



## Effect of amine containing compatibilizers on mechanical and rheological properties of a two-component silyl-terminated polyether/epoxy resin system

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**Abstract.** In this work we study the influence of compatibilizers on tensile and rheological properties of new silyl-terminated polyether/epoxy resin two-component systems. Considering that in the investigated multicomponent systems silyl-terminated polyether cannot react directly with epoxy groups, use of appropriate compatibilizers is essential. The results of the current research showed that some of the investigated amine containing compatibilizers (*N*-(*n*-butyl)-3-aminopropyltrimethoxysilane and bis[3-(trimethoxysilyl)propyl]amine) improved the tensile strength of the silyl-terminated polyether/epoxy resin two-component systems by more than 2.5 times.

**Key words:** silyl-terminated polyether, silane, compatibilizers.

### 1. INTRODUCTION

The adhesives and sealants industry is constantly growing and so are the requirements for the respective materials. There are only a few materials that can reach high tensile strength values while maintaining a relatively high elongation, the behaviour highly required in the automotive, shipbuilding, construction, and many other industries. One of the materials that has a potential to be used for these applications is the two-component silyl-terminated polyether/epoxy resin system [1,2]. In our earlier work it was shown that a secondary amine compatibilizer, namely *N*-(*n*-butyl)-3-aminopropyltrimethoxysilane, can be successfully used to improve exploitation properties of silyl-terminated polyether/epoxy resin systems [3].

In the work reported here we investigated the effects of different types of aminosilanes (primary, secondary, and secondary amine with bifunctional silane groups) and their concentrations on the mechanical properties of various silyl-terminated polyether/epoxy resin two-component systems. We also investigated rheological properties of a neat polymer and blends of silyl-terminated polyether with epoxy resin compatibilized with different aminosilanes.

### 2. EXPERIMENTAL METHODS

Silyl-terminated polyether (SIL) was mixed with epoxy resin (EP) at various weight proportions starting from 100/0 to 30/70, respectively. Compatibilizers, namely 3-aminopropyltrimethoxysilane (*am*), *N*-(*n*-butyl)-3-aminopropyltrimethoxysilane (*sam*), and bis[3-(trimethoxysilyl)-

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propyl]amine (*bsa*), were added at different weights (0.5, 1.5, and 2.5 g) to 100 g of the polymer matrix and compared with a series without any compatibilizer. As catalysts Tibcat 216 (dioctyltin dilaurate), Ancamine K54 (tris(dimethylaminomethyl)phenol), and water were used. The mixture compositions are shown in Table 1.

The blends were mixed using a SpeedMixer DAC 150 centrifugal laboratory mixer, cast in Teflon moulds, and cured at standard conditions ( $23 \pm 2$  °C,  $50 \pm 5\%$  relative humidity) for 1, 7, and 28 days.

The rheological measurements were performed by using a Bohlin CVO 100 rotation rheometer. The instrument was equipped with a 20 mm parallel plates geometry spindle (gap size 1000  $\mu\text{m}$ ). The tests at 25 °C were performed in the oscillation mode at a frequency of 1 Hz and strain 0.006.

The tensile stress–strain measurements were done by using a Zwick/Roell Z010 universal testing machine. The tests were made according to ISO 527 [4] at test speed 100 mm/min. Curing dynamics was evaluated by performing Shore A hardness measurements.

