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RIGA TECHNICAL
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Ritvars Bērziņš

DEVELOPMENT OF TWO-COMPONENT SYSTEMS ON THE BASES OF SILYL TERMINATED PREPOLYMERS AND EPOXY GROUPS CONTAINING COMPOUNDS, CHARACTERIZATION OF THEIR MECHANICAL, ADHESIVE AND RHEOLOGICAL PROPERTIES

Summary of the Doctoral Thesis

RTU Press
Riga 2023

RIGA TECHNICAL UNIVERSITY

Faculty of Materials Science and Applied Chemistry

Institute of Polymer Materials

Ritvars Bērziņš

Doctoral Student of the Study Programme “Materials Science”

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Scientific supervisor:

Professor Dr. sc. ing.

REMO MERIJS-MERI

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Bērziņš, R. Development of Two-component Systems on the Bases of Silyl Terminated Prepolymers and Epoxy Groups Containing Compounds, Characterization of their Mechanical, Adhesive and Rheological Properties. Summary of the Doctoral Thesis
Riga: RTU Press, 2023. – 57 p.

Published in accordance with the decision of the Promotion Council "RTU P-02"of 21 April 2023, Minutes No. 04030-9.2.2/2.

Materials research, preparation and testing was done at the Institute of Polymer Materials of Riga Technical University and at Tenachem Ltd.

Cover photo by wirestock on Freepik

https://doi.org/10.7250/9789934229497

ISBN 978-9934-22-949-7 (pdf)

DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF SCIENCE

To be granted the scientific degree of Doctor of Science (Ph. D.), the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on 7 september 2023 at 14.15 at the Faculty of Materials Science and Applied Chemistry of Riga Technical University, 3/7 Paula Valdena Street, Room 272.

OFFICIAL REVIEWERS

Dr. chem. Bruno Andersons
Latvian State Institute of Wood Chemistry, Latvia

Dr. Virginija Jankauskaite
Kaunas University of Technology, Lithuania

Dr. chem. Ingars Reinholds
University of Latvia, Latvia

DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Science (Ph. D.) is my own. I confirm that this Doctoral Thesis has not been submitted to any other university for the promotion to a scientific degree.

Ritvars Bērziņš ……………………………. (signature)

Date: ………………………

The Doctoral Thesis has been written in Latvian. It consists of an introduction, 3 chapters, conclusions, 139 figures, 31 tables; the total number of pages is 171. The Bibliography contains 78 titles.

ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my scientific supervisor Dr. Sc. Ing. Professor Remo Merijs-Meri and the team of RTU Institute of Polymer Materials. I am grateful for the opportunity to develop knowledge about polymer industry and to create important materials, which can compete with the world’s best sealants and adhesives, as well develop new scientific sector in RTU Institute of Polymer Materials.

I would like to express gratitude to Werner Hollbeck Company for initial knowledge of two component silyl-terminated pre-polymer/epoxy resin systems.

I would like to express gratitude to the Tenachem/Soudal Company Ltd for financial and emotional support and chance to create one of the developed recipes at industrial scale.

Ritvars Bērziņš

USED ABBREVIATIONS

ABS – acrylonitrile butadiene styrene;

ASTM – American Society for Materials and Testing;

benOH – benzyl alcohol;

butOH – butanol;

CAS – a self-synthesized silyl-terminated prepolymer based on castor oil;

CR – central shaft;

DBU – 1,8 Diazabicyclo-7-decene;

DMDEE – 2,2' dimorpholine diethylether;

EP – epoxy group-containing prepolymer;

EPDM – ethylene propylene monomer rubber;

GEL – gel;

Integr. – integration;

IPDI – isophorone diisocyanate;

KOH – potassium hydroxyl number;

NCO – isocyanate groups;

MDI – methylene diphenyl diisocyanate;

m_s – model system;

pH – a scale that describes the concentration of hydrogen ions in a solution;

PMMA – polymethyl methacrylate;

PV – planetary gear shaft;

PVC – polyvinyl chloride;

RH – relative humidity;

r_s – the real/complete system;

Ltd – company with limited responsibility;

SIL – silyl-terminated pre-polymer;

SOL – sol;

TDI – tolene diisocyanate;

UV – ultraviolet radiation

CONTENTS

Introduction

Expansion of the world economy and increase in consumers' purchasing power dictates the demand for higher quality materials due to the immense quest for higher standard of living of humankind. Because of that sealant and adhesive industry is in a constant search for new more efficient alternatives capable to replace traditional materials. Combining different classes of materials within a joint system is one of the approaches for design of perspective materials with extensive range of functional properties. Consequently, within framework of the PhD Thesis two-component flexible block silyl-terminated pre-polymer (SIL) and rigid-block epoxy resin systems were developed and studied. One of key benefits of such systems is great versatility of commercially available pre-polymers whose combinations allow development of even broader range of perspective products for sealants and adhesives market competing with highly elastic materials like acrylates and relatively rigid materials like epoxy resins.

Problem statement

Every year volume of polymer industry is increasing. To be competitive, materials should correspond to broad spectrum of requirements, including not only mechanical, rheological, adhesive and durability aspects, but also environmental sustainability. In the area of adhesives and sealants one of the most perspective trends is materials developed on the bases of silyl-terminated pre-polymers, which offer high superelasticity and adhesion to broad range of substrates. Introducing in this flexible polymer macromolecular network elements of the rigid-chain polymer (e.g., epoxy resin), provides possibility of obtaining universal material, applicable in various branches of national economy.

The Aim of Thesis

The main aim of the Thesis was to create two-component SIL/EP systems by using both commercially available and laboratory synthesized pre-polymers, by developing the research from laboratory until commercially viable industrial scale product.

Thesis tasks

1. Analysis of two-component SIL/EP systems by studying their mechanical and polymer curing properties in dependence of the used
    a. catalysts systems;
    b. compatibilizers.
2. Synthesis and integration of silyl-terminated prepolymers into two-component SIL/EP model systems, studying their mechanical properties in tension and hardness.
3. Research on different drying technology of real two-component SIL/EP systems.
4. Development of real two-component SIL/EP systems from commercially available materials and study of their mechanical, rheological and adhesive properties.

5. Development of real two-component SIL/EP systems from self-synthesized SIL prepolymers from commercially available polyols Acclaim 4200-18200 and polyols that are biorenewable.
6. Development of an experimental batch of two-component SIL/EP system at industrial scale and investigation of its mechanical, adhesive and rheological properties.

Scientific novelty of the research

Society is constantly setting demands towards the developed materials such as adhesive with high strength, resistance in the aggressive media, etc. Due to these reasons, coatings, adhesives, sealants and elastomers industry (C.A.S.E.) is constantly seeking for new formulations capable to fulfil growing demands of the market. The systems developed in the current PhD Thesis would be a significant step towards an excellent alternative to existing adhesives on the market. Within the framework of the Thesis efficiency of different alternative catalysts and compatibilizers has been evaluated by obtaining in-depth information about the performance of two-component SIL/EP systems, new pre-polymers have been synthesized from biologically renewable raw materials, innovative two-component systems have been developed covering broad spectrum of mechanical properties and demonstrating adhesion to various substrates of different surface polarities.

Practical significance of the research

Possibilities of SIL pre-polymer use in two component sealants/adhesives so far have been very limited because of the Henkel Company patent of 1995. This patent has blocked practically all the opportunities to create two component sealants with SIL pre-polymer in it. Because of expired patent terms, at the moment a lot of attention is paid to the development of new two-component systems using SIL pre-polymers, which are competing with one component systems of the same pre-polymer as well as the systems based on acrylates, polyurethanes, epoxies and others.

Research findings of the Thesis allowed the design of a two-component SIL/EP sealant on an industrial scale. Both properties as well as self-costs of the developed sealant were competitive to the commercial products already available in the market.

Theses

By combining silyl-terminated polyether/polyurethane type pre-polymers (SIL) and epoxy resins (EP) it is possible to obtain promising innovative two-component adhesives/sealants by considering the following:

1) compatibilizing SIL/EP two-component systems with secondary amine-containing silanes (N-butyl-3-aminopropyltrimethoxysilane and bis(3-(trimethoxysilyl)propylamine) in certain pre-polymer SIL/EP ratios gives the

opportunity to obtain adhesives/sealants with significantly improved tensile mechanical properties;

2) the synthesized SIL pre-polymers are a perspective alternative to the currently used commercial SIL pre-polymers, providing satisfactory storage stability and showing high mechanical properties in tension of the developed two-component SIL/EP systems;
3) SIL pre-polymers can be synthesized from naturally renewable raw materials (castor oil and farnesene) and integrated into two-component SIL/EP systems, thus improving their mechanical and adhesive properties;
4) in the two-component SIL/EP systems, it is possible to replace widely used bisphenol A-containing epoxy resins with more environmentally friendly epoxy-type compounds, thus maintaining general mechanical and adhesive properties of the end material;
5) tresults obtained in the laboratory experiments of the two-component SIL/EP system can be transferred to the industrial level; obtaining an adhesive/sealant that is stable during storage provides relatively high mechanical properties and adhesion to a wide variety of substrates, making it competitive in the adhesives/sealants market.

Strucure and scope of the Thesis

The Doctoral Thesis has been written in Latvian. It consists of introduction, literature review, methodological part and experimental part with results summary and discussions, as well as conclusions. The volume of the Thesis is 166 pages, including 139 images, 31 tables; 78 literature sources were used.

Approbation of the results of the Thesis and publications

The results of the PhD Thesis have been summarized in 7 publications and presented in 4 international conferences. Pedagogical experience (3 full semesters) has been gained by delivering lectures on several subjects at Riga Technical University – Adhesives and Coatings, Textile Chemistry, Chemistry and Technology of Technical Textile Materials, Chemistry and Technology of Fibrous Materials. A commercial prototype of one of the most perspective two-component SIL/EP sealants has been produced at industrial scale.

1. Literature review

The Literature review contains information about general properties of adhesives and sealants and their commercial importance, paying special attention to polyurethane type systems, which were chosen as a reference for the materials developed within the Thesis. In the literature review synthesis of silyl-terminated pre-polymers and epoxy resins and their catalysis mechanisms, mechanical and adhesive properties are thoroughly described.

2. Methodology

In this chapter raw materials used for development of the investigated SIL/EP systems as well as the methods used for characterization of their rheological, mechanical and adhesive properties have been summarized.

2.1.Raw materials and development of two-component systems

The chemicals used in the PhD Thesis used chemicals are summarized in Table 2.1.1.

Table 2.2.1

Raw materials for development of two-component systems

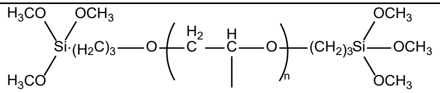
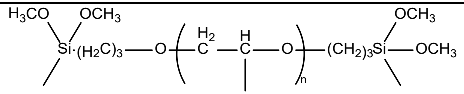
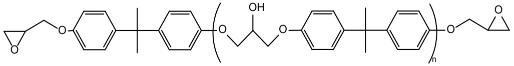
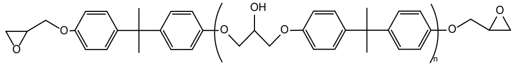
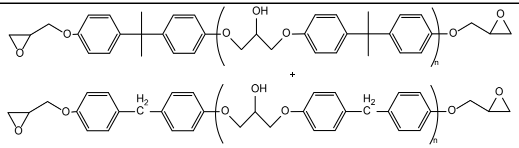
Trademark	*Producer*	*Raw material application*	*Raw material chemical structure*
SAX 520	Kaneka	SIL pre-polymer	
SAX 260	Kaneka	SIL pre-polymer	
D.E.R. 331	DOW	EP pre-polymer	
D.E.R. 321	DOW	EP pre-polymer	
D.E.R. 3412	DOW	EP pre-polymer	

Table 2.2.1. continued

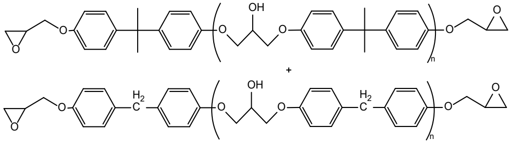
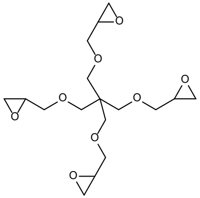
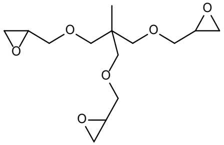
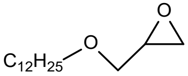
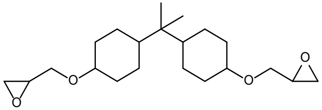
D.E.R. 351	DOW	EP pre-polymer	
D.E.R. 749	DOW	EP pre-polymer	
D.E.R. 732P	DOW	EP pre-polymer	
D.E.R. 721	DOW	EP pre-polymer	
Eponex 1510	DOW	EP pre-polymer	

Table 2.2.1 continued

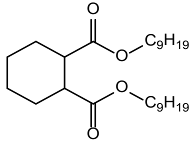
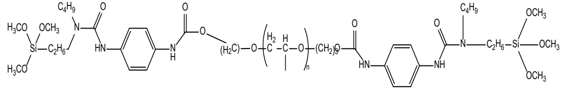
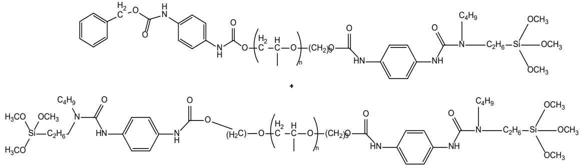
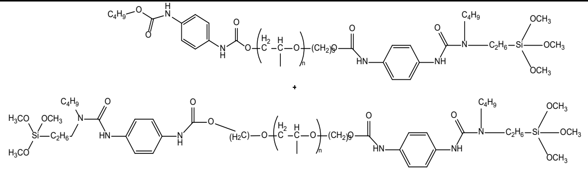
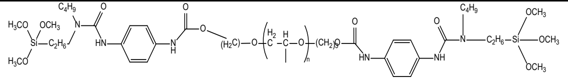
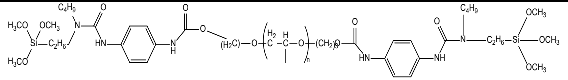
Hexamoll DINCH	BASF	Plasticizer	
Acclaim 4200	Self-synthesized	SIL pre-polymer	
Acclaim 4200 benOH	Self-synthesized	SIL pre-polymer	
Acclaim 4200 butOH	Self-synthesized	SIL prepolymer	
Acclaim 8200	Self-synthesized	SIL prepolymer	
Acclaim 12200	Self-synthesized	SIL prepolymer	

