



Viscosity Testing of HTPB Rubber Based Pre-binders

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Abstract: This paper presents the test results of viscosity changes, versus time and temperature, for the HTPB rubber based pre-binders used in the manufacture of heterogeneous solid rocket propellants (HSRP). A Brookfield HADV-II+PRO viscometer with a small sample adapter (SSA) and SC4-18 spindle, including a TC-550SD water bath, was used for the tests. The components of the pre-binders tested were: HTPB-K domestic liquid synthetic rubber, R45M rubber, dioctyl adipate as the plasticizer, diisocyanate curing agents (DDI, IPDI) and various additives: triethanolamine (TEA), iron compounds, lecithin, glycerine and a solution of oxalic acid in glycerine, and difunctional aziridine amide. As a result of these tests, it was found that the additives have an influence on the viscosity versus time dependence. Moreover, the influence of temperature on the viscosity changes with time were compared for HTPB-K domestic rubber and R45M rubber based pre-binders. The experimental equations describing these changes were also determined.

Keywords: pre-binder, HTPB rubber, viscosity, heterogeneous solid rocket propellant

1 Introduction

In the technological process of manufacturing heterogeneous solid rocket propellants (HSRP), during the mixing process at elevated temperature, we are faced with a two-phase mixture of liquid and solid chemical substances. This has a semi-fluid consistency that becomes a compact liquid mass of a highly filled type of suspension after a definite period of time. By using the suspension casting process it is possible to form different shapes and sizes for special applications (propellants). Thus composite solid bodies with specific properties after a definite

period of time, depending on the curing temperature, can be created, *e.g.* ballistic properties that depend on the content of the burning rate modifiers in the HSRP.

The mixed liquid phase fulfilling the pre-binder function is a synthetic prepolymer with hydroxyl functional groups (α,ω -dihydroxypolybutadiene, known as HTPB), together with a plasticizer, a curing agent (diisocyanate) and/or a cross-linking agent (*e.g.* chemical compounds incorporating three hydroxyl groups or three isocyanate groups), that forms the polymer matrix after the curing process at elevated temperature (323-348 K).

The above suspension is characterized by a specific pot life. The latter is connected with the chemical reaction occurring between the rubber and the curing agent (*e.g.* between the OH and NCO groups) and with the apparent viscosity – important parameters for technological reasons.

The plasticizers used in an HSRP are typically esters such as dioctyl adipate ($[\text{C}_8\text{H}_{17}\text{OOC}(\text{CH}_2)_2]_2$, DOA), isodecyl pelargonate ($\text{CH}_3(\text{CH}_2)_7\text{COO}(\text{CH}_2)_7\text{CH}(\text{CH}_3)_2$) or tri-isooctyl phosphate ($(\text{C}_8\text{H}_{17}\text{O})_3\text{PO}$). The most appropriate and compatible plasticizer turns out to be DOA, whilst the most often used curing agents are dimeryl diisocyanate (DDI) or isophorone diisocyanate (IPDI) [1, 2].

Iron compounds (oxides), ferrocene and its derivatives, amongst others 2,2'-bis(ethylferrocenyl)propane (catocene), and copper chromate, $\text{Cu}_2\text{Cr}_2\text{O}_5$, are used as the burning rate modifiers. However, modifiers cause the curing process to accelerate, increasing the viscosity and at the same time shortening the pot life [2-6]. A strong catalytic influence of 2,2'-bis(ethylferrocenyl)propane on the cure process is observed for DDI cured pre-binders [7].

The aforementioned suspension is by nature a non-Newtonian fluid whose apparent viscosity (η_{av}) is the sum of the liquid phase viscosity (η_l) and the structural viscosity (η_s) [8]. Such a suspension viscosity is determined by the liquid phase viscosity (pre-binder) and its dependence on time and temperature.

2 Results and Discussion

The following materials were selected for testing: HTPB type rubbers *i.e.* R45M (from IPI) and HTPB-K manufactured under laboratory conditions in Poland [9], DOA plasticizer (from Boryszew ERG SA), curing agents DDI (from IPI) and IPDI (from Alfa Aesar GmbH & Co. KG), catocene (from Neo Organics) and TEA cross-linking agent (from POCH S.A.).

