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**RHEOLOGICAL PROPERTIES
OF THE POLYURETHANE ADHESIVES**

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In this contribution, the results of measurements are presented concerning rheological and mechanical properties of polyurethane adhesives used in the automotive industry. The work is focused on the determination of rheological characteristics of the individual components of polymeric adhesives tested and on rheological and mechanical properties of the adhesives in the hardening process. Experiments were performed with one type of single-component adhesive and three types of two-component adhesives. All the components of PUR adhesives tested were viscoplastic with a certain degree of yield stress. The respective flow curves showed a shear-thinning and thixotropic behaviour; the results of oscillatory tests demonstrating that elastic behaviour dominated for all adhesive components. The elasticity of an adhesive evidently depended on their mixing ratio. Finally, it has been found out that adhesive gelation points measured in the hardening process could be detected much faster at a higher temperature than at a lower one.

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Introduction

Adhesives are used by mankind for thousands years. In recent years, the possibility of joining materials with the aid of adhesives has rapidly increased in all industry sectors; glued joints becoming a great alternative to mechanical connections in many engineering applications.

They provide uniform distribution of a tension along the bonded area, thus enhancing rigidity, a better distribution of the load, as well as reducing the weight and cost of acquisition and operation of the item of interest [1-3]. Proper determination of rheological properties of the adhesive and its components can be a good guide for application design and specification of apparatus technology nodes in the bonding process.

Experimental

The rheological and mechanical properties of polyurethane adhesives were measured for a description of behaviour of the samples tested, when the respective experiments were performed with one type of the single-component adhesive and three types of two-component adhesives. Typical features of the adhesives tested are summarized in Table I.

For measuring rheological properties of the individual adhesive components — i.e., yield stress, flow curves, thixotropy, three-step thixotropy, oscillatory tests, creep and recovery, plus stickiness —, a rotational rheometer Haake Mars (Thermo Fisher Scientific, USA) was employed using the cone-plate and plate-plate measuring systems at the temperatures of 23, 37, and 50 °C. To obtain the adhesive gelation times, a rheometer Ares (TA Instruments, USA) was employed with the plate-plate measuring system at the temperatures of 23 °C and 50 °C.

The dynamic mechanical analyser DMA DX04T (RMI, the Czech Republic) was used for glass transition determination; the adhesive tensile tests in the hardening process being performed on universal testing machine Zwick Z050 Roell (Zwick Roell Group, Germany).

Results and Discussion

Flow Curves

In this case, equilibrium flow curves were measured, the purpose of which was to stabilize the balance (shear stress values) between the individual measurement steps. The measurement range of deformation rates was 0.01-300 s⁻¹ and back. The experiment always took thirty steps, both in the range of increasing and decreasing

deformation rate. Time to reach equilibrium for a given measured point of the curve was set to a maximum of 20 s.

Table I Tested materials

The number of components	Type adhesive	Component	Composition	Mixing ratio (A : B)
1	Sikaflex (Sika Automotive)	Sikaflex	Isocyanate functional groups and additives	100 : 2
		Sikaflex booster	Hydroxyl functional groups	
2	Sikaforce (Sika Automotive)	Sikaforce A	Polyols containing inorganic fillers and additives	100 : 17
		Sikaforce B	Isocyanates and additives	
	Axson (Axson Technologies)	Axson A	Polyols containing inorganic fillers and additives	100 : 53
		Axson B	Isocyanate mixtures containing inorganic fillers and additives	
Betamate (Dow Automotive)	Betamate A	Isocyanate functional groups and additives	100 : 100	
	Betamate B	Polyols containing inorganic fillers and additives		

All the tested components of PUR adhesives were viscoplastic with a certain degree of the yield stress (see Fig.1). The pathway of the flow curves (upward) showed a shear–thinning behavior. With the increasing temperature, the measured value of viscosity decreased; the shear–thinning behavior having also decreased. This information was also confirmed by calculations of parameters according to the Herschel–Bulkley’s model.

