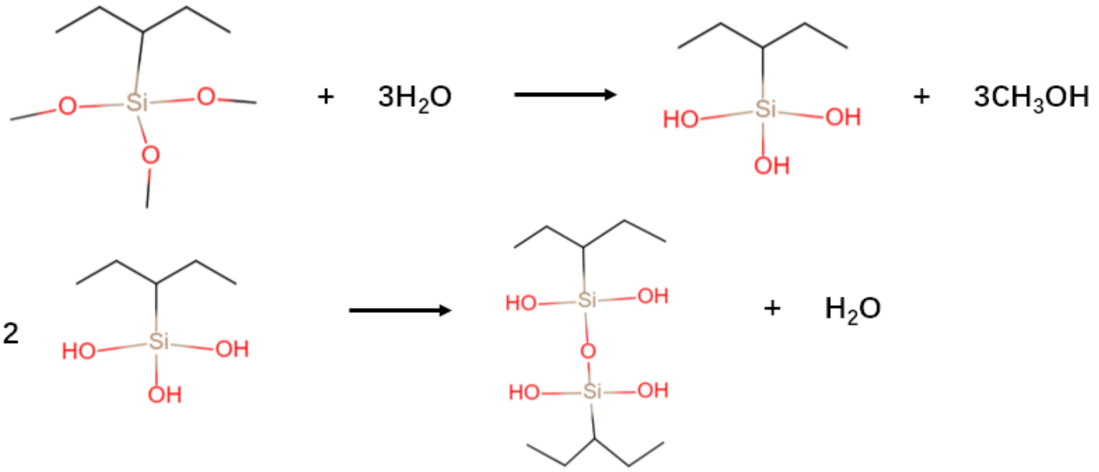


Figure 2.2: Cross-linking reaction of copolymerized silane polymer.

2.3.3.1 Dioctyltin dilaurate

Dioctyltin dilaurate (DOTL) is a commercial and commonly used organotin catalyst to crosslink silane-based polymers. The tin atom in DOTL is in the oxidation state of four. Four is the highest oxidation state of tin in a catalyst and is very stable. The tin atom is connected to the ligand with covalent bonds (Sn-C), which is why DOTL is categorized as an organotin catalyst. DOTL contains laurate ligands, which have longer-chain fatty acids with 12 carbon atoms. This catalyst is reprotoxic and harmful to the human immune system [16].

This organotin catalyst is believed to have a similar reaction mechanism to Lewis acids. This catalyst can accept or withdraw electrons from water molecules and generate a carboxylic acid and a by-product. The acid produced from the hydrolysis step is the substance that catalyzes cross-linking reactions [17].

2.3.3.2 Studied catalysts

In this study, three types of Tin (IV) free catalysts are investigated. Unlike DOTL, the catalysts are not reprotoxic. Catalyst 1 and 2 are metal based compounds. The catalysts have a fast-catalyzing effect in silicone condensation reactions [18]. The main active substance in Catalyst 1 is chemical A, while for catalyst 2, it is a mixture of chemical A and chemical B. Catalyst 3 is a nontoxic base and contains a metal different from the other two catalysts. This catalyst shows promising curing effects in ambient conditions, used for methoxy and ethoxy silane systems [19].

2.4 Analyzing methods

Three analyzing methods are used in this project. The theoretical background of each method is explained in this subsection. The aim is to highlight the advantages and limitations of each method.

2.4.1 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is an analytical technique that identifies and characterizes chemical substances by measuring their infrared absorption spectra [20]. It works by passing an infrared (IR) beam through a sample. As the light interacts with the sample, specific wavelengths are absorbed by different chemical bonds within the molecules. The light that passes through the sample is detected and transformed into a spectrum through a mathematical process called Fourier transformation. The resulting spectrum represents a molecular fingerprint of the sample, with unique absorption bands corresponding to specific molecular vibrations [20][21].

One of the main advantages of FTIR is its ability to provide precise and detailed information about the chemical composition and molecular structure of a sample [22]. FTIR can be used for both qualitative and quantitative analysis, offering insights into functional groups, molecular bonding, and chemical interactions. It is widely applied in various fields such as chemistry, materials science, and environmental science. Furthermore, the technique is relatively quick, non-destructive, and requires minimal sample preparation, making it highly efficient and suitable for a wide range of applications [23].

However, FTIR also has its limitations. FTIR spectroscopy is primarily limited to analyzing materials that are infrared active, meaning they have dipole moments that change during vibration [21]. Non-polar molecules or symmetrical molecules that do not exhibit changes in dipole moment during vibration are not easily detected by FTIR. This restricts the range of compounds that can be analyzed using this technique. Another significant limitation is its sensitivity to water and other polar solvents, as they can produce strong absorption bands that can obscure the spectral regions of interest [24]. This makes the analysis of aqueous samples particularly challenging. Additionally, FTIR typically requires samples to be prepared in a manner that allows the infrared light to pass through, which can sometimes be a limitation for solid or highly absorbent materials [25]. The spectral resolution, while generally sufficient for many applications, might not be adequate for distinguishing compounds with similar chemical structures.

Moreover, the interpretation of FTIR spectra can be complex and often requires a well-trained analyst [24][26]. The overlapping of absorption bands can make it difficult to assign specific peaks to exact functional groups, especially in complex mixtures. Although modern software and extensive spectral libraries have alleviated some of these issues, accurate analysis still relies heavily on the expertise of the operator. Despite these limitations, FTIR remains a powerful and versatile tool in the field of chemical analysis [27].

2.4.2 X-ray fluorescence

X-ray fluorescence (XRF) is a widely used spectrochemical technique for various materials, such as geological materials [28], dental and medical materials [29], and alloys [30]. It can determine the elemental composition of a complex qualitatively and quantitatively, and has the advantage of rapidly providing high-resolution assessment results. This technique does not require complex sample preparations and specimens can be in the form of a solid, powder or liquid [31][32].

The principle behind XRF is based on electron migration between atom layers. When high energy X-ray beams scan the samples, electrons in the inner layers are activated and injected into the outer layers and create vacancies. Since the element atom is in an unstable state after electron injecting, its outer shell electrons thus migrate from the outer to the inner layers, lose some energy and occupy those vacancies. During this migration process, secondary photon electrons are emitted in the form of light with specific wavelengths and detected by the detector. Energy dispersive (ED) and wavelength dispersive (WD) are two of the most commonly used detectors [32]. The principle of XRF is described in Equation 2.1, where E(ev) is the electron's energy in the unit of electrons volts, h is the Plank constant, c is the speed of light in vacuum conditions, λ is the wavelength of X-rays, and e is the electron charge. It is clear from the equation that wavelength is inversely proportional to the energy of electrons [31].

$$E(ev) = hc \div (\lambda \cdot e) \tag{2.1}$$

The XRF technique is an indirect method to determine the concentration of chemical elements. In Equation 2.1, the elemental concentration is calculated by measuring the intensity of characteristic X-ray lines. However, this proportional coefficient is not constant in practice and is influenced by several factors. The coefficient highly depends on the sample matrix. For example, the number of specific element atoms that can interact with X-ray irradiation in the sample is very critical because the total influence is the sum of all elements [31]. The homogeneity of the specimens can also affect this coefficient, such as water content, grain-size variation in bulk and specimen surface defects [33]. Furthermore, intensive calibrations are required to eliminate the influence of background or sample matrix [32].

2.4.3 Hot set test

Hot set test is a method typically used in cable industries to estimate the cross-linking degree of polyolefin materials. It is a very fast method and requires only around 15 minutes for each measurement. In this thesis, the hot set testing is based on standard EN 60811-507.

The schematic of the testing process is shown in Figure 2.3 [34]. In the first step, the material is stamped into a dumbbell shape and an initial length of around 20mm (L_0) is marked in the central part of the specimen between two silver lines without any loading. The dumbbell is hung in an oven at 200 °C for 15 mins with a constant tensile force applied in the end of the specimen (20 N/cm^2) [35] [36]. The final distance between the marked lines is measured after 15 minutes, which is L_1. Elongation is defined as the percentage of length change to the initial length and is calculated by Equation 2.2 [35]. The elongation indicates the cross-linking of the samples, the higher the elongation, the lower the cross-linking degree. After removing the load, the dumbbell remains in the oven for another 5 minutes to relax. The distance between the marked lines is measured again after the sample cools down to room temperature. Equation 2.2 is then used to calculate the elongation after relaxation, which is defined as permanent deformation.

$$Elongation = \frac{L1-L0}{\mathrm{L0}} \times 100\% \tag{2.2}$$

Regarding the limitation of the hot set test, one is that the result is sensitive to sample defects, such as cracks. When stretched by an external force and heated, cracks can expand and cause the specimen to fracture earlier than 15 minutes even in the presence of cross-linking in the sample [37]. In addition, the standard heating temperature (200 °C) in the oven is higher than the decomposition temperature for the components in some polymer materials and thus breaks up the sample and fails the testing.