The curing agent quantity in relation to the HTPB prepolymer used was calculated in accordance with the following formula:

$$m_c = (\text{IR}) \text{EW}_c \sum (m_n / \text{EW}_n) \quad (1)$$

where:

m_c – curing agent mass,

IR – NCO/OH ratio,

EW_c – NCO mass equivalent of the curing agent,

m_n – mass of each liquid component containing OH groups,

EW_n – OH mass equivalent for the HTPB prepolymer and other liquid components containing OH groups.

The pre-binders were prepared in quantities of 7 cm³. The components were precisely measured into a beaker on a KERN EMB 600-2 electronic scale in the following sequence: HTPB prepolymer, DOA plasticizer, modifiers, curing agent, triethanolamine (TEA) cross-linking agent and other additives. The compositions of the mixtures prepared are presented in Tables 1 and 2.

The viscosity measurements were carried out by using a Brookfield HADV-II+PRO viscometer with a small sample adapter (SSA) and a SC4-18 spindle, and including a TC-550SD water bath. All measurements were carried out using Brookfield Rheocalc software and the same spindle type and model. The tests were performed in the automatic viscosity measurement mode, according to the programmed measurement procedure with the simple B.E.A.V.I.S (*Brookfield Engineering Advanced Viscometer Instruction Set*) programming language. The rotational speed of the spindle used was changed, depending on the maximum permissible viscosity measured at a particular rotational speed (in accordance with the programmed procedure).

According to Tajima and Crozier's suggestion [10] it was assumed that the variation of the viscosity (η_t) with the cure reaction time (t) has the following form:

$$\eta_t(t, T) = \eta_0(T) e^{k_\eta(T) \cdot t} \quad (2)$$

$$\ln[\eta_t(t, T)] = \ln[\eta_0(T)] + k_\eta(T) \cdot t \quad (3)$$

where $\eta_0(T)$ is the viscosity at $t=0$, and $k_\eta(T)$ is the rate constant for the increasing viscosity and the set initial temperature T .

Table 1. Compositions of the different HTPB rubber

Composition, [%]					
HTPB-K	R45M	TEA	DOA	Catocene	DDI
60.1875	-	1.25	12.5	3.125	22.9375
-	62.1875	1.25	12.5	3.125	20.9375

Table 2. Compositions of the pre-binders (test temperature T = 333 K)

Mixture	Composition, %										
	R45M	DOA	DDI	IPDI	Additives						
					TEA	nFe ₂ O ₃	Cu ₂ Cr ₂ O ₅	Catocene	OA+G	G	HX 752
L3	60.65	21.70	13.61		0.67			3.37			
L4	62.76	22.45	14.09		0.70						
L5	60.57	19.25	16.15		0.67			3.36			
L6	60.57	23.55	12.52					3.36			
L7	60.36	23.47	12.48					3.35	0.34		
L8	60.57	21.27	12.92	1.21	0.67			3.36			
L9	60.57	23.55	12.52			3.36					
L10	60	20 ^L	16		0.67			3.33			
L12	60	20 ^L	16		0.67		3.33				
L14	62.07	20.69 ^L	16.55		0.69						
L15	59.80	19.94 ^L	15.95					3.32	0.33		
L16	59.80	19.94 ^L	15.95			3.32			0.33		
L17	66.67	22.22		6.67	0.74			3.7			
L18	61.43	21.23	13.92					3.42			
L19	61.224	21.156	13.88					3.4	0.34		
L20	61.224	21.156	13.88					3.4		0.34	
L21	63.6	21.98	14.42								
L22	61.43	21.23	13.92			3.42					
L23	61.43	21.23	13.92					3.42 ¹			
L24	61.43	21.23	13.92					3.42 ²			
L25	61.43	21.23	13.92					3.42 ³			
L26	65.50	15.28	14.85					3.64			0.73
L27 T= 323 K	65.50	15.28	14.85					3.64			0.73
L28 T= 323 K	65.03	15.25	14.74					3.61	0.65		0.72
L29	65.03	15.25	14.74					3.61	0.65		0.72
L30 T= 343 K	65.03	15.25	14.74					3.61	0.65		0.72

OA – oxalic acid, G – glycerine, L – lecithin added to DOA, ¹ ferrocene, ² FeO, ³ Fe₂O₃

The viscosity changes with time, recorded during the tests for the pre-binders tested, are presented in: Figure 1 – L3, L4 and L17; Figure 2 – L5-L9; Figure 3 – L10, L12 and L14-L16; Figure 4 – L18-L25; Figure 5 – L26 and L27 and Figure 6 – L28-L30.