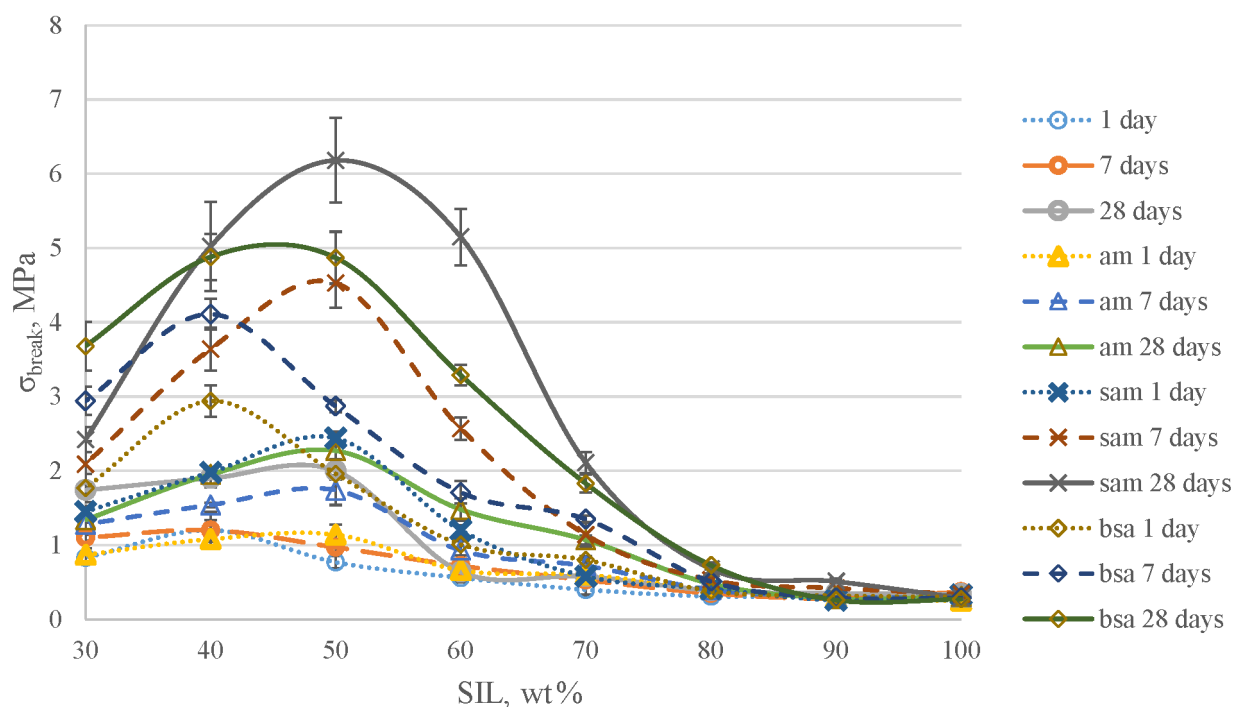
### 3. RESULTS AND DISCUSSION

#### 3.1. Tensile stress–strain test of SAX 520/D.E.R. 331 blends with compatibilizers

The tensile strength increased when the EP amount in the composition was higher and reached its maximum values depending on the compatibilizer type when the prepolymers ratio was 50/50 or 40/60, whereas at higher epoxy resin contents  $\sigma_{\text{break}}$  started to decrease (Fig. 1).

**Table 1.** Compositions of the investigated silyl-terminated polymer/epoxy resin (SAX 520/D.E.R. 331) systems

Component	Weight proportion								
SAX 520	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	
Ancamine K54	0	0.66	1.33	2	2.66	3.33	4	4.66	
Water	0.67	0.6	0.53	0.47	0.4	0.33	0.27	0.2	



**Fig. 1.** Tensile strength ( $\sigma_{\text{break}}$ ) of silyl-terminated polyether/epoxy resin (SIL/EP: SAX 520/D.E.R. 331) blends without and with 3-aminopropyltrimethoxysilane (*am*), *N*-(*n*-butyl)-3-aminopropylmethoxysilane (*sam*), and bis[3-(trimethoxysilyl)propyl]amine (*bsa*) compatibilizers.

After 1 day of curing the blend without a compatibilizer showed a maximum tensile strength of 1.2 MPa (prepolymers ratio 40/60). The tensile strength increased with time and reached its maximum value of 2.15 MPa after 28 days at the SIL/EP ratio of 50/50.

The impact of *am* on mechanical properties was small during the whole testing time compared to compositions without silane. This compatibilizer only contributed to the branching of the system and its maximum tensile strength value in time changed from 1.14 to 2.27 MPa. The maximum in the  $\sigma_{\text{break}}(\text{SIL})$  relationship of the silane *am* compatibilized systems was observed at the SIL/EP ratio of 50/50.

Silanes with secondary amine groups *sam* and *bsa* had a larger impact on tensile strength values of the material. Even after 1 day of curing blends with *sam*, the tensile strength was 2.27 MPa at the SIL/EP ratio of 50/50, and also the blend with *bsa* showed an excellent tensile strength value of 2.94 MPa at the polymers ratio of 40/60. After 1 day of curing, these values were 1.6 (*sam*) and 2.4 (*bsa*) times larger than the maximal value without a compatibilizer. After 28 days, the blends with *sam* and *bsa* silanes showed at the SIL/EP ratio of 50/50 their maximal tensile strength values of 6.18 and 4.87 MPa, respectively, which are 3 and 2.5 times larger than the maximum value of the blend without a compatibilizer.

