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The effect of curing agents on solid composite rocket propellant characteristics

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Three different types of curing agents have been discussed in this work, along with their effects on viscosity, maximum stress, strain at maximum load and on the level of burning rate and pressure exponent in the burning rate law of composite rocket propellants.
Dymeril-diisocyanate, isophorone-diisocyanate and toluene-diisocyanate curing agents were used. Hydroxyterminated polybutadiene is used as binder matrix, bimodal mixture of ammonium-perchlorate (ratio 70:30) as oxidant and mixture of aluminium powder (ratio 50:50) as metal component.

Key words: **composite rocket propellant, curing agents, dymeril-diisocyanate, isophorone-diisocyanate, toluene-diisocyanate, hydroxyterminated polybutadiene, ammonium-perchlorate, viscosity, maximum stress, burning rate, pressure exponent.**

Introduction

A lot of different components are combined in the composite rocket propellant (CRP) formulation which affects the propellant characteristics and has to be examined meticulously. Some of them are involved in chemical reactions to produce a final product or improving propellant quality. Complexity of the generated dependences is influenced by many factors such as solid component quantities, type of binder, curing agent, particle size distributions and theirs shapes, quantity and type of bonding agent and the like.

Many variables are responsible for characteristics such as viscosity and mechanical characteristics of the propellant, so they should be combined while analysing and defining new compositions, but also in component ration optimizations and solid fraction packages.

The effects of three different types of curing agents of binder in CRP, namely on viscosity level and time-changed, on maximum stress and strain at maximum load, on burning rates and pressure exponents in the burning rate law [1] are examinated and compared in this peper.

Experiment

Experimentation was conducted on propellants including hydroxyterminated polybutadiene (HTPB) as binder, solid ingredients consisting of bimodal mixture of ammonium-perchlorate (AP), the mean particle size of $200\mu m$ and $5\mu m$ (in ratio 70:30), and bimodal mixture of aluminium (Al), the mean particle size of $15\mu m$ and $30\mu m$, (in ratio 50:50). As curing agents in the binder dymeril-diisocyanate (DDI), isophorone-diisocyanate (IPDI), toluenediisocyanate (TDI) were used. All propellant formulations were cured for 120 hours at 70°C [2].

For viscosity measuring of uncured propellant Brookfield HBT viscometer was used, at spindle revolution of $5 min^{-1}$, at examination temperature of 50°C. Determining the apparent viscosity is exerted according to ASTM standard [3].

Uniaxial mechanical characteristics were measured on universal tester type Instron 1122 at JANAF "C" specimen, at tension rate of 50 mm/min and at two test temperatures [4].

Values in the burning rate law are determined at 2″ experimental motors at the ambient temperature [4].

Compositions given in Table 1 are casted with each of the specified curing agents.

Table 1. Compositions of CRP based on HTPB/DDI, HTPB/IPDI and HTPB/TDI

Composition number (CN)	Al, [mas.%]	AP, [mas.%]	solid phase [mas.%]
1	13.5	72.5	86.0
2	3.5	72.5	76.0
3	16.9	72.5	89.4
4	8.5	72.5	81.0
5	8.0	68.0	76.0
6	9.0	77.0	86.0

Results and discussion

Corresponding viscosity curves for compositions from Table 1 are given in Figures 1-3.

The initial viscosity value of composition number (CN) 3 based on DDI (Fig.1) is greater than CN viscosity values obtained at the end of measuring. (2500 Pas).

Compositions with IPDI (Fig.2) demonstrate considerably lower viscosity (at 90 minutes up to 500 Pas). The only exception is CN 3 which value changes from 900 Pas to 1400 Pas, but it remains good for casting, i.e. it has quite good pot life, even up to 90 minutes after adding the curing agent.