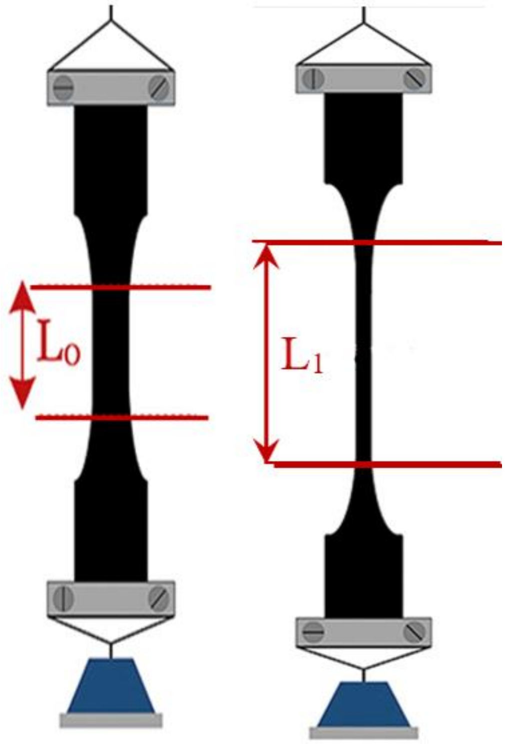


Figure 2.3: The schematic of the hot set testing (adapted from [34]).

3 Methods

Four different catalysts were used to cross-link silane-based polymers, including DOTL as a reference. CMB containing a polymer resin, antioxidant, scorch retarder and catalyst was compounded in a kneader. In some CMBs, an acid scavenger was added. The CMBs were then mixed with four different silane-based polymers, filled and unfilled, in a tape extruder. Subsequently, the polymers were cross-linked in hot water and in ambient conditions.

Different testing methods were conducted. Fourier transform infrared spectroscopy (FTIR) was used to evaluate the dispersion of catalyst in the CMBs and to check how well the CMBs were compounded. X-ray fluorescence (XRF) was performed to examine if the expected concentrations in the CMBs were obtained. The surface quality of the tapes was visually evaluated after the tape extrusion. Hot set tests were performed to estimate the cross-linking degree of the tapes.

3.1 Materials

All catalysts and additives used in this project are presented in Table 3.1. All materials were from unopened packages except for reference CMB and the antioxidant stabilizer. It should also be noted that catalyst 1 and catalyst 2 were dissolved in their respective solutions. The exact amount of active substance in the catalyst packages is not provided by the manufacturer.

Table 3.1: Description of the materials used in CMBs.

Components	Form
Polymer resin	Transparent pellet
Catalyst 1	Viscous yellow liquid
Catalyst 2	Viscous amber liquid
Catalyst 3	Yellow pellet
Reference catalyst (DOTL)	Transparent pellet
Antioxidant stabilizer	White powder
Scorch retarder	Transparent liquid
Acid scavenger	white pellet

The different polymers used in this study are listed in Table 3.2. The appearances of the polymers and the fillers in each polymer are presented in the table as well. All used polymers were from unopened packages and manufactured by Borealis.

Table 3.2: Description of the studied silane-based polymers.

Polymer	Form	Description
Polymer A	Transparent pellet	No fillers
Polymer B	White pellet	Highly filled with filler 1
Polymer C	White pellet	Highly filled with filler 2
Polymer D	White pellet	Low filled with filler 3

3.2 Kneading

Most CMBs were compounded with Thermo Scientific™ HAAKE™ PolyLab™ QC Rheomix3000 containing a driving unit with chamber. The kneader has a 310 cm^3 chamber with co-rotating roller rotors. The kneading temperature for all the CMB was 130 ℃, which is enough to melt the polymer resin. The chemicals in the CMBs were weighed with an analysis scale, with an accuracy of 0.01g, in zipper bags made of PE. The total mass of the weighted chemicals for all the CMBs was 236g. The weight percentages of the substances in the CMBs compounded in the kneader are presented in Table 3.3. They were chosen based on previous studies in Borealis.

Table 3.3: The contents of the kneaded CMBs and their respective weight percentages.

Substance (wt%)	CMB 1	CMB 2	CMB 3	CMB 4	CMB 5	CMB 6	CMB 7
Polymer resin	91.3	93.3	90.3	88.3	93.5	92.5	91.9
Catalyst 1	5	-	-	-	1.8	-	2.4
Catalyst 2	-	3	5	7	-	1.8	-
Scorch retarder	2	2	3	3	2	3	3
Antioxidant stabilizer	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Acid scavenger	-	-	-	-	1	1	1

All additives were added into the kneader at 5 rpm with their respective zipper bags. Half of the weighted polymer resin was added first in the kneader. After 3 minutes when the polymer resin was fully melted, each additive was subsequently added every 3 minutes. Lastly, the rest of the polymer resin was added into the kneader. After all components had been added to the kneader, the kneading speed was increased to 20 rpm for 10 minutes in order for the substances to be kneaded properly.

After the kneading, the chamber was disassembled, and the kneaded material was collected with a clean spatula. The kneaded material was cut into small pieces with scissors and then placed on a mylar polyester foil for the pieces to cool down. The material was thereafter stored in a sealed aluminum bag to minimize the exposure to humidity that could promote scorch and affect the results.

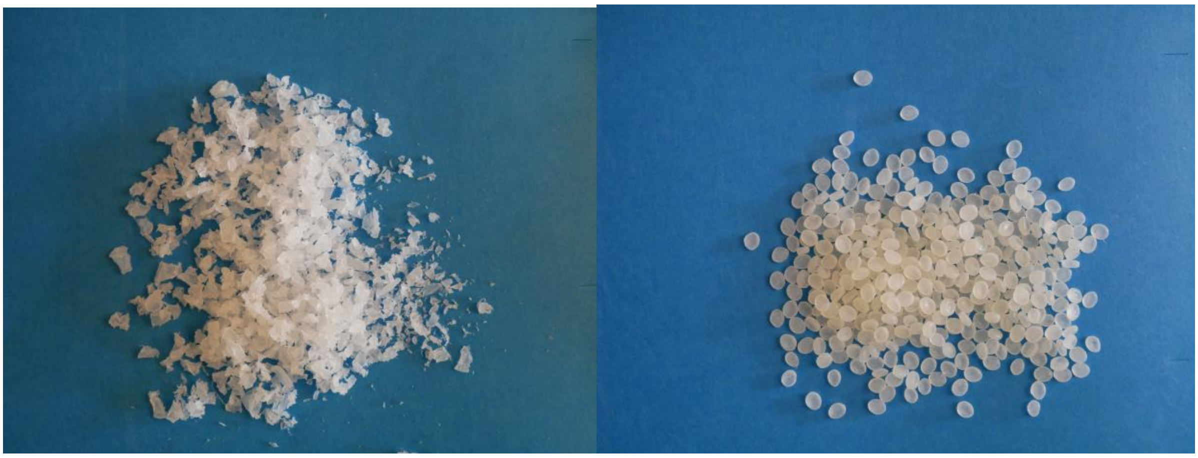
Other CMBs were compounded in the compounding line in Borealis, including CMB 8, CMB 9 and the reference CMB. The CMBs were compounded using a co-rotating twin compounder. The reference CMB contains a polymer resin, a scorch retarder, an antioxidant stabilizer, an acid scavenger and the reference catalyst. The contents of CMB 8 and 9 and their respective weight percentages are presented in Table 3.4.

Table 3.4: The contents of CMBs compounded in the compounding line and their respective weight percentages.

Substance (wt%)	CMB 8	CMB 9
Polymer resin	92.3	90.3
Scorch retarder	2	2
Antioxidant stabilizer	1.7	1.7
Catalyst 3	4	6

3.3 Preparing flakes

The kneaded material was much bigger than the polymers which are in pellet form, even after cutting the material into small pieces with scissors. For the CMBs to mix well with the polymers in the tape extrusion, they should have the same size and form. Figure 3.1 presents how flakes looked compared to pellets. Making pellets of the CMBs was not possible because pellets are only made by compounder for larger scale production. Instead, the CMBs were cut into flakes using a Rapid granulator. The kneaded pieces were added in the instrument and were cut into flakes with a length no more than 0.7 cm.



(a) (b)

Figure 3.1: Illustration of flakes (a) and pellets (b).

3.4 Tape extrusion

The aim of tape extrusion is to produce a homogenous tape that can be used for further testing, such as the hot set test. In the first part of the extruder, the material melts and then a screw processes the material until it is homogenous. The extruder used for tape extrusion was a Collin Teach-line E-20T extruder with a 20x25 mm screw and a 2mm flat nozzle. Norolex haul off is used to pull out the material from the extruder and to cool down the material with compressed air. The speed of the rollers in the Norolex haul off was adjusted until the thickness of the extruded tapes was around 1.8 mm. The thickness of the tapes was measured with a caliper. A scissor was used to cut the tapes to a length of 20 cm.

The CMBs were premixed with each polymer by shaking them in a plastic bag, before they were fed in the extruder. The total mass of the weighed mix of CMB and polymer was 700 g. The materials were weighed on an analysis scale with an accuracy of 0.01 g. The weight percentages of all extrusions for polymer A are listed in Table 3.5. The temperature in different zones of the tape extruder was set to 150/160/170 ℃ for all extrusions with polymer A. The rotating speed of the screw in the tape extruder was set to 55 rpm.

Table 3.5: The weight percentages of polymer A and CMBs in tapes 1-12.

Tape	CMB	wt% CMB	wt% polymer A
Tape 1	5	3	97
Tape 2	5	5	95
Tape 3	7	5	95
Tape 4	1	3	97
Tape 5	1	5	95
Tape 6	2	3	97
Tape 7	6	5	95
Tape 8	2	5	95
Tape 9	3	5	95
Tape 10	8	5	95
Tape 11	9	5	95
Tape 12	Reference	5	95

The weight percentages of polymer B and CMBs in tapes are listed in Table 3.6. The temperature in different zones of the tape extruder was set at 120/130/140 ℃ for all extrusions with polymer B. The surface quality of the tapes changes a lot for this polymer when adding the different CMBs. By adjusting the rotation speed of the screw, the surface quality can be improved. The speed of the screw was therefore not the same for all the extrusions. The rpm for each run is presented in Table 3.6.

