

Rheological, mechanical and adhesion properties of two component adhesive based on modified silyl terminated polyether polymer and epoxy resin

J Bitenieks¹, R Merijs Meri¹, J Zicans¹, R Berzins², J Umbraško² and U Reknors²

¹Institute of Polymer Materials, Faculty of Material Science and Applied Chemistry, Riga Technical University, Riga, Latvia

²TENACHEM Ltd., TENAX group, Dobeles, Latvia

Abstract. 4 types of two component adhesives based on modified silyl-terminated polyether polymer (MS Polymer) and epoxy resin are formulated. Rheological and mechanical properties as well as weathering resistance of the developed adhesives are investigated. It is shown that curing times vary in a wide range depending on the type of MS Polymer. It is also demonstrated that kinetics of cross-linked network formation of the investigated adhesives, depending on the type of MS Polymer, considerably affects mechanical characteristics of the system: Shore A hardness, tensile strength and tensile elongation. Although under the influence of UV weathering mechanical properties of the investigated systems are decreased, the remaining tensile elongation values are not less than 30%. In parallel it is revealed that adhesive formulations, developed in the framework of this research, are most suitable for bonding with stainless steel, partially suitable for bonding with aluminium and less suitable for bonding with polyvinyl chloride.

1. Introduction

Modified silyl-terminated polyether polymer (MS Polymer) as a widespread material in adhesive industry may offer advantages over two-component polyurethane adhesives. MS Polymer has a polyether backbone that carries telechelic methoxysilyl groups, which can crosslink by moisture from the air under ambient temperatures. The polymerisation reaction of MS Polymer is provided by tin catalyst. The elastic behavior of MS Polymer, its inherent good adhesion and stability in combination with epoxy resin has a potential for use in several application areas. Typical epoxy resins usually show an elongation at break of less than 10%. On the other hand their unmatched strength, better heat resistance, reduced tendency to swell when immersed in water, as well as good adhesion to some specialty substrates are properties that are highly appreciated. The combination of epoxy resins with MS Polymer is supposed to deliver a blend that shows superior strength compared to pure MS Polymer based adhesives, while combining all the other positive features from both polymer resin types [1 - 3].

The two-component MS Polymer/epoxy system can be made by incorporating MS Polymer and epoxy hardener in one component and epoxy, MS Polymer catalyst and water in other component [4]. The system is expected to be superb substitute for many (moisture-cure) one-component systems, which can cause problems through slow hardening processes.



Main advantages of such two-component systems are that they can be made for fast curing to eliminate waiting time especially on large work-pieces. Other benefits include high initial strength and cost effectiveness that are important in modern and automated production [5 - 6].

2. Materials

To evaluate the MS Polymer possibilities for two-component adhesive development various types of MS Polymer grades, as shown in Table 1 and Fig. 1, were chosen depending on their physical properties and functionality.

Table 1. Properties of MS Polymer types (manufacturer's information)

MS Polymer type	Structure	Modulus, MPa	Viscosity, Pa·s
SAX 350	DMS	0.25 at 50% elongation	6
SAX 530	TMS	0.27 at 50% elongation	7
S327	DMS	0.16 at 100% elongation	34
SAX 520	TMS	0.33 at 100% elongation	46

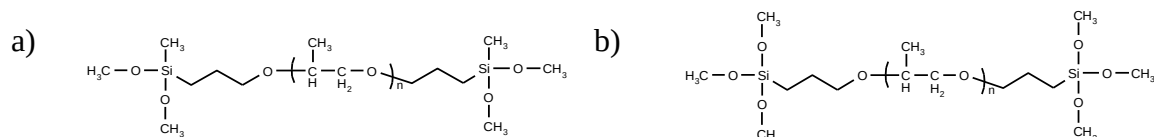


Figure 1. Structural formulas of a) di-functional MS Polymer (DMS) and b) tri-functional MS Polymer (TMS)

General purpose bisphenol A diglycidyl ether (DGEBA) epoxy resin DER 331 was chosen for the second component of the system. Other ingredients were reinforcing fillers, rheology modifier, silane compatibilizer, antioxidant, catalyst, hardener and UV-stabilizer (Table 2).