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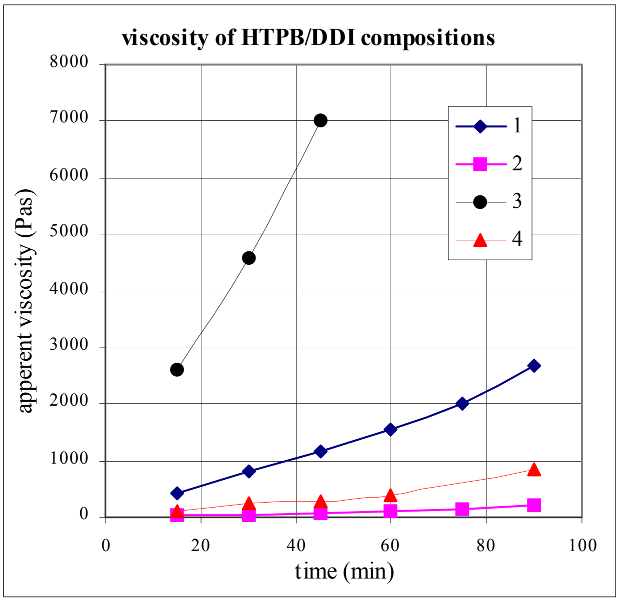

Figure 1. Time-dependence viscosity values of propellants based on HTPB/DDI

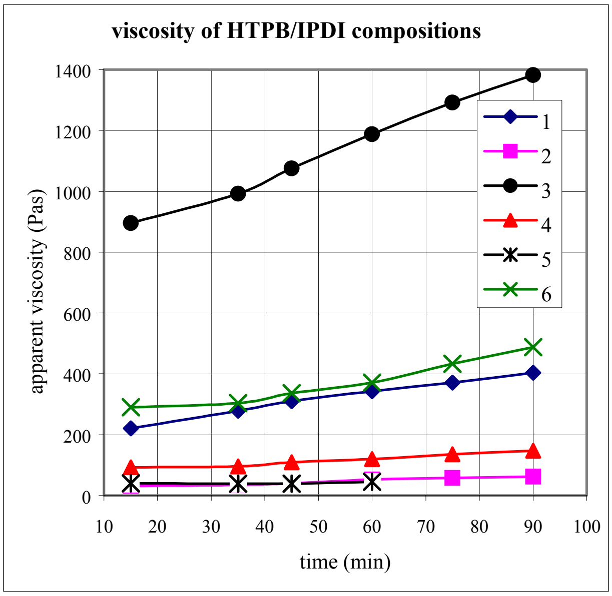

Figure 2. Time-dependence viscosity values of propellants based on HTPB/IPDI

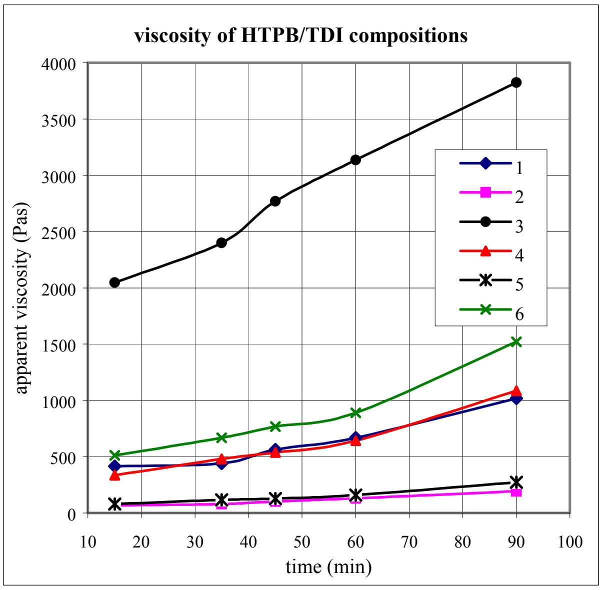

Figure 3. Time-dependence viscosity values of propellants based on HTPB/TDI

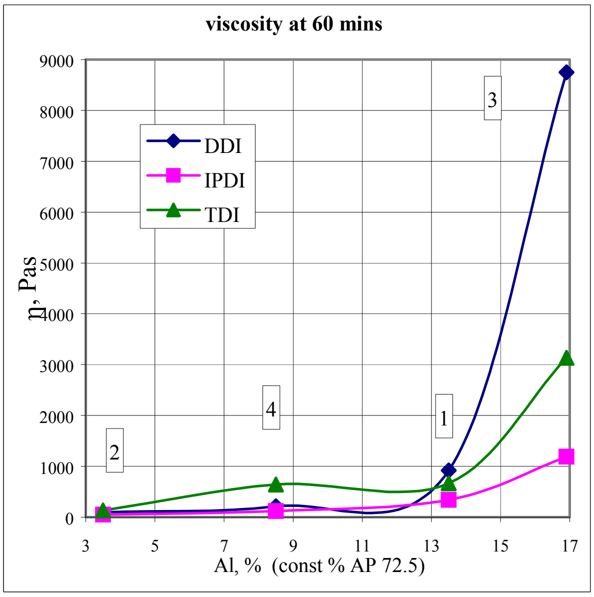

Figure 4. Comparative viscosity values of CRP after 60 minutes

Viscosity values of propellants based on TDI (Fig.3) are in between the values of the two prior types, which is particularly noticable when increasing solid phase content from 76 mas.% to 89 mas.%. The initial values of viscosity are up to 500 Pas, and after the examination time 1500 Pas is not exceded, except for CN with 89 mas.% which differs greatly in this case, achieving up to 4000 Pas.

Diagrams of viscosity alterations in time show considerable differences for all of three curing agent types. These values from the beginning until the end of the measuring period for DDI propellants are increased about seven times in average, for IPDI and TDI propellants only two, and three times respectively. Due to theirs chemical structures, i.e. reaction rate with polymer, values of viscosity have the different levels and changing rate in time, the effects of DDI, IPDI and TDI through CN 1, 2, 3 and 4 (Table 1).

The viscosity values for propellants based on DDI, IPDI and TDI 60 minutes after adding the curing agent are shown in Fig. 4. It can be seen that the propellant based on DDI up to 81 mas.% (CN 4), obes not deviate significantly from the same viscosity values of propellants with IPDI and TDI. However by adding the solid components up to 89 mas.