Thixotropy

The area between the upward and downward pass of flow curves also pointed to thixotropic behaviour, decreasing with the increasing temperature. The results of loop area are listed in Table II, showing that sample Betamate B has the maximum at all measured temperatures.

Table II Thixotropy loop areas

Material	Thixotropy loop area, Pa s ⁻¹		
	23 °C	37 °C	50 °C
Axson A	2.10×10 ⁵	5.88×10 ⁴	3.93×10 ⁴
Axson B	6.02×10 ⁵	1.46×10 ⁵	2.64×10 ⁴
Betamate A	9.18×10 ⁵	8.12×10 ⁴	1.38×10 ⁴
Betamate B	1.37×10 ⁶	5.53×10 ⁵	3.95×10 ⁵
Sikaforce A	5.24×10 ⁵	3.09×10 ⁴	1.24×10 ⁴
Sikaforce B	7.78×10 ³	2.38×10 ³	1.31×10 ³

To obtain information about thixotropy, the three-step tests were made, too. Such tests can provide information about whether the structure is to be fully restored within the test time range. The rotor maintained a constant deformation velocity in three subsequent sequences: 0.1 s⁻¹ for 60 s; then, 100 s⁻¹ for 30 s, and finally again 0.1 s⁻¹ for 60 s. These three-step tests had showed that the structure of majority tested adhesives did not regenerate completely, which could be detected as a false thixotropy (partial regeneration). The values of the renewed viscosity were about 70 % of the original ones (see Fig.2).

Oscillatory Tests

At first, the amplitude sweep test for finding a region of linear visco-elasticity was made (see Fig.3); the respective measurement being performed in the CS mode, which means a shear stress control within a range of 0.01-100 Pa and a constant frequency of 1 Hz. The dependence of the accumulated modulus, the loss modulus and the complex viscosity on the shear stress was also measured, where the subsequent evaluation revealed a linear region in which the shear stress value from the linear viscoelasticity range can be determined. This value was later used for the frequency oscillatory test.

The second oscillation test was based on the previously determined shear stress value in the linear viscoelasticity region, in this case being set as a constant

shear stress value; the measurements themselves ranging from 0.1-80 Hz. The same dependence was recorded as that in the previous case.