Tensile deformation values were quite similar. The impact of compatibilizers on the material deformation was not great.

The Shore A values of the investigated compositions rose at the higher EP amounts in the composition. Figure 2 shows that the addition of *am* silane did not have any considerable effect on the compositions hardness, whereas the addition of *sam* and *bsa* silanes increased the Shore A hardness compared to the composition without a compatibilizer. Increased values of mechanical properties, including hardness, may be evidence of better reactivity between the functional groups of the compatibilizer and terminal epoxy and silyl groups of the respective polymers.

According to previous results [1–3], the composition with *sam* has the greatest impact on the mechanical properties of the material. In all previous experiments the silane content was 1.5 g. As this amount of silane might be not optimal, we made compositions with different concentrations of *sam*. Mechanical properties were analysed after 1 day and 28 days of curing.

Figure 3 illustrates differences in tensile strength after 1 day and 28 days of curing with *sam* as the compatibilizer. After 1 day of curing the highest value (3.04 MPa) was shown by the blend with a *sam* content of 2.5 g at the SIL/EP ratio of 40/60. When the silane amount was smaller, the values of the tensile strength

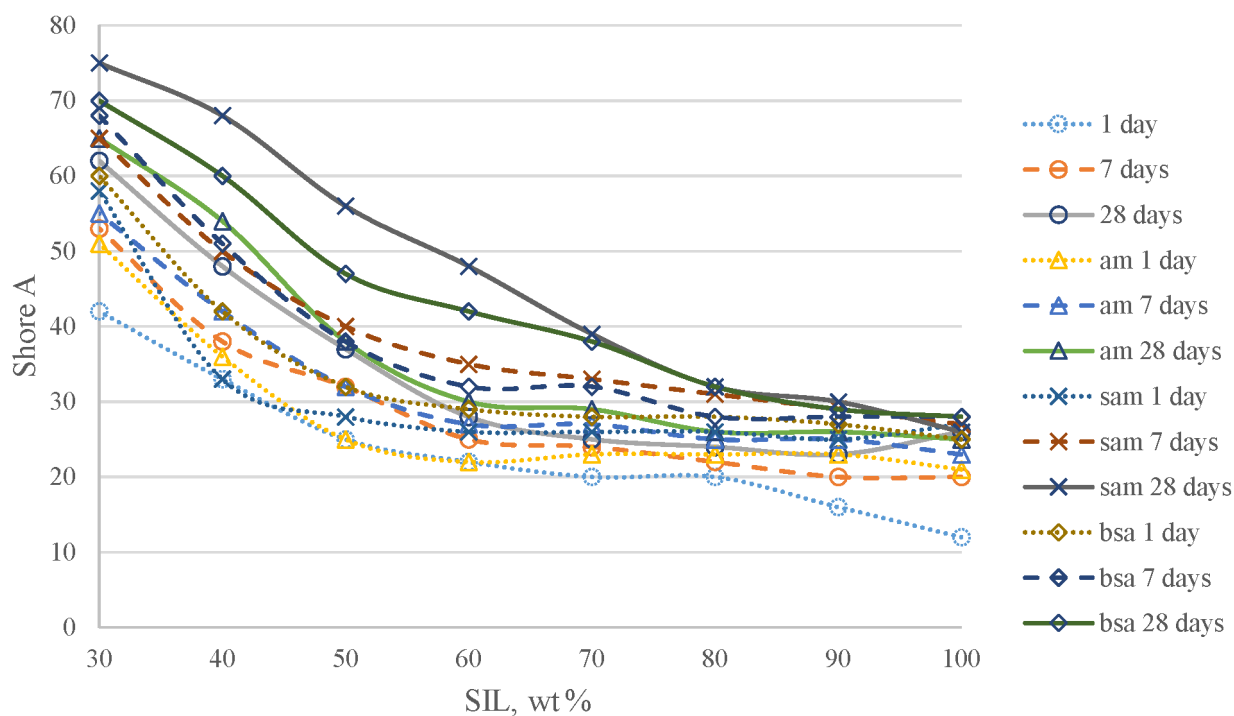
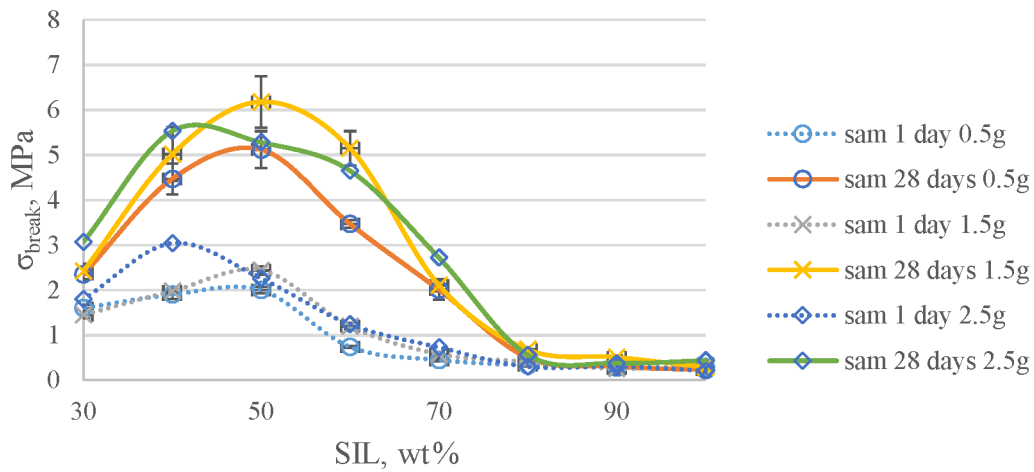