Table 2.2.1. continued

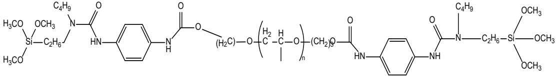
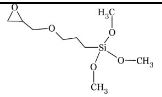
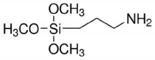
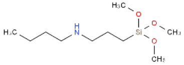
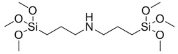
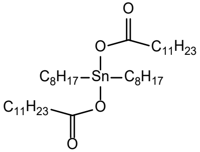
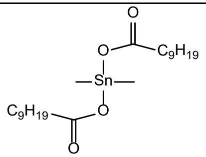
Acclaim 18200	Self-synthesized	SIL prepolymer	
Dynasylan GLYMO	Evonik	Compatibilizer	
Dynasylan AMMO	Evonik	Compatibilizer	
Dynasylan 1189	Evonik	Compatibilizer	
Dynasylan 1124	Evonik	Compatibilizer	
Tibcat 216	TIB chemicals	Catalyst	
Tibcat 318	TIB chemicals	Catalyst	
Tibcat 410	TIB chemicals	Catalyst	SnO

Table 2.2.1. continued

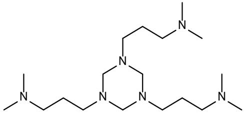
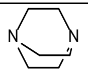
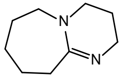
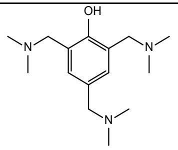
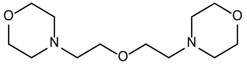
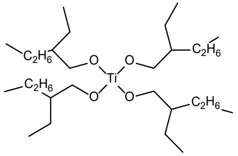
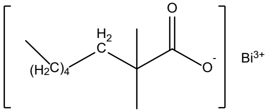
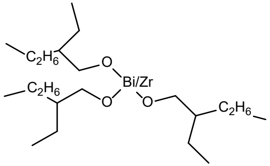
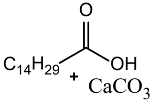
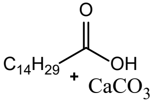
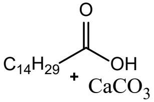
Niax C41	Air products	Catalyst	
Dabco 33LV	Air products	Catalyst	
DBU	Air products	Catalyst	
Ancamine K54	Evonik	Catalyst	
DMDEE	Jeffcat catalysts	Catalyst	
Tyzor TOT	Shephard Chemicals	Catalyst	

Table 2.2.1 continued

Bicat 8108M	Shephard Chemicals	Catalyst	
Bicat 3184	Shephard Chemicals	Catalyst	
Omycarb 1TVA	Omya	Filler	
Hakuenka CCR-S10	Omya	Filler	
Microdol 5	Omya	Filler	CaCO3
Hydrocarb 95T	Omya	Filler	

Eight pre-polymers were synthesized with molecular weights from 4200 g/mol to 18200 g/mol, two of them were from renewable raw materials (castor oil, Krasol F3000).

Within the framework of the research, mechanical properties of two-component SIL/EP systems (model and completed systems) at the pre-polymer mixing range from 100/0 to 30/70 (SIL/EP) were tested.

The model systems were mixed for 60 seconds at 2800 rpm using centrifuge type laboratory mixer Speedmixer DAC 150.

The completed systems were mixed using 3 L laboratory mixer by Teja Enginnering. At first, all raw materials in a liquid phase (pre-polymer, plasticizer, drying agent) were mixed for 5 min (speed at central axis 1000 rpm, speed of planetary mixer 5 rpm). After 5 min, solid fillers were added, mixing speed was increased to 3500 rpm (speed at central shaft CR) and 35 rpm (speed of planetary mixing elements, PV) and mixing was continued for 20 minutes, then vacuum was applied to the system and mixing was continued for another 30 minutes at 3500 rpm (speed at CR) and 35 rpm (speed at PV).

Two-component SIL/EP adhesive at industrial scale was made in a 1 m^3 reactor. First, plasticizer and pre-polymer were loaded in the reactor. The components were mixed (250 rpm at CR and 70 rpm at PV) for 5 minutes until the homogeneous solution, then the solid ingredients were added, the mixing speed was increased (1000 rpm at CR and 70 rpm at PV), vacuum was applied (vacuum at least 50 bar) and the system was mixed for 10 minutes. In the next step 80 % of the drying agents were added at low speed (300 rpm at central axis, 50 rpm at planetary axles) by continuing the mixing for 4 minutes. Then, the mixing speed was increased (600 rpm at CR, 100 rpm at PV), vacuum was applied and mixing was continued for 25 minutes. After that, the rest of the drying agent (20 %) and the catalyst were added and mixing was continued at low mixing speed (speed at CR – 300 rpm, speed at PV – 50 rpm) for 5 minutes. After that, mixing speed was increased (speed at CR – 1000 rpm, speed of PV –100 rpm), vacuum was applied and mixing was continued for another 15 minutes. After the mixing process the material was filled in the packing provided specifically for that purpose.

2.2. Pre-polymers synthesis

In a three-neck flask, 1 equivalent of polyol, 2 equivalents of isocyanate (Ongronate 1010) and the catalyst (Dabco 33 LV) 0.03 % from the total amount of the reaction mass were added. The solution was mixed for 5 hours at 60 °C in an inert atmosphere using static mixer (200 rpm). The conversion degree of the reagents was controlled in the mixing process by measuring isocyanate percent concentration using titration. In the second stage of the synthesis, N-butyl-3-aminopropyltrimetoxysilane was added to the reaction mixture. Termination of the synthesis was controlled by measuring the concentration of isocyanate groups using infrared spectrometer.

2.3. Materials' stress-strain properties using tensile test

Tensile properties were determined using Zwick/Roell Z010 universal testing machine. The tests were performed according to ISO 527. Testing was made for both the model systems and the completed systems after 1, 7 and 28 days of storage at 23 ºC and 50 % RH.

2.4. Materials' hardness

Shore-A hardness was tested according to ISO 7619, using SCHMIDT PHPSA durometer. Testing was made for both the model systems and the completed systems after 1, 7 and 28 days of storage at 23 ºC and 50 % RH.

2.5. Materials' adhesion properties using peel test

The test was made manually by peeling the sealant from substrate surface (express industrial testing method). Delamination character was evaluated by visual inspection of the delaminated surfaces. Accordingly, material's fracture was characterized either as cohesive (sealant/adhesive material remains on the surface of the substrate) or adhesive (sealant/adhesive material does not remain on the surface of the substrate) or thin layer (sealant/adhesive material remains on the surface of the substrate as thin layer). Substrates used in the research: metal substrates – alloy 5005, alloy MS 63, stainless steel, copper, aluminium, anodized aluminium; polymer substrates – glass fiber reinforced epoxide composite, polyvinyl chloride (PVC), ethylene propylene diene terpolymer rubber (EPDM), polyamide, polymethylmethacrylate. Samples were tested after 1, 7 and 28 days of storage at 23 ºC and 50 % RH.

2.6. Materials' adhesive properties using shear test

The test was made according to EN 1465. Substrates used in the research were: stainless steel, anodized aluminium, PVC and wood. Samples were tested after 7 and 28 days of storing at 23 ºC and 50% RH.

2.7. Pre-polymer's viscosity

Pre-polymers viscosity was tested using rheometer Bohlin CVO 100. The instrument was equipped with 20 mm diameter spindle with plate-plate geometry (gap size 1000 µm). The tests were made at constant shear rate 5 s^{-1} and temperature 25 ºC for 60 seconds.

2.8. Materials' complex viscosity, elastic and viscous modulus

Rheological properties were tested using Bohlin CVO 100 rheometer in oscillation method. The tests were performed at a constant frequency of 1 Hz, strain amplitude of 0.006 and temperature of 25 ºC. During the tests, 20 mm spindle with plate-plate geometry (gap between 1000 µm) was used. Testing was made to study the effects of the addition of different catalyst systems and compatibilizers on rheological properties of both the model systems and the completed systems.

2.9. Titration method for measuring percentage of isocyanate concentration

Isocyanate containing pre-polymer was dissolved in 5 ml of acetone. Two to five drops of methyl orange indicator and 2 ml of diethylamine were added to the mixture and titration with 1N hydrochloric acid solution was performed until the mixture colour turns light orange.

2.10. Isocyanate concentration testing using IR spectroscopy

IR spectra were taken in a range from 4000 cm^{-1} to 400 cm^{-1}, scanning time 24, and resolution 4 cm^{-1}. Previously obtained titration results were attributed to the parallel recorded IR spectrum. For data analysis integration method L was used, calculating the highest peak height in the interval: left boarder 2405.5 cm^{-1}, right border 2161.5 cm^{-1}, first base line 2486.8 cm^{-1}, second base line 2098.2 cm^{-1}. During the evaluation the peak discussed above was compared to the peak which did not change during the synthesis: left boarder 3038 cm^{-1}, right boarder 2730.7 cm^{-1}, first base line 3173.5 cm^{-1}, and second base line 2649.4 cm^{-1}. After IR spectrometer data were calibrated according to the results of titration, IR spectroscopy was solely used for control of completeness of the reactions.

2.11. Aging of two-component systems

Accelerated ageing tests were performed at a temperature of 55 °C, RH of 95 % and UV irradiance within spectrum 290 – 400 nm, spectra peak at 340 nm. In these conditions materials were aged for 504 hours, and the effect of accelerated ageing was evaluated by determining the change of hardness and tensile properties.

3. Results and discussion

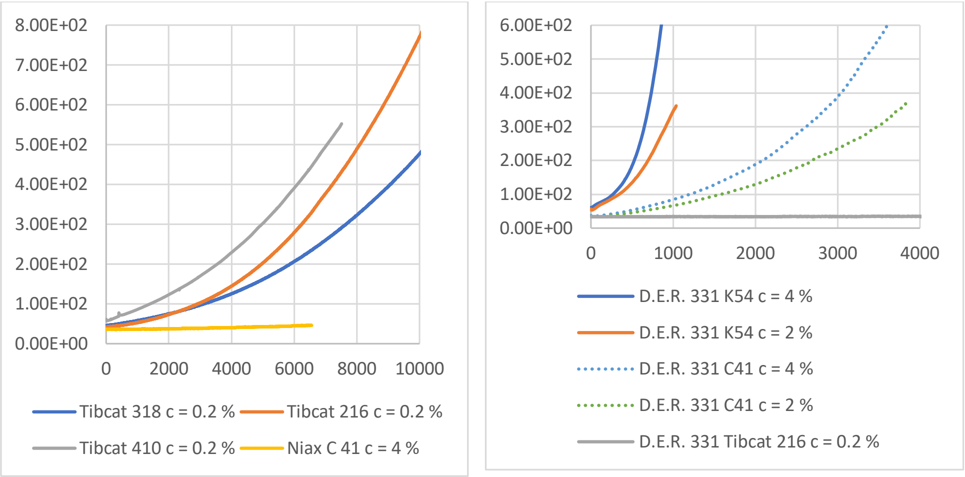
Within the framework of the Doctoral Thesis perspective two-component SIL/EP systems were developed; by analysing the effects of different catalyst systems and compatibilizers, several model and completed systems were obtained by using both commercial and laboratory synthesized pre-polymers and their mechanical, adhesive and rheological properties were analysed. Finally, a two-component SIL/EP adhesive prototype was produced at industrial scale and its properties were characterized.

3.1. Catalyst evaluation for the two-component SIL/EP systems

Catalyst evaluation was done on the basis of commercially available SIL pre-polymer SAX 520 and EP pre-polymer D.E.R. 331. Catalytic activity was studied for different types of catalysts.

1. Amine containing catalysts:
    a) N,N',N''-Dimethylaminopropylhexahydrotriazine (Niax C41);
    b) 1,4-Diazabicyclo[2.2.2]octane solution in dipropylene glycol (Dabco 33LV), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU);
    c) 2,4,6-Tris(dimethylaminomethyl)phenol (Ancamine K54);
    d) 4,4′-(Oxydi-2,1-ethanediyl)bismorpholine (DMDEE).
2. Tin containing catalysts:
    a) dioctyltin dilaurate (Tibcat 216);
    b) dioctyltin neodecanoate (Tibcat 318);
    c) tin oxide (Tibcat 410).
3. Organometallic catalysts of titanium, zinc, bismuth, zirconium:
    a) titanium chelate (Tyzor TOT);
    b) bismuth neodecanoate (Bicat 8108M);
    c) zirconium/bismuth/zinc neodecanoate mix (Bicat 3184M).