%, the viscosity of DDI compositions are increased four to five times compared to the corresponding CN containing IPDI and TDI. This means that at a great solid components concentration a long aliphatic chain of DDI cannot realise a satisfactory contact with solid particles, so the flow becomes complicated [5].

Comparative viscosity values of CN 4, 5 and 6 for IPDI and TDI based propellants, with constant ratio of AP and Al, are show in Fig.5. In relation to the formulations of constant AP content but different Al content (CN 1, Fig.4), a smooth viscosity increment for the same solid content, but

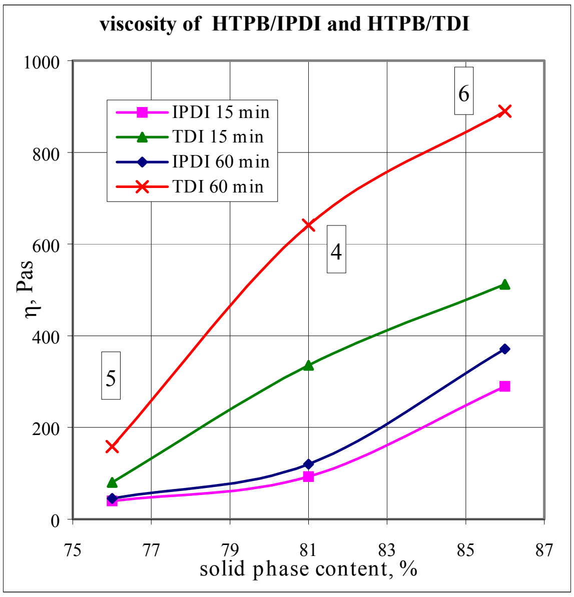

Figure 5. Comparative viscosity values for IPDI and TDI based CRP

less Al amount can be noticed (CN 6, Fig.5). The larger Al amount in the same solid content is a more favoured combination for the viscosity level, so its level is higher in CN 6 than in CN 1. Due to greater Al density in relation to AP, the first one has a less volume participation and therefore lower viscosity. In case of small solid quotient (76 mas.%), a slight viscosity distinction of CN 2 and 5 occures for a long curing period with propellants based on TDI.

The values of uniaxial mechanical characteristics: maximum stress, (σ_m) and strain at maximum load, (ε_m) for the propellants including all types of curing agents are represented in Tables 2-4.

The used curing agent types have different structures; therefore, the mechanical characteristics at tension depend on the formed polymer network between polymer and the curing agents, and also the secondary links existing in the itself polymer and in relation to solid particles.

