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Different epoxide compound influence on two component silyl-terminated polymer/epoxide systems mechanical, rheological and adhesion properties

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Abstract. Polyether silyl-terminated pre-polymer (SIL) and epoxy resin (EP) based two component systems are most perspective alternatives to the dominant polyurethane adhesive and sealant materials. This study focuses on the influence of the amount of epoxide component on the rheological, indentation, tensile and adhesion properties of SIL/EP composites within a whole range of the component weight to weight ratios. Results show that epoxide content and structure both considerably affect all the investigated properties of the material. Depending on its composition, the obtained materials demonstrate tensile strength in the range of 0.22-4.06 MPa, tensile deformation in the range of 25-1527 % and Shore A hardness in the range of 4-96.

1. Introduction

Sealant and adhesive market are constantly growing, because of new material development, increasing quality requirements and environmental issues. Despite wide range of adhesives in the market, only few materials (mostly polyurethane type) simultaneously can provide good adhesion to various substrates, high tensile strength (>3 MPa) and deformation (>100%). Previous publications [1-2] showed that two component silyl-terminated polymer /epoxy resin systems (SIL/EP) are able to achieve the above mentioned properties. Consequently, in the current research attention is paid to revealing the effects of various structurally different EP addition on the rheological, indentation, tensile and adhesion properties of SIL based two-component systems.

2. Experimental methods

Formulations of component A, based on SIL (SAX 520), and component B, based on structurally different EPs (bisphenol A epoxy resin (D.E.R. 331), hexion cycloaliphatic epoxy resin (Eponex 1510), tetra-functional aliphatic epoxy compound (D.E.R. 749), mono-functional aliphatic epoxy compound (D.E.R. 721)), are summarized in Table 1, where the particular epoxide groups containing raw material is labelled as epoxy compound.

A and B components were made by using 3-liter laboratory mixer TEJA Engineering. First, all liquid raw materials (resin/pre-polymer, plasticizer, adhesion promoters, drying agent) were stirred for 5 minutes at 1000 (dissolver)/ 5 (planetary) rpm, then fillers were added and the composition was stirred

20 minutes at 3500 (dissolver)/ 35 (planetary) rpm, then mixing was continued under vacuum for 30 minutes at 3500 (dissolver)/ 35 (planetary) rpm.

Table 1. Two-component SIL/EP formulations (in weight percentage)

Polymers percentage	100/0	90/10	80/20	70/30	60/40	50/50	40/60
A component							
SAX 520 (Kaneka Belgium)	40	36	32	28	24	20	16
Hexamol DINCH (BASF)	15.0	13.5	12.0	10.5	9.0	7.5	6.0
Dynsylan 1189 (Evonik)	1	1	1	1	1	1	1
Omycarb 1T (Omya)	17.13	15.00	13.80	12.00	10.30	8.60	6.80
Hakuenka CCR-S10 (Omya)	25.0	22.5	20.0	17.5	15.0	12.5	10.0
Dynasilan VTMO (Evonik)	1.0	0,9	0,8	0,7	0,6	0,5	0,4
Lupragen N600 (Air products)		0,62	1,33	2	2,66	3,33	4
B component							
Epoxy compound (see in text)	0	4	8	12	16	20	24
Hexamol DINCH (BASF)	0	1.5	3.0	4.5	6.0	7.5	9.0
Omycarb 1T (Omya)	0	1.70	2.38	3.69	4.92	6.14	7.45
Hakuenka CCR-S10 (Omya)	0	2.5	5.0	7.5	10.0	12.5	15.0
Tibcat 216 (Tibchemicals)	0.20	0.18	0.16	0.14	0.12	0.10	0.08
Water	0.67	0.60	0.53	0.47	0.40	0.33	0.27

SIL/EP compositions were mixed using SpeedMixer DAC 150 centrifugal laboratory mixer at room temperature 23 ºC and 3000 rpm, casted in Teflon moulds and cured at standard conditions – 23±2 ºC, 50 ±5% RH – for 1, 7 and 28 days.

Shore A hardness was measured after 1, 7 and 28 days of curing by using durometer (SCHMIDT) according to ISO 7619.

Rheological measurements were performed by using Bohlin CVO 100 rheometer. Instrument was equipped with 20 mm diameter spindle with plate-plate geometry (gap size 1000 μm). Tests at 25 ºC were performed in oscillation mode – frequency 1 Hz and strain 0.006.

Tensile stress-strain measurements were done by using Zwick /Roell Z010 universal testing machine. Tests were made according to ISO 527 at test speed 100 mm/min. Tensile strength measurements were made after 1, 7 and 28 days of curing.

