

Modern high-energetic polymers

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The concept of high-energetic polymers

“High-energetic polymers” is term describing a specific group of polymeric compounds which properties do not always corresponding to that notion. This group includes some compounds with lower combustion energy per kilo than combustion energy of many engineering polymers, which do not belong to the group of high-energetic polymers (eg PTFE). High-energetic polymer are characterized by dynamics of combustion process, which mean combustion energy expressed by the pulse is high (heat of combustion per time). The explosive energy is described by parameter “heat of an explosive reaction”. Polymers, for which explosive combustion is possible, are called high-energetic polymers.

Also an ambiguous term “energetic polymers” is sometimes used. It is mainly biochemistry term and refers to the natural polymers (energy reserve material for living organisms). The term “explosive polymers” is also incorrect because decomposition of these polymers is not always explosive [1].

“Exploforic group” and “piroforic group” theory

High-energetic polymers are macromolecular compounds having the ability for rapid chemical transformation, with energy that can be used to perform work. A compound or material is capable of doing work when gaseous explosion products occurs during explosive transformation. Similar requirement: rapid decomposition, its egzothermic and gaseous reaction products are for low-molecular weight explosives. It can be assumed that the chemical structure of high-energetic polymers is analogous to the chemical structure of explosives.

Classical chemistry of explosives classifies certain groups of atoms as an “exploforic group”. These groups, when present in organic compounds give them explosive properties. On the otherh and piroforic groups, not give the explosive properties, but increase these properties.

Important exploforic groups:

- nitro -NO₂
- nitrate -ONO₂
- chlorate -ClO₃
- peroxide -O-O-
- azido -N₃

Important piroforic groups:

- amine -NH₂
- carboxylic -COOH
- hydroxyl -OH
- carbonyl =CO
- carbon-carbon multiple bond

This statement does not exhaust the exploforic and piroforic groups theory. Isocyanate groups are classified as both exploforic and piroforic [2].

Exploforic and piroforic groups theory can be applied without modifications to macromolecular compounds. The same groups can improve explosive properties of polymers and low-molecular-weight compounds.

Oxygen balance

Balance between reducing atoms (or group of atoms) and oxidizing atoms (or group of atoms) is an important as presence specific functional group in explosive. Balancing can be illustrated as follows: well

balanced compounds decompose to the simple compounds in which the atoms are in a typical oxidation-number (molecular nitrogen, water, carbon dioxide, etc.). Appropriately balanced relationship will burn up with a maximal energy of combustion. Balance is often expressed through a numerical balance of oxygen that is ratio (in percentage) of oxygen contained in the substance to the amount of oxygen required to burn all combustible atoms [3].

Balance between oxidizing and reducing groups might be expressed by concentration of carbon atoms in the molecule as well. It is the quantity of carbon atoms in the molecule, after reduction of the amount of carbon atoms that are oxidized intramolecular.

Oxygen balance factor can not be regarded as a determinant of the explosive, but well balanced is very important in macromolecular compounds. If the compound is not balanced, the polymer main chain is not decomposed during explosion. It is favourable if the polymer side chain oxygen balance is positive, this gives the possibility of oxidation of the polymer main chain.

Typical polymers have negative oxygen balance in the main chain, which is inherent to macromolecular compounds, however presence of oxygen atoms in the main chain has positive impact on high energetic properties.

New high-energetic polymers.

The first new type high-energetic polymer was synthesized in 1929, nitrated polyvinyl alcohol (PVN). A great part of research on this compound comes from World War II. Studies include also others compounds such nitrated polystyrene and poly(nitrophenyl), but without any positive results. The breakthrough came when polymer with azidomethyl side chain was first synthesized and patented in 1972 by E. Vandenburg [4]. The patent reserve the right to synthesis of poly(glycidyl azide). This compound can be obtained by the reaction of polyepichlorohydrin solution in dimethylformamide with sodium azide. Structure of poly(glycidyl azide) is shown in Figure 1.

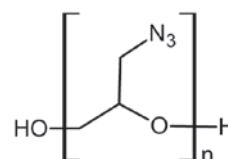


Fig 1. Structure of poly(glycidyl azide)

Due to presence of the exploforic azido group, polymer has explosive potential, but the first application of this compound was based on properties characteristics for macromolecular compounds. Polymers addition reduce sensitivity and improve the mechanical properties. Explosive formed by mixing RDX and poly(glycidyl azide) (0.864 / 0.136) have similar characteristics (sensitivity and mechanical properties) as the explosive formed by mixing RDX and hydroxide-terminated polybutadiene (0.864 / 0.136) [5]. However, the mixture of RDX with azide polymer have higher explosive parameters (higher energy of decomposition and higher volume of gaseous products of explosion).