Table 2. Mechanical characteristics of CRP/DDI

T [°C]	Composition number (CN)	DDI σ_m [daN/cm^2]	DDI ε_m [%]
-50	1	21.59	13.20
	2	11.94	33.75
	3	27.81	5.03
	4	16.11	17.34
20	1	7.68	15.88
	2	4.51	30.46
	3	11.25	4.97
	4	6.18	15.72

Table 3. Mechanical characteristics of CRP/IPDI

T [°C]	Composition number (CN)	IPDI σ_m [daN/cm^2]	IPDI ε_m [%]
-50	1	26.25	8.203
	2	14.99	24.83
	3	37.46	6.19
	4	22.24	12.83
	5	17.75	20.03
	6	29.19	9.68
20	1	10.88	23.58
	2	4.97	40.79
	3	14.39	14.19
	4	7.43	27.37
	5	6.04	43.48
	6	9.73	20.35

Table 4. Mechanical characteristics of CRP/TDI

T [°C]	Composition number (CN)	TDI σ_m [daN/cm^2]	TDI ε_m [%]
-50	1	26.60	10.63
	2	15.79	19.56
	3	33.74	8.89
	4	22.42	14.80
	5	16.72	25.43
	6	29.10	11.96
20	1	11.75	12.75
	2	5.88	16.00
	3	15.19	14.34
	4	9.23	17.29
	5	6.84	27.73
	6	11.27	14.01

The effect of the used curing agent types on the measured mechanical characteristics of the propellant are given in Figures 6 and 7. The same figures also show the values of the corresponding response (maximum stress or strain at maximum load) at two test temperatures: 20°C i –50°C for four compositions (CN 2, 4, 1 and 3).

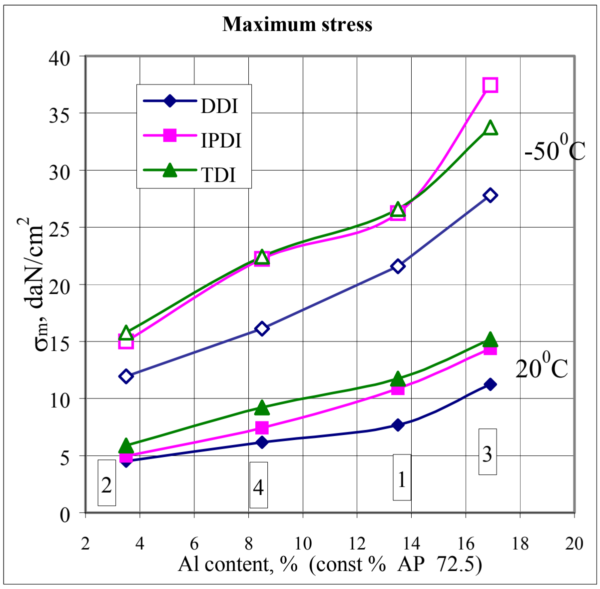

Figure 6. Comparative values of maximum stress of CRP

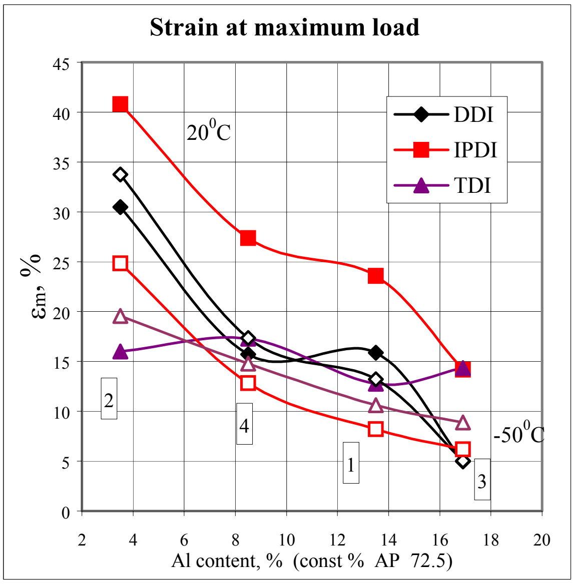

Figure 7. Comparative values of strain at maximum load of CRP

The largest maximum stress values at 20°C have been reached in formulations involving TDI as aromatic isocyanate (Fig.6), since benzene's rings diminish the chain mobility and then restore intensive secondary bonds. IPDI provides similar urethane groups densities, but polymer segment orientation is reduced due to the cyclic structure, creating difficulties at establishing the secondary bonds and lower maximum stress values. The lowest values of σ_m are always realised using DDI, due to its branchy aliphatic sequence (dodecile groups), so the molecular masses between the network nodal point are increased, and the urethane bond concentrations and secondary attachments diminished. The level of maximum stress depends on the ballance of all these effects and the intensity of solid particles-polymer links. In case of a low solid content, the maximum stress differences are small at the same test temperature.