In the case of the investigated A + B type two-component systems the pre-polymer catalyst should be selective, i.e., it should be inactive within the embodied component composition (let us say, e.g., within the composition of the A component), whereas it should initiate curing reaction if combined with the other component (i.e., component B). To evaluate the catalysts efficiency, individual systems of SIL or EP pre-polymers with selected catalysts were developed and their rheological properties were analysed; viscosity increase over time testified that the chosen catalyst catalyzed a particular system. For catalysis of SIL pre-polymer, different tin catalysts were used, known to catalyze SIL one-component systems even at low concentrations; concentration of 0.2 wt.% was chosen based on commercial information. Consequently, Tibcat 216 at 0.2 wt.% concentration was used for development of the model and the completed systems due to both the low required concentration, enough large gelling time (considerably larger than for Tibcat 410 and similar to Tibcat 318) and faster curing in comparison to Tibcat 318 (Fig. 3.1.1 a). As tertiary amine type compounds are well-known EP catalysts, various representatives from this group were chosen as catalysts for EP pre-polymers. Analysis of viscosity data revealed two effective catalysts for EP system – Ancamine K54 and Niax C41 (Fig. 3.1.21 b); 2 wt.% of Niax C41 was chosen for further research due to both more comparable gelling time (in comparison to SIL-prepolymer) and its lower toxicity.



a b

Fig. 3.1.1. Viscosity changes of mixtures (a) based on SAX 520 pre-polymer and (b) based on D.E.R. pre-polymer using tin and amine type catalysts.

From Fig. 3.1.1 it is clearly seen that the selected catalysts will efficiently promote curing if the components of two-component system will be combined, but will remain stable within each individual component.

3.2. Studies on the effect of compatibilizers on the properties of the SIL/EP model system

3.2.1. Mechanical properties of the two-component SIL/EP model systems with compatibilizers, containing

To study the effects of different compatibilizers on the mechanical properties of SIL/EP systems, model systems were designed at different SIL (SAX 520)/ EP (D.E.R. 331) pre-polymers ratios 100/0 to 30/70. Decreasing of SIL pre-polymer concentration below 30 wt.% resulted in inacceptable brittlening (after 28 days 50 % RH $\sigma_{break} = 2.3$ MPa; $\varepsilon_{break} = 3$ %; Shore A 96); consequently, these compositions were not considered for further research. To catalyze SIL pre-polymer Tibcat 216 (w = 0.2 %) was used, whereas to catalyse EP pre-polymer Niax C41 (w = 2 %) was used. Four different silanes – 3-glycidyloxypropyltrimethoxysilane (*es*), 3-aminopropyltrimethoxysilane (*am*), N-butyl-3-aminopropyltrimethoxysilane (*sam*), and Bis[3-(trimethoxysilyl)propyl] amine (*bsa*) – were chosen as compatibilizers. Due to a number of functional groups, silanes work not only as compatibilizers, but also as crosslinking agents, which might increase material tensile strength and hardness as well as decrease tensile deformation at break. Because of dual influence of the silanes, several compatibilizer concentrations (0.5 %, 1.5 %, 2.5 %) were assessed to find out the most effective one. Results showed that the most effective silane compatibilizer concentration was 1.5 %. Consequently, Figs. 3.2.1.1–3.2.1.3 summarize the relationships of various indicators of mechanical properties as functions of SIL/EP content. Results of tensile tests and hardness measurements show that the systems compatibilized with *sam* and *bsa* (Fig. 3.2.1.1) demonstrate greater efficiency. Consequently, all the compatibilized systems demonstrated increased tensile strength, being 1.03 (*es*), 1.04 (*am*), 2.27 (*bsa*) and 2.87 (*sam*) times higher in comparison to the system without compatibilizer. Tensile deformations at maximal tensile strength values of the systems with compatibilizers decreased by 32 % (*es*), 29 % (bsa), and 9 % (am) or remained unchanged (*sam*) in comparison to the unmodified system (Fig. 3.2.1.2). Hardness of the systems compatibilized with *bsa* and *sam* demonstrated the highest values all over the investigated SIL/EP range, denoting to higher efficiency of the mentioned compatibilizers (Fig. 3.2.1.3).

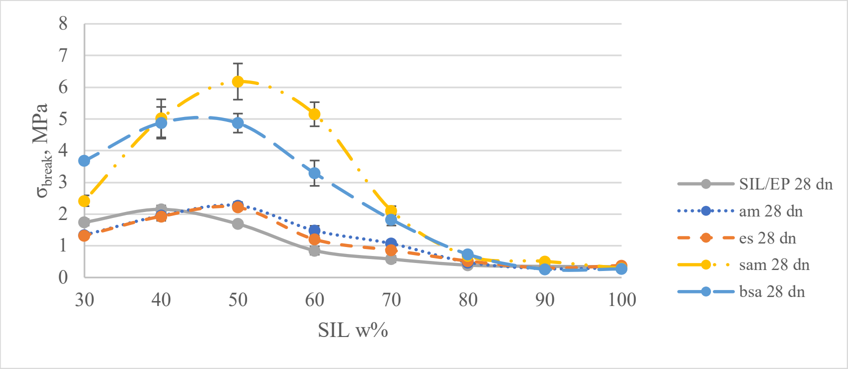


Fig. 3.2.1.1. Tensile strength at break of the two-component SIL/EP systems with compatibilizers *es*, *am*, *sam* and *bsa* after 28 days of curing at 23 °C and 50 % RH.

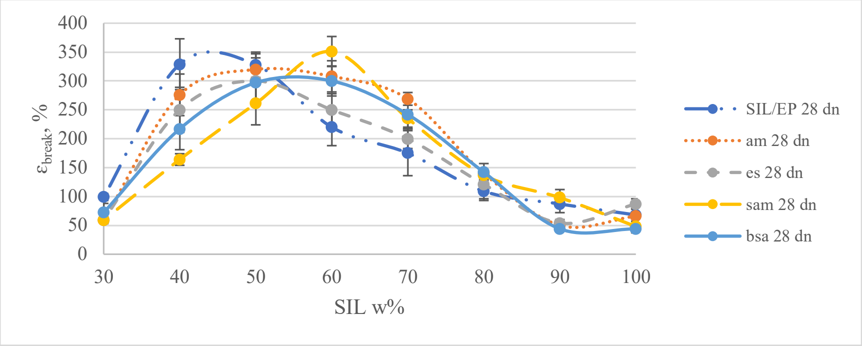


Fig. 3.2.1.2. Tensile deformation at break of the two-component SIL/EP systems with compatibilizers *es*, *am*, *sam* and *bsa* after 28 days of curing at 23 °C and 50 % RH.

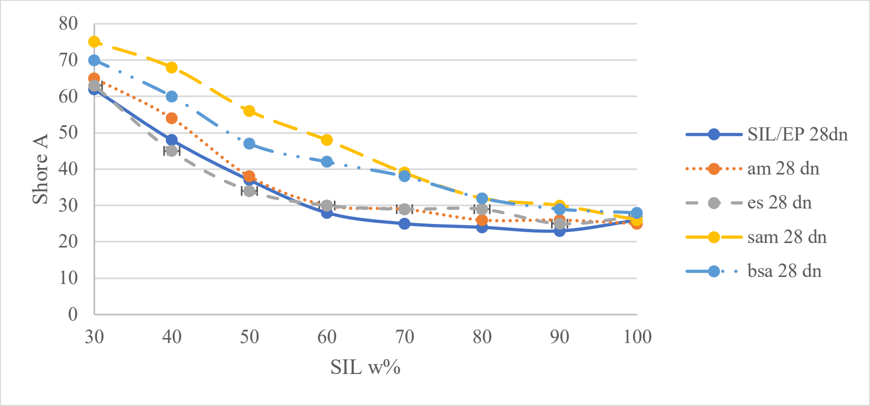


Fig. 3.2.1.3. Hardness of the two-component SIL/EP systems with compatibilizers *es*, *am*, *sam* and *bsa* after 28 days of curing at 23 °C and 50 % RH.

3.2.2. Rheological properties of the two-component SIL/EP model systems with compatibilizers

Rheological testing in oscillatory mode was made for two-component model systems with and without compatibilizers. Fig. 3.2.2.1 shows that, when the compatibilizers are added to the system, viscosity decreases in time (SIL/EP ratio 50/50), denoting to the fact that in the presence of the chosen compatibilizers development of 3D network within the systems occurs slower, i.e., extra time is required for development of chemical bonds between SIL and EP pre-polymers in addition to the development of SIL-SIL and EP-EP networks.

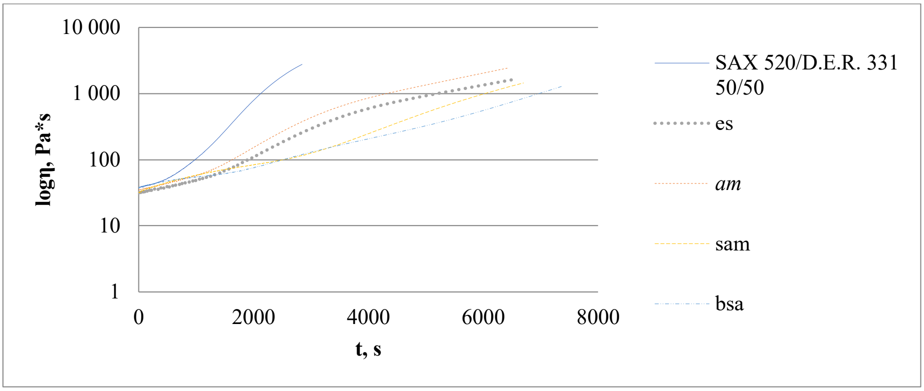


Fig. 3.2.2.1. Viscosity-time relationships of the two-component SIL/EP 50/50 system with compatibilizers *es*, *am*, *sam* and *bsa*.

As revealed in previous chapter, in respect of mechanical properties greater efficiency was demonstrated by two of the investigated compatibilizers (*bsa* and *sam*). Results of rheological measurements show that both of these two systems demonstrate cross-over modulus practically in the same time despite of SIL and EP ratio (as shown in Fig. 3.2.2.2 for the case of *sam* containing system). This effect denotes to the development of joint 3D network within the system including the elements of the both pre-polymers. In contradiction, in the case of unmodified systems as well as *am* and *es* compatibilized systems, the cross-over modulus changes over SIL/EP ratio depending of the contributions of the development speeds of SIL and EP pre-polymer networks. This could be explained by the different effect of the *es* and *am* functional groups on the epoxy resin, resulting in a different formation of the polymer network compared to the monofunctional amino silane.

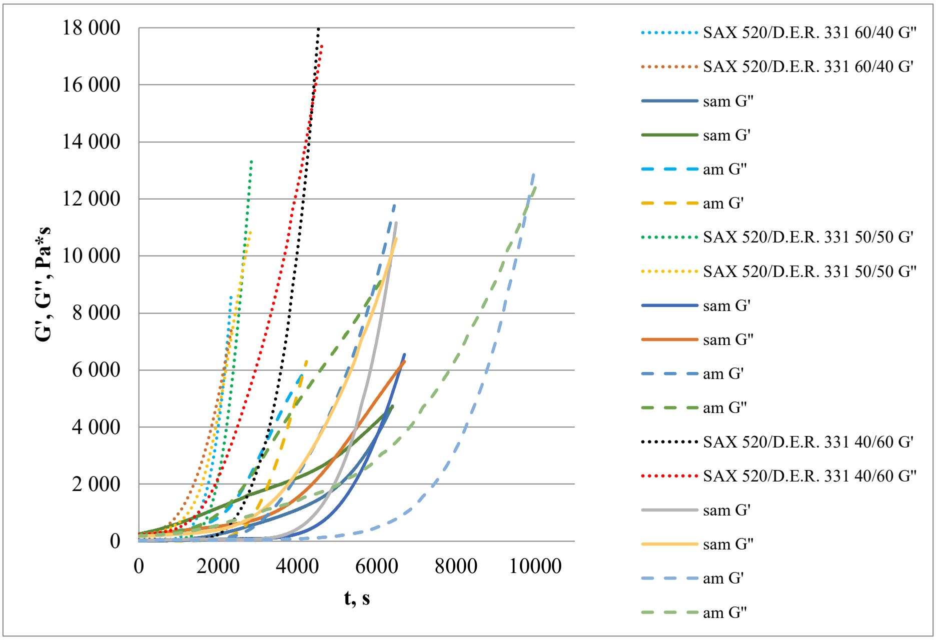


Fig. 3.2.2.2. Time relationships of viscous modulus (G”) and elastic modulus (G’) of the two-component SIL/EP systems with compatibilizers *es*, *am*, *sam,* and *bsa.*

3.3. Mechanical and rheological properties of the two-component SIL/EP model systems with self-synthesized SIL pre-polymers

3.3.1. Mechanical properties of the two-component SIL/EP systems with self-synthesized SIL pre-polymers

During the Thesis research, several SIL pre-polymers were synthesized, which were further integrated into two-component SIL/EP model and completed systems using the previously described methodology. In Table 3.3.1.1, formulations of the used recipes are displayed.

Table 3.3.1.1

Recipes of the two-component SIL/EP model systems

	weight (g)							
	100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70
SIL	100	90	80	70	60	50	40	30
D.E.R. 331	0	10	20	30	40	50	60	70
Tibcat 216	0.2	0.18	0.16	0.14	0.12	0.1	0.08	0.06
Niax C41	0	0.2	0.4	0.6	0.8	0.1	1.2	1.4
sam	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Water	0.67	0.6	0.53	0.46	0.39	0.32	0.25	0.18

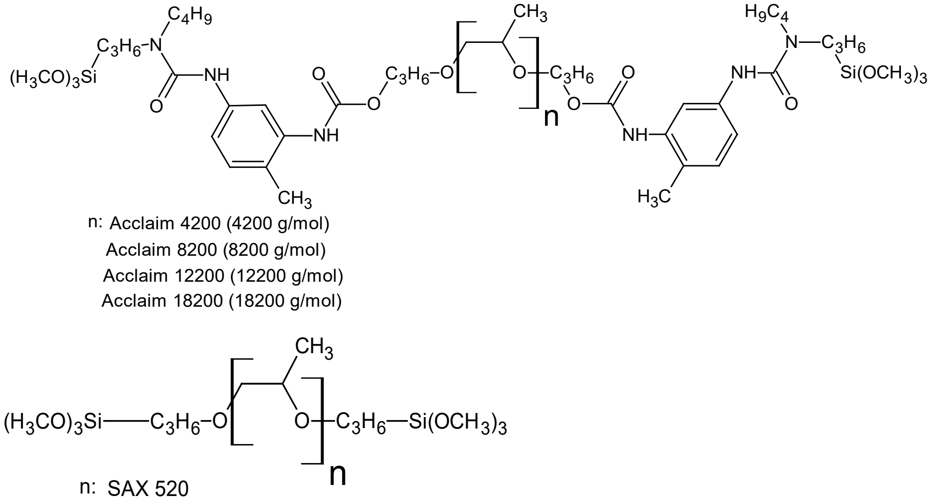


Fig. 3.3.1.1. Chemical structures of self-synthesized pre-polymers Acclaim 4200, Acclaim 8200, Acclaim 12200, Acclaim 18200, and commercially available *SAX 520.*

During the Thesis research, several commercially available polyol grades with different molecular weights in the range of 4200–18200 g/mol were used. These polyols were used for synthesis of SIL pre-polymers. Synthesis mechanism is shown in Fig. 3.3.1.2.