Table 3.6: The weight percentages of polymer B and CMBs in tapes 13-26.

Tape	CMB	wt% CMB	wt% polymer B	rpm
Tape 13	5	3	97	60
Tape 14	7	3	97	60
Tape 15	7	4	96	70
Tape 16	7	5	95	70
Tape 17	1	3	97	70
Tape 18	6	3	97	60
Tape 19	2	3	97	70
Tape 20	3	3	97	60
Tape 21	3	4	96	60
Tape 22	4	3	97	85
Tape 23	3	5	95	55
Tape 24	4	5	95	70
Tape 25	8	5	95	70
Tape 26	Reference	3	97	70

The weight percentages of polymer C and CMBs in tapes are listed in Table 3.7. The temperature in different zones of the tape extruder was set at 135/145/155 ℃ for all extrusions with polymer C. The rotating speed of the screw in the tape extruder was set to 70 rpm.

Table 3.7: The weight percentages of polymer C and CMBs in tapes 27-38.

Tape	CMB	wt% CMB	wt% polymer C
Tape 27	5	3	97
Tape 28	7	3	97
Tape 29	7	4	96
Tape 30	7	5	95
Tape 31	1	3	97
Tape 32	6	3	97
Tape 33	2	3	97
Tape 34	3	3	97
Tape 35	4	5	95
Tape 36	8	5	95
Tape 37	9	5	95
Tape 38	Reference	3	97

The weight percentages of all extrusions run for the polymer D base resin are listed in Table 3.8. The temperature in different zones of the tape extruder was set at 130/140/150 ℃ for all extrusions with polymer D. The rotating speed of the screw in the tape extruder was set to 70 rpm.

Table 3.8: The weight percentages of polymer D and CMBs in tapes 39-44.

Tape	CMB	wt% CMB	wt% polymer D
Tape 39	5	5	95
Tape 40	7	5	95
Tape 41	1	7	93
Tape 42	6	5	95
Tape 43	4	5	95
Tape 44	Reference	5	95

3.5 Cross-linking

Before the tapes can be tested with hot set test, they need to be in the shape of dumbbells as seen in Figure 2.3. Elastocon stans press was used to stamp and mold the tapes into dumbbells according to ISO-527-2-5A. Only the middle part of the tapes was stamped to make dumbbells with even thickness since the thickness is different on the edges of the tapes. For one 20 cm tape, two dumbbells were made. The dumbbells were then put in a hot water bath to cross-link. If dumbbells cross-linked well in the hot water bath, new dumbbells with the same recipes were placed in a room with ambient conditions to see if they could cross-link there as well.

3.5.1 Water bath

The dumbbells were first put in small aluminum bags. Distilled water was then poured in the aluminum bags until the bags were halfway full. The bags were thereafter sealed and placed in a hot water bath. The water bath temperature was not the same for all base resin since they have different melting temperatures. In Table 3.9, the water bath temperature and residence time for each base resin are presented.

Table 3.9: The water bath temperature and residence time for each base resin.

Polymer	Water bath temperature (℃)	Residence time (h)
Polymer A	90	48
Polymer B	70	48
Polymer C	70	48
Polymer D	90	48

3.5.2 Ambient conditions

For each tape, 24 dumbbells were made for cross-linking in ambient conditions. The dumbbells were placed standing on an aluminum plate in a room that kept 23 ℃ and 50% relative humidity. The dumbbells needed to be standing separately and not touching each in order to maximize the airflow around the dumbbells, as seen in Figure 3.2. The dumbbells were collected for a hot set test after 4, 7, 10, 14, 21 and 28 days respectively.

Figure 3.2: Dumbbells cross-linking in ambient conditions.

3.6 X-ray fluorescence

XRF was used to determine if the expected concentrations of the catalysts and scorch retarder in the CMBs were obtained. Firstly, the flakes were pressed at 120 ℃ and 5 bars using Specac hot press to produce plaques with a thickness of 3 mm. The plaques were then stamped and molded to circular plaques of 40 mm diameter using Elastocon stans press. The plaques were subsequently placed in a Zetium WDXRF (wavelength dispersive X-ray fluorescence), from Malvern Panalytical, to determine the contents of the plaques.

3.7 Fourier transform infrared spectroscopy

FTIR was used to evaluate the dispersion of the compounded CMBs. It was done by first pressing 10 flakes per CMB at 120 ℃ and 5 bars using a Specac hot press to produce thin plaques with a thickness of 0.2 mm. The plaques were then measured in a Bruker Tensor 27 FTIR spectrophotometer. CMB1 and the reference CMB were selected for the FTIR measurement. CMB1 was chosen to test how well the CMBs were compounded in the kneader and the reference CMB was selected to determine how well the CMBs were compounded in the compounding line.

3.8 Hot set test

Hot set tests were performed to estimate the degree of cross-linking, according to standard EN 60811-507: 2012. To perform the hot set test, three dumbbells were placed in a 200 ℃ oven with a downward stress of 20 N/cm^2. Weights were put on the dumbbells to achieve the desired stress. A Elastocon EB16 oven was used to perform the hot set tests. The elongation of the dumbbells was measured after 2 min and 15 min. After 15 min, the load on the dumbbells was removed. The dumbbells stayed in the oven for another 5 min and then were taken out of the oven to cool down at room temperature. The permanent deformation of the dumbbells was measured subsequently once they cooled down. In this study, 100% hot set elongation after 15 min is considered good cross-linking. This is in accordance with IEC 60811-2-1, a standard utilized for testing insulating and sheathing materials of electric and optical cables.

3.9 Surface quality evaluation

The surface quality of each tape was evaluated visually. The study aims to investigate how well the catalysts cross-link silane-based polymers, but the surface quality is critical as well. Recipes for tapes with poor surface qualities are not considered as possible solutions to replace DOTL in the final production. The criteria for the different levels of surface qualities, used in this project, is presented in Table 3.10. There is no uniform standard for the surface quality of filled polymer materials. The criteria used in this study may not be valid for other studies.

Table 3.10: The description of the criteria for the different surface qualities.

Surface quality level	**Description of the criteria for the surface quality**
Very good	smooth surface, no scorch, no wrinkles
Good	smooth surface, a small number of scorch or wrinkles
Okay	relatively smooth surface, some scorch or wrinkles
Bad	relatively rough surface, a lot of scorch or many small wrinkles
Very bad	very rough surface, a high number of scorch or many big wrinkles

4 Results & Discussion

This section is divided into three sections. Firstly, the characterization of the different polymeric systems is presented. Secondly, the compounding of the CMBs is assessed. Lastly, the environmental and ethical aspects of the catalysts are discussed.

4.1 Characterization of polymer systems

The results of the four silane-based polymers are presented in separate subsections. The subsections are further divided into four sections. Firstly, the hot set results for tapes cross-linked in water baths and in ambient conditions are presented and discussed separately. Subsequently, the surface qualities of the tapes are presented. Lastly, the catalyst candidates for each polymer are evaluated.

4.1.1 Polymer A

4.1.1.1 Cross-linking in water bath

Polymer A was extruded to tapes with different amounts of CMB carrying various amounts of active substances. As seen in Figure 4.1, five tapes made with catalyst 1 have good cross-linking results, no more than 100%. Even using a low amount of catalyst (0.054 wt% active substance in tape 1), good cross-linking was achieved. The results also indicate that it is possible to achieve good cross-linking with less amount of catalyst 1 since the hot set elongation was much lower than 100%.

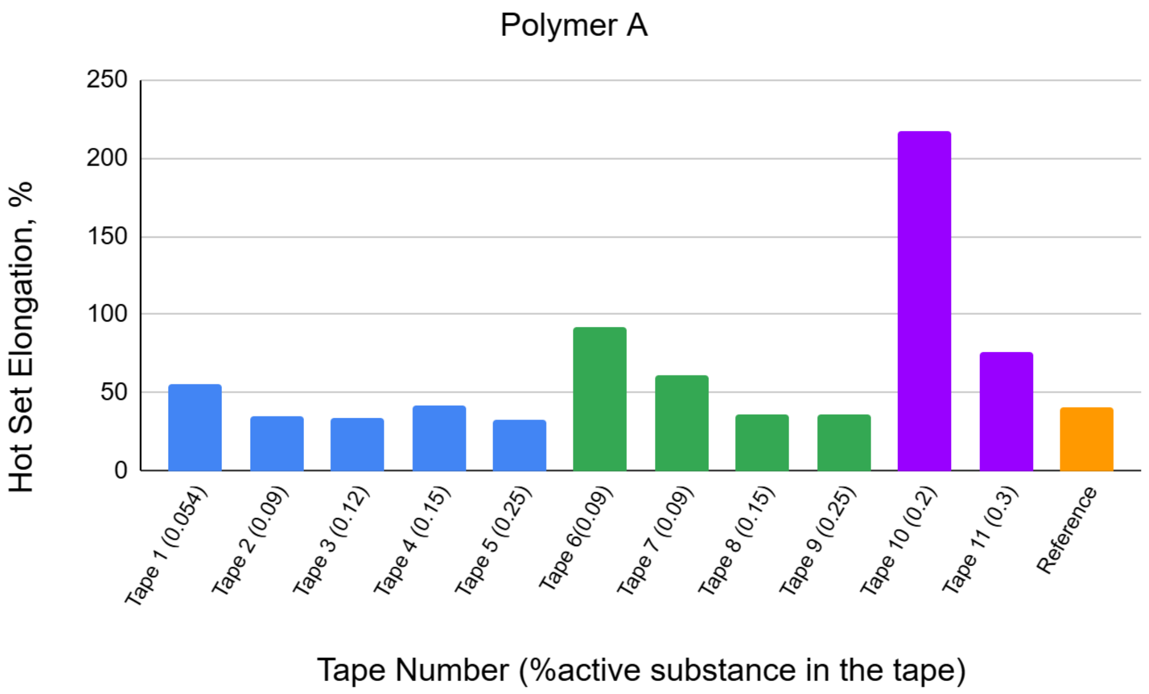


Figure 4.1: Hot set elongation of the tapes made with polymer A. The blue bars correspond to catalyst 1, the green to catalyst 2, the purple to catalyst 3, and the orange to the reference.