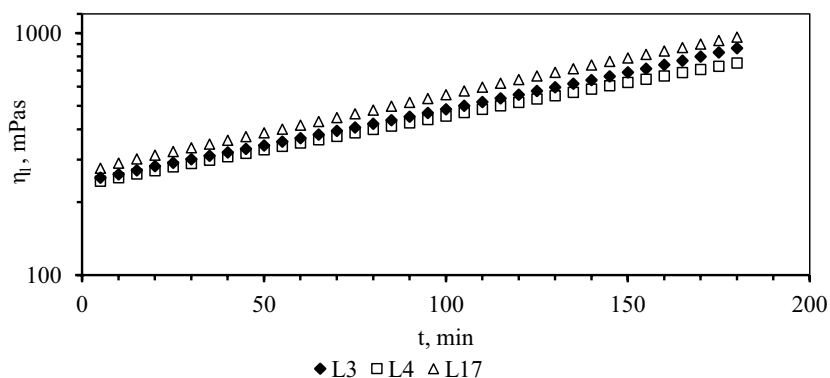


Figure 1. Viscosity versus time dependence for pre-binders L3, L4 and L17.

The dependences presented in Figure 1 show that all three binders have similar natures regarding viscosity change with time. They all contained catocene and TEA.

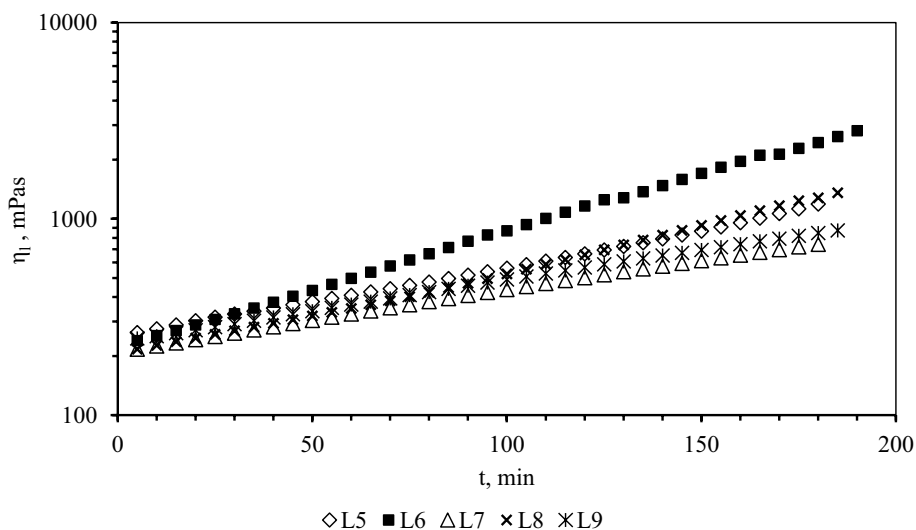


Figure 2. Viscosity versus time dependence for pre-binders L5-L9.

It is seen from the viscosity versus time dependences presented in Figure 2 that in the case of the pre-binder L6, which contains only catocene and no other additives, there is a faster increase in viscosity with time. The others, containing additionally TEA (L5, L8) or OA+G (L7) or nano iron oxides instead of catocene (L9), have comparable viscosity changes with time.

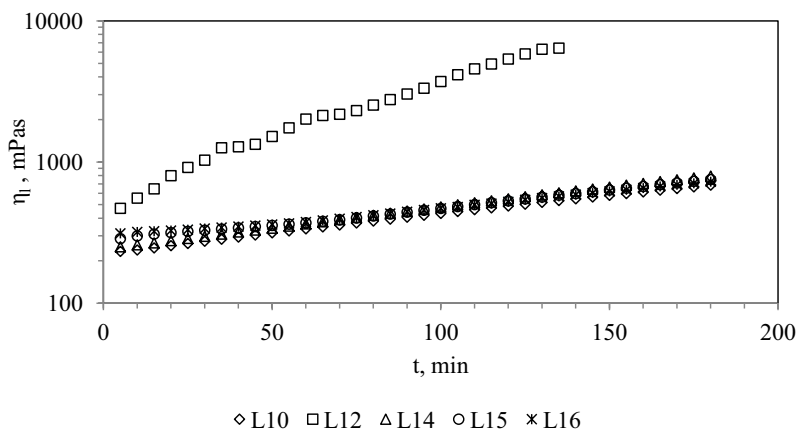


Figure 3. Viscosity versus time dependence for pre-binders L10, L12 and L14-L16.