Lap shear test was performed by using different substrates: stainless steel, PVC, wood (ash tree). Test was made according to EN 1465. Specimen overlap area was 12.5*25.0 mm and material thickness was 0.2 mm.

3. Results and discussion

3.1. Mechanical properties.

After 1, 7 and 28 days of curing systems show wide range of tensile strength values. In previous publication [2] it was shown that the most effective SIL/EP ratio from adhesion and aging perspective is 80/20. In this publication we will pay special attention to the corresponding polymer composition.

Tensile strength data (Fig. 1) show that addition of even 10-20 wt.% of epoxy group containing compound can cardinally change material properties. Thus after 28 days of curing of the investigated systems at SIL/EP ratio 80/20 following tensile strength values are obtained: 3.05 MPa (for D.E.R. 331 containing systems), 2.75 MPa (for D.E.R. 749 containing systems), 1.75 MPa (for D.E.R. 721 containing systems) and 3.78 MPa (for Eponex 1510 containing systems). SIL/EP compositions with three of four EPs, namely D.E.R. 331, D.E.R. 749 and Eponex 1510, show similar tendencies throughout

all hardening time. From the three previously mentioned, the systems with Eponex 1510 show some interesting properties. Because of alkyl type structure of Eponex 1510 it has lower reactivity comparing to bisphenol A type epoxy compounds (this effect is observed also from rheological data). Because of this effect Eponex 1510 containing system has different σ_{break}(SIL/EP ratio) relationship than that for the systems with D.E.R. 331 and D.E.R. 749. Continuous progress of the curing reaction between Eponex 1510 and SIL, especially in the systems with higher EP content, is confirmed by rising tensile strength value as curing time is increased: if after 1 day of curing minimum in σ_{break}(SIL/EP ratio) relationship is observed along SIL/EP ratio 70/30-40/60, than by increasing curing time this minimum range is getting narrower, namely tensile strength minimum is observed at SIL/EP ratio of 70/30 – 50/50 (7 days of curing) and 70/30 (28 days of curing). It can be hypothesized that by increasing curing time even more, tensile strength minimum will be lost and σ_{break}(SIL/EP ratio) relationship will show maximum values in the range 70/30- 40/60. In contradiction to other epoxy compounds, mono-functional D.E.R. 721 containing system show completely different trend of σ_{break}(SIL/EP ratio) relationship. Tensile strength decrement at EP contents above 10 wt.% of the systems with D.E.R. 721 can be explained with mono-functional chain of D.E.R. 721, preventing effective cross-linking within the system.

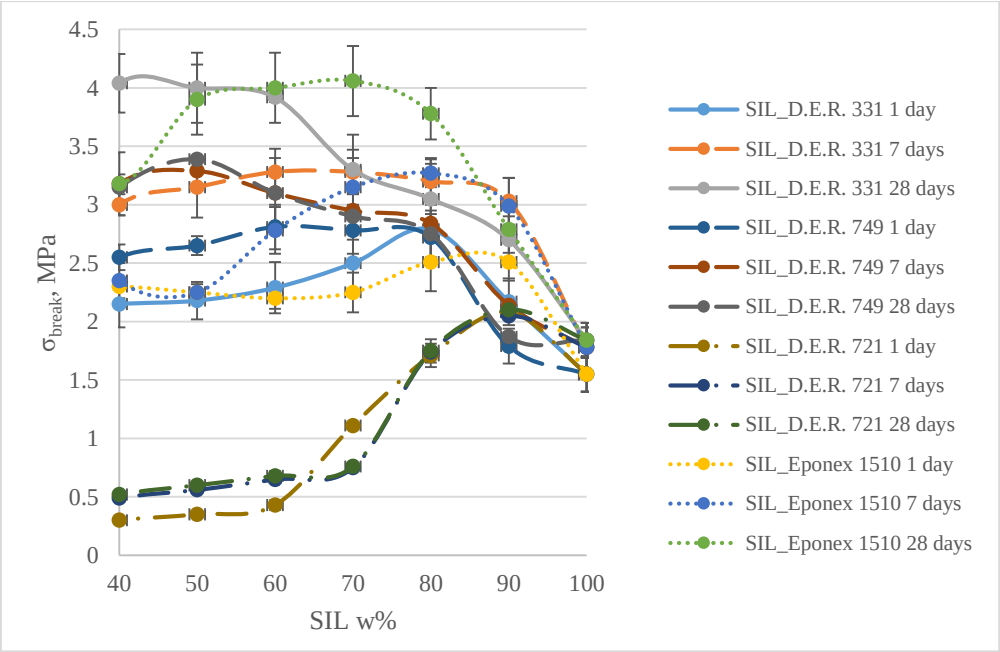

Figure 1. Tensile strength at break (σ_{break}) as a function of SIL weight content