Table 2. Materials used for two-component adhesive formulations

Ingredient	Type	Supplier
SAX 350	MS Polymer	Kaneka Belgium
SAX 530		
S327		
SAX 520		
DER 331	Epoxy resin	DOW Chemical
Tib Kat 318	MS Polymer catalyst	TIB Chemicals
Baxxodur EC 130	Epoxy hardener	BASF
AMMO	Aminosilane	Evonik Industries
Omyacarb 1T VA	Coarse filler	Omya AG
Hakuenka CCR-S10	Fine filler	Shiraishi-Omya GmbH
Cabosil TS-720	Thixotropic additive	Cabot Corporation
Irganox 245	Antioxidant	BASF
Tinuvin 328	UV-stabiliser	BASF

3. Experimental

For the development of adhesives (Table 3) total of four different formulations of component A were considered. Component B was formulated on the basis of DER 331 epoxy. Two different formulations of component B were prepared depending on the type of MS Polymer (DMS or TMS) in the component A. For TMS containing systems tin catalyst was added ten times less to obtain reasonable

pot life of the system after mixing of components A and B since TMS has three reactive methoxysilyl groups on each end of polyether chain whereas DMS has only two methoxysilyl group on each end of polyether chain.

Table 3. Two-component formulations for MS Polymer/Epoxy adhesive

Formulation for component A			Formulation for component B		
Ingredient	Type	wt, %	Ingredient	Type	wt, %
SAX 350/S327	MS Polymer	30.00	DER 331	Epoxy resin	15.00
Baxxodur EC 130	Epoxy hardener	4.50	Tib Kat 318	Catalyst	1.00
Irganox 245	Antioxidant	0.30	Irganox 245	Antioxidant	0.15
Tinuvin 328	Stabiliser	0.30	Tinuvin 328	Stabiliser	0.15
Omyacarb 1T VA	Coarse filler	19.30	Omyacarb 1T VA	Coarse filler	14.70
Hakuenka CCR-S10	Fine filler	9.50	Hakuenka CCR-S10	Fine filler	2.00
Cabosil TS-720	Thixotropic agent	1.50	H ₂ O		0.30
AMMO	Compatibilizer	1.30			

Formulation for component A			Formulation for component B		
Ingredient	Type	wt, %	Ingredient	Type	wt, %
SAX 520/SAX530	MS Polymer	30.00	DER 331	Epoxy resin	15.00
Baxxodur EC 130	Epoxy hardener	4.50	Tib Kat 318	Catalyst	0.10
Irganox 245	Antioxidant	0.30	Irganox 245	Antioxidant	0.15
Tinuvin 328	Stabiliser	0.30	Tinuvin 328	Stabiliser	0.15
Omyacarb 1T VA	Coarse filler	19.30	Omyacarb 1T VA	Coarse filler	15.60
Hakuenka CCR-S10	Fine filler	9.50	Hakuenka CCR-S10	Fine filler	2.00
Cabosil TS-720	Thixotropic agent	1.50	H ₂ O		0.30
AMMO	Compatibilizer	1.30			

Components A and B of MS Polymer/Epoxy adhesive each was mixed with SpeedMixer DAC 150 centrifugal laboratory mixer to obtain homogeneous mixture of the ingredients. Components A and B were then mixed at a ratio of 2:1 by weight. Samples for mechanical characterisation were casted in Teflon moulds and left for curing for determined duration at 23°C ± 2°C and ~ 50% ± 5%RH.

Rheological characteristics were measured using Bohlin CVO 100 rheometer. Instrument was equipped with 20 mm diameter spindle in plate-plate geometry. The gap size between plates was set to 1000 µm. Tests at 23°C were performed in oscillatory shear mode at frequency 1.5 Hz and strain 0.15. The dynamic storage G' and loss moduli G'' were recorded as a function of the reaction times.

Tensile stress-strain and adhesive characteristics were determined using Zwick/Roell Z010 universal testing machine. Tensile tests were made according to DIN 53504 at a test speed 200 mm/min. Samples were tested after 14 days of curing. Lap shear tests were made according to EN 1465. Some of the most commonly used materials – stainless steel grade 1.4301, aluminium grade AlMg1 and polyvinylchloride (PVC) grade KömaDur - were chosen as bonded joint substrates. Sample bonding area was 12.5x25 mm with adhesive layer thickness 1 mm. The joint strength was expressed as a maximum force applied to the adhesive area. To observe the development of lap shear strength the tests were made 1, 7, 14, 21 and 28 days after manufacturing.

Shore A hardness was measured according to ISO 868 using Zwick/Roell 3114/5 durometer.