Fig. 2. Shore A value of SIL/EP blends without and with *am*, *sam*, and *bsa* compatibilizers. For abbreviations, see Fig. 1.



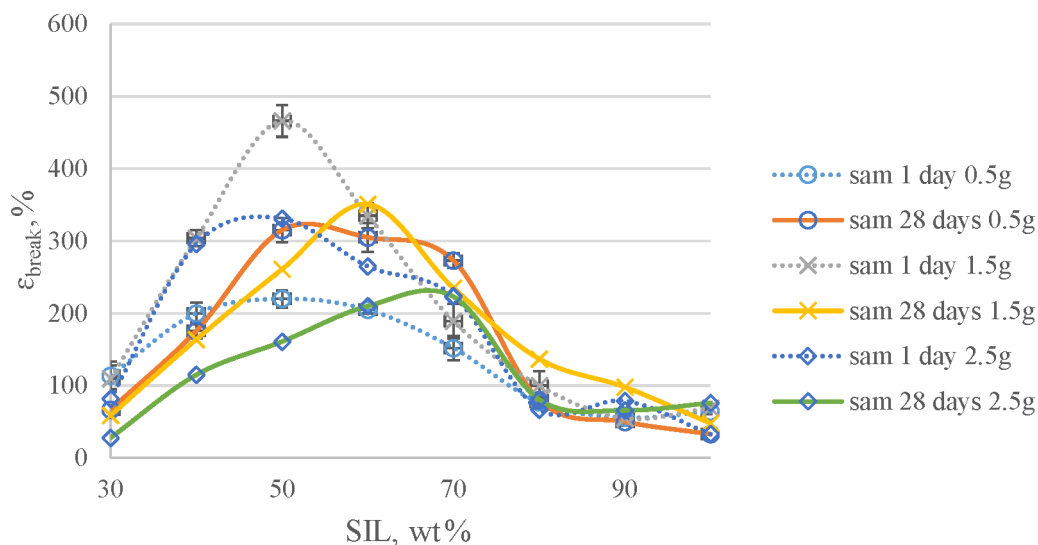
**Fig. 3.** Tensile strength ( $\sigma_{\text{break}}$ ) of SIL/EP blends with the *sam* compatibilizer at different silane contents per 100 g of the polymer. For abbreviations, see Fig. 1.

were lower. This effect indicates that silane is an important part of the system and at a higher silane content the polymer network will be built faster.

After 28 days of curing, the most effective blend was at a silane *sam* concentration of 1.5 g per 100 g of the polymer (6.18 MPa) at the SIL/EP ratio of 50/50. When the silane content was 2.5 g, the tensile strength value dropped to 5.53 MPa because silane works also as a crosslinking agent and so the material became too rigid (see Fig. 4). Figures 3 and 4 also

show that the silane the content of 0.5 g is too small to reach the potentially maximal mechanical values of the system.

Shore A values for all the compositions showed a similar trend: they increased when the amount of silane was raised in the composition. After 28 days of curing the highest value of Shore A hardness (80 units) was observed for silane *sam* compatibilized blends at the SAX 520/D.E.R. 331 ratio of 30/70.