Pure poly(glycidyl azide) not detonates in the usual manner. It decomposes rapidly, with nitrogen emitting as after-effect of the side chain decomposition. The reaction heat of decomposition is 957 kJ / kg (isobaric reaction at 5 MPa) [6]. Burning is rapid, though only the 40% of polymer mass is used. This compound is also characterized by relatively high concentration of carbon atoms and the presence of oxygen

atoms in the main chain (3 carbon atoms and 1 oxygen atom for each mer). Complete combustion of the polymer requires the participation of outside oxidant, which is not characteristic of individual explosives.

Properties of poly(glycidyl azide) are shown in Table 1.

Location of the azide group affects on the characteristics of glycidyl azide polymer. Compounds in which the azide group is substituted directly into the main chain, such as azidoPVC are not explosives. This means that an azidomethyl group ($-\text{CH}_2-\text{N}_3$) is considered to be explosive group.

Others new high-energetic polymers contain explosive nitrate (V) group (O-nitro, $-\text{NO}_2$). An example of a such polymer is poly(3-nitratometyl-3-metyl oxetane), synthesized by cationic polymerization of a monomer which contains in his structure heterocyclic ring (oxetane). The catalyst of the reaction is Lewis acid [8]. Structure of poly(3-nitratometyl-3-metyl oxetane) is shown in Figure 2.

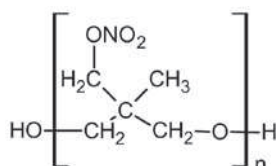


Fig. 2. Structure of poly(3-nitratometyl-3-metyl oxetane)

Poly(3-nitratometyl-3-metyl oxetane) is potentially explosive as a result of nitratomethyl side chain. First application of this polymer was analogous to poly(glycidyl azide), and also as an ingredient of insensitive plastic bonded explosives by mixing with classic explosive. The polymer decomposed differently than poly(glycidyl azide), the reaction depending on the stimulus and the polymer main chain might decomposed as well. This is result of the basic mechanism for the decomposition of the $-\text{CH}_2-\text{O}-\text{NO}_2$ group, which involves the radical ($\bullet \text{NO}_2$) initiation of intra molecular oxidation processes. This reaction proceeds rapidly at temperature over than 120°C . At room temperature the polymer is not explosive. Artificial ageing at 60°C in an inert atmosphere results decomposition to the compounds such like peroxides or alcohols [9]. Calculated enthalpy of explosion is $818 \text{ kJ} / \text{kg}$ [5].

This compound, as the only one described, is not classified as explosive, and is commercially available.

Polymer with similar physical and chemical properties poly(glycidyl nitrate) which is synthesized by heterocyclic ring (oxiran) mer. This compound is similar to oxiran polymers, such a polyepichlorohidrine, which is the poly(glycidyl azide) raw material. In both cases, the polymerization is initiated by HBF_4 , and gives prepolymer containing approximately 11 mers. Prepolymers are joined together with a multifunctional alcohol [10]. Structure of the polymer is shown in Figure 3.

Properties of the polymer are determined by nitrooxymethylene side chain. The polymer is potentially explosive, with similar properties like the poly(glycidyl azide), and similar decomposition like the

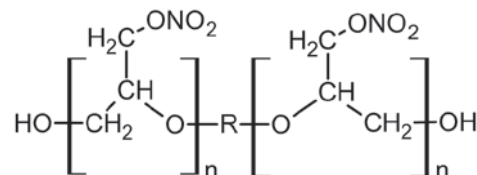


Fig. 3. Structure of poly(glycidyl nitrate), R – multifunctional alcohol poly(3-nitratometyl-3-metyl oxetane). Polymer decomposes explosively (the detonation wave initiation). Its combustion does not involve the additional oxidizer, although oxygen balance factor is -60.5 . Properties of polymer are shown in Table 2.

Calculated energy of explosion of poly(glycidyl nitrate) is lower than both the poly(glycidyl azide) and the poly(3-nitratometyl-3-metyl oxetane). However polymer resistance to simple stimuli (friction and shock) is higher. The application of polymer is limited by very low stability.

The methyl group linker ($-\text{CH}_2-$) between polymer chain and explosive group is based on characteristics of presented high energetic polymers. This is related to the specificity of reaction of decomposition. In this case, side chains is decomposed and also main chain is decomposed within limits. However, the methyl group decrease the oxygen balance factor of side chain. There are also polymers, in which the nitro group is substituted directly to the main chain. According to the theory, those polymers should have a greater explosive properties because of fact that the reaction will cover the whole molecule.

Some differences are noticed for azido polymers. Compound synthesised by the reaction of sodium azide with polyvinyl chloride (80% azido groups in product) does not have higher explosive properties than polymer with azidomethyl side chain [11].