Figure 3 presents the viscosity versus time changes for the pre-binders containing lecithin as the additive. The pre-binder that contains $\text{Cu}_2\text{Cr}_2\text{O}_5$ shows a faster increase in viscosity with time, which proves that copper chromate acts catalytically on the cure process, accelerating the reaction between the OH and NCO groups.

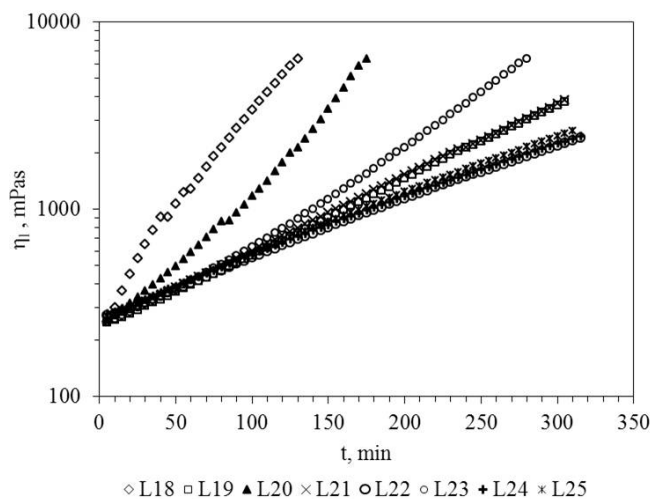


Figure 4. Viscosity versus time dependence for pre-binders L18-L25.

It is seen from the nature of the viscosity changes with time presented in Figure 4 that catocene and ferrocene (FRR), in the absence of TEA and OA+G,

accelerate the cure reaction. A comparison of the curves for pre-binders L18, L19 and L20 indicates that addition of OA+G or G results in a slowing of the cure reaction, and that addition of OA+G has a greater influence on this process than G alone.

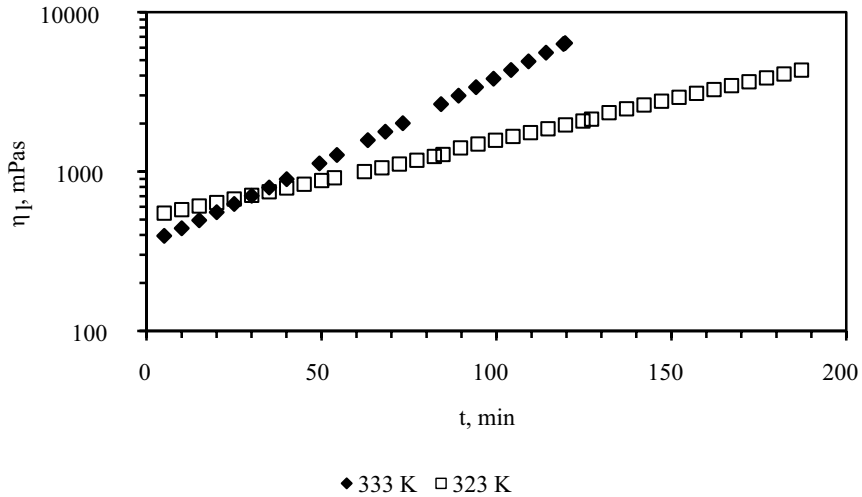


Figure 5. Viscosity versus time dependence for pre-binders L26, L27.