Owing to varied chemical structures, the chain lengths between the curing sites and mobility of chains, there are considerable differences at propellant tension ability (Fig.7). At low solid content, the polymer characteristics are dominant in propellant behavior determining. The largest values of ε_m at 20°C are obtained for propellants based on IPDI, while propellants including DDI up to 81 mas.% solid content show greater tension behavior than TDI propellants (the larger molecular mass between the nodes). However, increasing the solid content above 86 mas.% demonstrates it is not convenient to of DDI, because of a considerable strain decrease due to greater unsatisfactorily polymer package. Decreasing the test temperature, propellants with DDI, due to chain mobility and squatness, biggest tension ability is provided, while the combinations with smaller density have even greater values than those at 20°C.

Ballistic characteristics of some of the mentioned propellant formulations based on HTPB/DDI have been determined at 2” experimental motors at ambient temperature. The abtained values of the measured mean pressures, corresponding burning rates along with the evaluated burning rate lows are presented in Table 5.

Table 5. Examination ballistic results of KRG based on DDI

1		2		3		4	
p (bar)	*v* (mm/s)	*p* (bar)	*v* (mm/s)	*p* (bar)	*v* (mm/s)	*p* (bar)	*v* (mm/s)
32,45	6,35	13,45	3,35	43,95	7,91	22,59	4,25
44,84	6,58	29,22	3,45	56,22	8,39	33,99	4,59
65,1	7,52	37,28	3,49	80,52	9,53	62,33	4,99
88,59	7,95	58,25	3,67	101,24	10,45	73,35	5,29
100,14	8,34	73,11	3,72	119,75	10,49	101,32	5,87
125,97	8,64	101,12	4,2	147,16	11,56	131,05	6,27
v=2,6881$p^{0.2430}$ v_{70}=7,55 mm/s		v=2,5072$p^{0.0989}$ v_{70}=3,82 mm/s		v=2,4046$p^{0.3120}$ v_{70}=9,10 mm/s		v=2,1186$p^{0.2176}$ v_{70}=5,34 mm/s	
n-pressure exponent; v_{70}*-burning rate at 70 ba;* $v=Bp^n$							

Table 6. Experimental results of KRG based on IPDI and TDI

1 (IPDI)		1 (TDI)	
p (bar)	v (mm/s)	p (bar)	v (mm/s)
41,99	7,71	44,00	8,46
63,72	8,74	66,86	9,88
89,00	10,07	96,88	10,69
92,37	10,13	104,77	11,33
145,42	12,32	166,62	14,14
v=1,8391$p^{0,3793}$ v_{70}=9,21 mm/s		v=2,0413$p^{0,3719}$ v_{70}=9,91 mm/s	

Ballistic measurements are made for CN 1 based on IPDI and TDI and the results are shown in Table 6.

It has been noticed that the values of burning rate at 70 bar and pressure exponent of DDI propellants are significantly lower than the two others, which can be seen from the results given in Table 4 for the 86 mas.% solid content (CN 1).

Conclusion

This paper analyses the viscosity and mechanical characteristics CRP based on HTPB and three different types of curing agents including isocyanate's groups: DDI, IPDI i TDI, along with the burning rate and pressure exponent levels, considering also the appropriacy of these formulations for application.

The largest change of viscosity throughout measuring occured in DDI propellants: it mounts aproximately seven times, and for IPDI and TDI propellants only two, i.e. three times respectively. Up to 81 mas. % solid content viscosity values for all of the three propellant types are very close. However, for heavy formulations (86 mas. % solids and more), DDI propellants have the highest viscosity and therefore it can be concluded that this curing agent is not suitable for application in case of extremely heavy formulations. Larger Al amount for the same solid content is a more advantageous combination for the viscosity level.