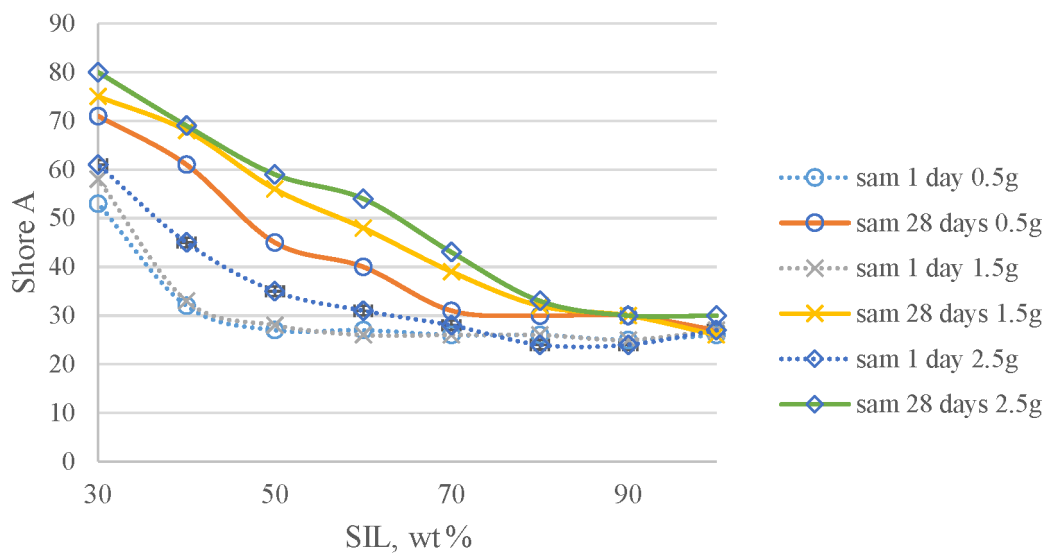
**Fig. 4.** Tensile deformation ( $\epsilon_{\text{break}}$ , %) of SIL/EP blends with the *sam* compatibilizer at different silane contents per 100 g of the polymer. For abbreviations, see Fig. 1.

### 3.2. Rheological characteristics

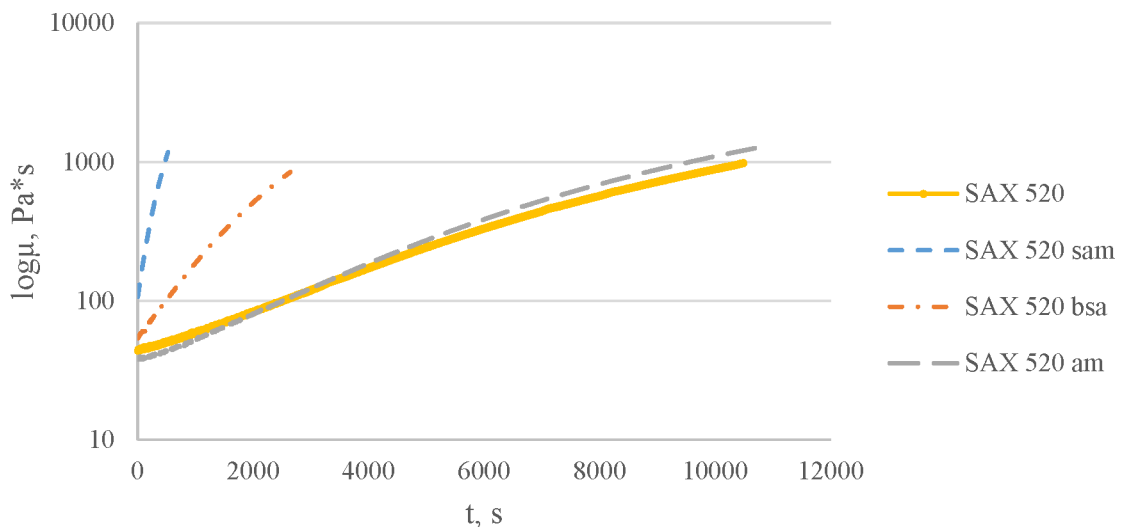
For rheological tests we analysed neat SAX 520 based blends and their compositions with D.E.R. 331 in the range of ratios from 60/40 to 40/60. The compatibilizers *sam* and *bsa* had a significant influence on the curing speed of the neat SAX 520 based blend. Complex viscosity as well as elastic and viscous moduli time relationships of SAX 520 blends (Figs 6 and 7) show that the silanes *bsa* and, especially, *sam* made curing

faster by reaching crossover moduli 3470 Pa at 2549 s and 4700 Pa at 491 s, respectively.