Tensile deformation data make good correlation with tensile strength data. The systems, containing D.E.R. 331, 749 and Eponex 1510, show similar results after curing for 7 and 28 days. Considerably higher tensile deformation values of the system with Eponex 1510 after 1 day of curing are most probably explained with lower curing rate. Addition of D.E.R. 721 to SIL results in sharply increased tensile deformation values, especially after 1 day of curing of the 80/20 SIL/EP system. By increasing the curing time up to 7 days, tensile deformation values of D.E.R. 721 containing systems may even increase due to the increment of overall toughness of the system, especially at higher EP contents (60/40-40/60 SIL/EP ratio). However, at 28 days of curing this this effect is somewhat reduced, especially at lower EP contents (60/40-70/30 SIL/EP ratio), due to the development of tighter cross-linked network.

In comparison to tensile strength at break and ultimate elongation, showing complex non-monotonous relationships in respects to SIL/EP content, Shore A hardness as function of SIL/EP ratio of the investigated compositions is characterized by almost linear relationships. This could be probably

attributed to the fact that tensile stress-strain behaviour characterizes materials in bulk, while indentation related Shore A hardness characterizes materials surface, where hardening occurs at the first. Interestingly, that in the case of D.E.R. 331, D.E.R. 749 and Eponex 1510 containing systems Shore A hardness increases along with EP content, concomitant in the case of D.E.R. 721 decrease in Shore A hardness values is observed. This could be explained with distinct curing dynamics in the case of mono-functional (D.E.R. 721) and bi- (D.E.R. 331 and Eponex 1510) or tetra-functional (D.E.R. 749) epoxy compounds. By increasing the content of mono-functional epoxy compound, which cures mainly by homo-polymerization, SIL/EP two-component system is not efficiently cross-linked, as indirectly confirmed also by low tensile strength at break and ultimate deformation values. In contradiction, in the case of bi- and tetra-functional EPs, effective cross-link network is developed resulting in increased values of Shore A hardness, concomitant to tensile strength at break and ultimate hardness. Increase in curing time causes increment in Shore A hardness of all the investigated systems, irrespectively from the epoxy compound used.

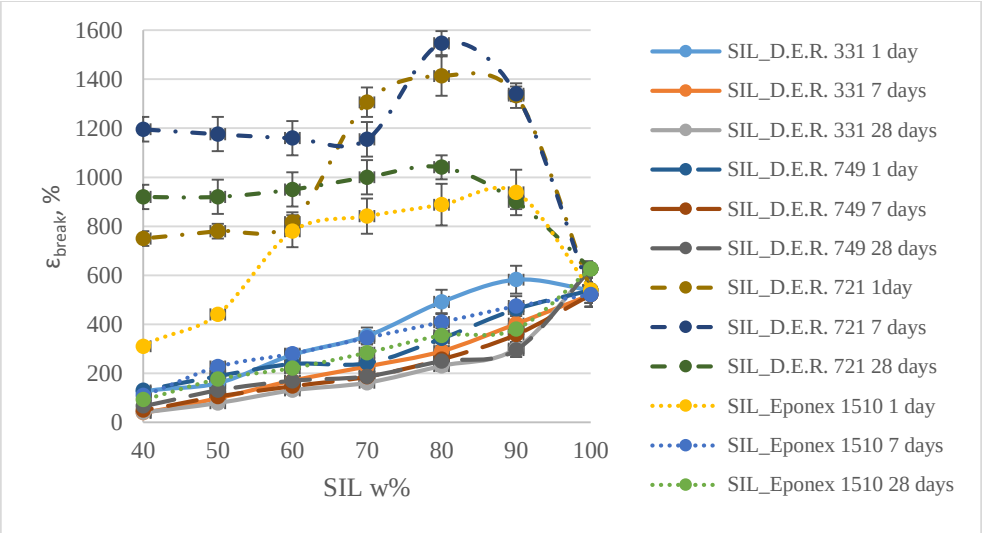

Figure 2. Tensile deformation at break (ε_{break}) as a function of SIL weight content