Weathering of adhesives was tested according to ISO 4892-3 using Q-Lab QUV accelerated weathering tester. The test samples were cured for 21 days and then were subjected to periodically repeating cycles of 8 h UV exposure (0.76 W·m⁻²·nm⁻¹ irradiance at 340 nm wavelength) and 4 h condensation. Temperature at UV exposure was 45°C and at condensation step was 40°C. Overall test duration was 672 h. Samples for mechanical testing according to DIN 53504, were taken after 7, 14, 21 and 28 days of weathering.

4. Results

4.1. Rheological characteristics

As seen from the G' , G'' curves in Fig. 2, in the beginning of time sweep analysis mixtures of the components A and B of the MS Polymer/epoxy system are in liquid state and the values of G' and G'' are small. Consequently in the beginning of the experiment viscous behaviour of the systems dominates ($G'' > G'$). Later with progression of curing reaction both moduli increase to the moment where elastic modulus starts to take advantage over viscous modulus. The time where G' crosses G'' ($G' = G''$) is then recorded as a gel point (t_{gel}). At t_{gel} stable 3D network is formed however material is not completely cured. After intersection of G' and G'' , curing starts to develop sharply ($G' > G''$). Curing behaviour is different for the systems based on TMS and DMS polymers. In comparison to the systems with DMS polymers, systems with TMS polymers exhibit faster increase of G' and G'' in the beginning of the experiment, but slower modulus gain after t_{gel} is reached. After t_{gel} curing may proceed up to many hours when G' and G'' modules reach plateau. Lower t_{gel} values can be achieved with more reactive TMS MS Polymers like SAX 530 and SAX 520. It is worth mentioning that the use of low-viscous systems with fast curing times could give considerable advantages for development of perspective easy workable adhesives, highly demanded in the market [7].

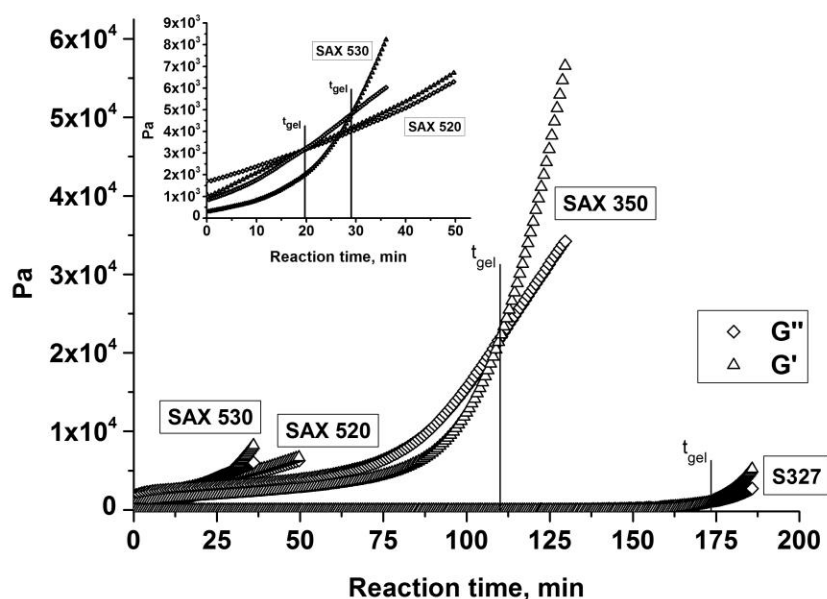


Figure 2. Gel point t_{gel} depending on MS Polymer type.

4.2. Mechanical properties

As already expected, combination of MS Polymer with epoxide resin at the formulations denoted in Table 2 allows obtaining the systems with increased strength and hardness in comparison to neat MS Polymers (10-fold increment in average) [8], thus following the market trends on the developing of high-strength adhesives for high demanding applications [7].

Shore A hardness of the developed MS Polymer/epoxy adhesives is shown in Fig.3. Although all the MS Polymer containing systems show relatively high levels of Shore A hardness already after the 1st day of curing, development of 3D cross-linked network proceeds during the whole observation time, i.e., 28 days, as can be judged from continuously increasing Shore A hardness values. Increase of Shore A hardness of the investigated adhesives can be approximated by exponential relationships. Curing is most intensive during the first 7 days.