In the case of a nitro group substitution for the main chain increases the heat of combustion, which triggered the explosive reaction, in opposition to combustion of compounds with nitro group substituted to side chain. This is related to the oxidation potential of nitro group. An example of such polymer product is nitration polybutadiene with hydroxyl end groups. Hydroxy terminated polybutadiene is used for many years in the technology of explosives as a binder of plastic explosives. It is not explosive, but it is fuel, and mixed with oxidizer gives propellant. Explosive is get in nitration process, where ratio of nitration is 1/9. Structure of hydroksy-terminated polybutadien nitrated in part is shown in Fig 4.

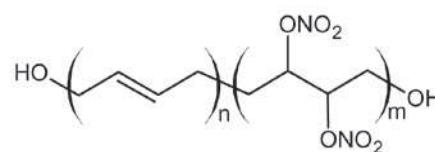


Fig. 4. Hydroksy-terminated polybutadien nitrated in part.

Properties of poly(glycidyl azide)

Table 1

Test / Property	Result	Score
Density		$1,29 \text{ g/cm}^3$
Form, colour	Light yellow liquid	
Glass temperature		-45°C
Blasting cup	Did not detonate	
Unconfined burning	Burns rapidly	
Friction sensitivity (Peters' test)		360 kN
Impact sensitivity (Kast's test)		20 Nm
Thermal stability (weight loss after 8 days at $73,9^\circ\text{C}$ at inert atmosphere)[7]		0,5 %
Enthalpy of detonation (calculated)[5]		2500 kJ/kg

Propeites of poly(glycidyl nitrate)

Test / property	Result	Score
Density		1,46 g/cm ³
Form, colour	Yellow liquid	
Glass temperature		-35 °C
Blasting cup	Detonate	
Unconfined burning	Burns rapidly	
Friction sensitivity (Peters' test)		360 kN
Impact sensitivity (Kast's test)		20 Nm
Thermal stability (weight loss after 8 days at 60 °C at inert atmosphere)[9]	Decomposition	
Enthalpy of detonation (calculated)[5]		2661 kJ/kg

Polymer has simple structure. The parameters of explosives are able to determine in a wide range by changing the degree of substitution. It is the most promising high energetic polymer. However, physical and chemical properties are similar to properites of hydroksy-terminated polybutadien, like: low viscosity, low glass transmission temperature the possibility of cross-linking. Mechanical properties and stability are retained by polymer with nitration degree up to 15%, it is possible to use this polymer as a matrix of plastics bonded explosive [12].

Summary

Both, azido and nitro group, are used in new high-energetic polymers. In the case of the azido group, it should be linked by methyl (azidomethyl group is created). Azide group itself may not be enough for explosive properties of polymer.

Balance between oxidizing and reducing elements of the structure is important in macromolecular compounds. Valuable factor that expresses this balanced is the oxygen balance of side chain.

An important group of high energetic polymers are compound with nitro group. New polymers based on this kind of exploforic group have a chance to become new generation of explosives.

Also poly(glycidyl azide) is seen to be advanced explosive because of oxidation and reducing balance, physical and chemical properties and reduced sensitivity.

Literature

- Colclough M. i inni: Energetic polymers as binders in composite propellants and explosives. *Polymers for Advanced Technologies*, 1994, 5, 9, 554-560.
- Korzun M.: 1000 słów o materiałach wybuchowych i wybuchu. MON, Warszawa, 1986.
- Urbański T: Wstęp do technologii materiałów wybuchowych. MON, Warszawa, 1954.

- Vandenburg E. J.: Polymers Containing Azidomethyl Side Chains. US Patent 3 645 917.
- Desai H. i inni: Synthesis of narrow molecular weight á,ù-hydroxy telechelic poly(glycidyl nitrate) and estimation of theoretical heat of explosion. *Polymer*, 1996, 37, 15, 3471-3476.
- Kubota N.: Combustion mechanism of azide polymer. *Prop. Explos. Pyyro.*, 1988, 13, 172.
- Frankel M. i inni: Historical Development of Glycidyl Azide Polymer. *J. Prop. Power*, 1992, 8, 3, 560.
- Kubista P. i inni: Kinetics and Mechanism of oxetanes polymerization catalyzed by R₃Al. *Die Makromolekulare Chemie*, 1967, 100, 286-289.
- Bunyan P i inni: Analytical Techniques for the Study of the Aging and degradation of an energetic polyoxetane. TTCP, W-4, 20th Meeting, 1995, TTCP, USA.
- Millar R., Stern A., Day R.: Process for Producing Improved Poly(glycidyl Nitrate). US Patent 5017356.
- Agrawal J.: Some new high energetic materials and their formulation for specialized applications. *Propellant, Explosives, Pyrotechnics*, 2005, 30, 5, 316-328.

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