Catalyst 2 also exhibited a good curing effect on unfilled polymer A. Considering the results for tape 6 and tape 7, 0.09 wt% of catalyst 2 appears to be the minimum amount needed to achieve effective cross-linking, as indicated by the elongation values being close to 100%. It is important to note that although tape 6 and tape 7 contain the same amount of active substance, they exhibited different hot set elongation results. This discrepancy could be attributed to poor dispersion of the CMB in the tape. Firstly, CMB and polymer A were in different physical forms: Polymer A was in pellet form, while CMB was in flake form. Secondly, different amounts of CMB were added to polymer A: 3 wt% CMB was used in tape 6, whereas 5 wt% was used in tape 7. The impact of poor dispersion is more pronounced when a lower wt% of CMB is added into the tape.

Regarding catalyst 3, it shows a significant influence on the cross-linking speed of polymer A system. Hot set elongation decreased dramatically from over 200% to around 80%, when the catalyst amount changed from 0.20 wt% to 0.30 wt%. Tape 11 showcased a good cross-linking result with 0.30 wt% of catalyst 3.

4.1.1.2 Cross-linking in ambient conditions

To investigate the cross-linking speed of every catalyst in ambient conditions, 5 wt% of each CMB was tape-extruded with polymer A. It is clear in Figure 4.2 that the reference catalyst cross-links very slowly in ambient conditions compared with the other three catalysts. The tape made with reference catalyst still has a very high hot set elongation even after 28 days, with over 300 % elongation.

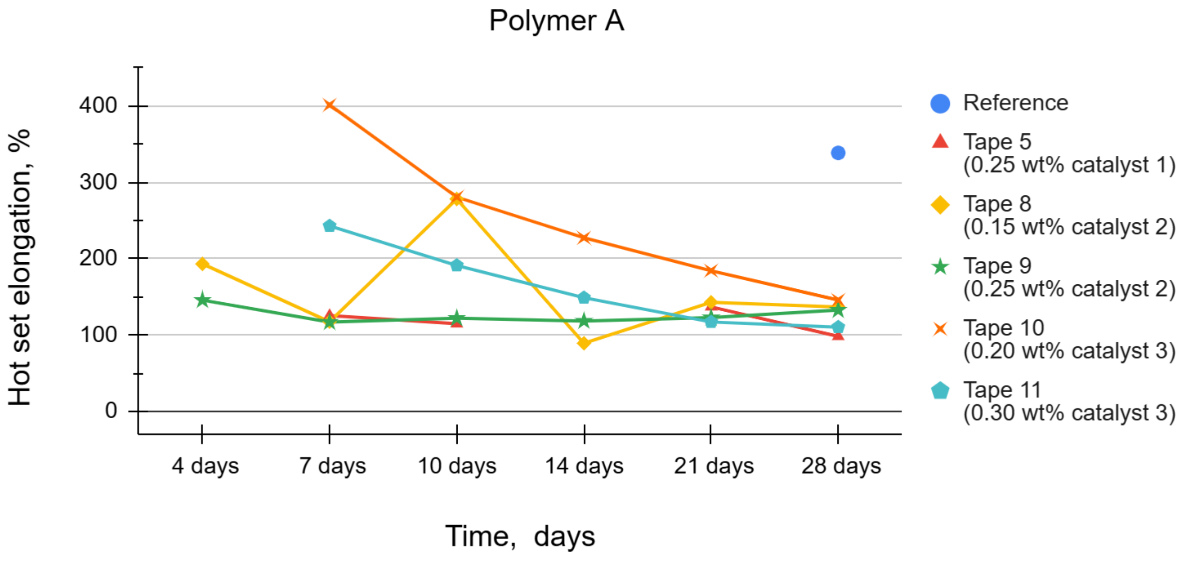


Figure 4.2: Cross-linking speed in ambient conditions for tapes with polymer A.

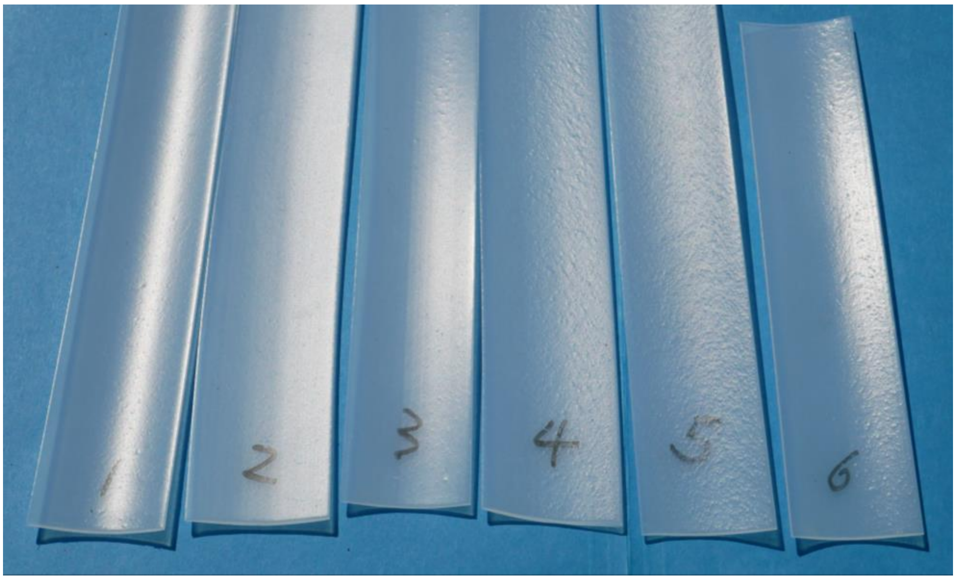
Figure 4.2 also shows that in ambient conditions, catalyst 1 and 2 have comparable cross-linking speeds for polymer A. In only 7 days, the elongation of tapes composed of catalyst 1 (0.25 wt%) and catalyst 2 (0.15 wt% and 0.25 wt%) approaches the same level, at about 120% elongation. Regarding the curve of catalyst 2 (0.15 wt%), the elongation reaches a peak after 10 days. A possible explanation is that some samples contain less amount of catalyst than others, which is caused by the bad dispersion of CMB in the tape. In addition, tape 2 (0.09 wt%), tape 3 (0.12 wt%) and tape 7 (0.09 wt%) which contain lower amount of catalyst failed the hot set test even after maintaining 28 days in ambient conditions, and the tapes are not shown in the figure.

Whereas for catalyst 3, both curves show a downward trend with increasing cross-linking time. After 21 days, the hot set elongation of tapes made with catalyst 3 (0.30 wt%) is around 120%, which indicates the tape has good cross-linking. It also can be seen that the hot set elongation of polymer A made with 0.30 wt% of catalyst 3 is always lower than that made with 0.20 wt%. This indicates that the higher the amount of the catalyst in the tape, the faster the cross-linking speed.

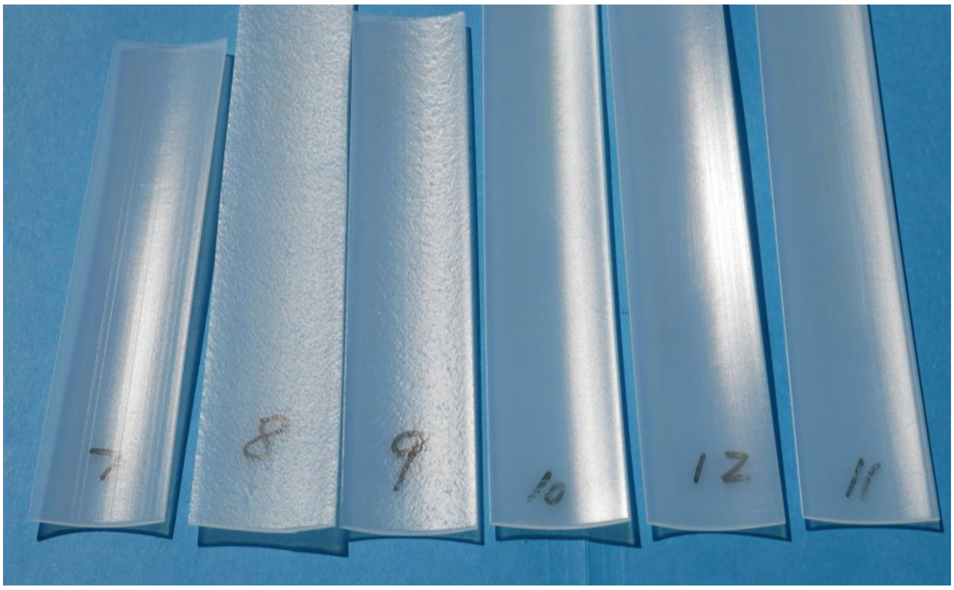
4.1.1.3 Surface quality

The tapes exhibiting good cross-linking in water bath are shown in Figure 4.3. It is clear from the figure that tape 10 and tape 11 display as good surface quality as the reference (tape 12), smooth surface and almost no scorch. This indicates that tapes have very good surface quality even when the amount of catalyst 3 is as high as 0.30 wt%.