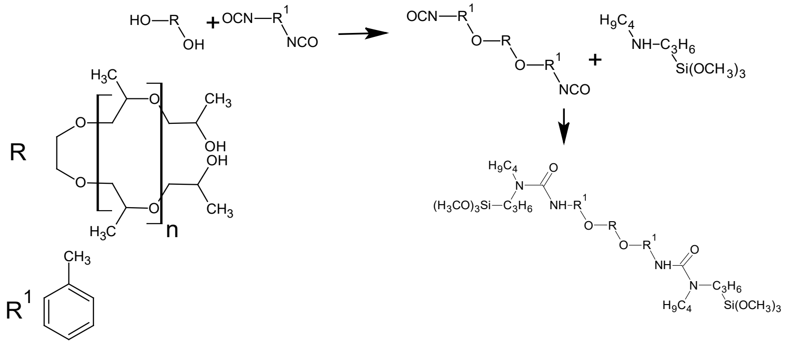


Fig. 3.3.1.2. Synthesis mechanism of SIL pre-polymer.

Two-component SIL/EP system with commercially available SAX 520 and D.E.R. 331 pre-polymers showed high tensile strength of 6.15 MPa (maximum) at high deformation value 261 %. By replacing SAX 520 with a number of self-synthesized SIL pre-polymers, namely Acclaim 4200, Acclaim 8200, and Acclaim 12200, tensile strength of the system was increased even more, i.e., 1.26, 1.5, and 1.05 times, respectively, in comparison to the standard system, whereas the corresponding deformation at break values decreased 17.4, 21.8, and 11.9 times (Fig. 3.3.1.3). Considerable decrement of ultimate deformation values can be explained by the following:

- self-synthesized SIL pre-polymers contain rigid TDI molecules, which decreases molecular mobility, resulting in loss of deformation;
- molecular weights of self-synthesized SIL pre-polymers are smaller in comparison to *SAX 520*, but the number of crosslinking groups is not changed, resulting in decrease of deformations.

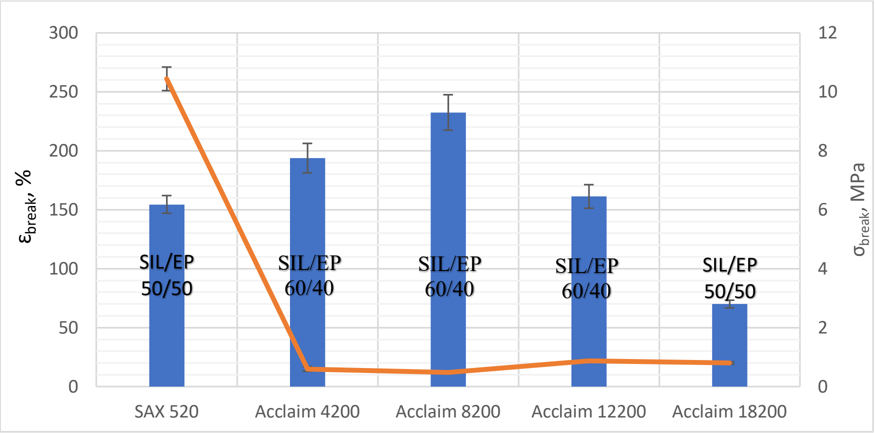


Fig. 3.3.1.3. Tensile strength (bars) and ultimate deformation (trendline) values of the two-component SIL/EP model systems at maximum tensile strength value after 28 days of curing at 23 °C and 50 % RH.

The data show that the most effective in the group of self-synthesized pre-polymers was Acclaim 8200, which allowed to ensure the highest tensile strength values. The system with Acclaim 18200 showed relatively low values comparing to the other tested systems, which can be explained by low compatibility of Acclaim 18200 with D.E.R. 331.

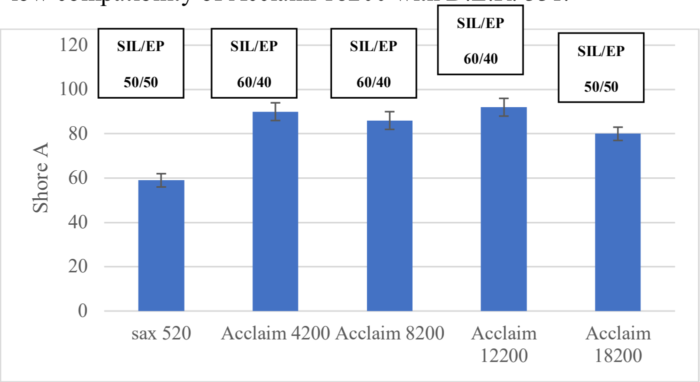


Fig. 3.3.1.4. Hardness of the two-component SIL/EP systems after 28 days of curing at 23 °C and 50 % RH.

The systems with self-synthesized SIL pre-polymers showed higher hardness (Fig. 3.3.1.4), which can be explained because of integrated aromatic ring (rigid element) within the structure of self-synthesized pre-polymers.

3.3.2. Rheological properties of the self-synthesized pre-polymers and it model systems

To understand better influence of self-synthesized SIL pre-polymers on the rheological behaviour of two-component SIL/EP systems, viscosity of individual SIL pre-polymers was initially determined (Fig. 3.3.2.1).

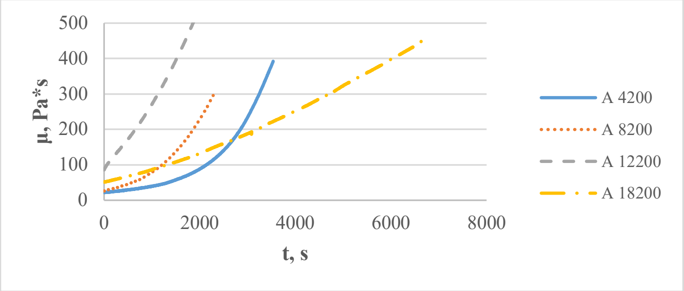


Fig. 3.3.2.1. Viscosity changes in time of the self-synthesized SIL pre-polymers.

Viscosity changes in time show that by increasing molecular weight of the pre-polymer from 4200 g/mol to 12200 g/mol, viscosity increases faster. The exception from this relationship is related to Acclaim 18200, because of its poor compatibility with D.E.R. 331.

By considering that highest tensile strength values for the investigated systems are observed at close-to-equal SIL/EP ratio 40/60–60/40, rheological properties of the self-synthesized SIL pre-polymer containing systems are compared for the SIL/EP 50/50 system (Fig. 3.3.2.2).

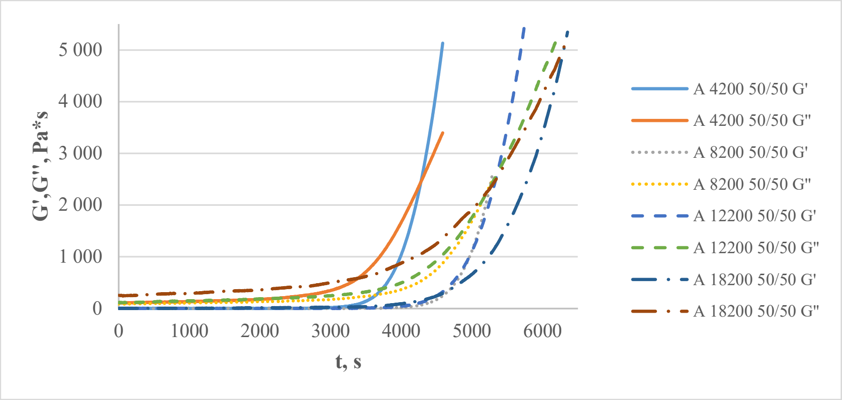


Fig. 3.3.2.2. Elastic and viscous modules in time of the two-component SIL/EP systems with the self-synthesized SIL pre-polymers.

Results of oscillatory shear tests testify that the lowest value of gelling time (the lowest value of cross-over modulus observed at 4235 s) is observed for the system with Acclaim 4200 because of its smallest molecular weight; consequently, if combined with rigid EP phase, faster development of 3D molecular network occurs in comparison to other Acclaim pre-polymers. In general, if molecular weight of the synthesized Acclaim pre-polymers is increased, it will decrease cross-linking density and the system will become more flexible, however it will not be always the case, because of a compatibility with epoxy resin molecule.

3.3.3. Mechanical properties of the two-component SIL/EP systems with containing self-synthesized pre-polymer with reduced functionality

As it was mentioned in previous chapters, substitution of *SAX520* by self-synthesised Acclaim pre-polymers resulted in higher tensile strength values but significantly decreased ultimate deformation values. To improve flexibility of the resulting system, the number of functional groups of Acclaim 4200 pre-polymer was reduced by 1/3 by blocking with n-butanol or benzyl alcohol, as depicted in Fig. 3.3.3.1.

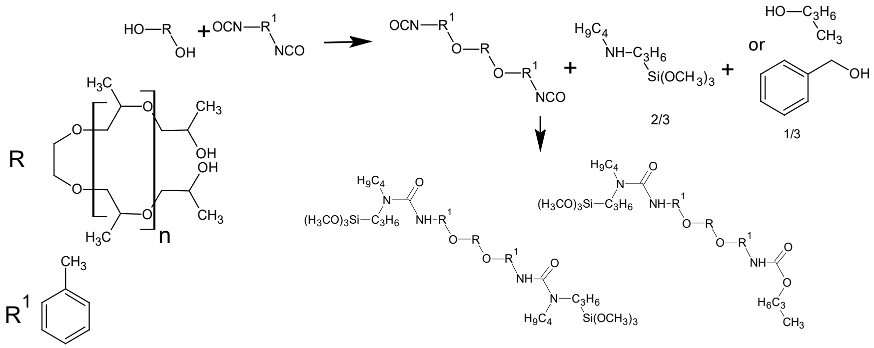


Fig. 3.3.3.1. SIL pre-polymer synthesis with reduced 1/3 functionality.

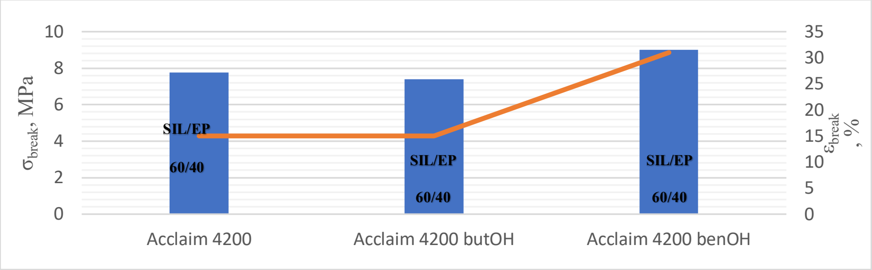


Fig. 3.3.3.2. Tensile strength (bars) and ultimate deformation (trendline) of the two-component SIL/EP model systems at their maximum tensile strength value after 28 days of storage at 23 °C and 50 % RH.

Depicted data show that blocking 1/3 of functional groups of pre-polymer Acclaim 4200 with n-butanol practically does not influence mechanical properties of the system, whereas if the pre-polymer is blocked with benzyl alcohol, tensile strength and ultimate deformation values both are increased. This can be explained because of benzyl alcohol aromatic group affecting the spherical position of the molecule and orienting the polymer network.

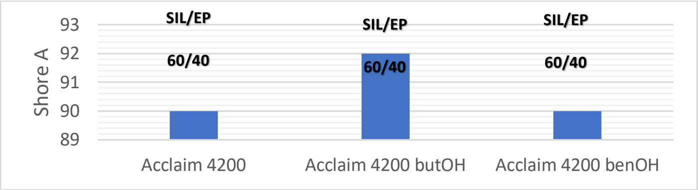


Fig. 3.3.3.3. Hardness of the two-component SIL/EP systems with blocked functional groups after 28 days of storage at 23 °C and 50 % RH.

By decreasing functionality of SIL pre-polymers, materials hardness practically does not change, indirectly indicating that crosslinking density has not changed.

3.4. Mechanical, rheological, and adhesive properties of the two-component SIL/EP completed systems

In addition to the model systems, more realistic, completed two-component SIL/EP systems also were developed within the framework of the PhD Thesis. These systems, apart from the pre-polymers, catalysts, and compatibilizers, contained also plasticizers, fillers and moisture sorption agents and silanes, which act as adhesion promoters, compatibilizers, and drying agents, all ingredients traditionally used in commercial adhesives/sealants compositions (Table 3.3.4.1).