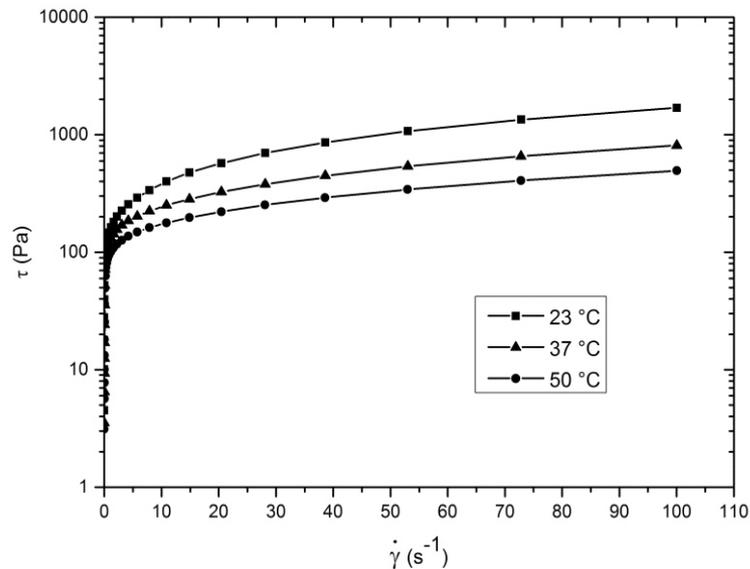


Fig. 1 Example of the flow curve of Sikaforce A component

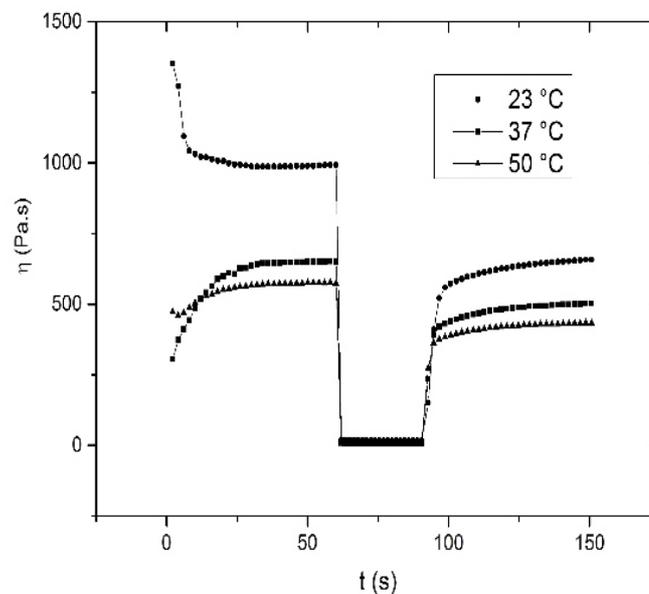


Fig. 2 The three-step test of Sikaforce A component

The intersection of the accumulated and loss modul ($G' = G''$) could be recorded, allowing us to determine change of the response of the material at a different time scale. In general, the frequency tests could infer the degree of elasticity of the adhesive at various frequencies. The results of frequency tests demonstrated that elastic behaviour had been dominant for all adhesive components. The values of the accumulated modules were many times higher than those for the loss modulus and also the value of the loss angle sometimes exceeded

45°. It was obvious that the isocyanate based components exhibited a significantly higher elasticity compared to the components based on polyols (Fig. 4).