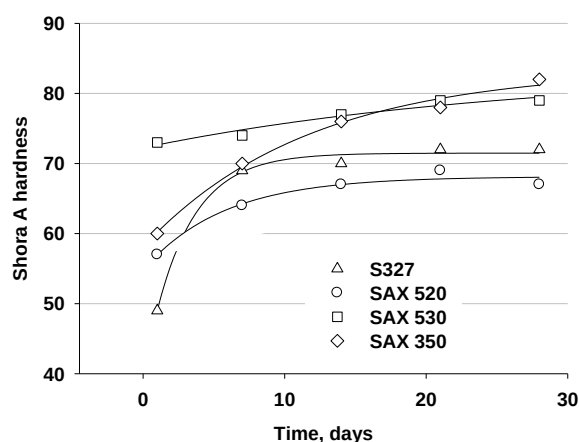


Figure 3. Shore A hardness of MS Polymer/epoxy adhesives.

Tensile stress-strain characteristics of the investigated MS Polymer/epoxy adhesives vary in a similar manner to Shore A hardness. In Fig. 4, tensile stress-strain characteristics of the investigated adhesives are shown after 14 days of curing. The systems containing low viscosity MS Polymers SAX 350 and SAX 530 provide strengths close to 2.5 MPa (namely 2.37 and 2.39 MPa, respectively), while the systems, containing higher viscosity MS Polymer grades, S327 and SAX 520, show ultimate strengths in the range of 2 MPa (namely 1.98 and 1.91 MPa respectively). In the same time adhesives with S327 and SAX520 possess higher tensile elongations in comparison to those containing SAX 350 and SAX 530.

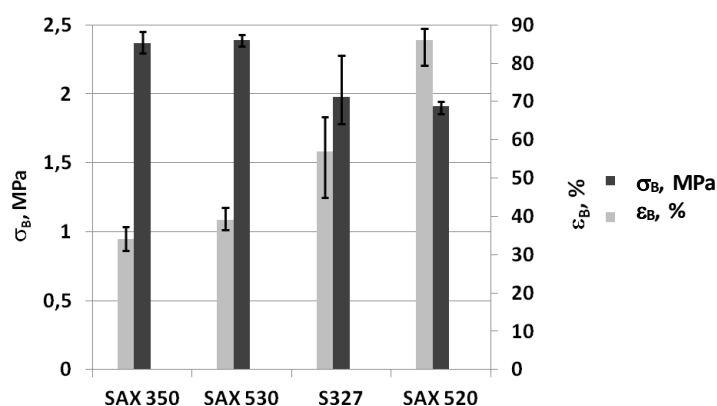


Figure 4. Tensile strength σ_B and tensile elongation ϵ_B of MS Polymer/epoxy adhesives.

In general Shore A hardness as well as tensile strength and elongation variations denote that main factors determining mechanical characteristics of the developed adhesives are interaction between epoxy resin and MS Polymer during development of the adhesive systems as well as curing kinetics itself.

Lap shear strength experiment was applied as a basis for making some predictions about the reliability of adhesives formulated on MS Polymer. As shown in Fig. 5, increase of adhesive strength to various substrates (stainless steel, aluminium, PVC) is gradually rising along with progression of the cure as well as development of bonding between the adhesive and substrate. Change of adhesive strength of the investigated formulations can be approximated by exponential functions.