Table 3.3.4.1

Recipes of the two-component SIL/EP completed systems

Trade name	Manufacturer	Chemical structure	Function	SIL/EP ratio (wt %)							
Component A				100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70
SAX 520	Kaneka Belgium NV	Silyl-terminated polymer	Polymer	40	36	32	28	24	20	16	12
Hexamoll Dinch	BASF	1,2-Cyclohexane dicarboxylic acid	Non-phtalate plasticizer	15	13.50	12	10.50	9	7.50	6	4.50
Dynsylan 1189	Evonik Industries AG	N-(n-Butyl)-3-amino propyltrimethoxysilane	Compatibi-lizer/adhesion promoter	1	1	1	1	1	1	1	1
Omycarb 1T	Omya AG	Ground $CaCO_3$	Filler	17.13	15	13.8	12	10.30	8.60	6.80	5.00
Hakuenka CCR-S10	Omya AG	Precipitated $CaCO_3$ coated with fatty acids	Filler	25	22.5	20	17.5	15	12.5	10	7.5
Dynasilan VTMO	Evonik Industries AG	Vinyltrimethoxysilane	Drying agent	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3
Lupragen N600	BASF	N,N',N”-tris-(dimethylaminopropyl) hexahydrotriazine	Catalyst	0	0.62	1.33	2	2.66	3.33	4	4.6

Table 3.3.4.1. continued

Component B											
D.E.R. 331	The Dow Chemical Company	Epoxy resin	Polymer	0	4	8	12	16	20	24	28
Hexamoll Dinch	BASF	1,2-Cyclohexane dicarboxylic acid	Non-phtalate plasticizer	0	1.5	3	4.5	6	7.5	9	10.5
Omycarb 1T	Omya AG	Ground $CaCO_3$	Filler	0	1.7	2.38	3.69	4.92	6.14	7.45	8.76
Hakuenka CCR-S10	Omya AG	Precipitated $CaCO_3$ coated with fatty acids	Filler	0	2.5	5	7.5	10	12.5	15	17.5
Tibcat 216	TIB Chemicals AG	Dioctyltin dilaurate (DOTL)	Catalyst	0.2	0.18	0.16	0.14	0.12	0.1	0.08	0.06
Water	-	Water	Catalyst	0.67	0.6	0.53	0.46	0.39	0.32	0.25	0.18

3.4.1. Moisture control in the two-component SIL/EP completed systems

Two-component completed systems, investigated within the framework of PhD Thesis, apart from pre-polymers, catalysts and compatibilizers, contained fillers (2 types of $CaCO_3$), plasticizers and water absorption agents. By considering that water can initiate self-catalysis of SIL pre-polymer, special attention was paid to the control of the amount of water within the investigated sealants/adhesives formulations. Several water absorption approaches were analyzed, including physical drying approach (drying at increased temperature and with vacuuming) and chemical approaches (either addition of a component acting as molecular sieve, or addition of a component capable to absorb water chemically, such as monofunctional isocyanate or silane). In respect to aggregative state, water absorbing agents were used in solid form (3 angstrom molecular sieve in the amount of 5 % in respect to total composition weight), or liquid form (in the amount of 1wt.% in respect to total composition). Concentrations of the used water absorption agents were chosen based on recommendations of the raw material suppliers.

The effectiveness of the said water control approaches was evaluated by measuring viscosity of SIL at 4 different rotation speeds (0.2, 0.5, 1.0 and 10 s^{-1}) immediately after preparation of the SIL component containing typical ingredients for the completed system and after thermal aging for 7 and 28 days at 50 °C. The lowest speed indicates material's viscosity practically at stationary position, but the higher speeds characterize material's pumping and transporting abilities. It is industrially accepted that such thermal ageing protocol allows prediction of viscosity change of the material after 6 month and 2 years storage at room temperature, respectively.

Table 3.4.1.1

Viscosity change of SIL component before and after thermal aging

Water adsorption process	Viscosity of SIL immediately after preparation (Pa×s)				Viscosity of SIL after 7 days of thermal aging (Pa×s)				Viscosity of SIL after 28 days of thermal aging (Pa×s)			
	0.2 s^{-1}	0.5 s^{-1}	1 s^{-1}	10 s^{-1}	0.2 s^{-1}	0.5 s^{-1}	1 s^{-1}	10 s^{-1}	0.2 s^{-1}	0.5 s^{-1}	1 s^{-1}	10 s^{-1}
24h mixing + vacuuming at 50 °C	230	110	71	31	529	253	170	59	1036	454	291	77
Addition of 5 % molecular sieve	225	108	75	30	540	327	360	76	952	403	265	98
Addition of 1 % monofunctional isocyanate	198	113	78	40	160	95	80	54	273	211	176	97
Addition of 1% silane mix	180	105	70	72	154	104	85	50	135	101	85	58

Data on viscosity change after aging shows that the most effective drying method was using 1 % silane mix (Dynasylan VTMO 80 %, Dynasylan AMMO 20 %). The most ineffective method was moisture control by using molecular sieves – viscosity after 28 days of aging increased by 226 %. When monofunctional isocyanate was used, viscosity changes were relatively small after 7 days of aging, but after 28 days, viscosity increment was already 142 %. Using silane mix after 28 days of aging, viscosity increment was only 38 %, this can be explained by the fact that silanes not only dry material but also stabilize it due to the same functional groups (methoxy silanol) as SIL pre-polymer. Based on the results in further studies, silane mix was used to dry the component with SIL pre-polymer.

3.4.2. Mechanical properties of two-component SIL/EP full system compared with model system

Integrating into the system fillers, plasticizers and other additives significantly changed the material's properties. Figures 3.4.2.1 and 3.4.2.2 show concentration relationships of tensile strength and ultimate elongation of completed and model systems.

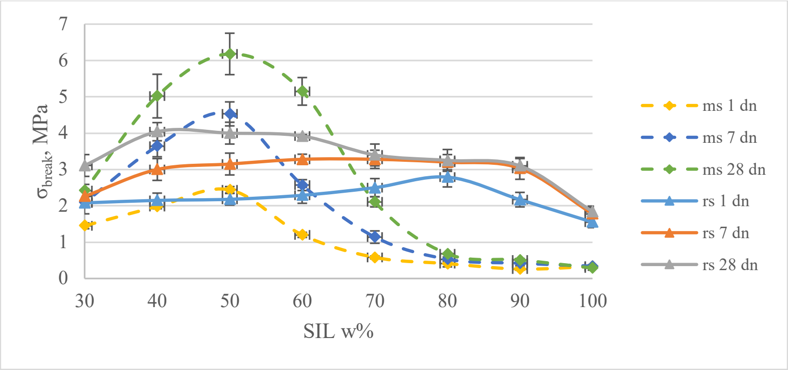


Fig. 3.4.2.1. Tensile strength of the two-component SIL/EP full and completed systems after 28 days of storage at 23 ºC and 50 % RH.

In the model systems at low EP concentrations, tensile strength values are low because linear SIL pre-polymer does not have a necessary number of rigid elements to build structured polymer network with high tensile strength. When concentration of rigid element (EP pre-polymer) is increased, tensile strength increases, reaching maximum values at SIL/EP range 60/40 to 40/60. In complete systems, fillers act as rigid elements structuring the material already at low EP concentrations. Because of that even after 1 day of curing the system with only SIL pre-polymer demonstrates at least 5 times higher tensile strength values (1.55 MPa) in comparison to the model system (0.3 MPa) after 28 days of curing at 23 ºC and 50 % RH. Considering that there is no considerable change in tensile strength values of the completed systems along the whole SIL/EP concentration range, it may be concluded that the additive package plays an important role by ensuring tensile strength of the adhesive. However, by increasing the concentration of rigid elements (EP) as well as cross-linking sites, within the SIL/EP concentration range 60/40–40/60 tensile strength values of the model systems exceed those of the respective complete systems. This effect appears because additives limit development of polymer network.

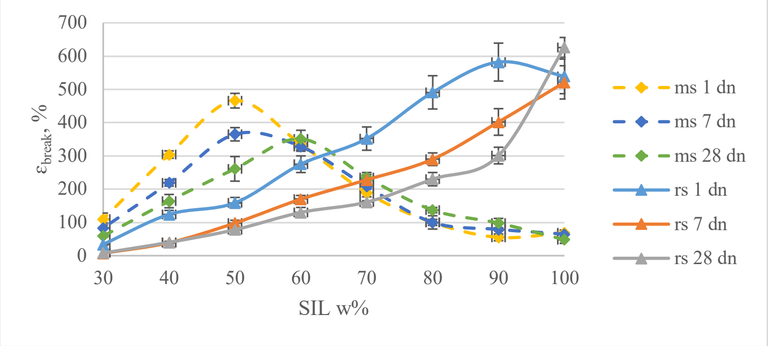


Fig. 3.4.2.2. Tensile deformation of two-component SIL/EP complete and model systems.

The additive package influence on the systems' ultimate tensile deformation values (Fig. 3.4.2.2.) confirms the previous statement that the fillers act as rigid elements in the completed system. At lower EP concentration range the system is structured mainly by the additive package, as a result, complete systems demonstrate higher ultimate elongation values in comparison to the respective model systems. However, increased amount of rigid structural elements (increased concentration of EP groups as well as cross-links) in the system further limits its deformability. At SIL/EP concentration range 40/60 to 60/40 ultimate deformation values of the model systems are higher in comparison to the complete systems, which contain rigid fillers.

3.4.3. Adhesion properties of the two component SIL/EP full systems

Table 3.4.3.1 demonstrates the two-component SIL/EP systems' adhesion properties in shear test on different substrates (tested at 3 different mixing ratios of SIL/EP: 100/0, 80/20, and 50/50).

Table 3.4.3.1

Lap shear test results of two-component SIL/EP systems after 28 days of curing

Substrate	Parameter	SIL/EP		
		100/0	80/20	50/50
PVC	σ_{break} [MPa]	0.09	0.21	0.25
	ε_{break} [%]	13	9	8
	Fracture failure	A100	C20A80	C30A70
Stainless steel	σ_{break} [MPa]	1.42	5.5	6.2
	ε_{break} [%]	124	14	10
	Fracture failure	C100	C100	C100
Wood (ash)	σ_{break} [MPa]	1.6	4.3	4.7
	ε_{break} [%]	210	30	15
	Fracture failure	C100	C100	C100

All analyzed two-component SIL/EP systems show good adhesion against stainless steel and wood substrates, but poor – against PVC. Adhesion strength correlates with tensile test results, i.e., by increasing EP content, shear strength increases and deformation decreases.

3.4.4. Rheological properties of the two-component SIL/EP full systems

Rheological properties of the two-component full systems were tested in SIL/EP range from 100/0 to 30/70.

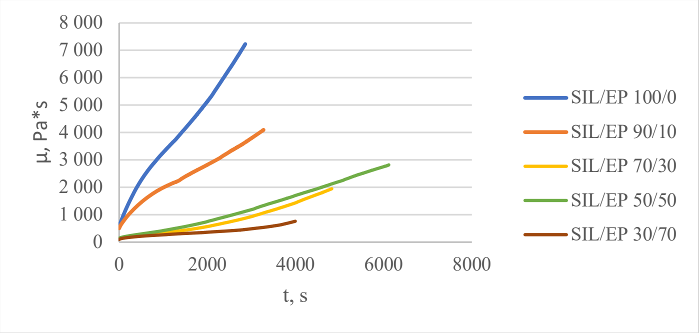


Fig. 3.4.4.1. Viscosity change during curing of two-component full systems in the SIL/EP range from 100/0 to 30/70.

Viscosity-time relationships in Fig. 3.4.4.1 show that materials' viscosity increases during curing time and curing speed increases by increasing SIL component concentration. In SIL/EP range 70/30–30/70, curing speed levels off indicating that the curing speed of EP component is lower comparing to that of SIL component. SIL pre-polymer has higher number of functional groups and, when in the system there are two pre-polymers, they cure via compatibilizer and it takes longer time to form polymer network.

3.4.5. Aging properties of the two-component SIL/EP full systems

Two-component SIL/EP systems (SIL/EP range from 100/0 to 30/70) were aged for 504 hours in an accelerated weathering test chamber. The tested compositions did not contain any UV stabilizers or hindered amines, allowing to evaluate UV and moisture stability of the polymer composition itself.

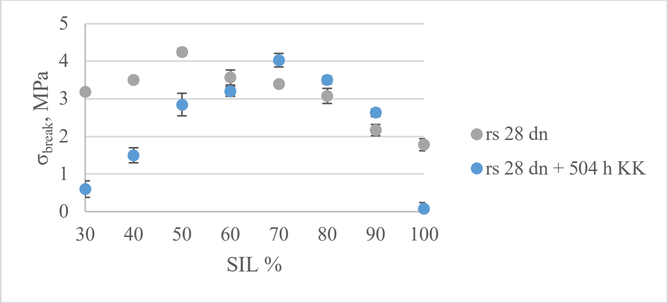


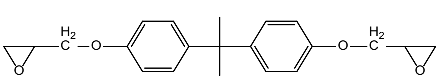
Fig. 3.4.5.1. Tensile strength of two-component SIL/EP full system before (rs 28 dn) and after aging (rs 28dn + 504h KK).

In Fig. 3.4.5.1, it is shown that at certain SIL/EP ratios, the tested material demonstrates considerable stability to aging. In SIL/EP range from 90/10 to 60/40, ultimate tensile strength changes of the material were less than 16 % by maintaining considerable ultimate deformation values (above 100 %). The results indicate that EP pre-polymer works not only as a rigid element of the system, but also as UV stabilizer. However, by increasing EP component's content above SIL/EP ratio 60/40, the material becomes brittle, because under test conditions (increased temperature and UV light) post-curing is promoted and the number of cross-links is increased. Tensile strength of the aged 100 % SIL pre-polymer is decreased by 2125 %, indicating poor UV stability of the neat SIL pre-polymer.

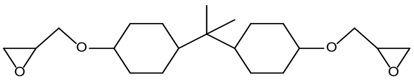
3.5. Mechanical, rheological and adhesion properties of the two-component SIL/EP full systems, using different types of EP pre-polymers

3.5.1. Mechanical properties of the two-component SIL/EP full systems, using different types of EP pre-polymers

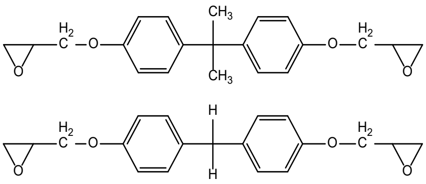
In previous chapters main attention was paid to SIL pre-polymers; however SIL/EP system contains two pre-polymers which influence final adhesive properties. In the following research, we used *SAX 520* as the constant element in the two-component system because it gave the highest deformation values.



