

Rheological and thermal properties of mixtures of hydroxyl-terminated polybutadiene and plasticizer*) (Rapid communication)

Tomasz Gołofit¹⁾, Katarzyna Gańczyk-Specjalska^{2), **)}, Karolina Jamroga¹⁾, Łukasz Kufel¹⁾

DOI: [dx.doi.org/10.14314/polimery.2018.1.9](https://doi.org/10.14314/polimery.2018.1.9)

Abstract: Mixtures of hydroxyl-terminated polybutadiene (HTPB) and dioctyladipate (DOA) as a plasticizer, which after crosslinking are applied as binders in heterogeneous propellants, were studied. The influence of mixture composition on rheological and thermal properties, important from technological and utility viewpoint were specified. The temperature dependence of prepared mixtures viscosity were studied. Systems were subjected to crosslinking and values of pot life (t_{pl}) were determined. It was stated that t_{pl} rose with increasing plasticizer content. Differential scanning calorimetry and thermogravimetry techniques were used to analyze thermal stability of mixtures. It was concluded that applied components could not decompose in the temperature range of 290–350 K and studied mixtures did not cause the hazard of thermal explosion.

Keywords: rheology, thermal stability, hydroxyl-terminated polybutadiene, curing.

Właściwości reologiczne i termiczne mieszanin polibutadienu z końcowymi grupami hydroksylowymi oraz plastyfikatora

Streszczenie: Zbadano mieszaniny polibutadienu z końcowymi grupami hydroksylowymi (HTPB) oraz adypinianu dioktylu (DOA) jako plastyfikatora, które po usieciowaniu wykorzystywane są jako lepiszcza w heterogenicznych paliwach rakietowych. Określono wpływ składu na reologiczne i termiczne właściwości mieszanin, mające istotne znaczenie z technologicznego i użytkowego punktu widzenia. Zbadano zależność lepkości przygotowanych mieszanin od temperatury. Badane układy poddano sieciowaniu i wyznaczono wartości czasu życia technologicznego (t_{pl}). Wykazano, że t_{pl} wydłuża się ze wzrostem zawartości plastyfikatora. Stabilność termiczną mieszanin zbadano za pomocą różnicowej kalorymetrii skaningowej i termogravimetrii. Stwierdzono, że zastosowane składniki nie ulegają rozkładowi w temperaturze od 290 do 350 K i badane mieszaniny nie powodują zagrożenia eksplozją.

Słowa kluczowe: reologia, stabilność termiczna, polibutadien z końcowymi grupami hydroksylowymi, sieciowanie.

Heterogeneous solid rocket propellants (HSRP) are the crosslinked mixtures of solid and liquid components. Rocket propellants consist primarily of solid, inorganic oxidizer and organic polymer [e.g., hydroxyl-terminated polybutadiene (HTPB)]. Besides these components, there are additions which improve operational parameters and simplify technological operations: metal powders, plasticizers, antioxidants, combustion modifiers, and cross-

linkers [1]. This last group of substances usually consists of 2,4-toluene diisocyanate (TDI) [2], isophorone diisocyanate (IPDI) [3] or diphenylmethane diisocyanate (MDI) [4].

HTPB is commonly used in HSRP [5], because of its good physicochemical and mechanical properties after crosslinking with isocyanates [6, 7]. It is chemically inactive, with low glass transition temperature, high elasticity and moisture resistant [8]. Plasticizer is the substance which increases polymer chains mobility and reduces intermolecular impacts. Plasticizers improve binder physical properties and its behavior at the very low temperatures and high pressures. Following ester plasticizers are applied in propellant composition: dioctyl adipate (DOA), dibutyl phthalate or trioctyl phosphate [9].

The reaction between hydroxyl and isocyanate groups (crosslinking) is the process which determines the duration of HSRP formation. The mixture viscosity increases during the reaction of crosslinking. Three-dimension-

¹⁾ Warsaw University of Technology, Department of High-Energetic Materials, Noakowskiego 3, 00-664, Warsaw, Poland.

²⁾ Institute of Industrial Organic Chemistry, Annopol 6, 03-236 Warsaw, Poland.

*) Material contained in this article was presented at XXIst International Science-Technology Conference Armament'2017, The Issues of Development, Production and Maintenance of Weapon Systems, 19–22 June 2017, Jachranka, Poland.