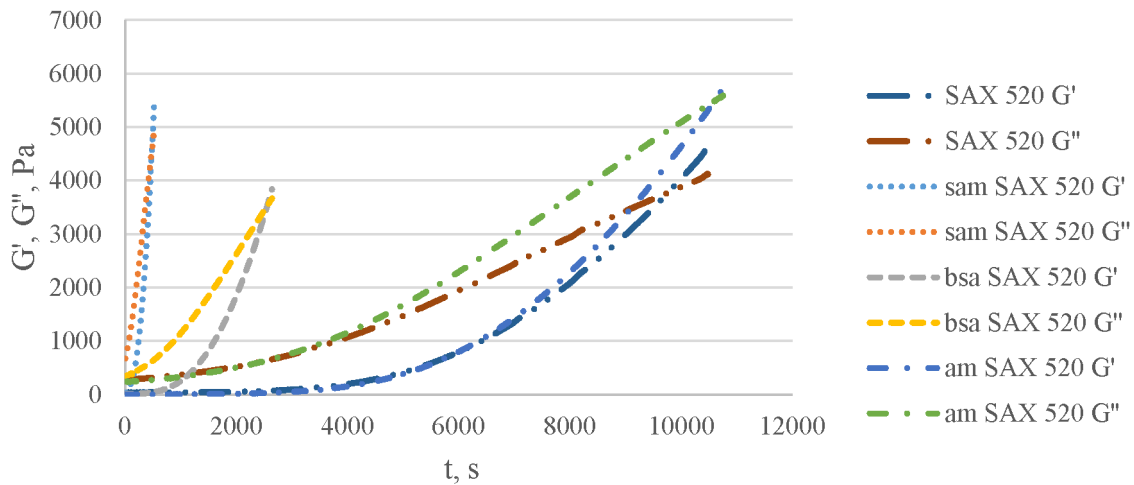
Figures 8, 9, and 10 show the growth of the elastic and viscous moduli of SIL/EP blends (60/40; 50/50; 40/60). Compositions with a larger EP content showed higher Shore A values (see Fig. 5). The same analogy can be attributed to crossover moduli. As an example, the composition with silane *sam* at the SIL/EP ratio of 60/40 has a crossover modulus 4600 Pa (Fig. 8), while by increasing the EP content to 60% the crossover



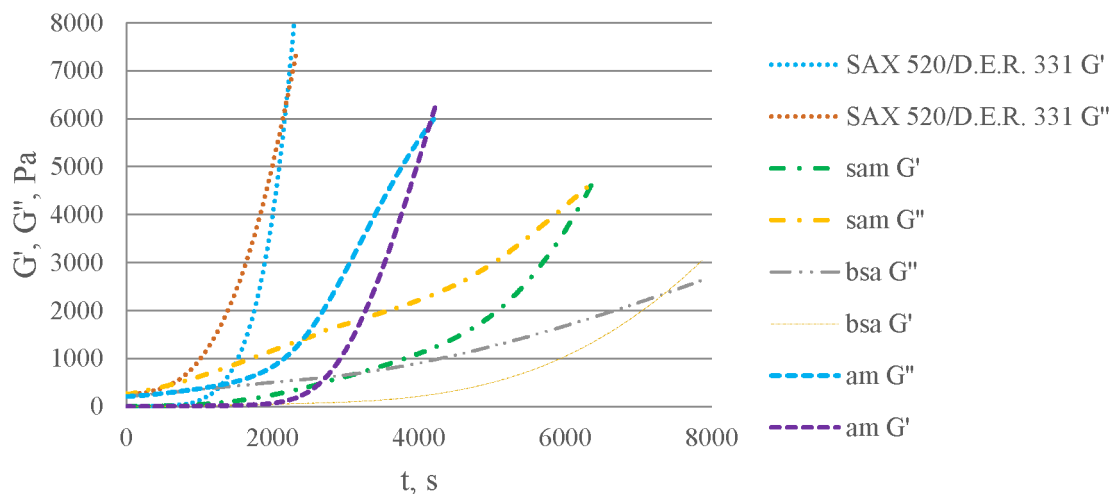
**Fig. 5.** Shore A hardness of SIL/EP blends with the *sam* compatibilizer at different silane contents per 100 g of the polymer. For abbreviations, see Fig. 1.