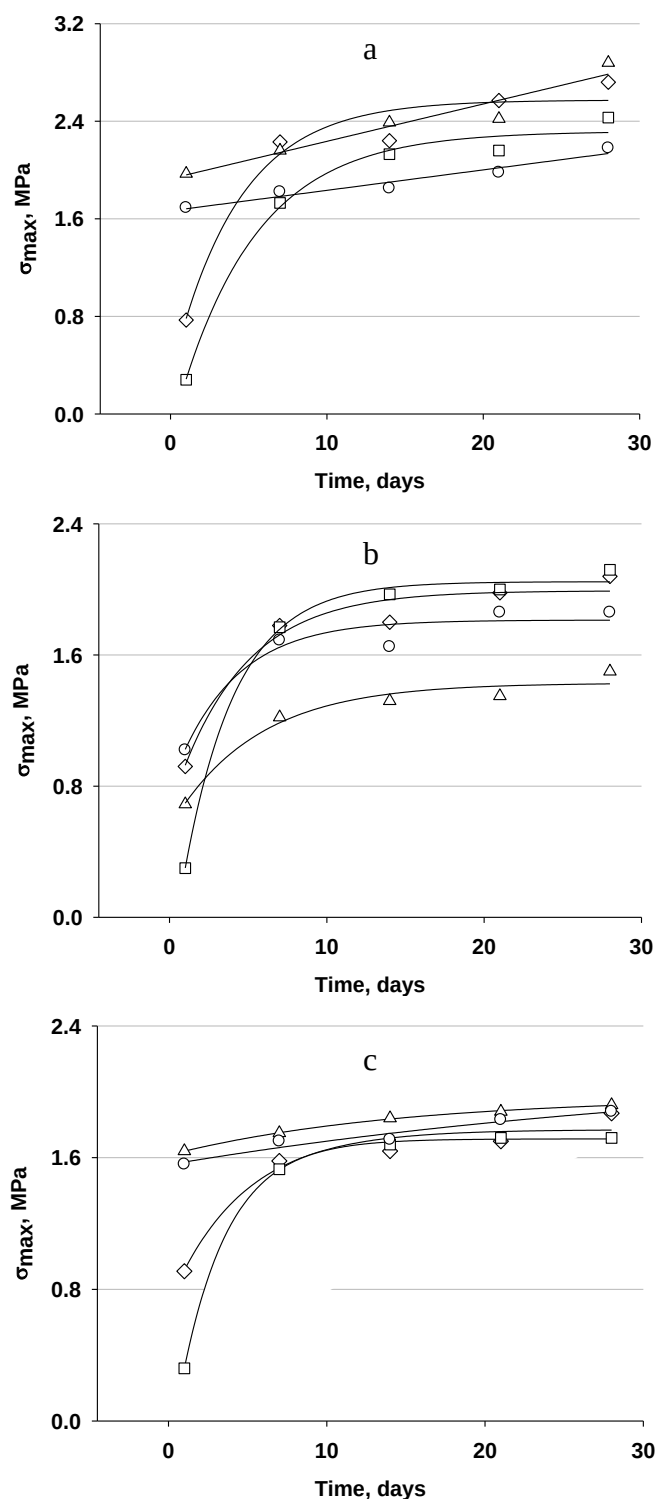


Figure 5. Lap shear strength $\sigma_{\max}$ of MS Polymer/epoxy adhesives to steel (a), aluminium (b) and polyvinyl chloride (c): $\diamond$ - SAX350; $\square$ - S327; Δ - SAX530; $\circ$ - SAX520.

By considering the importance on the development of fast curing adhesives it is interesting to look on the change of adhesion strength within the bonded system as a function of reaction time. As shown in

Fig. 5, already after the 1st day of curing some of the adhesives show reasonable strength to certain substrates, e. g. formulations with SAX 530 and SAX 520 MS Polymers to stainless steel and PVC substrates. Adhesion of the formulations containing di-functional MS Polymers, especially S327, to these substrates is somewhat smaller. Although after the 1st day of curing adhesion of the investigated adhesives (especially in the case of tri-functional MS-Polymer based systems) to aluminium substrate in general is lower, situation changes after 7 days of curing. Since this adhesive strengths of the investigated formulations (except of the adhesive formulation based on SAX 530) to aluminium and PVC substrates are rather close each to other. Simultaneously adhesion strengths of all the investigated adhesives to steel are the highest; especially this is attributed to the systems containing MS Polymers with lower viscosities. It is also worth mentioning that above 7 days of curing changes of adhesive strengths of the investigated formulations to various substrates are comparatively small. By considering the results obtained, it can be concluded that adhesive formulations, developed in the framework of this research, are most suitable for bonding with stainless steel, partially suitable for bonding with aluminium and less suitable for bonding with PVC. In general the effectiveness of the investigated adhesives to the most promising substrate, i.e., stainless steel, can be arranged in following order: SAX 530 (tri-functional low-viscosity MS-Polymer) > SAX 350 (di-functional low-viscosity MS-Polymer) > S327 (di-functional high-viscosity MS-Polymer) > SAX520 (tri-functional high-viscosity MS-Polymer).