***) Author for correspondence; e-mail: specjalska@ipo.waw.pl

al network is formed and it gives relevant mechanical properties to the finished product [10]. It is assumed that suitable flow properties (which allow the propellant load formation) are assured for viscosity not exceeding $1.5 \text{ kPa} \cdot \text{s}$ [11]. The parameter of pot life (t_{pl}) was introduced to compare flow parameters of analyzed mixtures. It defines the time of reaching limit mentioned above ($\eta_{max} = 1.5 \text{ kPa} \cdot \text{s}$). Curing process can be monitored by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR) or viscometry [12, 13]. The crosslinking rate increases with the raising value of isocyanate and hydroxyl groups ratio (r) [14]. The highest value was observed for $r = 1.1$ (HTPB-TDI system) [12]. Bandgar *et al.* stated that the formation of rocket propellants was optimal in the temperature range of 313–323 K. Significant viscosity increase was observed for mixtures with dioctyl adipate (DOA) as a plasticizer, *i.e.*, for HTPB-DOA-TDI systems at temperatures above 323 K. Studies were performed for two different plasticizer contents: 30 and 40 % [15].

The values of t_{pl} were studied for the system of HTPB and two crosslinking agents: TDI and IPDI. It was defined as the time for the viscosity to reach the value of $70 \text{ Pa} \cdot \text{s}$. For all of examined mixtures r value was 1. For the mixtures with TDI and IPDI t_{pl} were determined to be, respectively, 240 and 1890 min at the temperature of 303 K, but 124 and 575 min at the temperature of 333 K. It was demonstrated that t_{pl} for mixtures with different TDI : IPDI molar ratios increased with the IPDI content raising. The application of crosslinking mixture with the suitable isocyanates ratio allows the modification of the t_{pl} [16].

Thermal stability of a mixture influences the safety of HSRP exploitation and storage. Thermal analysis is often applied to analyze the thermal stability. These may be performed using following techniques: DSC, microcalorimetry or thermogravimetry (TG) [17–19]. Uncontrolled decomposition of the mixture may lead to the thermal explosion. It is related to the thermal power generated in the system and discharged to the environment. When the thermal power generated is higher than discharged, uncontrolled increase of the temperature occurs [20]. It may lead to the thermal explosion, even at low conversion degrees of the substance [21]. That's why the compatibility of the mixture component is important.

Following systems are described in the relevant literature: HTPB-TDI, HTPB-IPDI, HTPB-TDI-IPDI, HTPB-DOA-TDI, HTPB-DOA-MDI. However, not all data required to determine parameters significant during HSRP formation are given. Rheological and thermal properties are significant from the technological point of view.

The aim of this paper was to determine the influence of plasticizer content on the flow and thermal properties before and after crosslinking process. Binary systems with polymer (HTPB) and plasticizer (DOA) as well as ternary systems with the addition of crosslinking agent (TDI) were studied.

EXPERIMENTAL PART

Materials

Polybutadiene terminated with hydroxyl groups (HTPB) from Mesko S.A. was characterized by glass transition temperature $T_g = 198 \text{ K}$, non-volatile residue 99.9 %, moisture content $\leq 0.02 \%$, hydroxyl number $L_{OH} = 47.1 \text{ mg}_{\text{KOH}}/\text{g}$ and functionality of 2.4–2.6.

Bis(2-ethylhexyl) adipate (DOA) from Boryszew S.A. with purity min 99.5 % had a density of $0.922\text{--}0.930 \text{ g/cm}^3$, moisture content did not exceed 0.1 %.

Toluene 2,4-diisocyanate (TDI) from Mesko S.A. had a density of 1.214 g/cm^3 and purity of 95 %.

HTPB, DOA and units required for the viscosity measurements were stored in the desiccator above phosphorus pentoxide for at least a week to eliminate the influence of moisture on the crosslinking reaction. Binary systems containing HTPB and DOA with plasticizer content from 5 to 35 wt % were prepared. TDI was used to perform the crosslinking process. Constant mass ratio of TDI and HTPB was kept.

Methods of testing

Viscosity measurements were performed with the HB-DV2T Brookfield viscometer, using small samples adapter (SSA) and SC4-21 spindle. Examined mixture in amount approximately 6 g was placed in SC4-13R(P) pan. Measurements were performed in the temperature range of 298–343 K. Each system was subjected to the crosslinking process at the temperature of 343 K. Before measurements mixtures were stirred for 1 min and were degassed (1 hPa) for 30 min. Spindle rotation speed was constant and equal to 0.093 1/s.

Simultaneous thermogravimetric and differential scanning calorimetry measurements (TG/DSC) were carried out using SDT Q600 TA Instruments device. Analyses were performed in open aluminum pans at heating rate of 5 K/min in the temperature range of 303–823 K, under nitrogen with the $100 \text{ cm}^3/\text{min}$ flow. This method was applied to examine particular mixture components and both binary and ternary systems.