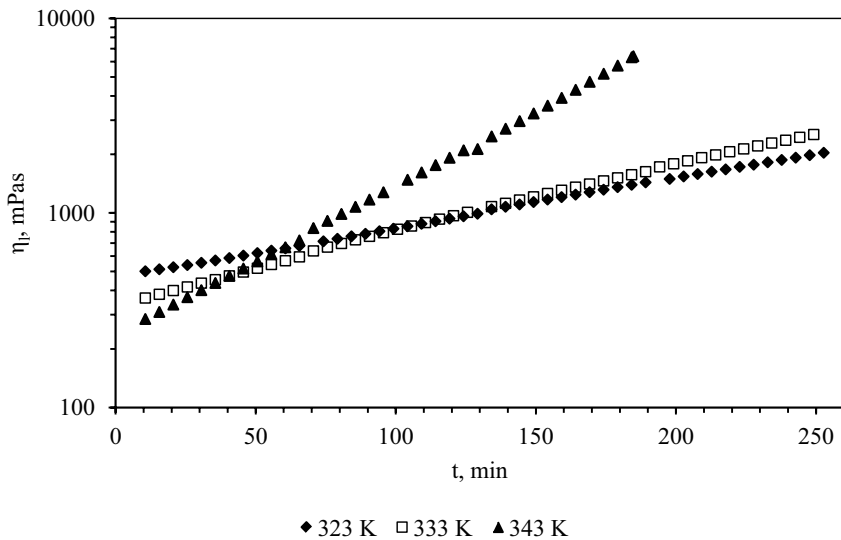


Figure 6. Viscosity versus time dependence for pre-binders L28-L30.

Figures 5 and 6 show the influence of temperature on the cure process of the pre-binders.

Tables 3 and 4 present the values of η_0 and k_η evaluated using Equation (3) and based on the viscosity dependencies for the pre-binders presented in Figures 1-6.

Table 3. Values of constant ($\eta_0(T)$) and rate constant ($k_\eta(T)$) for the pre-binders L3-L10, L12 and L14-L25

Mixture	$\eta_0(T)$, [mPas]	$k_\eta(T)$, [min ⁻¹]	R ²
L3	242.67	0.007	0.9997
L4	238.19	0.0064	0.9999
L5	249.33	0.0083	0.9975
L6	222.71	0.0135	0.9993
L7	212.81	0.0071	0.9992
L8	192.87	0.0104	0.9965
L9	237.18	0.0072	0.9994
L10	228.8	0.0062	0.9986
L12	545.57	0.0192	0.9856
L14	244.21	0.0067	0.9994
L15	273.39	0.0055	0.9956
L16	287.23	0.005	0.9919
L17	271.28	0.0071	0.9997
L18	283.76	0.0248	0.9905
L19	228.39	0.0092	0.9998
L20	199.44	0.0188	0.9907
L21	243.50	0.0091	0.9998
L22	266.53	0.0071	0.9985
L23	203.32	0.0119	0.9957
L24	277.11	0.0071	0.9983
L25	269.29	0.0075	0.9984

Table 4. Values of constant (η_0) and rate constant (k_η) for the R45M rubber based pre-binders L26-L30 at three different temperatures (T)

T [K]	L26, L27			L28-L30		
	η_0 [mPas]	k_η [min ⁻¹]	R ²	η_0 [mPas]	k_η [min ⁻¹]	R ²
323	498.39	0.0115	0.9992	464.64	0.0059	0.9995
333	340.56	0.0244	0.9999	351.21	0.0081	0.9977
343				232.29	0.0178	0.9996

The results recorded from testing the viscosity changes with time at five different temperatures (318, 323, 328, 333 and 338 K) for the HTPB-K and R45M rubber based pre-binders (Table 1) are presented in Figures 7 and 8.

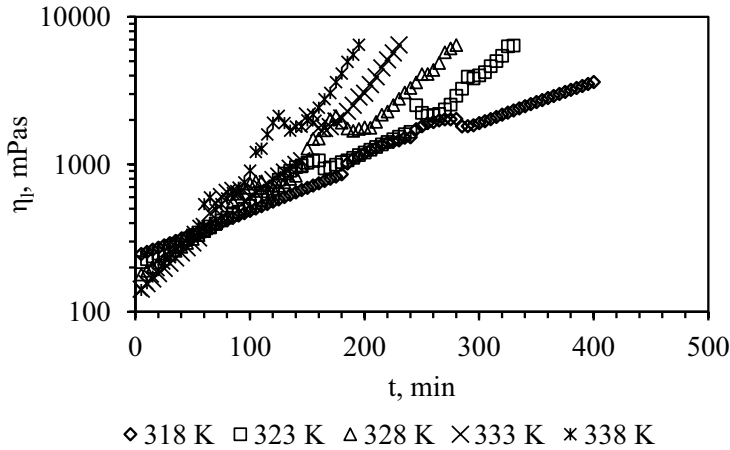


Figure 7. Viscosity versus time and temperature dependence for the HTPB-K based pre-binder.