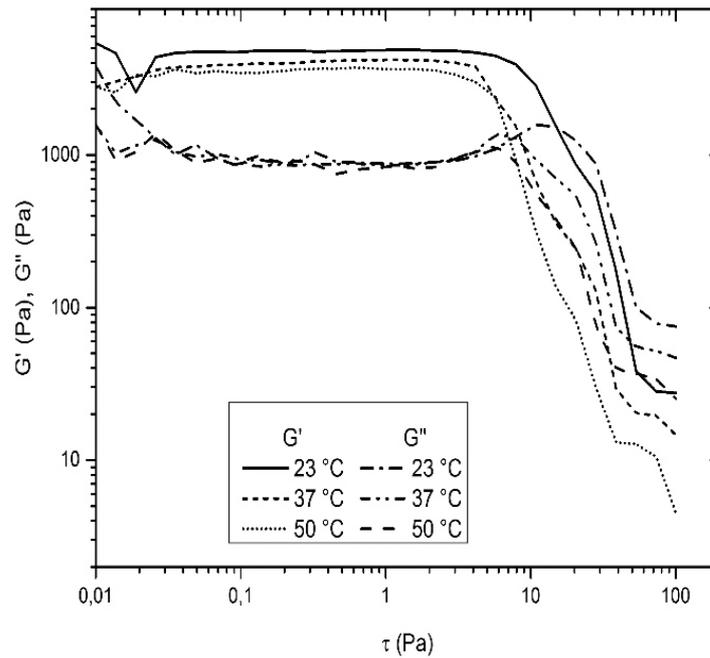


Fig. 3 The amplitude sweep test of Sikaforce B component

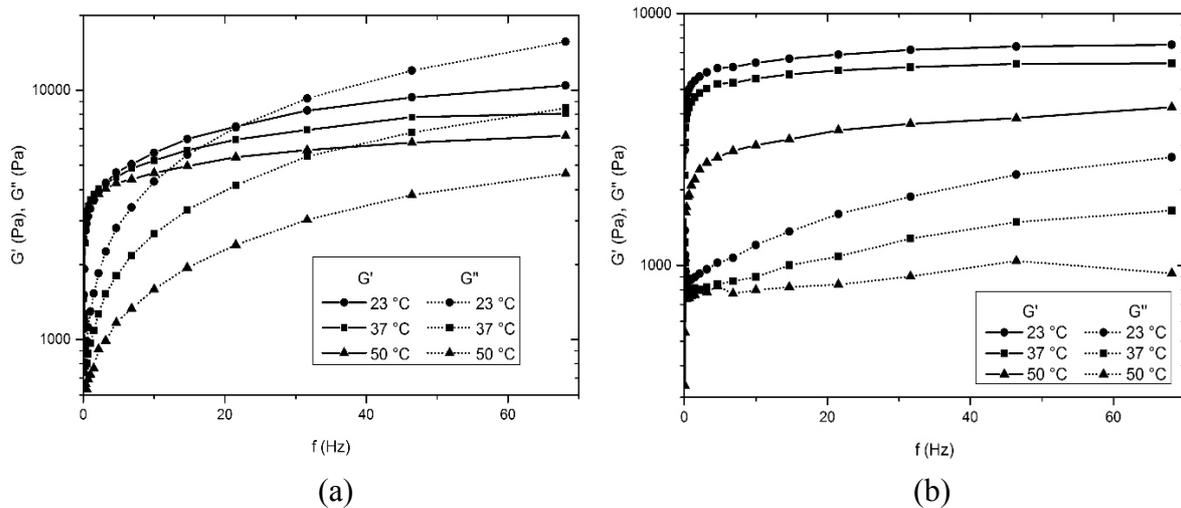


Fig. 4 The frequency sweep test of Sikaforce A (a) and Sikaforce B (b) components

Finally, the values of the intersections of the accumulated and loss moduli have provided optimal conditions for the mixing of individual components together, because the predominant viscous properties of components ensure a better coverage of the substrate and a common handling of the adhesive.

Creep and Recovery Test

The creep and recovery test was carried out in the CS mode and the measurement itself consisted of two parts. The first part of the creep comprised the application of a constant shear stress 1 Pa on a given sample for 120 s. The stress value was then determined by the amplitude sweep test within the range of linear viscoelasticity. In the second phase of the test, the tension was released and the sample left to recover for 120 s. Creep and recovery test have confirmed the elastic behavior of the polyurethane adhesives and, with the increasing temperature, the deformation also increased.

Gelation Times

The gelation point was determined with the ARES rheometer using oscillatory torsional stress of the sample with a constant frequency of 1 Hz and a maximum deformation of 10 %. Gelation times were determined for each adhesive, always at two different temperatures. It was found out that adhesive gelation points measured in the hardening process could be detected much faster at a higher temperature than at a lower one (see Fig.5).