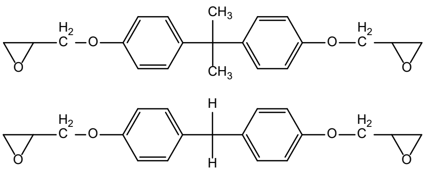
D.E.R. 331



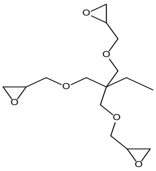
Eponex 1510



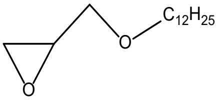
D.E.R. 3412



D.E.R. 351



D.E.R. 749



D.E.R. 721

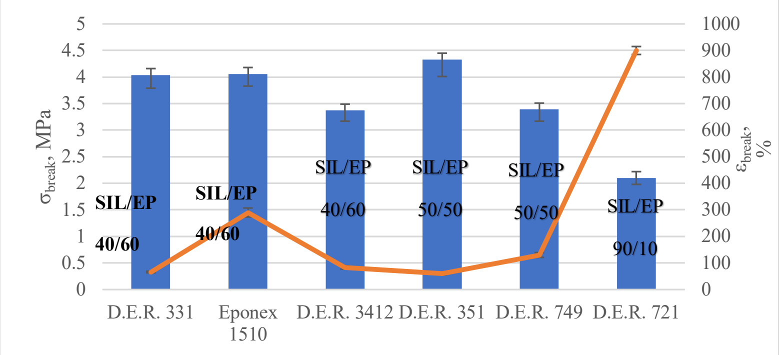


Fig. 3.5.1.1. Tensile strength and deformation of SIL/EP compositions after 28 days curing at 23 ºC and 50 % RH (blue histogram – tensile strength; orange curve – tensile deformation).

One of the goals of the Doctoral Thesis was to replace bisphenol-A containing pre-polymer D.E.R. 331 with environmentally more suitable alternative. Assessment of the epoxide mechanical properties showed that 4 of 5 alternatives potentially can replace D.E.R. 331. D.E.R. 721 showed significantly lower tensile strength values at increased tensile deformation values. This effect may be explained because of D.E.R. 721 mono-functionality. The functional group decreases SIL pre-polymer functionality, consequently, by increasing the EP pre-polymer concentration, tensile deformation values increases.

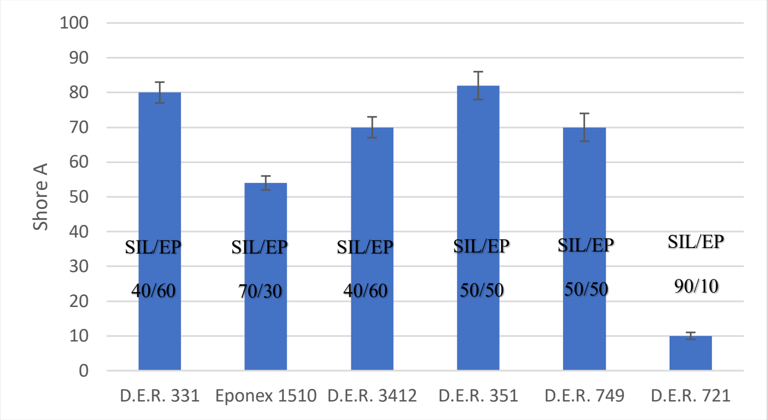


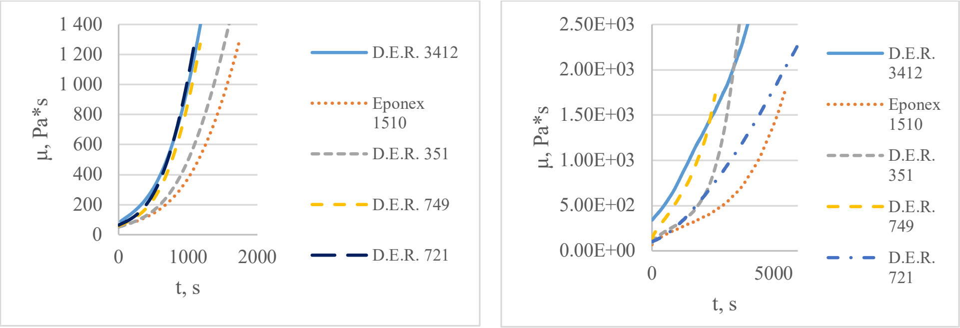
Fig. 3.5.1.2. Hardness of two-component SIL/EP full systems after 28 days of curing at 23 ºC and 50 % RH.

Analogous to tensile strength 4 of 5 EP pre-polymers (D.E.R. 3412, D.E.R. 351, D.E.R. 749) in combination with *SAX520* at certain SIL/EP ratios showed similar hardness values to the system with D.E.R. 331 pre-polymer. One of the systems (D.E.R. 721) showed significantly lower Shore A values indicating that the material has fewer crosslinks.

Analyzing mechanical properties of the alternative EP pre-polymers containing systems, the best substitute of D.E.R. 331 is D.E.R. 351, however pre-polymers Eponex 1510, D.E.R. 3412 and D.E.R. 749 also could be considered for replacement of D.E.R. 331.

3.5.2. Rheological properties of the two component SIL/EP full system, using different types of EP prepolymers

Viscosity changes of the full systems were tested at two SIL/EP ratios 80/20 and 50/50, because at these two concentrations material mechanical properties changed more significantly depending on EP pre-polymer concentration.



a) b)

Fig. 3.5.2.1. Viscosity changes of various two-component compositions at SIL/EP ratio a) 80/20 and b) 50/50 b).

The results at SIL/EP ratio 80/20 show that two of EP pre-polymers (D.E.R. 351 and Eponex 1510) influence viscosity of the system more than other pre-polymers. By increasing EP pre-polymer concentration, curing speed of the system decreases, indicating that EP pre-polymers curing speed is slower. Viscosity of the system with D.E.R. 749 increases at the fastest rate because of its higher functionality (3) comparing to other EP pre-polymers. However, alkyl group-based EP pre-polymers, Eponex 1510 (cyclo hexane) and D.E.R. 721 showed even lower curing speeds.

3.5.3. Adhesion properties of the two-component SIL/EP full system, using different types of EP pre-polymers

To analyze two-component SIL/EP full systems' adhesion properties, 3 different substrates were used: polyvinyl chloride (PVC), stainless steel and wood (ash). Based on the previously obtained mechanical properties, SIL/EP ratio 80/20 was chosen to evaluate adhesion properties of two-component SIL/EP full systems. Tests were performed using the lap shear test.

Table 3.5.3.1

Lap shear test results of the two-component SIL/EP full systems at ratio 80/20 after 28 days of curing

		Epoxide type					
Substrate	Parameter	D.E.R. 331	D.E.R. 3412	D.E.R. 351	D.E.R. 749	D.E.R. 721	Eponex 1510
PVC	σ_{break}, MPa	0.21	0.36	0.58	3.51	0.5	0.38
	ε_{break}, %	9	8.66	11.50	42	32	4.69
	Fracture failure	C10A90	C15A95	C25A75	C100	C20A80	C20A80
Stainless steel	σ_{break}, MPa	5.5	4.37	5.85	4.34	0.47	5.81
	ε_{break}, %	14.5	41.43	17.50	27.1	30	36
	Fracture failure	C100	C100	C100	C100	C10A90	C100
Wood (ash)	σ_{break}, MPa	4.3	3.98	5.20	3.52	0.49	4.62
	ε_{break}, %	30	30.50	21.08	30.8	30.2	26.3
	Fracture failure	C100	C100	C100	C100	C15A85	C100

Only one system (D.E.R. 749) formed adhesion to all the substrates, showing 100 % adhesion even to PVC. All other systems, except of the system with D.E.R. 721, also formed good adhesion to wood and stainless steel.

3.6. Mechanical and adhesion properties of the two-component SIL/EP full systems using self-synthesized SIL pre-polymers

3.6.1. Mechanical properties of the two-component SIL/EP full system using self-synthesized SIL pre-polymers

Previous results showed that when fillers are integrated into the system, the plasticizer's tensile strength decreases and deformation increases. This could be very beneficial for the model systems with self-synthesized pre-polymers, which demonstrated increased tensile strength (the highest one achieved during the investigations), but on the account of significantly decreased tensile deformation.

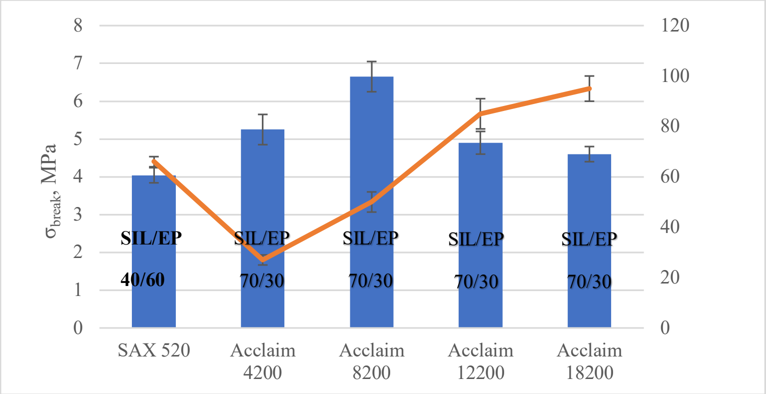


Fig. 3.6.1.1. Tensile strength and deformation of SIL/EP compositions after 28 days of curing at 23 ºC and 50 % RH (blue histogram – tensile strength, orange curve – tensile deformation).

Similar to the previously obtained results, when fillers and plasticizer are added, tensile deformation of the system increases at lower EP concentrations. Analyzing mechanical properties of self-synthesized pre-polymers, it is possible to conclude that by increasing their molecular weight, the tensile deformation value increases: Acclaim 4200 ($\varepsilon_{break} = 27$ %) < Acclaim 8200 ($\varepsilon_{break} = 50$ %) < Acclaim 12200 ($\varepsilon_{break} = 85$ %) < Acclaim 18200 ($\varepsilon_{break} = 95$ %). Tensile deformation and strength increment in comparison to SAX520 extends potential application areas of the material.

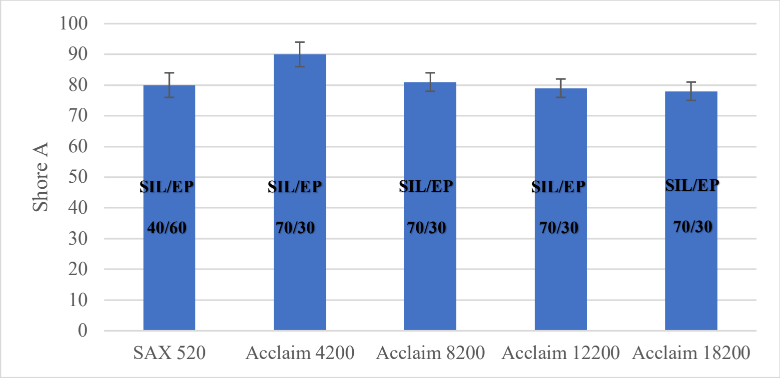


Fig. 3.6.1.2. Hardness of the two-component SIL/EP full systems after 28 days of curing at 23 °C and 50 % RH.

At tensile strength, maximum three of the four SIL/EP systems showed practically the same hardness values, comparable to *SAX520*/D.E.R.331. Only the system with Acclaim 4200 demonstrated higher hardness indicating to denser polymer network.

3.6.2. Adhesion properties of the two-component SIL/EP full systems using self-synthesized SIL prepolymers

Similar to previously used approach, three substrates – PVC, stainless steel, and wood (ash) – were used to evaluate adhesion properties of two-component SIL/EP full systems, obtained using self-synthesized SIL pre-polymers. The tests were performed at SIL/EP ratio 80/20.

Table 3.6.2.1

Two-component SIL80/EP20 full systems' lap shear tests using self-synthesized pre-polymers after 28 days of curing

		SIL prepolymer			
Substrate	Parameter	Acclaim 4200	Acclaim 8200	Acclaim 12200	Acclaim 18200
PVC	σ_{break}, MPa	0.23	0.43	0.9	0.63
	ε_{break}, %	1.94	4.8	12.1	6.1
	Fracture failure	C20A80	C20A80	C70A30	C60A40
Stainless steel	σ_{break}, MPa	4.83	5.98	3.92	2.23
	ε_{break}, %	8.19	14.37	17.5	12.95
	Fracture failure	C100	C100	C100	C90A10
Wood (ash)	σ_{break}, MPa	3.74	4.84	3.47	1.95
	ε_{break}, %	8.84	11.36	14.28	12.1
	Fracture failure	C100	C100	C100	C100

As shown in Table 3.6.2.1, all the investigated compositions formed good adhesion to stainless steel and wood, but relatively poor to PVC. Lower shear strength values showed the material with Acclaim 18200 pre-polymer, which can be explained with poorer systems compability with EP. By analyzing adhesive properties of the systems with Acclaim 4200, Acclaim 8200, and Acclaim *12200*, it may be concluded that the limiting factor is not the material's adhesion to wood and stainless steel substrates but tensile strength of the adhesive/sealant itself.

3.7. Mechanical and adhesion properties of the two-component SIL/EP full systems containing self-synthesized SIL pre-polymer obtained from biobased polyols

One of the goals of the PhD Thesis was to synthesize pre-polymers from renewable sources and integrate them into two-component SIL/EP system. In the course of this work, two different polyols – castor oil and farnesene Krasol – were chosen.