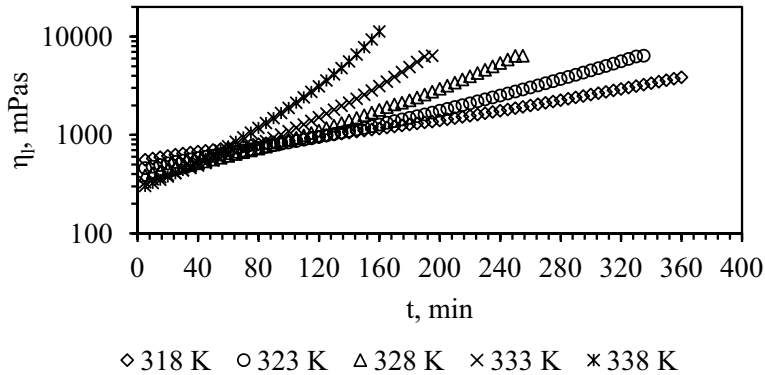


Figure 8. Viscosity versus time and temperature dependence for the R45M based pre-binder.

The curves (straight lines in logarithmic form) presented can be described by Equation (3). The calculated values of constant ($\eta_0(T)$) and rate constant ($k_\eta(T)$) are presented in Table 5.

Table 5. Values of constant ($\eta_0(T)$) and rate constant ($k_\eta(T)$) for the HTPB-K and R45M rubber based pre-binders at five different temperatures (T)

T, [K]	HTPB-K		R45M	
	$\eta_0(T)$, [mPas]	$k_\eta(T)$, [min ⁻¹]	$\eta_0(T)$, [mPas]	$k_\eta(T)$, [min ⁻¹]
318	250.85	0.007	521.68	0.0053
323	201.08	0.009	392.43	0.0079
328	172.32	0.0125	312.41	0.0113
333	136.87	0.0158	254.76	0.0157
338	136.89	0.0191	213.33	0.0229

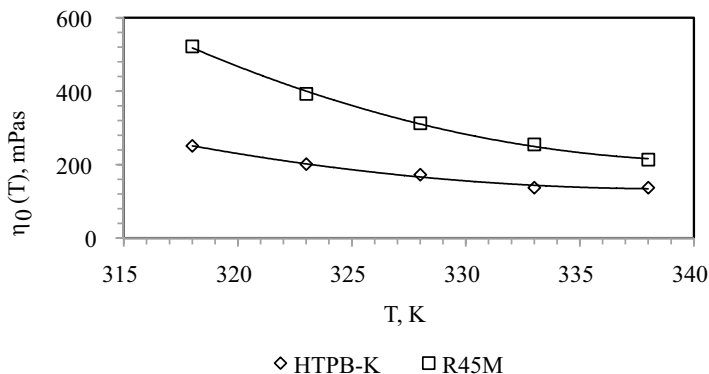


Figure 9. $\eta_0(T)$ versus temperature dependence for the pre-binders tested (Table 1).

The $\eta_0(T)$ values versus temperature (Figure 9) can be described by a quadratic function, and the $k_\eta(T)$ values versus temperature (Figure 10), characterizing the cure reaction rate, by the general dependence:

$$k_\eta(T) = A e^{-E_a/RT} \quad (4)$$

where:

A – constant,

E_a – cure activation energy,

R – universal gas constant,

T – temperature.

The activation energies (E_a) evaluated were 45.99 kJ/mol and 64.6 kJ/mol, respectively.

The HTPB-K rubber based pre-binder is characterised by a lower activation energy than the R45M rubber based pre-binder.

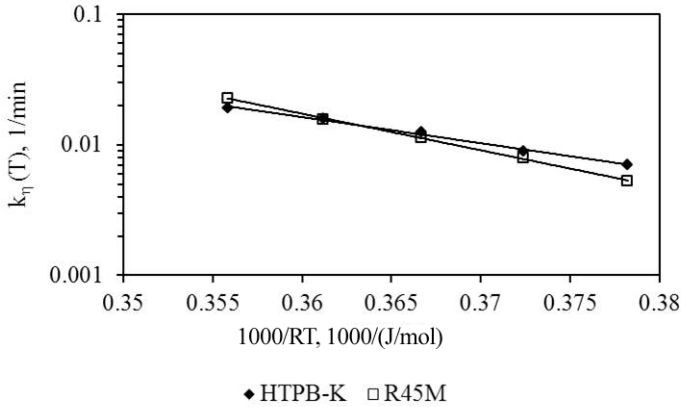


Figure 10. $k_{\eta}(T)$ versus temperature dependence for the pre-binders tested (Table 1).