The apparent activation energy of viscous flow and pre-exponential factor were determined on the basis of Arrhenius-Guzman equation [22]:

$$\eta = A \cdot e^{\frac{U}{RT}} \quad (1)$$

where: U – apparent activation energy for viscous flow, A – the constant dependent on the polymer molecular weight and independent on the temperature, T – temperature in Kelvin scale, η – viscosity, R – gas constant.

The dependence of the viscosity during crosslinking on time is described by equation:

$$\eta = a \cdot e^{\frac{b}{t-t_{max}}} \quad (2)$$

where: t_{max} – time required for total mixture crosslinking (determined on the basis of this equation), t_{pl} – pot life determined on the basis of this equation for the maximum value of the viscosity allowing to cast the mixture, $\eta_{max} = 1.5 \text{ kPa} \cdot \text{s}$, a , b – constant parameters.

RESULTS AND DISCUSSION

Influence of DOA content on the viscosity in the HTPB-DOA binary systems

The effect of temperature and DOA content on viscosity of prepared mixtures is shown in Fig. 1. The mixture viscosity clearly decreased with increasing content of DOA plasticizer. According to the anticipation, the viscosity also decreased with the raising temperature. The strongest dependence of the plasticizer content was observed at the temperature of 298 K. The viscosity of the system with 5 wt % of DOA addition decreased sevenfold in the temperature range of 298–333 K, while for the mixture with 35 wt % of DOA – fivefold. The dependence of viscosity on the temperature is described by the eq. (1), where values of U of viscous flow and A factor are determined. The obtained results are collected in Table 1. The value of U of the viscous flow rose in the HTPB-DOA system with 0 to 5 wt % of DOA and then decreased with the increase of the plasticizer amount. The most significant difference was denoted between values obtained for mixtures with 5 and 10 wt % of DOA (4.1 kJ/mol) and the least for those with 10 and 15 wt % (0.5–0.8 kJ/mol). Pre-exponential A factor increased with the DOA content in the binary system.

Table 1. Apparent activation energy of the viscous flow (U) and pre-exponential factor (A) calculated for HTPB-DOA mixtures

wt % of DOA	U , kJ/mol	$A \cdot 10^{-8}$, Pa · s
0	44.5 ± 0.1	4.0 ± 0.6
5	46.1 ± 0.4	4.0 ± 0.6
10	42.0 ± 0.4	16.5 ± 2.7
15	41.5 ± 0.5	15.8 ± 3.2
15	41.2 ± 1.8	15.0 ± 10.1
25	38.3 ± 0.8	32.7 ± 10.3
35	37.0 ± 0.5	33.0 ± 6.5

Influence of DOA content on t_{pl} and t_{max} in the HTPB-DOA-TDI ternary systems

The time dependencies of HTPB-DOA-TDI systems viscosity for mixtures with DOA content in the range of 0–30 wt % are plotted in Fig. 2. Experimental points are described by the eq. (2), which was used to determine of t_{max} of the mixture and t_{pl} for the maximum value of the viscosity being equal to $\eta_{max} = 1.5 \text{ kPa} \cdot \text{s}$, which allowed the mixture casting. Values of t_{pl} and t_{max} increased with the raising DOA content, as expected. The biggest values (above 6.5 h) were observed for the mixtures with DOA

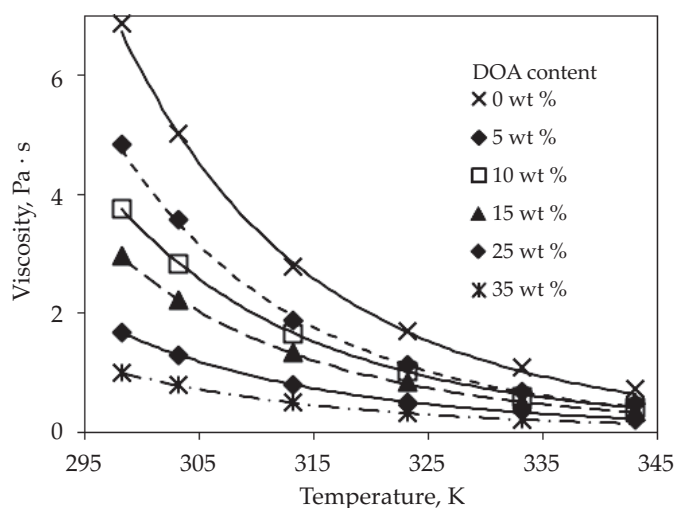


Fig. 1. The effect of temperature and DOA content on viscosity of HTPB-DOA mixtures

content of 30 wt %. Obtained experimental values of t_{pl} and t_{max} were described by linear eqs. (3) and (4), respectively:

$$t_{pl} = 0.1 \cdot x_{wDOA} + 4.59 \quad R^2 = 0.9127 \quad (3)$$

$$t_{max} = 0.1 \cdot x_{wDOA} + 4.09 \quad R^2 = 0.8437 \quad (4)$$

where: x_{wDOA} – content of DOA in the mixture.