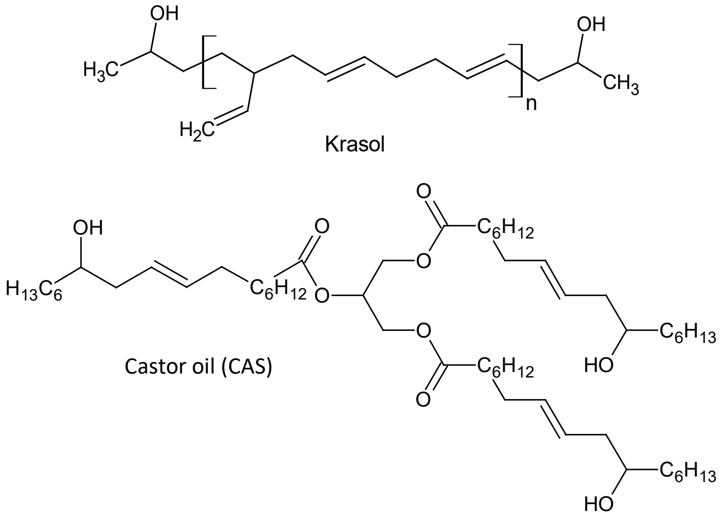


Fig. 3.7.1. Renewable polyols Krasol and castor oil.

As oil reserves decline increasingly, an important role is to search for new alternatives to replace fossil oil-based chemicals. Within the framework of the Tthesis two renewable compounds containing hydroxyl groups – Krasol and castor oil – were silylated. Krasol has been fully integrated into the SIL/EP system but the castor oil-based pre-polymer was integrated only partially because of its high initial viscosity (400 Pa*s) in comparison to viscosities of other pre-polymers (5–30 MPa*s). To analyze the influence of CAS pre-polymer addition on the materials properties, three different replacement degrees (1 %, 5 % and 10 %) from the SIL pre-polymer concentrations were evaluated.

3.7.1. Mechanical properties of the two-component SIL/EP full system containing self-synthesized SIL pre-polymers obtained from biobased polyols

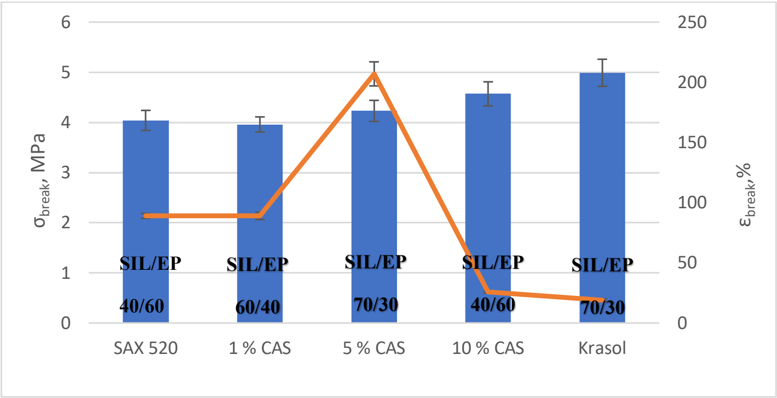


Fig. 3.7.1.1. Tensile strength and deformation of SIL/EP after 28 days of curing at 23 ºC and 50 % RH (blue histogram – tensile strength, orange curve – tensile deformation).

The results, depicted in Fig. 3.7.1.1, show that by partial replacement of *SAX 520* with CAS, it is possible to increase tensile strength at its maximum peak value. Unfortunately, the systems with 10 % of CAS, as well as Krasol pre-polymer, are characterized by increased tensile strength, but significantly reduced tensile deformation.

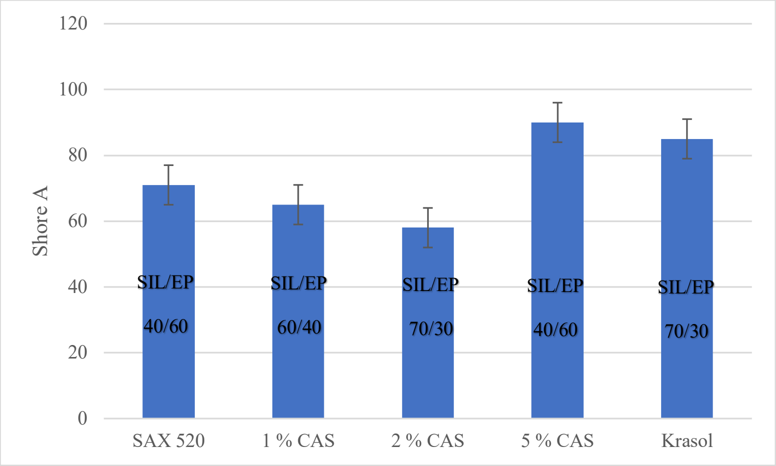


Fig. 3.7.1.2. Hardness of two component SIL/EP full systems after 28 days of curing at 23 ºC and 50 % RH.

The results depicted in Fig. 3.7.1.2, show that the Shore A hardness is predominantly influenced by SIL/EP ratio, i.e., by increasing EP concentration, hardness of the material increases. The system with Krasol gives very high material hardness (83) at SIL/EP ratio 70/30, indicating to the dense polymer network.

By analyzing the results of materials' mechanical properties, it is possible to conclude that the most effective system is the one with 5 % CAS pre-polymer, characterized by both high tensile strength and deformation values.

3.7.2. Adhesion properties of the two-component SIL/EP full system containing self-synthesized SIL pre-polymer obtained from biobased polyols

Similar to other adhesion experiments SIL/EP ratio 80/20 was chosen to characterize adhesion properties of two-component SIL/EP full system with self-synthesized SIL pre-polymer, obtained by using renewable compounds containing hydroxyl groups, to 3 different substrates – PVC, stainless steel, and wood (ash).

Table 3.7.2.1

Lap shear test results of two-component SIL/EP full systems after 28 days of curing using self-synthesized pre-polymers from renewable polyols

Substrate	Parameter	SIL/EP	1% CAS	5 % CAS	10 % CAS	Krasol F3000
PVC	σ_{break}, MPa	0.41	0.46	0.57	0.81	0.43
	ε_{break}, %	5.1	6.11	5.97	11.21	5.4
	Fracture failure	C10A90	C10A90	C30A70	C100	C20A80
Stainless steel	σ_{break}, MPa	4.95	5.02	6.26	5.46	4.6
	ε_{break}, %	26.08	24.53	22.39	16.92	14.3
	Fracture failure	C100	C100	C100	C100	C100
Wood (ash)	σ_{break}, MPa	4.12	4.58	4.48	5.47	4.32
	ε_{break}, %	27.53	26.19	30.5	21.83	15.4
	Fracture failure	C100	C100	C100	C100	C100

The results in Table 3.7.2.1 show that significant adhesion improvement to PVC substrate can be achieved at CAS pre-polymer content of 5 %. Similar results were observed for the system with EP pre-polymer D.E.R. 749, because this pre-polymer has similar backbone as CAS. Material with Krasol F3000 did not improve significantly adhesion to PVC comparing to standard material. Similiarly to PVC, adhesion to wood is increased by increasing CAS content (the structure is polar and mobile enough to reach the surface of the substrate). Comparing to the standard recipe, adhesion to stainless steel substrates is also improved if CAS pre-polymer is added up to 5 %. At higher CAS concentration, adhesion is decreased because of increased crosslink density of the system.

3.8. Production of the two-component SIL/EP full system at industrial scale

With the support of SIA Tenachem industrial scale production of one of the industrially most viable two-component SIL/EP systems was realized. Although full spectrum of the determined properties of the material will not be shown due to confidentiality issues, the company agreed to share part of the data to demonstrate practical importance of the investigations.

3.8.1. Recipe and rheological properties of the two-component SIL/EP full system

Recipe of the developed industrially viable SIL/EP system is given in Table 3.8.1.1. Technology of manufacturing components A and B is described in the methodological part of the PhD Thesis. It is recommended to keep the following mixing ratio between the A and B components:

- 100 : 11.1 by volume (A : B);
- 100 : 10.48 by mass (A : B).

Table 3.8.1.1

Recipe of the two-component SIL/EP full system (components A and B).

SIL component
($\rho_{SIL} = 1.76$ g/cm^3)

Polymer	w%
SAX 260	16
Plasticizer	
Hexamol DINCH	9.5
Fillers	
Microdol 5	46.9
Hydrocarb 95T	25
Drying agents	
Dynasylan VTMO	0.6
Dynasylan 1189	1
Catalyst	
Niax C41	1

EP component
($\rho_{EP} = 1.66$ g/cm^3)

Polymer	w%
Eponex 1510	36
Plasticizers	
Hexamol DINCH	3
Benzyl alcohol	4
Fillers	
Omycarb 1T	52.55
Hakuenka CCR-S10	3.5
Catalysts	
Tibcat 216	0.65
Water	0.3

In Fig. 3.8.1.1 the recommended packing of the developed SIL/EP system is demonstrated, which ensures that components A and B are stored in individual cartridges equipped with extruder type mixer.

Fig. 3.8.1.1. Recommended packing of two-component SIL/EP composition.

Material's storage stability was tested by storing the material at elevated temperatures (70 ºC) for 7 and 28 days. Industrially it is accepted that storage at such conditions corresponds to 6 months and 2 years of storage at normal temperatures, respectively. Storage stability was evaluated by performing rheological measurements at 4 different shear speeds, of which the lowest one corresponds to practically stationary material, whereas the highest one – to the adhesive flow during extrusion.

Table 3.8.1.2

Viscosity change of the two-component SIL/EP full system over thermal ageing

	Unaged	After storage for 7 days at 70 °C	After storage for 28 days at 70 °C
A component			
0.2 s^{-1}, Pa*s	1551	1520	1490
0.5 s^{-1}, Pa*s	827	835	846
1 s^{-1}, Pa*s	515	523	537
10 s^{-1}, Pa*s	136	142	158
B component			
0.2 s^{-1}, Pa*s	569	573	550
0.5 s^{-1}, Pa*s	281	282	292
1 s^{-1}, Pa*s	173	172	189
10 s^{-1}, Pa*s	50	49	73

The results show that before ageing component A has a 3 times higher viscosity than component B. After aging for 7 days at elevated temperatures, viscosity of components A and B practically has not changed, indicating good storage stability of the material at least for 6 months. After aging for 28 days, viscosity at 0.2 s^{-1} speed practically did not change, whereas it increased at 10 s^{-1} speed, indicating that material undergoes dimerization, trimerisation, and formation of other higher molecular compounds. Pre-polymer viscosity at shear speed of 10 s^{-1} changes by 16 % (component A) and 46 % (component B) after 28 days, which is satisfactorily for this type of material and practically does not limit processability of materials using an extruder type mixer, which is integrated in the package. Viscosity of the systems should have been increased 5 times until processability is limited by the extruder mixer type.

3.8.2. Mechanical properties of the two-component SIL/EP full system

Change of mechanical properties of the two-component SIL/EP full system over thermal ageing is shown in Table 3.8.2.1.

Table 3.8.2.1

Change of mechanical properties of the two-component SIL/EP full system over thermal ageing

	Unaged	After storage for 7 days at 70 °C	After storage for 28 days at 70 °C
24 h			
σ_{break}, MPa	1.78	1.72	1.68
ε_{break}, %	526	480	470
Shore A	54	55	54
7 days			
σ_{break}, MPa	3.10	2.88	2.71
ε_{break}, %	128	115	105
Shore A	55	56	56
28 days			
σ_{break}, MPa	3.92	3.8	3.64
ε_{break}, %	95	91	82
Shore A	57	58	57

It has been determined that the material already after 24 hours of storage shows enough high tensile strength and deformation values at break. After 7 and 28 days of curing at 23 ºC and 50 % RH, tensile strength of the material increased and deformation values decreased. Tensile strength increment was 174 % and 220 %, respectively, while relatively high deformation values were maintained relatively high (95 %). When material was aged, its mechanical properties decreased due to branching and molecular weight increment of the pre-polymers, which decreases pot life and reduces capabilities of the effective development of 3D structure. However, decrement of the material's mechanical properties in tension (unaged material vs aged for 28 days at 70 ºC) is not large – 7 % (σ_{break}) and 13 % (ε_{break}), from which one may conclude that it is possible to use the material also after 2 years storage.

3.8.3. Adhesion properties of the two-component SIL/EP full system

The results of peel test of the two-component SIL/EP full system over thermal ageing is shown in Table 3.8.3.1.

Table 3.8.3.1

Peel test of the two-component SIL/EP full system

	Unaged	After storage for 7 days at 70 °C	After storage for 28 days at 70 °C
Concrete	C100	C100	C100
Zinc	C100	C100	C100
Stainless steel	C100	C90A10	C80A20
Anodized aluminium	C100	C90A10	C70A30
Aluminium	C100	C100	C90A10
PVC	C100	C80A20	C60A40
Wood	C100	C100	C90A10

Unaged material samples showed 100 % cohesive failure mode for all the substrates after 7 days of storage at standard conditions (23 °C temperature and 50 %RH). When the material was aged, adhesion to stainless steel, anodized aluminium, aluminium, PVC, and wood substrates decreased because of branching and molecular weight increase of the pre-polymers, making it more difficult to access the substrate surface due to reduced macromolecular mobility.

Lap shear strength tests also have been performed to evaluate the adhesive properties of industrial material towards three different substrates: anodized aluminium, PVC, and wood (Table 3.8.3.2). Lap shear strength to anodized aluminium and wood after 7 days of storage at standard conditions (23 °C temperature and 50 %RH) reached 3.47 and 3.58 MPa, which indicated that the limiting factor for these substrates is the strength of the material itself and not the adhesion to the substrate. Concomitant, lap shear strength to PVC after days of storage at standard conditions (23 °C temperature and 50 %RH) reached 1.51 MPa, testifying that adhesion against this substrate is lower in comparison to the adhesion to anodized aluminium and wood. After ageing, lap shear strength and deformation values decreased, denoting to the decreased adhesion because of aging. For aged materials (after storage for 28 days at 70 °C) shear strength to anodized aluminium decreased by 21 % (deformation decreased by 17 %), PVH by 42 % (deformation decreased by 15 %) and to wood by 14 % (deformation decreased by 7 %). It is estimated that the developed sealant/adhesive may find application in both construction and automotive sectors.