The viscosity versus time and temperature dependencies for the HTPB-K and R45M rubber based pre-binders tested can be described by the following equations:

- a) For the HTPB-K rubber based pre-binder

$$\eta_0(T) = 0.2654 T^2 - 179.95 \cdot T + 30635, R^2 = 0.9902 \quad (5)$$

$$k_{\eta}(T) = 252696 \cdot e^{-45990/RT}, R^2 = 0.9939 \quad (6)$$

$$\eta_i(t, T) = (0.2654 T^2 - 179.95 \cdot T + 30635) \cdot \exp[252696 \cdot t \cdot e^{-45990/RT}] \quad (7)$$

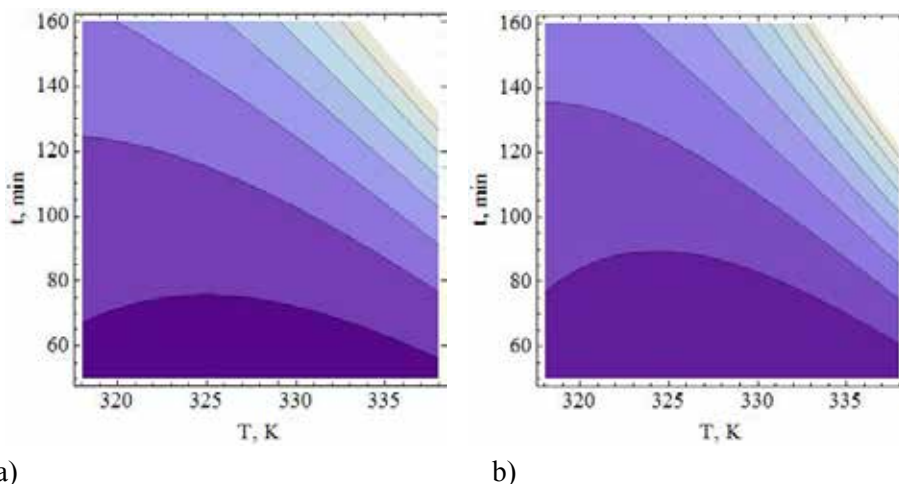
- b) For the R45M rubber based pre-binder

$$\eta_0(T) = 0.5657 \cdot T^2 - 386.21 \cdot T + 66124, R^2 = 0.9981 \quad (8)$$

$$k_{\eta}(T) = 2 \cdot 10^8 \cdot e^{-64600/RT}, R^2 = 0.9993 \quad (9)$$

$$\eta_i(t, T) = (0.5657 \cdot T^2 - 386.21 \cdot T + 66124) \cdot \exp[2 \cdot 10^8 \cdot t \cdot e^{-64600/RT}] \quad (10)$$

Figures 11a and 11b present the contour graphs of viscosity versus time and temperature for the HTPB-K based pre-binder (Equation 7) and the R45M based pre-binder (Equation 10) respectively, for the time range of 50-160 min and the temperature range of 318-338 K. Real differences in the rate of viscosity change versus time and temperature are observed during testing.



a) b)
Figure 11. Contour graphs for the liquid rubber based pre-binders a) HTPB-K, $\eta_l(t, T)$ dependence – Equation (7), and b) R45M, $\eta_l(t, T)$ dependence – Equation (10).

3 Conclusions

Additives such as glycerine and a solution of oxalic acid in glycerine result in slowing or blocking the cure process of the pre-binder accelerated by the presence of catocene. The more effective agent for slowing the reaction between the hydroxyl and isocyanate groups is the mixture of glycerine and oxalic acid. Iron oxides have no accelerating influence on the cure process of the pre-binders.

The viscosity (η_l) change with cure reaction time (t) can be satisfactorily described by Equation (2), and the rate constant $k_{\eta}(T)$ fully characterizes the viscosity change with time.

Tests of the viscosity versus time and temperature dependence for the pre-binders showed that temperatures above 328 K result in distinctly faster increases in viscosity after 80 minutes.

The HTPB-K rubber based pre-binder has characteristics of viscosity change versus time and temperature which differ from those of the R45M rubber based pre-binder. They exhibit anomalous changes for some time intervals.

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5 References

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