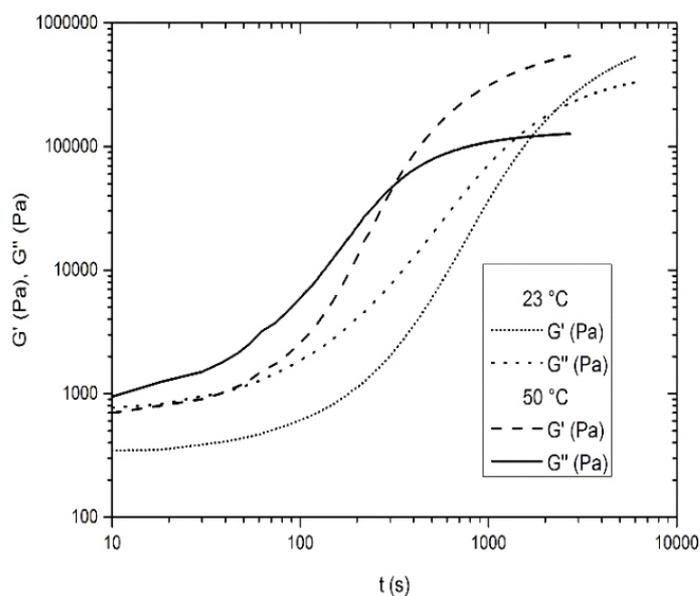


Fig. 5 Gelation times of the Sikaforce adhesive

As seen in the Table III, the gelation times for the two-component adhesives at room temperature (23 °C) were relatively long. At the temperature of 50 °C, the hardening process run in considerably shorter time, as the increased temperature greatly accelerated the hardening reaction. For one-component adhesives Sikaflex with booster, the hardening process was carried out at room temperature in a very

short time, when, at an elevated temperature, the gelation had occurred almost immediately. Without adding boosters to one-component adhesives Sikaflex, the hardening process did not appear.

Table III Gelation times of adhesives

Material	Gelation time, min	
	23 °C	50 °C
Axson	220.0	10.40
Betamate	15.4	0.97
Sikaflex + booster	2.2	-
Sikaforce	37.0	5.25

Glass Transition Temperature

The glass transition temperature was measured one and seven days after the beginning of the hardening process. The respective values were evaluated via the tangent of the loss angle. As found out, the glass transition temperature had the same value for measurements on the first and seventh day after the beginning of the hardening, except for the Axson sample, where the glass transition temperature decreased by 20 °C after seven days; see data in Table IV.

Table IV Glass transition temperature of adhesives tested

Material	Glass transition temperature, °C	
	After 1 day	After 7 days
Axson	-36	-56
Betamate	-39	-39
Sikaflex	-51	-51
Sikaforce	24	24

Tensile Tests

Test on the adhesive strength was carried out using the universal machine as mentioned above. Values of the adhesive strength were recorded again after one and seven days from the beginning of the hardening process as the relative value of the extension. The values of relative extension for adhesives used in the

automotive industry should achieve at least 150 %. After one day from the beginning of hardening, Axson adhesive showed a very small level of the tensile strength. A relative elongation, expressing the degree of elasticity of the adhesive, reached only 67 %. After seven days, the adhesive strength was more pronounced, but the relative elongation decreased by 40 %.

For other adhesives, the values of relative elongation had been significantly higher; the highest relative elongation, more than 400 %, was observed at the Sikaflex adhesive. This product also underwent the tensile test, revealing also a very good strength. The values of tensile strength and elongation are reported in Table V.

Table V The tensile strength and elongation of adhesive

Material	Characteristics	after 1 day	after 7 days
Axson	σ , MPa	0.33	3.10
	ε , %	67	22
Betamate	σ , MPa	6.25	7.97
	ε , %	140	126.5
Sikaflex	σ , MPa	4.8	4.91
	ε , %	472	403
Sikaforce	σ , MPa	2.13	2.52
	ε , %	188.5	193

Conclusion

All the components of the PUR adhesives tested have been found viscoplastic with a certain degree of yield stress. The character of the individual flow curves showed a shear-thinning and thixotropic behaviour. The three-step tests, carried out to obtain information about thixotropy, have revealed that the structure of a majority of the adhesives tested did not regenerate completely, which had been detected via the false thixotropy (partial regeneration). The values of the renewed viscosity were about 70 % of the original level.

The results of oscillatory tests have demonstrated that elastic behaviour is dominant for all the adhesive components; especially, the isocyanate-based components exhibited significantly higher elasticity compared to components based on polyols. Thus, the elasticity of an adhesive has evidently depended on the mixing ratio.

Furthermore, it has been found out that adhesive gelation points measured

in the hardening process could be detected much faster at a higher temperature than at a lower one. Finally, the glass transition temperatures of the adhesives were evaluated from the respective dependence by means of the tangent of the loss angle after one and after seven days from the beginning of the hardening process. From the tensile tests, the values of the tensile strength and of the relative elongation were obtained for each adhesive involved in the hardening process.

Acknowledgement

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