In contrast, the surface qualities of tapes within the catalyst 1 (tapes 1 to 5) and catalyst 2 (tapes 6 to 9) groups vary significantly. Increasing the amount of catalyst, as indicated by higher tape numbers, results in progressively rougher surface textures. Comparing tape 3 and tape 4, a transition from smooth to rough surface quality is observed. This suggests that for optimal surface quality, the amount of catalyst 1 should not exceed 0.12 wt%. Regarding catalyst 2, most tapes generally exhibit poor surface qualities except for tape 7 which shows acceptable quality with 0.09 wt% of the active substance.



(a)



(b)

Figure 4.3: Tapes made with polymer A and different CMBs, marked with tape numbers. (a) Tapes from 1 to 6; (b) Tapes from 7 to 12

4.1.1.4 Summary

For this polymer, three tapes show potential to be good candidates to replace DOTL in the unfilled silane cross-linked polymer system. Tape 11 is the best one among them. This tape has very good surface quality and faster cross-linking speed in ambient conditions than the reference tape. Although the elongation after hot water bath is a little higher than the result for DOTL, it is still a good cross-linking result based on the standard shown in section 3.8. The formulation for the best tape is 6 wt% catalyst 3 in CMB and 5 wt% CMB in the tape, containing 0.30 wt% active substance in total.

Since the goal is to obtain good cross-linking and good surface quality using as little amount of catalyst as possible, tape 2 (made with catalyst 1) and tape 7 (made with catalyst 2) are alternative solutions as potential sustainable catalysts to exchange DOTL. The formulation for the two tapes is the same, 1.8 wt% catalyst and 2 wt% scorch retarder in the CMB and 5 wt% CMB in the tape, containing 0.09 wt% active substance in total. These two tapes have acceptable surface quality and good cross-linking in a water bath. Moreover, the result for ambient conditions indicates that this catalyst has a faster cross-linking speed than DOTL. Therefore, they could be a choice as candidates to replace DOTL even though the surface quality is not as good as the one made with catalyst 3.

4.1.2 Polymer B

4.1.2.1 Cross-linking in water bath

Only four tapes, of all extruded tapes with polymer B, showcase good cross-linking. The hot set elongation of the tapes is presented in Figure 4.4. Catalyst 1 cross-linked the polymer very well, as seen in Figure 4.4. The lowest amount of catalyst 1 that cross-linked the polymer is 0.12 wt% active substance. For catalyst 2, good cross-linking was only achieved using a high amount of catalyst in tape 22 (0.21 wt% active substance). Compared to the reference, tape 17 and tape 22 had lower elongation as seen in Figure 4.4. However, a lower amount of catalyst was used in the reference tape.

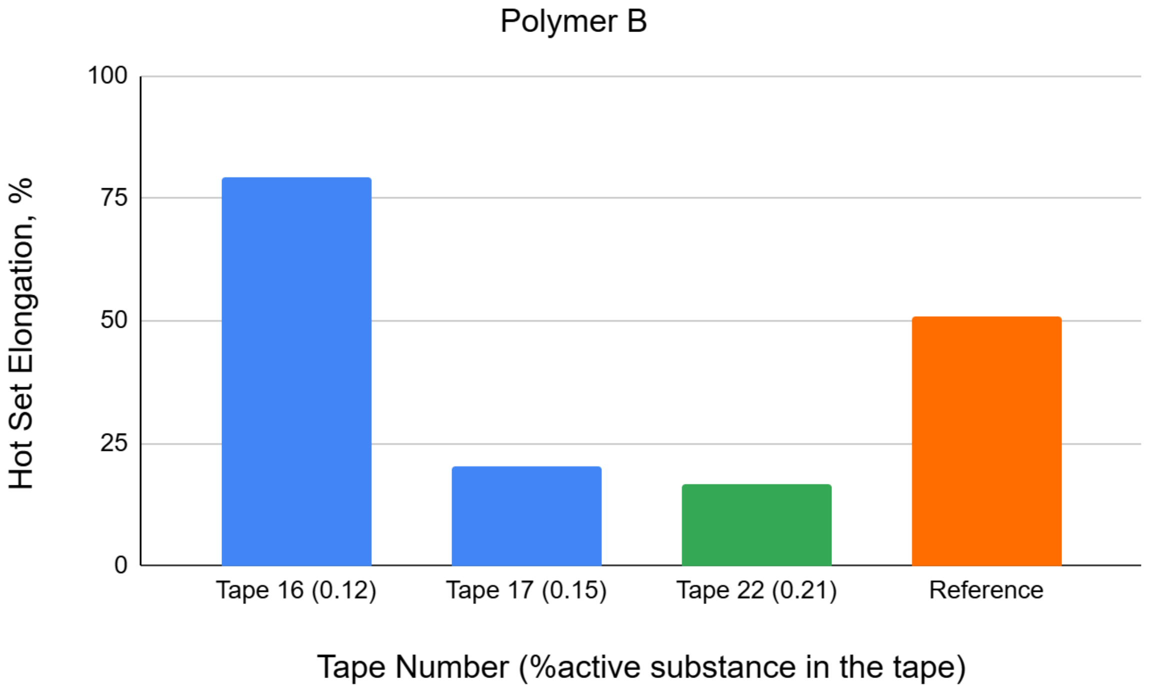


Figure 4.4: Hot set elongation of the tapes made with polymer B. The blue bars correspond to catalyst 1, the green to catalyst 2, and the orange to the reference catalyst.

4.1.2.2 Cross-linking in ambient conditions

The tapes that cross-linked well in the water bath were placed in a room with ambient conditions to see if they could cross-link there as well. It should be noted that tape 22 was not put in the room with ambient conditions even though the tape cross-linked well in the water bath. The reason behind that decision is that the surface quality of the tape was too bad to be a candidate for the replacement of DOTL. Further testing on the tape was therefore not conducted.

Figure 4.5 presents the hot set elongation results of the tapes, with polymer B, cross-linked in ambient conditions. Tape 17 with 0.15 wt% catalyst 1 had good cross-linking speed, as seen in Figure 4.5. Good cross-linking was already achieved after 4 days. Tape 25 with 0.20 wt% catalyst 3 displayed good cross-linking after 14 days. Both tape 17 and tape 25 had faster cross-linking speed than the reference tape. It should be noted that the reference tape consists of a lower amount of catalyst than tape 17 and tape 25. As seen in Figure 4.5, the hot set elongation for the reference tape increases between 7 days and 10 days. However, the expected trend for the curve is to decrease with time. The reason for this could be bad dispersion of the catalyst in the reference tapes.

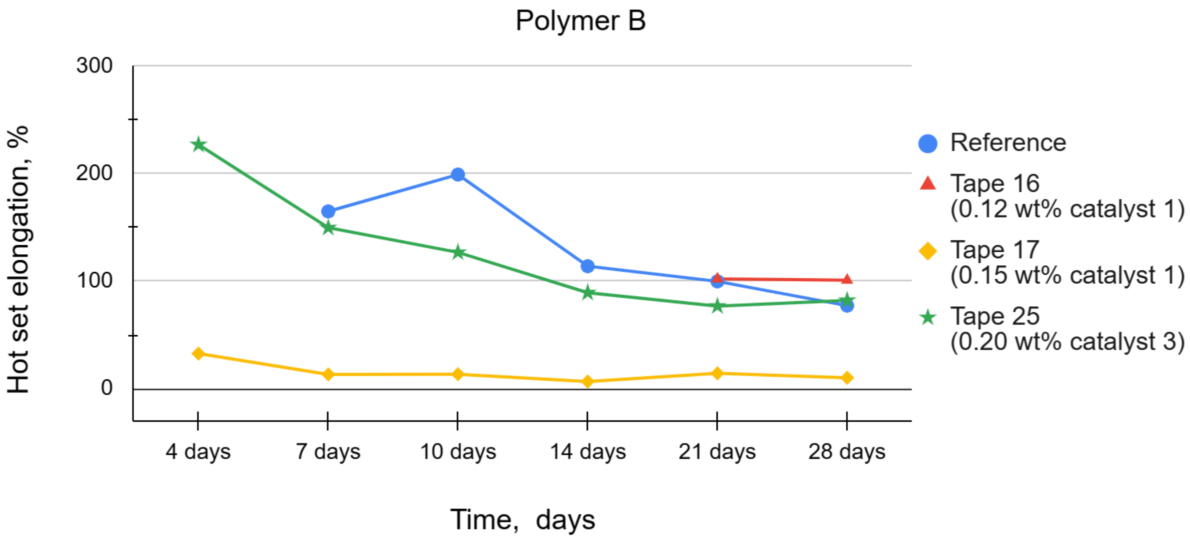


Figure 4.5: Cross-linking speed in ambient conditions for tapes with polymer B.

4.1.2.3 Surface quality

The cross-linked tapes with polymer B are presented in Figure 4.6. Tape 16, that consists of 0.12 wt% catalyst 1, has good surface quality as seen in the figure. However, some parts of the tape had bad surface quality. The reason for the uneven surface quality of tape 16 could be that the processing conditions, such as temperature and rpm, of the CMB and the polymer in the tape extruder were not optimal. Tape 17 with a higher amount of catalyst 1 displayed worse surface quality, as seen in Figure 4.6. The surface quality of tape 22 with the highest amount of catalyst 2 (0.21 wt%), had very bad surface quality but was the only tape with catalyst 2 that cross-linked. As shown in Figure 4.6, tape 25 with catalyst 3 had very good surface quality just like tape 26 with reference catalyst.