Table 3.8.3.2

Lap shear test results of two-component SIL/EP

	Unaged	After storage for 7 days at 70 ºC	After storage for 28 days at 70 ºC
7 days			
Anodized aluminium			
σ_{break}, MPa	3.47	3.12	2.73
ε_{break}, %	20.1	18.4	16.53
PVC			
σ_{break}, MPa	1.51	1.26	0.87
ε_{break}, %	11.72	10.53	9.97
Wood			
σ_{break}, MPa	3.58	3.26	3.05
ε_{break}, %	21.41	20.59	19.92

Conclusions

1. By evaluating the compatibilisation possibilities of SIL/EP two-component systems it has been concluded that in comparison to the systems without compatibilizer and the systems with epoxy or amine groups containing compatibilizers, N-butyl-3-aminopropyltrimetohysylane (*sam*) and bis(3-(trimetoxysilyl)propylamine (*bsa*) demonstrated the highest compatibilisation effect because they contained secondary amine groups, which selectively react with epoxy groups containing compounds:
   a) in the case of *sam* it was possible to increase tensile strength by 288 % (up to 6.18 MPa), but in the case of *bsa* it was possible to increase tensile strength by 248 % (5.43 MPa), practically without decreasing ultimate deformation values of the systems;

   b) the results of rheological analysis testified that *sam* and *bsa* compatibilisers promoted the development of gel point almost at the same time, independently from the pre-polymers SIL/EP ratio, thus denoting to the development of joint polymer network.
2. By substituting presently broadly used SAX 520 with SIL pre-polymers, synthesized from polyols with different molecular masses (4200–18200 g/mol), it has been concluded that
   a) the most suitable catalyst for SIL pre-polymer synthesis is Dabco 33LV, at concentration w = 0.003 %, which efficiently catalysed synthesis of the pre-polymer as well as ensured the best storage stability;

   b). three of the four synthesised pre-polymers (Acclaim 4200, Acclaim 8200 and Acclaim 12200) demonstrated by 25 %, 50 %, and 4 % improved ultimate tensile strength values, in comparison to the reference system SAX 520/D.E.R. 331 (6.18 MPa);

   c) in the case of self-synthesized SIL pre-polymers containing complete systems, it is possible to obtain high tensile strength values (>8 MPa), thus opening door for ultilisation of the developed real SIL/EP systems for gluing of car wind-shields as well as other high-responsibility engineering applications.
3. By integrating within the two-component systems microbially synthesized or from castor oil derived polyols, it is possible to improve certain mechanical and adhesive properties in comparison to SAX 520/D.E.R. 331 systems:
   a) two-component systems with the pre-polymer, synthesized from castor oil, are characterized not only by high tensile strength ($\sigma_{break} = 3.63$ MPa), but also improved adhesion to PVC (1.3 MPa in shear), which is 3 times larger than in the case of SAX 520/D.E.R. 331;

   b) two-component systems with commercial microbially synthesized pre-polymer Krasol F3000 are characterized by high tensile strength ($\sigma_{break} = 4.97$ MPa), although at comparatively lower ultimate deformation values ($\varepsilon_{break} = 46$ %) in comparison to the reference (SAX 520/D.E.R. 331), which possessed $\sigma_{break} = 4.4$ MPa and $\varepsilon_{break} = 66$ %.

4. By assessing replacement capabilities of bisphenol A containing epoxy resin with environmentally more friendly alternatives, it has been concluded that
    a) two of the three EP pre-polymers (Eponex 1510 and D.E.R. 3412) demonstrate very similar mechanical and adhesive properties to the reference resin and thus may be suggested as alternatives. Maximally achievable tensile strength was $\sigma_{break} = 4.06$ MPa at $\varepsilon_{break} = 290$ % for the systems with Eponex 1510 and $\sigma_{break} = 4.31$ MPa at $\varepsilon_{break} = 60$ % for the systems with D.E.R. 351 in comparison to $\sigma_{break} = 4.04$ MPa at $\varepsilon_{break} = 66$ % for the reference system (SAX 520/D.E.R. 331);
    b) substitution of D.E.R. 331 by D.E.R. 749 ensures not only high shear adhesion to stainless steel and wood but also to PVC, thus making it the most universal system from the adhesion viewpoint;
5. By evaluating the knowledge obtained within the Thesis research, up-scaling has been performed by developing an industrial sealant prototype with relatively high mechanical properties and adhesion to broad spectrum of different substrates, which has been tested by customer and used for gluing of metal frameworks.

Synopsis of PhD Thesis/recommendations

Two-component silyl-terminated pre-polymers (SIL)/epoxy resin (EP) systems were studied in the Doctoral Thesis. The main goal was to analyse mechanical, rheological and adhesive properties of the systems as a function of the content of pre-polymers (SIL, EP), catalysts, compatibilizers, plasticizers, fillers, and water absorption agents. In the Thesis, not only commercially available pre-polymers but also self-synthesized alternatives obtained from microbially synthesized or renewable polyols were examined.

Within the Thesis, influence of the mixtures of catalytic systems on the synthesis of SIL and EP pre-polymers has been carried out, demonstrating that:

a) the SIL pre-polymer used in the research (SAX 520) can be catalyzed already at relatively low concentration (w = 0.2 %) by tin-containing catalysts (e.g., Tibcat 216; Tibcat 318; Tibcat 410), whereas the amine containing catalyst (DBU) is effective only at high concentration (w = 4 %);

b) the EP pre-polymer used to create two-component systems (D.E.R. 331) can be catalyzed by amine-containing catalysts (Niax C41 and Ancamine K54), from which priority should be given to Niax C41 due to its lower toxicity;

c) the use of tin-type catalyst Tibcat 216 and amine-containing catalyst Niax C41 allows selectively catalyze only the opposing component pre-polymer, providing the possibility to create a two-component system.

The obtained results on the performance of various two-component SIL/EP system compatibilizers showed that:

a) the two-component SIL/EP system was most effectively compatibilized by compatibilizers containing a secondary amine group N-butyl-3-aminopropyltrimethoxysilane (*sam*) and bis(3-(trimethoxysilyl)propylamine (*bsa*), allowing to obtain the systems with higher tensile mechanical properties compared to the systems without a compatibilizer and with compatibilizers that contained epoxy or primary amino groups;

b) within a SIL/EP ratio range from 100/0 to 30/70, the tensile strength of *sam* and *bsa* catalysed systems respectively increased by 288 % (6.18 MPa) and by 248 % (5.43 MPa) without reducing the deformation values compared to the reference system without compatibilizer;

c) by increasing the compatibilizer content, deformative properties of the system decreased, denoting that *sam* and *bsa* act not only as compatibilizers but also cross-linkers of the system;

d) rheological experiments confirmed the results of the testing of mechanical properties, showing that *sam* and *bsa* compatibilizers practically formed the gel point in the same time interval, regardless of the SIL/EP ratio, thus indirectly indicating that a uniform polymer network was formed;

e) it is advantageous to use the *sam* type compatibilizer at a concentration of w = 1.5 % for developing of the investigated two-component system because of its higher efficiency.

Within the Doctoral Thesis, the synthesis of several SIL pre-polymers from various polyols with different molecular weights (4200–18200 g/mol) also was performed to create model and real systems and to investigate their mechanical properties. The obtained results showed that:

a) the most effective and stable catalyst for the synthesis of SIL pre-polymers is Dabco 33LV at concentration w = 0.003 %, because the pre-polymer which was catalyzed with Dabco 33LV did not significantly increase the viscosity during storage;
b) by increasing molecular mass of the self-synthesized SIL pre-polymers, their solubility/compatibility with epoxides decreased;
c) the synthesized pre-polymers with molecular weights of 4200 g/mol and 8200 g/mol showed highest tensile strength values, 7.75 MPa and 9.3 MPa, respectively, but significantly decreased deformation values, 15 % and 12 %, respectively, compared to the reference system;
d) decreasing the functionality of the SIL pre-polymer (Acclaim 4200) with butanol did not significantly change ultimate deformation values ε_{break} = 18%, but blocking the pre-polymer with benzyl alcohol not only increased the deformation values (at the maximum tensile breaking strength – 31 %), but also increased tensile strength values, at the maximum reaching 9.02 MPa (after storage for 28 days at 23 ºC and 50 % RH);
e) two-component SIL/EP systems were able to reach high tensile strength values, and depending on the applied SIL pre-polymer, it was possible to change the properties of the system in a wide range depending on the composition of pre-polymers, which allows the material to be used in various industries.

Several water absorption methods have been studied in the Thesis, which may be used to reduce the water content of the complete system, ensuring its long-term stability. The research results showed that chemical water absorption methods are more effective, especially the mixture of silanes (AMMO + VTMO), which not only absorbed water most effectively, but also may contribute to the improved adhesion of the material.

Initial research was done using a model system, but adhesives and sealants commonly are not offered in this form in the market, so full two-component systems with pre-polymers, fillers, plasticizers, and other additives were created and their mechanical, rheological, aging, and adhesive properties were determined. The research results showed that:

a) by adding fillers to the systems, the content of rigid elements increases, as a result of which materials become stiffer, thereby reducing the possible concentration of EP pre-polymer, which can be integrated into the system without significantly losing the superelasticity of the material;
b) the complete two-component SIL/EP system with pre-polymers SAX 520/D.E.R. 331 showed tensile strength values ranging from σ_{break}= 1.84 (SIL/EP 100/0) to σ_{break} = 4.04 MPa (after storage for 28 days at 23 ºC and 50 % RH), without showing a distinct maximum peak value at certain SIL/EP ratio, which may be explained by complicated interaction between the SIL and EP polymers with the components of the additive

package, including plasticizers mineral fillers, water absorption agent, catalysts, and compatibilizer;

c) increasing of the EP concentration to a certain value (SIL/EP 50/50) improves adhesion to all the studied substrates – PVC, alloys MS 63 and 5005, stainless steel, copper, glass fiber reinforced epoxy composite, EPDM, polyamide and PMMA, whereas at higher EP concentration, the system becomes stiffer, thus the adhesion considerably decreases against all the studied substrates;
d) at certain SIL/EP content, shear strength of two-component systems against stainless steel and wood substrates may exceed 4 MPa;
e) changing of the EP pre-polymer concentration within certain interval (SIL/EP 90/10 to 50/50) improves UV resistance of the corresponding complete systems in comparison to the system with the 100 % SIL pre-polymer due to the protection provided by aromatic rings of the EP pre-polymer, working as UV absorber.

As part of the Doctoral Thesis, not only the effect of SIL pre-polymers but also different EP pre-polymers on the properties of two-component SIL/EP system were studied. The research results showed that:

a) by changing the type and concentration of EP pre-polymer in the system, it is possible to vary the mechanical properties in a wide range: σ_{break} = 0.35–4.33 MPa, ε_{break} = 25–1041 %, Shore A = 10–95 units;
b) two of the investigated EP pre-polymers (Eponex 1510 and D.E.R. 3412) allowed to obtain two-component systems with similar mechanical and adhesive properties comparing to the D.E.R. 331/SAX 520 based systems, testifying that they can be used for replacement of bisphenol-A containing D.E.R. 331;
c) D.E.R. 749 improved adhesion of the two-component SIL/EP system the most, showing good shear adhesion not only to stainless steel and wood substrates, but also to PVC, reaching a shear strength of 3.51 MPa (after 28 days storage at 23 ºC and 50 % RH).

Complete systems were created not only with commercially available SIL and EP pre-polymers, but also with self-synthesized Acclaim 4200– 8200 SIL pre-polymers, as well as SIL pre-polymers synthesized from biologically renewable resources (castor oil and farnesene). The results of the obtained materials showed that:

a) similar to the model system experiments, three of the four synthesized pre-polymers (Acclaim 4200, Acclaim 8200, and Acclaim 12200) allowed to obtain the systems with higher tensile strength values but lower deformation values comparing to the reference system SAX 520/D.E.R. 331;
b) complete systems with the synthesized SIL pre-polymers reach high tensile strength values, allowing to consider their use as car windshield sealants (>8 MPa), instead of presently used polyurethane adhesives;
c) two-component systems with a pre-polymer synthesized from castor oil, demonstrated not only increased tensile strength (σ_{break} = 3.63 MPa at SIL/EP ratio 80/20), but also improved adhesion to PVC (1.3 MPa in shear), which was 3 times higher than for the SIL/EP system without castor oil-based SIL pre-polymer;

d) two-component systems with Krasol F3000 pre-polymer possessed increased tensile strength values ($\sigma_{break} = 4.97$ MPa), though at decreased deformation capability ($\varepsilon_{break} = 46$ %, at breaking strength maximum).

To evaluate practical applicability of the investigated SIL/EP systems, an industrial two-component SIL/EP adhesive was developed, the storage, mechanical, rheological and adhesive properties of which were evaluated. The results showed that the created two-component SIL/EP adhesive meets all the necessary properties ($\sigma_{break} = 3.92$MPa, $\varepsilon_{break} = 95$ %, Shore A = 57, adhesion to anodized aluminium, PVC and wood – 3.47 MPa, 1.51 MPa, and 3.58 MPa, respectively) to be used both in construction and for sealing of metal frameworks, for which the material was intended.

Ritvars Bērziņš was born in 1988 in Tukums. He holds a Bachelor's degree in Chemical Technology (2011 year) and a Master's degree in Chemical Technology (2013 year). From 2014–2016 he was a chemical engineer researcher and from 2016–2020 a product development manager at Tenachem Ltd; from 2020–2021 he was a product development manager and technologist at Skonto CC Ltd and from 2021–2022 a development manager at Skonto Prefab Ltd. He is currently a lecturer and research assistant with the Department of Polymers of Riga Technical University, as well as a project development manager at Valmiera Glass Corporation and a leading product development engineer at Tenachem Ltd. His scientific interests are related to textile chemistry and adhesive industries.