The binder composition may be determined on the basis of the dependence of t_{pl} on the DOA content. Such a binder will hold the t_{pl} value required for the technological process.

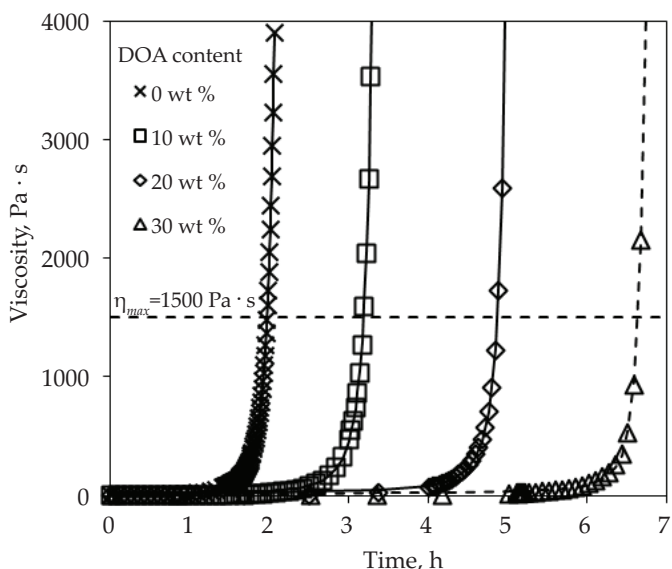


Fig. 2. Dependence of the HTPB-DOA-TDI systems viscosity on time during crosslinking at the temperature of 343 K

Thermal properties in binary and ternary systems

TG/DSC analysis was applied to study the thermal properties of HTPB-DOA and HTPB-DOA-TDI systems. The dependence of mass loss (TG) and heat flow (DSC)

on the temperature for DOA, HTPB, HTPB-DOA (15 wt %) and HTPB-DOA (35 wt %) are shown in Fig. 3. Each of the binary mixtures showed three-stage mass loss process. The first stage corresponded to the endothermic process of DOA evaporation from the mixture in temperature range 395–567 K. The second stage was related to the beginning of HTPB exothermic decomposition observed in the temperature range 567–662 K. The third stage was the evaporation of HTPB observed at temperatures from 662 to 772 K.

No significant differences were observed for particular stages of HTPB-DOA mixtures mass loss before and after the crosslinking. Values were similar within the margin of error. The highest temperature of the technological process performance was limited with the process of low-molecular component evaporation. Propellant curing was usually carried out at the temperature of 343 K, 130 K lower than DOA evaporation point. Examined HTPB-DOA and HTPB-DOA-TDI systems were thermally stable and there was no hazard of the thermal explosion.

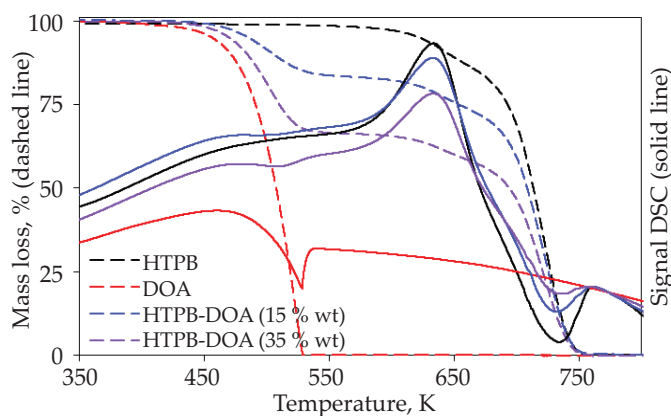


Fig. 3. TG/DSC curves of HTPB-DOA mixtures

CONCLUSIONS

Rheological and thermal properties of HTPB and HTPB-TDI mixtures were studied and the influence of DOA plasticizer content on these properties was determined. The increase of DOA content in the binary system caused the decrease of η and U . Values of t_{pl} and t_{max} of ternary HTPB-DOA-TDI systems increased linearly with the increase of DOA content in the system. The temperature dependence of mass loss showed that for the binary and ternary systems it was the three-stage process. No influence of the crosslinking on the mass loss values was observed.