Figure 4.6: Tapes made with polymer B and different CMBs, marked with tape numbers.

4.1.2.3 Summary

The goal of the study is to find a catalyst that can cross-link polymer B both in water bath and in ambient conditions. It is also important that the surface quality of the tapes is good and that as low amount of catalyst as possible is used. Comparing the tapes in Figure 4.4 and Figure 4.6, only tape 16 with catalyst 1 showcases a good cross-linking degree in water bath and good surface quality. The tape consists of 0.12 wt% active substance, which is 2.4 wt% catalyst in CMB and 5 wt% CMB in the tape. However, the tape had slow cross-linking speed in ambient conditions since good cross-linking appeared after 21 days as seen in Figure 4.5.

Tape 25 with 0.2 wt% active substance of catalyst 3, which is 4 wt% catalyst in CMB and 5 wt% CMB in the tape, had very good surface quality as seen in Figure 4.6. The tape also cross-linked well in ambient conditions. Good cross-linking was achieved after 14 days. The cross-linking speed of tape 25 in ambient conditions even exceeded the tape with the reference catalyst. However, the tape did not cross-link in the water bath.

4.1.3 Polymer C

4.1.3.1 Cross-linking in water bath

The tapes with polymer C that cross-linked in the water bath are presented in Figure 4.7. Catalyst 1 did not cross-link the polymer when a low amount of catalyst was used. Only the tape with the highest amount of catalyst 1 (0.15 wt% active substance) had good cross-linking in the water bath as seen in Figure 4.7. Catalyst 2 did not cross-link the polymer, even with a high amount of catalyst (0.35 wt% active substance). As seen in Figure 4.7, catalyst 3 showcased good cross-linking using 0.2 wt% active surface in the tape. Tape 37 with a higher amount of catalyst 3 displayed even better cross-linking. However, the reference tape, with less amount of catalyst compared to the other tapes, had the best cross-linking degree as shown in Figure 4.7.

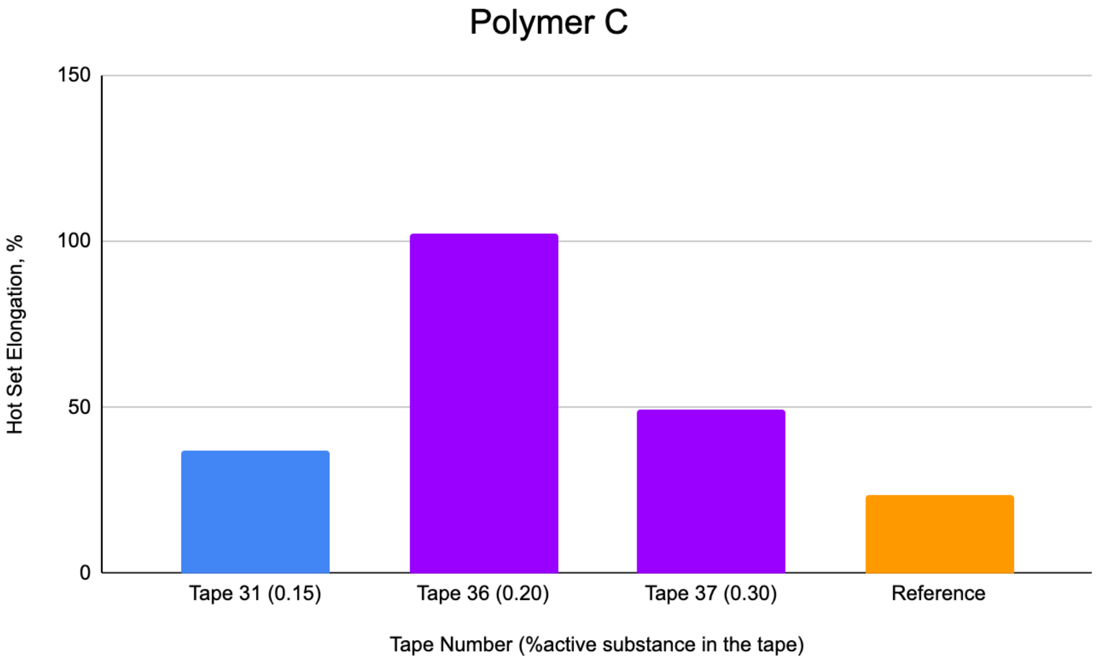


Figure 4.7: Hot set elongation of the tapes made with polymer C. The blue bars correspond to catalyst 1, the purple to catalyst 3, and the orange to the reference catalyst.

4.1.3.2 Cross-linking in ambient conditions

The tapes with polymer C that cross-linked in ambient conditions are shown in Figure 4.8. Catalyst 1 only achieved good cross-linking after 14 days when a high amount of catalyst (0.15 wt% active substance) was used in tape 31. Catalyst 3 showcased good cross-linking after 7 days when 0.2 wt% active substance was used in tape 36. Tape 37 with a higher amount of catalyst 3 had an even faster cross-linking speed as seen in Figure 4.8. Good cross-linking was already reached after 4 days. The cross-linking speed of tape 37 exceeds the reference tape which achieved good cross-linking after 7 days as shown in Figure 4.8.

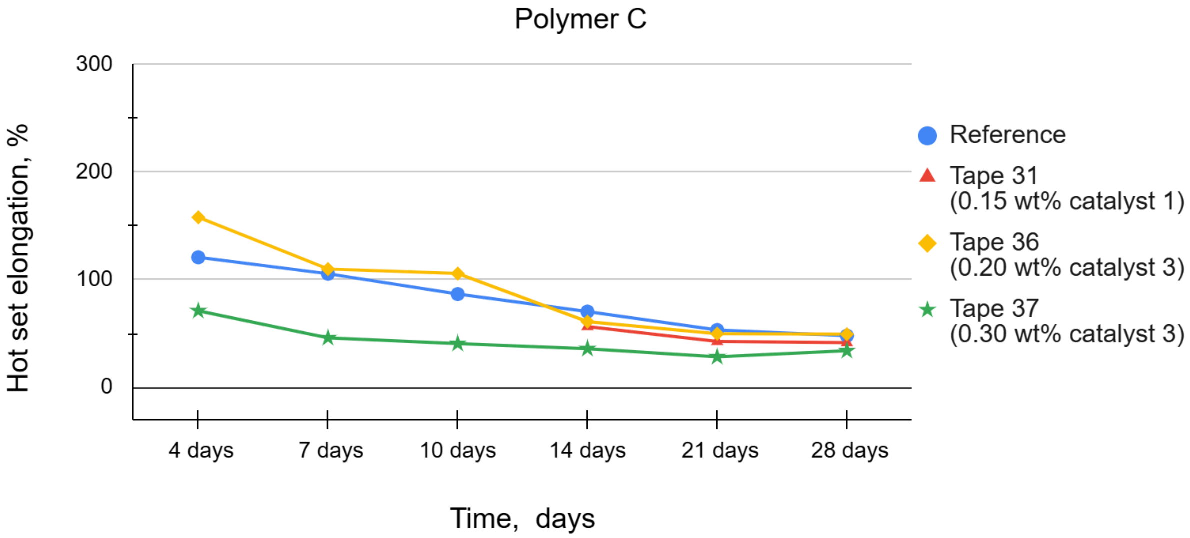


Figure 4.8: Cross-linking speed in ambient conditions for tapes with polymer C.

4.1.3.3 Surface quality

The cross-linked tapes with polymer C are shown in Figure 4.9. Tape 31 is the only tape with catalyst 1 that achieved good cross-linking and the surface quality of the tape was very bad as seen in the figure. Tape 36 and tape 37 with catalyst 3 have good surface qualities just like the tape 38 with the reference catalyst.

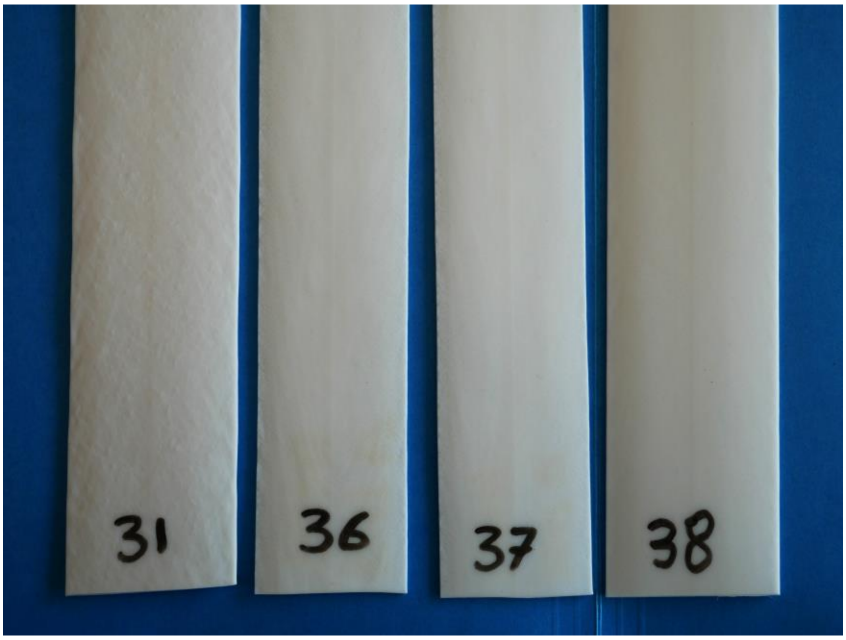


Figure 4.9: Tapes made with polymer C and different CMBs, marked with tape numbers.