Compositions based on HTPB/DDI provide the smallest maximum stress values in the whole domain of examinated solids at both test temperatures. A significant rise of σ_m (2-2,5 times) for all three propellant types at –50 °C is present.

Compositions based on HTPB/DDI containing up to 86 mas.% solids provide the tension potential very similar to that of TDI propellants. However when using extremely heavy formulations DDI propellants are not suitable, due to a very severe drop of strain – more than 6 times, contrary to the drop in IPDI propellants – 3 times and TDI propellants with only 10% reduction. DDI propellants up to 86 mas. % solids at -50 °C take the largest values of ε_m, but they are decreased by filler enhancing and become smaller than those for IPDI and TDI which are very close.

Further more, compositions based on HTPB/DDI including 86 mas. % of solids provide over 30% lower pressure exponent values and over 20% lower burning rate values than the corresponding IPDI and TDI propellants, providing large application possibilities.

These examination results prove that the available variety of composite rocket propellant compositions could be extended with a new one containing DDI curing agent, especialy for the solid content up to 80 mas. %.

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Uticaj umreživača na karakteristike kompozitnog raketnog goriva

U ovom radu su razmatrana tri tipa umreživača. Ispitivan je njihov uticaj na viskozitet, zateznu čvrstoću, izduženje pri maksimalnoj sili i kako utiču na nivo brzine sagorevanja i eksponenta pritiska u zakonu brzine sagorevanja kompozitnih raketnih goriva.

Kao umreživači su korišćeni dimeril-diizocijanat, izoforon-diizocijanat i toluen-diizocijanat. Kao vezivo je korišćen prepolimer na bazi hidroksiterminiranog polibutadiena, kao oksidator bimodalna smeša amonijum-perhlorata (odnos 70 : 30), a smeša aluminijumskog praha (odnos 50 : 50) kao metalna komponenta.

Ključne reči: **kompozitno raketno gorivo, umreživači, dimeril-diizocijanat, izoforon-diizocijanat i toluen-diizocijanat, hidroksiterminirani polibutadien, amonijum-perhlorat, viskozitet, zatezna čvrstoća, brzina sagorevanja, eksponent pritiska**

Inflence des agents de liage sur les caractéristiques de la propulsion composite de fusées

Ce papier prend en considération trois types d'agents de liage. On a examiné leur influence sur viscosité, résistence à la tension et allongement à la force maximale. On a étudié aussi comment ils influencent sur le niveau de la vitesse de combustion ainsi que l'exposant de pression selon la loi de vitesse de combustion des propulsions composites de fusées.

En tant qu'agents de liage ont été utilisés dimeril-diisocianat, isoforon-diisocianat et toluène-diisocianat. Le liant utilisé est un prépolymère dont la base est hydroxiterminal polybutadi-ène; oxidant utilisé est un mélange bimodal d'ammonium perchlorate (dans le rapport 70 :30). Le mélange de poudre d'alluminium (dans le rapport 50 :50) servait de composante métallique.

Mots clés: **propulsion composite de fusées, agents de liage, dimeril-diisocianat; toluène-diisocianat, isoforon-diisocianat, polybutadène hydroxiterminal, ammonium perchlorate,viscosité,résistence à la tension, vitesse de combustion, exposant de pression**

Влияние интегрирующих элементов на характеристики многокомпонентного ракетного топлива

В этой работе испытывано влияние трёх типов интегрирующих элементов на вязкость, на затяжную прочность, на удлинение при максимально допустимой нагрузке, на уровень полученных скоростей горения и показателя степени давления в законе скорости горения многокомпонентного ракетного топлива.

В роли интегрирующих элементов использованы димерил-диизоцианат, изофон- диизоцианат и толуен-диизоцианат. Топливо-вяжущая составляющая была на основании гидрокситерминированного полибутадиена, а твёрдая фаза (различных содержаний в топливе) была составлена из двоичных смесь аммония перхлората в роли оксиданса, в отношении частиц 70:30 и пороховой смеси алюминия как металлической составляющей, в отношении частиц 50:50.

Ключевые слова: многокомпонентное ракетное топливо, интегрирующие элементы, димерил-диизоцианат, изофон- диизоцианат, толуен- диизоцианат, гидрокситерминированный полибутадиен, аммония перхлорат, вязкость, затяжная прочность, скорость горения, показатель степени давления