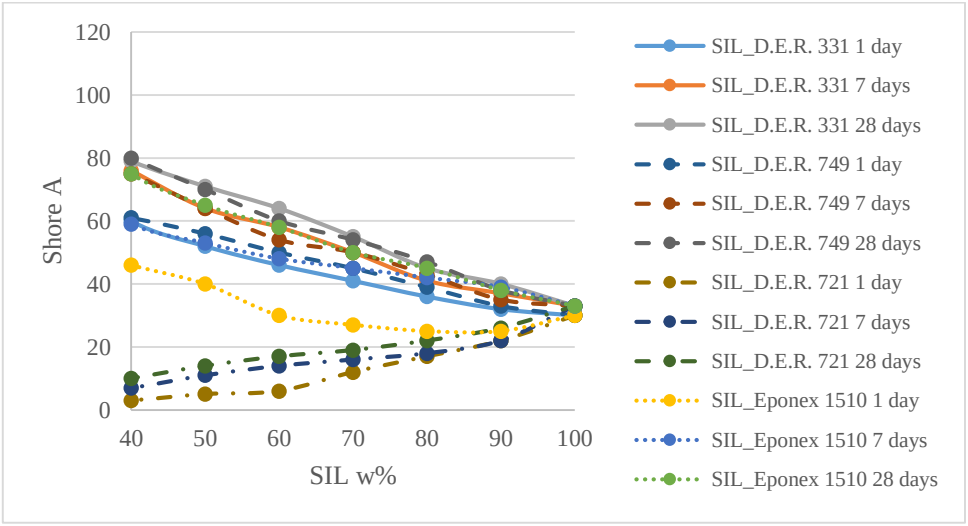

Figure 3. Shore A hardness value as a function of SIL weight content

3.2. Rheological characteristics.

Viscosity-time relationships of the investigated epoxy compounds and respective SIL/EP compositions at 80/20 ratio are demonstrated in Fig. 4 and Fig. 5 respectively. The composition with SIL/EP ratio 80/20 is chosen, because in previous publication [2] it was shown that this particular concentration was the most effective from adhesion perspective.

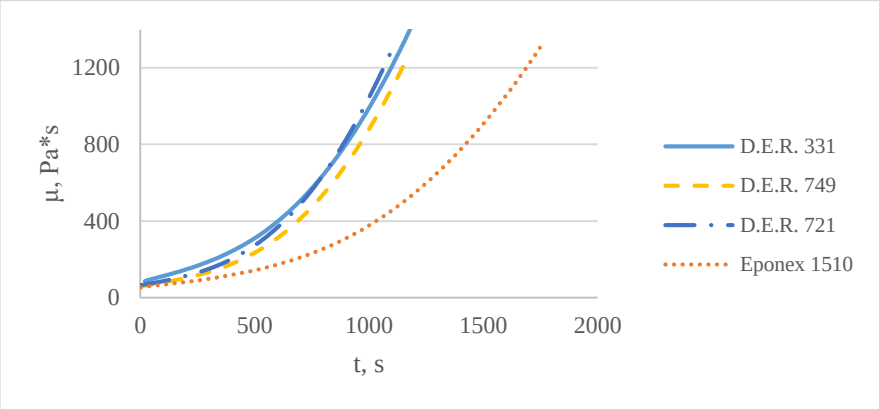

Figure 4. Viscosity change in time of two component SIL/EP system

Results show that three of four epoxide type raw materials (D.E.R. 331, D.E.R. 749 and D.E.R. 721), when mixed with SIL, influence viscosity growth of the respective two-component systems almost in the same way, testifying that these epoxy compounds influence SIL curing similiary. Viscosity growth rate of Eponex 1510 containing SIL is considerably smaller in comparison to the rest of the recipes, i.e., time at cross-over point of Eponex 1510 containing system is ca 1500 s in respect to ca 800-1000 s, characteristic for other investigated two-component systems. Besides it one can observe that cross-over moluli of D.E.R. 331, D.E.R. 749 and Eponex 1510 containing systems are higher than that of D.E.R. 721 containing system, denoting to the development of more resistant 3D network in the former case, which is also consistent with tensile strength at break values of the respective SIL/EP two-component systems.