4.1.3.4 Summary

Comparing the tapes in Figure 4.7, Figure 4.8 and Figure 4.9, tapes with catalyst 3 are the only ones that showcase good surface quality and good cross-linking in both water bath and in ambient conditions. Tape 36 with 0.20 wt% active substance, which is 4 wt% catalyst in CMB and 5 wt% CMB in the tape, displayed fast cross-linking speed in ambient conditions. Good cross-linking was achieved after 7 days, as seen in Figure 4.8. Tape 37 with 0.3 wt% active substance, which is 6 wt% catalyst in CMB and 5 wt% CMB in the tape, had better cross-linking in water bath and a faster cross-linking speed in ambient conditions than tape 36. When weighing the two tapes with catalyst 3, the one with the lowest amount of catalyst is preferred since it is less expensive.

4.1.4 Polymer D

For polymer D, limited results were collected although a new batch of this polymer resin was tried to eliminate the possible influence of the aging problem. In addition, Catalyst 3 was not considered with this polymer because most tapes made with this catalyst failed hot set testing in previous project [19].

4.1.4.1 Cross-linking in water bath

Figure 4.10 shows the hot set results of tape 41 and reference tape after cross-linking in a hot water bath at 90℃ for 48h. It should be noted that all other tapes made with catalyst 1 (0.09 wt% and 0.12 wt% active substance) and all tapes made with catalyst 2 (0.09 wt% and 0.35 wt% active substance) have no cross-linking result, and are not shown in the figure.

It is clear from Figure 4.10 that the reference tape has the best cross-linking among all tapes, with elongation at around 35%. Tape 41 made with catalyst 1 (0.35 wt% active substance) also got a good cross-linking result, with elongation much lower than 100%.

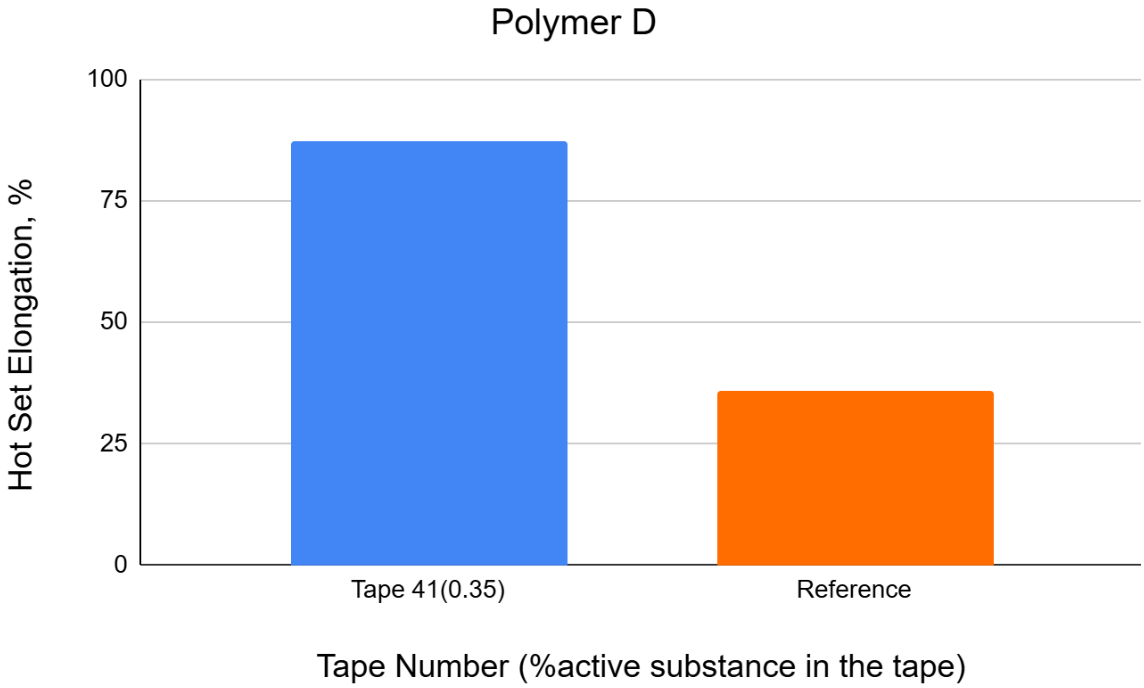


Figure 4.10: Hot set elongation of the tapes made with polymer D. The blue bars correspond to catalyst 1, and the orange to the reference catalyst.

As mentioned in the limitation of hot set test, section 2.7, the reason behind the failed hot set test could be attributed to side-reactions between the catalysts and the polymers and thus a decomposition of some components upon heating. As shown in Figure 4.11, when heated in the oven at 200 °C, bubbles appeared on elongated samples for tape 40 with catalyst 1 and tape 42 with catalyst 2, while not valid for tape 44 with the reference catalyst. The reference tape had smooth surface after hot set test. Therefore, in order to confirm if cross-linking for tapes with catalyst 1 and 2 was achieved after hot water bath, other methods to test cross-linking should be considered.

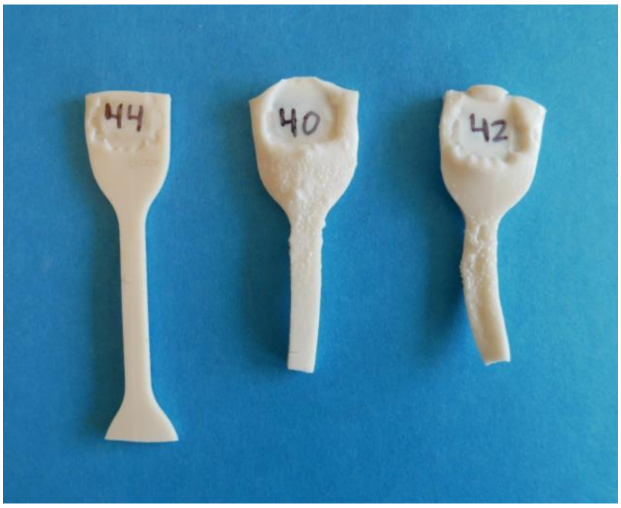


Figure 4.11: Dumbbell samples after hot set test, marked with tape numbers.

4.1.4.2 Surface quality

For tapes that cross-linked in hot water bath, the surface quality of the tapes is evaluated according to criteria in section 3.9 and shown in Figure 4.12. The figure demonstrates that the reference tape has good surface quality. However, for tape 41, the surface quality is very bad when the highest amount of catalyst 1 (0.35 wt% active substance) is added to the tape, with many scorches.

Figure 4.12: Tapes made with polymer D and different CMBs, marked with tape numbers.

4.1.4.3 Summary

Polymer D is thought to be the most difficult base resin to process among the four polymer systems according to previous experiences. This base resin is very sensitive to the environment. Good surface quality of tapes can only be made in a very small processing window during the extrusion. It is clear from the result that none of the catalysts have comparable cross-linking effects as the reference considering the surface quality after extrusion and the cross-linking degree after the water bath. Furthermore, tapes made with this polymer were not placed in ambient conditions because of the poor catalyst performances in hot water baths.

4.2 Assessment of the compounding

The compounding of the CMBs, in the kneader and compounding line, is evaluated in this subsection. Firstly, the dispersion of CMB 1 compounded in the kneader and the reference CMB produced in the compounding line is examined using FTIR. Subsequently, the concentrations of the catalysts and the scorch retarder in CMBs from XRF analysis are compared with the expected concentrations.

4.2.1 Dispersion of the catalyst masterbaches

The results from the FTIR test of CMB 1 are presented in Figure 4.13. The spectra display the peaks of the 10 flakes tested in FTIR. The interesting wavenumber range is between 1650 cm^{-1} and 1500 cm^{-1}, where some functional groups of the catalyst appear in FTIR. As seen in Figure 4.13, the peaks of flakes do not overlap. However, the peaks in the figure show that the catalyst was found in all flakes and the amount of catalyst in the flakes does not differ much. This indicates that the compounding in the kneader was successful.

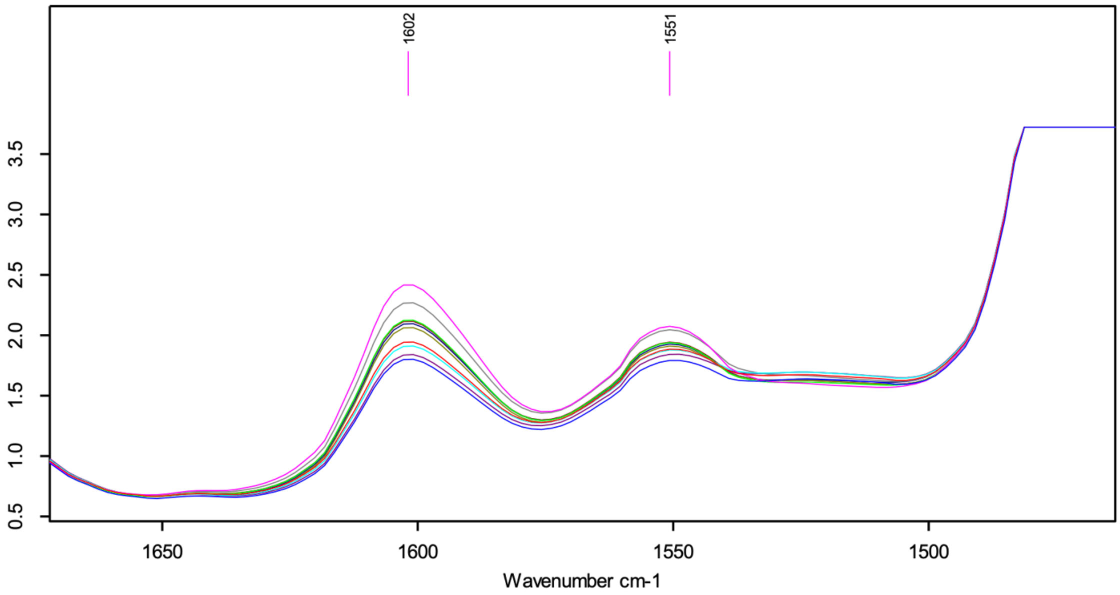


Figure 4.13: FTIR results of CMB 1 normalized at 2020 cm^{-1} polyethylene peak. The spectra show the peaks of 10 flakes between 1650 cm^{-1} and 1500 cm^{-1}.