**Fig. 6.** Growth of the logarithm of complex viscosity of SIL blends with and without compatibilizers as a function of time. For abbreviations, see Fig. 1.



**Fig. 7.** Growth of elastic ( $G'$ ) and viscous ( $G''$ ) moduli of SIL blends with and without compatibilizers as functions of time. For abbreviations, see Fig. 1.

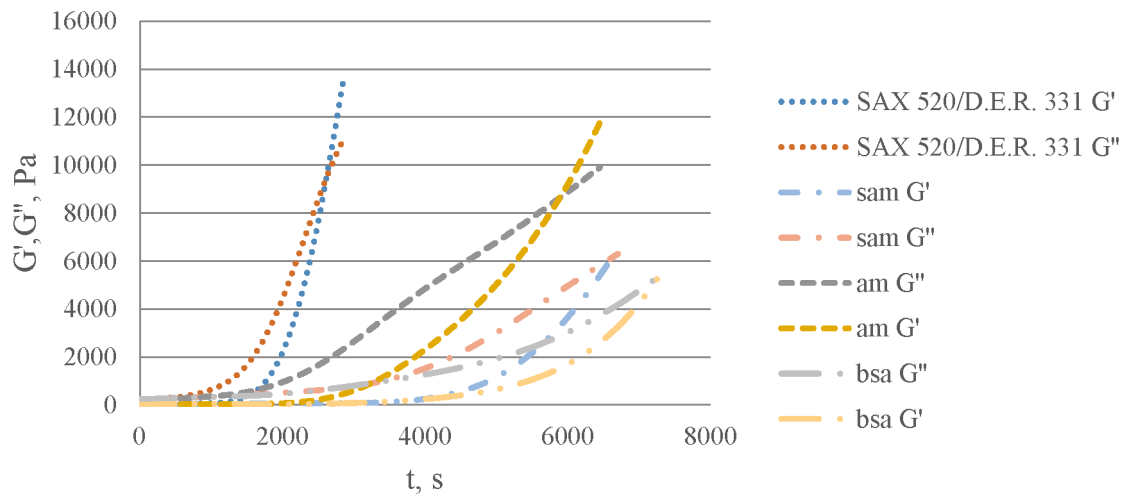


**Fig. 8.** Growth of elastic ( $G'$ ) and viscous ( $G''$ ) moduli of SIL/EP (60/40) compositions with and without compatibilizer as functions of time. For abbreviations, see Fig. 1.

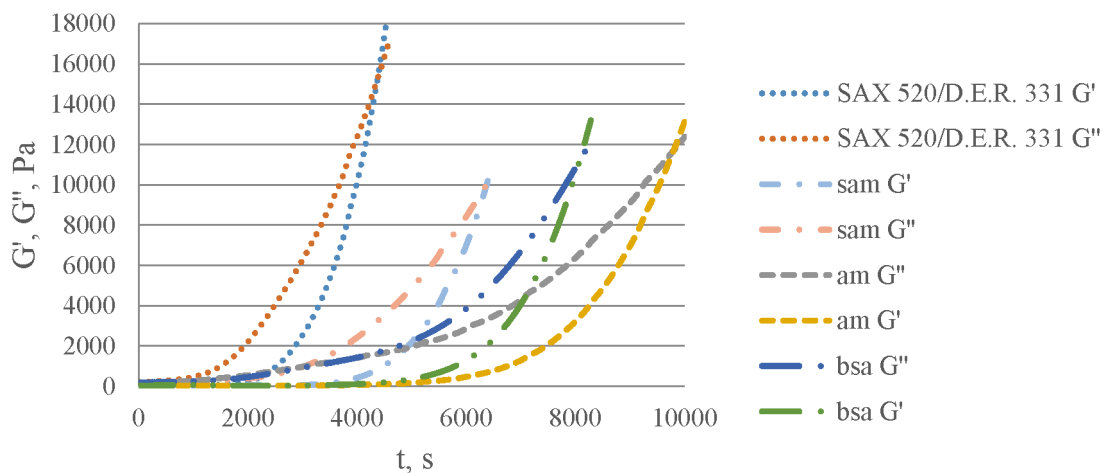
modulus reaches 9860 Pa (Fig. 10). This confirms that the system becomes more rigid if the EP content is higher.