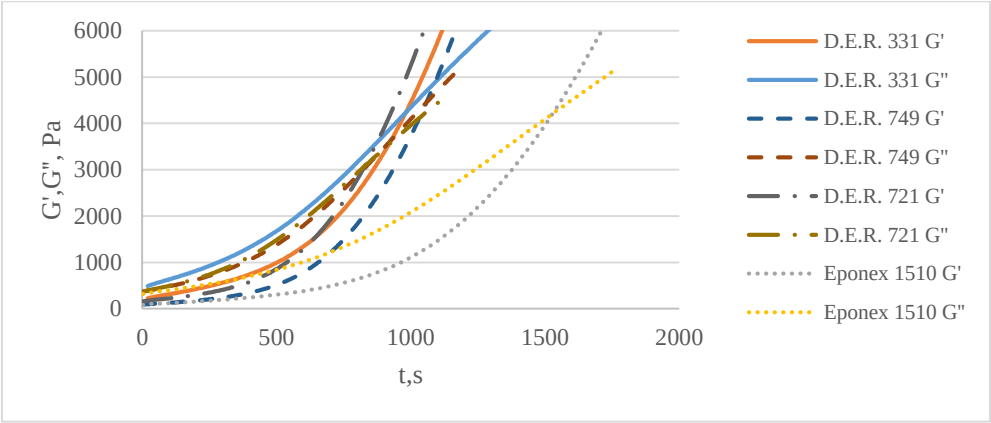

Figure 5. Elastic and viscous moduli growth in time of two component SIL/EP system

3.3. Lap shear test.

Lap shear test results show that addition of three (D.E.R. 331, D.E.R. 749 and Eponex 1510) of four EPs to SIL at ratio of 20/80 ensures good adhesion to stainless steel and wood. Eponex 1510 containing system possesses the highest shear strength values to the both previously mentioned substrates. Let's

mention that this composition demonstrates also the highest values of tensile strength at break and cross-over modulus. It is especially interesting to note that D.E.R. 749 containing system ensures also good adhesion to PVC after 28 days of curing, although its overall shear strength values to stainless steel and wood are somewhat lower in comparison to those with D.E.R. 331 and Eponex 1510. Better adhesion of D.E.R. 749 containing systems to PVC could be explained by considering its greater polarity in comparison to other epoxy compounds, considered in this research. It is also hypothesized that shear strength to stainless steel and wood as well as tensile strength at break of this high functionality (4) epoxy compound containing systems potentially could be increased by using structurally similar 3-functional epoxy compound due to the reduced density of the 3D network and hence increased evolution of tensile strength because of greater flexibility of the structure. In contradiction to other investigated systems the system with D.E.R. 721 shows low adhesion to all the substrates, which is one more indication that mono-functional epoxy compounds can't ensure the necessary adhesion to the substrates, highly attractive in the adhesives and sealants market, because they tend to block chain ends of the SIL.

Table 2. Lap shear test results of the investigated SIL/EP 80/20 compositions to various substrates

Substrate	Days	Epoxide type							
		D.E.R. 331		D.E.R. 749		D.E.R. 721		Eponex 1510	
		σ_{break} [MPa]	ε_{break} [%]	σ_{break} [MPa]	ε_{break} [%]	σ_{break} [MPa]	ε_{break} [%]	σ_{break} [MPa]	ε_{break} [%]
PVC	7	0.16	1.52	0.33	5.26	0.44	36.0	0.29	8.13
	28	0.21	9.00	3.51	42.0	0.50	32,0	0.38	4.69
Stainless steel	7	5.78	17.1	4.26	20.4	0.48	20,7	5.95	23.6
	28	5.50	14.5	4.34	27.1	0.47	30.0	5.81	36.0
Wood	7	4.20	21.1	3.32	32.4	0.28	16.0	4.43	36.4
	28	4.30	30.0	3.52	30.8	0.49	30.2	4.62	26.3

4. Conclusions

The influence of the addition of various structurally different epoxy compounds (mono-functional D.E.R. 721, bi-functional D.E.R. 331 and Eponex 1510 and tetra-functional D.E.R. 749) on the rheological, indentation, tensile and adhesion properties of polyether silyl-terminated pre-polymer two-component systems is investigated.

It has been revealed that:

- epoxide content and structure both significantly affect mechanical properties of the silyl-terminated polymer composite - values of the tensile strength at break change in the range of 0.22-4.06 MPa, tensile deformation in the range of 25-1527% and Shore A hardness in the range of 4-96;
- curing speed of the three of four epoxide compounds is practically the same, except of Eponex 1510, which cures slower;
- D.E.R. 749 containing composition ensures adhesion to all the tested substrates, including stainless steel, wood and polyvinylchloride, showing shear strength above 3 MPa after 28 days of curing;
- D.E.R. 721 containing system shows decreased adhesion to all the substrates, but because of high elongation values these compositions are perspective to create materials with exceptionally high flexibility.

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