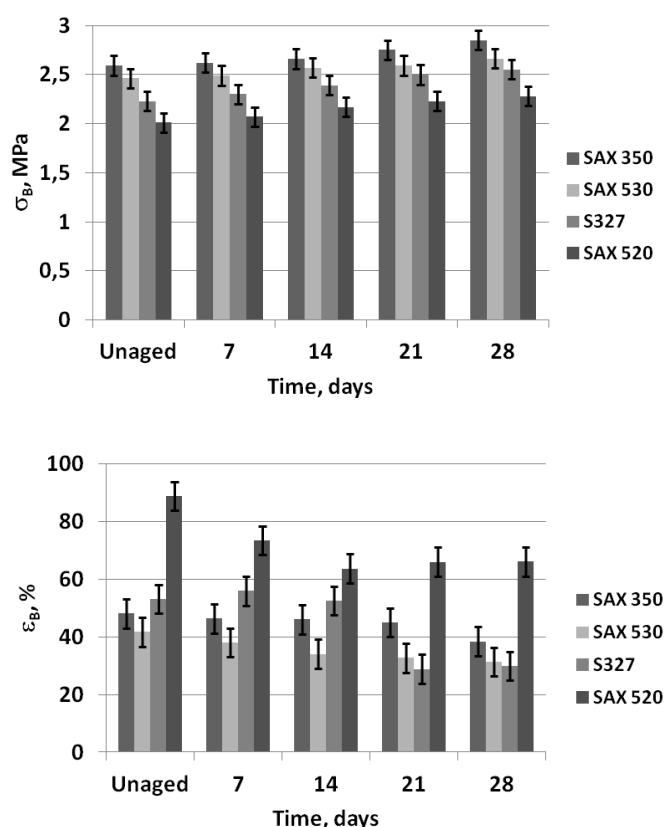


Figure 6. Tensile strength σ_B and tensile elongation ϵ_B of MS Polymer/epoxy adhesives after UV weathering.

4.3. Weathering resistance

Weathering resistance of the developed adhesives has been evaluated by following the changes of stress-strain characteristics. As shown in Fig. 6, by increasing aging time, tensile strength of all the developed adhesive formulations is slightly increased but respective tensile deformation is decreased in comparison to unaged systems, which is evidently a result of structural impairment of the investigated systems due to the complex behaviour of the detrimental effects of UV irradiation, temperature and moisture. It should be however mentioned that all the investigated adhesive formulations maintained considerable deformations (in the range of 30% at least) even after 28 days of UV exposure. It is also worth mentioning that the composition, containing SAX 530, demonstrating low gel time and possessing the best adhesive properties to steel, showed also one of the highest resistances to UV irradiation (only slightly lagging behind the composition with SAX 350).

5. Conclusions

By investigating rheological and mechanical properties of MS Polymer/epoxy adhesive formulations the following can be concluded:

- 1) curing times vary in a wide range depending on the type of MS Polymer used;
- 2) kinetics of cross-linked network formation, depending on the type of MS Polymer, considerably affects mechanical characteristics of the system: Shore A hardness, tensile strength and tensile elongation;
- 3) although UV weathering detrimentally affects mechanical properties of the investigated systems, the remaining tensile elongation values are not less than 30%;
- 4) herein defined adhesive formulations exhibit the greatest adhesion to stainless steel, somewhat reduced adhesion to aluminium and the worst adhesion to polyvinylchloride.

6. Acknowledgments

This work was supported by EU-Project No 2013/0070/2DP/2.1.1.1.0/13/APIA/VIAA/004

7. References

- [1] Yail J K, Seung W H, Isamu Y and Jae-Yoon K 2014 *Int. J. Adhes. Adhes.* **51** 117
- [2] Nečasová B, Kovářová B, Liška P and Šlanhof J 2015 *Procedia Eng.* **108** 410
- [3] Acebo C, Fernandez-Francos X, Messori M, Ramis X and Serra A 2014 *Polymer* **55** 5028
- [4] Devroey D R E, Homma M 2001 *Int. J. Adhes. Adhes.* **21** 275
- [5] Petrie E M 2006 *Epoxy Adhesive Formulations* New York: McGraw-Hill 554
- [6] Kohl M, Reichenbach-Klinke R, Steigerwald P, Kern G and Proebster M 2007 *Two-component adhesive/sealant* US 2007/0088110 A1
- [7] Peeters L 2013 *adhesion Adhesives & Sealants* **1** 14
- [8] Bitenieks J, Merijs Meri R, Zicans J, Berzins R, Umbraško J and Reknors U 2015 *IOP Conf. Series: Materials Science and Engineering* (submitted)