Rheological properties of SIL/EP blends show that the addition of silanes *sam* and *bsa* to the system did not change the reaction speed significantly when the polymer was changed. The crossover modulus of *sam* compatibilized systems was observed after 6338 s (4600 Pa) at the SIL/EP ratio of 60/40, after 6440 s (6030 Pa) at the SIL/EP ratio of 50/50, and after 6362 s (9860 Pa) at the SIL/EP ratio of 40/60. For the *bsa* compatibilized systems the crossover modulus was

observed after 7352 s (2320 Pa) at the SIL/EP ratio of 60/40, after 7229 s (5170 Pa) at the SIL/EP ratio of 50/50, and after 7954 s (10 100 Pa) at the SIL/EP ratio of 40/60. In the case of the blend without a compatibilizer and the silane *am* treated system the crossover moduli changed to a greater extent as a function of the polymer content. Compositions with the compatibilizer *am* showed the crossover modulus after 4058 s (5450 Pa) at the SIL/EP ratio of 60/40, after 5822 s (8340 Pa) at the SIL/EP ratio of 50/50, and after 9700 s (11 100 Pa) at the SIL/EP ratio of 40/60. This leads to a conclusion that *sam* and *bsa* are preferable to *am* as compatibilizers.



**Fig. 9.** Growth of elastic ( $G'$ ) and viscous ( $G''$ ) moduli of SIL/EP (50/50) compositions with and without compatibilizer as functions of time. For abbreviations, see Fig. 1.



**Fig. 10.** Growth of elastic ( $G'$ ) and viscous ( $G''$ ) moduli of SIL/EP (40/60) compositions with and without compatibilizer as functions of time. For abbreviations, see Fig. 1.

#### 4. CONCLUSIONS

Compatibilizers containing an amine group (*am*, *sam*, *bsa*) had different impacts on mechanical and rheological properties of SIL/EP systems. We observed that *sam* and *bsa* significantly improved the mechanical properties compared to blends without a compatibilizer and with *am*. For example, after 28 days of curing the maximal tensile strength of *sam* compatibilized compositions was 6.18 MPa, which is 2.72 times higher than for the blend without a compatibilizer. The most

effective concentration of *sam* was 1.5 g per 100 g of the polymer.

The *sam* and *bsa* compatibilizers significantly influenced also the rheological behaviour of the investigated SIL/EP systems. For example, in the *sam* compatibilized SIL/EP systems the crossover modulus was observed approximately at the same time regardless of the SIL/EP ratio, indicating that *sam* silane is a good compatibilizer for a SIL/EP system. Blends without a compatibilizer and *am* compatibilized systems had crossover moduli at different times.

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## REFERENCES

1. Bitenieks, J., Merijs Meri, R., Zicans, J., Berzins, R., Umbraško, J., and Reknens, U. Modified silyl-terminated polyether polymer blends with bisphenol A diglycidyl ether epoxy for adhesive applications. *IOP Conf. Ser.: Mater. Sci. Eng.*, 2016, **111**, 012017.
2. Bitenieks, J., Merijs Meri, R., Zicans, J., Berzins, R., Umbraško, J., and Reknens, U. Rheological, mechanical and adhesion properties of two component adhesive based on modified silyl-terminated polyether polymer and epoxy resin. *IOP Conf. Ser.: Mater. Sci. Eng.*, 2016, **111**, 012018.
3. Berzins, R., Merijs Meri, R., and Zicans, J. Compatibilizers effect on silyl-terminated polyether/epoxy resin system mechanical and rheological properties. *Key Eng. Mater.*, 2017, **721**, 441–445.
4. International Organization for Standardization. ISO 527-1:2012. Plastics -- Determination of tensile properties -- Part 1: General principles.

## Amiine sisaldavate sidusainete mõju kahekomponentsele silüül-lõpurühmadega polüetrile

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On uuritud sobitusainete mõju uute, silüül-lõpurühmadega kahekomponentsete polümeer/epoksüvaiksüsteemide tõmbe- ja reoloogilistele omadustele. Asjakohaste sobitusainete kasutamine on hädavajalik, kuna uuritud mitmekomponentsetes süsteemides ei saa silüül-lõpurühmadega polüeeter epoksüvaigu epoksürühmadega vahetult reageerida. Käesoleva uuringu tulemused näitasid, et mõned amiini sisaldavad sobitusained (*N*-(*n*-butüül)-3-aminopropüül-trimetoksüsilan ja bis[3-(trimetoksüsilüül)propüül]amiin) suurendavad silüül-lõpurühmadega kahekomponentsete polümeer/epoksüvaiksüsteemide tõmbetugevust enam kui 2,5 korda.