The technological process of rocket propellant casting is carried out in the temperature range of 290 to 350 K. Applied components cannot decompose and have high vapor pressure. Our experiments did not show any mass loss or substances decomposition in this temperature range. The mass loss related to endothermic process occurred at higher temperatures, that's why the mixtures of HTPB-DOA and HTPB-DOA-TDI do not cause the hazard of thermal explosion.

Researches on the rheological properties and thermal stability are ones of the fundamental analyses that allow to elaborate new, efficient rocket propellants.

REFERENCES

- [1] Saravanakumar D., Sengottuvelan N., Narayanan V. *et al.*: *Journal of Applied Polymer Science* **2001**, 119, 2517. <http://dx.doi.org/10.1002/app.32859>
- [2] Czub P., Kasza P.: *Polimery* **2014**, 59, 466. <http://dx.doi.org/10.14314/polimery.2014.466>
- [3] Kozakiewicz J., Rokicki G., Przybylski J. *et al.*: *Polimery* **2011**, 56, 564.
- [4] Chai T., Liu Y.C., Ma H. *et al.*: "Rheokinetic analysis on the curing process of HTPB-DOA-MDI binder system", IOP Conference Series: Materials Science and Engineering, IOP Publishing, Hangzhou, China, 20–23 May 2016, p. 1.
- [5] Chaturvedi S., Dave P.N.: *Arabian Journal of Chemistry* **2015**. <http://dx.doi.org/10.1016/j.arabj.2014.12.033>
- [6] Cao Z., Zhou Q., Jie S. *et al.*: *Industrial & Engineering Chemistry Research* **2016**, 55, 1582. <http://dx.doi.org/10.1021/acs.iecr.5b04921>
- [7] Yang L., Xie K., Pei J. *et al.*: *Journal of Applied Polymer Science* **2016**, 133, 43 512. <https://dx.doi.org/10.1002/app.43512>
- [8] Tanver A., Rehman F., Wazir A. *et al.*: *RSC Advances* **2016**, 6, 11 032. <http://dx.doi.org/10.1039/C5RA23250C>
- [9] Kumari D., Balakshe R., Banerjee S. *et al.*: *Review Journal of Chemistry* **2012**, 2, 240. <http://dx.doi.org/10.1134/S207997801203003X>
- [10] Florczak B., Bednarczyk E., Maranda A.: *Chemik* **2015**, 69, 136.
- [11] Florczak B., Bogusz R., Skupiński W. *et al.*: *Central European Journal of Energetic Materials* **2015**, 12, 841.
- [12] Singh M., Kanungo B.K., Bansal T.K.: *Journal of Applied Polymer Science* **2002**, 85, 842. <http://dx.doi.org/10.1002/app.10719>
- [13] Saeb M.R., Rastin H., Nonahal M. *et al.*: *Journal of Applied Polymer Science* **2017**, 134, 45 221. <http://dx.doi.org/10.1002/app.45221>
- [14] Sekkar V., Alex A.S., Kumar V. *et al.*: *Journal of Macromolecular Science, Part A* **2017**, 54, 171. <http://dx.doi.org/10.1080/10601325.2017.1265403>
- [15] Bandgar B.M., Sharma K.C., Mukundan T. *et al.*: *Journal of Applied Polymer Science* **2003**, 89, 1331. <http://dx.doi.org/10.1002/app.12254>
- [16] Sekkar V., Raunija T.S.K.: *Propellants, Explosives, Pyrotechnics* **2015**, 40, 267. <http://dx.doi.org/10.1002/prep.201400054>
- [17] Xu Z.-X., Wang Q., Fu X.-Q.: *Journal of Hazardous Materials* **2015**, 300, 702. <http://dx.doi.org/10.1016/j.jhazmat.2015.07.069>
- [18] Gańczyk K., Zygmunt A., Gołofit T.: *Journal of Thermal Analysis and Calorimetry* **2016**, 125, 967. <http://dx.doi.org/10.1007/s10973-016-5476-9>
- [19] Gołofit T., Zyśk K.: *Journal of Thermal Analysis and Calorimetry* **2015**, 119, 1931. <http://dx.doi.org/10.1007/s10973-015-4418-2>
- [20] Gołofit T., Książczak A.: *Problemy Mechatroniki: Uzbrojenie, Lotnictwo, Inżynieria Bezpieczeństwa* **2011**, 2, 31.
- [21] Semenov N.N.: "Chemical Kinetics and Chain Reactions", Oxford University Press, London 1935, p. 489.
- [22] Cepeda E., Hermosa M., Llorens F. *et al.*: *International Journal of Food Science and Technology* **2002**, 37, 271. <http://doi.org/10.1046/j.1365-2621.2002.00566.x>

Received 5 IX 2017.