The results from the FTIR of the 10 pellets containing reference CMB are shown in Figure 4.14. The interesting wavenumber range is between 1650 cm^{-1} and 1500 cm^{-1}, where some functional groups of the catalyst can be found in FTIR. As seen in Figure 4.14, the peaks of the pellets overlap with each other which indicates good dispersion. The results indicate that there is good mixing in the compounding line. Compared to the CMB 1 compounded in the kneader, the dispersion is better in the reference CMB from the compounding line. This is expected since the conditions in the compounding line are well-optimized by technical experts.

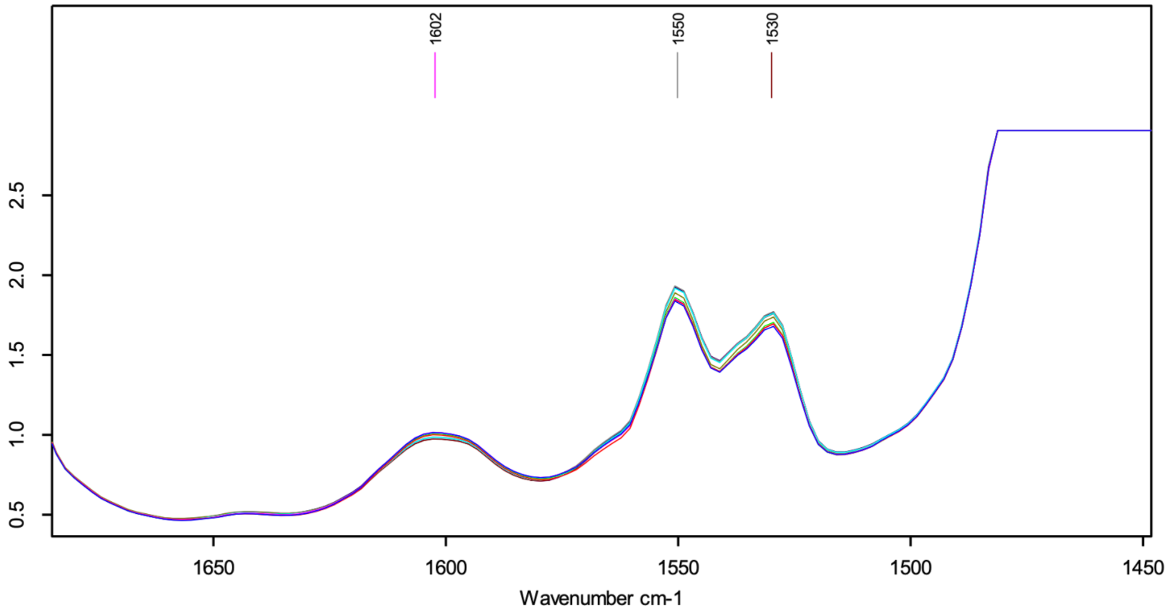


Figure 4.14: FTIR results of the reference CMB normalized at 2020 cm^{-1} polyethylene peak. The spectra show the peaks of 10 pellets between 1650 cm^{-1} and 1500 cm^{-1}.

4.2.2 Concentration verification

To determine the concentration of the catalysts and scorch retarder in CMBs, four CMBs were tested by XRF analysis. The results of these two components in CMB 1, 2 and 3 are shown in Table 4.1. CMB 1, 2 and 3 were compounded in the kneader whereas reference CMB (DOTL) was manufactured in the compounding line. CMB 1 contains catalyst 1 while CMB 2 and 3 contain catalyst 2. The results of the components in the reference CMB are not shown in Figure 4.1.

Table 4.1: The concentration of catalysts and scorch retarder in four CMBs from XRF analysis

CMB	Expected amount of catalyst (%)	Detected amount of catalyst (%)	Expected amount of scorch retarder (%)	Detected amount of scorch retarder (%)
1	5	4.20	2	2.38
2	3	2.30	2	2.58
3	5	3.40	3	3.15

Regarding the amount of catalyst in each CMB, Table 4.1 shows that the detected catalyst concentration is lower than the expected amount for CMB 1, 2, and 3 respectively. However, the XRF results showed that the concentration of DOTL in reference CMB is the same as the expected value that was added into the mixture. This demonstrates that the compounding quality in a commercial compounding line is better than the one in a small kneader.

One possible reason for the differences between the detected and expected concentration of catalyst 1 and 2 is that the catalysts are dissolved in solutions to keep the right viscosity. According to the safety data sheets provided by the manufacturing company, the mixture of catalyst 1 contains 20 wt% solvent while the amount of solvent in the mixture of catalyst 2 is not disclosed by the manufacturer. Another reason for the variance of the expected and detected concentration of the catalysts is that the substances may have stuck in corners of the chamber during kneading.

Table 4.1 clearly shows that the amount of scorch retarder in CMB produced in the kneader is higher than the expected concentration in the mixture. It should be noted that the detected amount of scorch retarder is a little higher than the expected amount in the three CMBs compounded in the kneader. Moreover, the XRF results showed that the detected amount of scorch retarder is much higher in the reference CMB that was produced in the compounding line. The reason for this variation is still under investigation at Borealis.

4.3 Environmental and ethical aspects

Environmental and ethical perspectives need to be taken into consideration when dealing with chemicals. The currently used catalyst for filled silane-based polymers, DOTL, is a hazardous chemical that is on the REACH blacklist. The substance has adverse effects on reproduction and offspring. According to the safety data sheet of DOTL, it may also cause damage to organs. This is tremendously concerning since there is a risk of exposure to the chemical during production or utilization. Since DOTL has not been replaced yet in commercial products, prevention actions are essential when using this substance. It is, for example, important for employees to notify the employer if they are pregnant. The employer must then make sure that pregnant employees abstain from work that could expose them to the chemical.

In case of a leakage in a production or transport where DOTL is involved, the chemical can be released to the environment. Once the chemical is released, the risk of exposure increases. The chemical could for example spread through water systems and affect more people. It would also be difficult to control the exposure once the chemical is released to the environment. This emphasizes why it is so important to replace DOTL with other catalysts.

The other catalysts studied in this project are not reprotoxic. However, the catalysts are not completely harmless. Catalyst 1, 2 and 3 are corrosive and can cause skin irritation, according to their safety data sheet. Catalyst 2 may also cause long lasting harmful effects to aquatic life. These hazards are important to consider when dealing with the catalysts. However, there are safety procedures that can minimize the exposure of the studied catalyst. Using gloves when dealing with catalysts is an example of a prevention action. Although the risk of exposure increases in case of leakage, the catalysts are not on the REACH blacklist.

5 Conclusion

- Catalyst 1 cross-linked filled and unfilled polymer systems, in both hot water bath and ambient conditions. Only tapes with lower amount of catalyst 1 displayed good surface qualities.

- Catalyst 2 cross-linked the unfilled polymer A in hot water bath and ambient conditions. When a high amount of catalyst 2 was used, the catalyst cross-linked the highly filled polymer B in the hot water bath. However, the surface qualities of tapes made with this catalyst were bad. Moreover, catalyst 2 did not cross-link the highly filled polymer C and low filled polymer D.

- Tapes with catalyst 3 showcased very good surface quality and cross-linking in ambient conditions for unfilled polymer A and highly filled polymer B and C. Furthermore, the catalyst displayed good cross-linking in hot water bath for polymer A and C.

6 Future studies

Scorch retarder has been proven to reduce scorches on tape surfaces [38]. Therefore, further research should be conducted to determine if better surface quality can be achieved by increasing the amount of scorch retarder additives in the CMBs. For example, tape 2 and 7, which were made with catalyst 1 and 2 respectively using two wt% of scorch retarder in CMBs, have okay surface qualities. The weight percentage of scorch retarder in the CMBs should be increased while keeping the same amount of catalyst in the CMBs to verify if the surface quality can be improved while maintaining good cross-linking.

The higher amount of catalyst in the tape, the better cross-linking degree. When the amount of active substances catalyst 3 ranges from 0.20 wt% to 0.30 wt% in the tape, the hot set elongation changed significantly. The amount of catalyst 3 that falls between these two ranges should thus be investigated to see if using less of catalyst still results in hot set elongation that is close to 100%. The goal is to lower catalyst costs thus achieving.

In order to minimize the influence of bad dispersion, CMBs should be compounded into pellets instead of flakes to get better mixing in the extruder and thus better tapes. Recipes should also be verified in the cable line, since previous projects have shown that the surface quality is better when produced as cables instead of tapes because the processing conditions are optimal in the cable extruder [19].

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