Polyolefin composites for special applications

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Taking into consideration tonnage, the biggest part of the world production have olefin polymers and among them polyethylene and polypropylene. Regarding their properties, polyolefins are very diverse group of polymers; each polymer occurs in at least few types, this is why we can find polymers in solid and liquid state, hard, brittle, flexible. Basic polymers properties can be additionally changed by the use of fillers and modifiers. Because of that, polyolefins are a good base for obtaining material with the desired properties. The possibility of regulation of physico-chemical properties in a wide range, relatively low price and easy processing decided about prevalence of polyolefin materials, and simultaneously their classification as a raw materials for production of every day articles [1].

The development of military industry proceeds according to the concept of sword and shield, that is action and contraction. This conception lies in that, preparation of a new weapon (sword) implies designing of a better protective measure (shield), allowing to degrade action of created arms. In turn, appearance of a new shield determines works on more effective combat measures, enabling its elimination. In consequence, that leads to fast and incessant development of military technique [2]. Military technique is a strong progress engine, not only for the military branch, but also for several branches of industry, also including plastics.

The aim of the following work is to show the wide possibility of application of polyolefin composites, not only in standard manner, but also as materials for special applications e.g. in military branch. Chosen applications show, how diverse materials can be obtain on the basis of polyolefin polymers.

Binders for plastic bonded explosives and propellants

For over a hundred years polymers have been used as a components of propellants in artillery and small-caliber ammo, in explosives with decreased sensitivity for mechanical stimuli, and since the forties, it is since rockets were introduced, also in rocket propellants. Modern plastic bonded explosives (PBX) and also propellants are mixtures of oxidizer, polymeric binder, modifiers and blasting explosives, balanced depending on its function. The binder content, depending on application, varies most often in the range 5-30 % by weight in relation to the whole mass of the mixture. [3, 4]

Binder, also commonly called fuel, in solid propellants and plastic bonded explosives, is a flammable ingredient, acting as a structure-creating agent. Its purpose is to give appropriate mechanical strength and compactness to the whole mixture. Good binder selection has a crucial influence on explosives phlegmatization, that is decreasing its sensitivity for initiation of explosion by accidental mechanical stimulus. As a flammable component, it is an agent allowing for appropriate oxygen balance, which is especially crucial, if the mixture is going to be used as propellant or PBX for ammunition elaboration. Binder choice determines processing of the whole mixture, which is connected to the most important requirement for the materials: the method of forming. Here casting is preferred, though proccessing or injection could also be used [4].

Other requirements often set for binders:

- high phlegmatization ability,
- ability of chemical conversion with a large amount of gases production,
- relatively high density at simultaneous lack of solid products of combustion, that affects ability fr execussion of work by the mixture,
- small corrosive aggression,
- relatively low toxicity of the binder and the products of its combustion.

For plastic explosives, such as C4 (Composition 4), used by counter-terrorist and military engineering groups, there are additionally set three requirements, which directly connect to binder choice:

- can be formed by hands,
- can be stuck to items, but do not stick to hands (like plasticine),
- preservation of plastic properties in a wide temperature range.

Materials used as binders are not able to meet all requirements at the same time, that is why depending on their application, the significance of particular requirements is changeable.

At first, in plastic bonded explosive mixtures as a binder natural polymers have been used. The development of knowledge on synthetic polymers, caused that in the fifties of the last century began research on their application in explosive agents also. Mixtures obtained on the basis of synthetic polymers characterized by higher time durability and were more waterproof, than those with natural polymers. Intense studies lasted up to the seventies. During that time have been elaborated a great number of PBX recipes based on epoxide resins or polyurethanes; it also turned out that majority of requirements set for binders were met by olefin polymers or their mixtures. At present, among polyolefin binders, most commonly used are the mixtures comprising of polybutadiene terminated by hydroxyl groups (HTPB) or polyisobuthylene (PIB)), Fig. 1. This fact is caused, mostly by two factors, i.e. simplicity of obtaining mixture with explosive and the ability for maintaining good operational parameters in a wide temperature range [4-7].

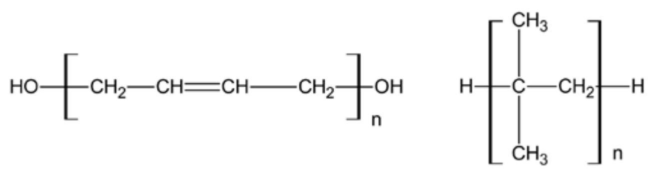

Fig. 1. Structure of HTPB (left) and PIB (right)

These polymers are also characterized by high ability to phlegmatize an explosive. Fig. 2 shows friction sensitivity (value in N) of pure pentaerythritol nitrate(V) (PETN) and its mixtures (30 cg/g of binder) with polyisobuthylene (PIB), polyglycerol (PG), polybutene terminated by hydroxyl groups (HTPB) as well as co-polymer glycidyl azide with ethylene oxide (Poli(GAcoEtOX).

As shown in the below graph, mixture based on polyolefin polymers, PIB and HTPB, demonstrate half the friction sensitivity in comparison to pure explosive.

Polyolefins, are used as binders as well, in such a specialized plastic mixtures as initiating agents activated by small power lasers. The main component of such mixtures is the most often high ener-

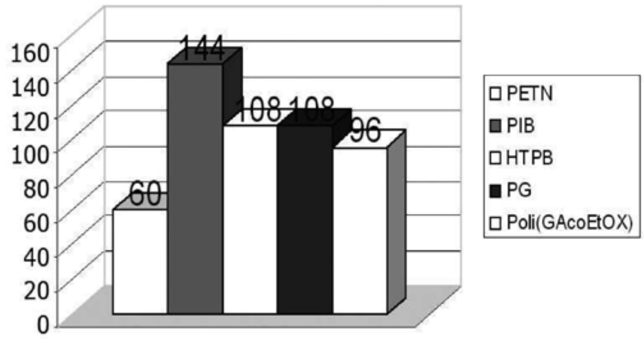

Fig. 2. Comparison of friction sensitivity of pure PETN and its mixtures

getic complex sensitive to laser light e.g. ***cis***-bis-(5-nitrotetrazolato-***N²)***tetraminecobalt(III) perchlorate, BNCP (fig. 3).

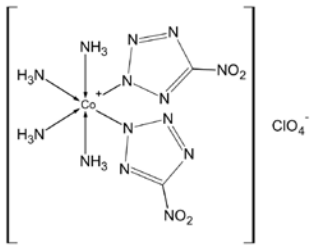

Fig. 3. Structure of BNCP

Explosives of this type, in contrast to classical primary explosives, are characterized by small sensitivity, for easy to generation, mechanical stimuli. However, they can be initiated by laser light with appropriate wave length. In this application binder should let the laser through beam, preferably leading to its reflections inside the mixture. This will allow the light to act on complex crystals and initiate explosive. The binder is very good at explosions initiated by laser, ating on the aforementioned HTPB. Significantly worse results are obtained using PIB [8-10].

Shaped charges constructional elements

Polyolefin composites are a good material for production of elements of specialized explosives for sapper purpose, especially flexible linear shaped charges. First of all linear shaped charges are used during engineering works to cut concrete and steel profiles as well to destroy carrier elements during demolition by the use of explosive technique. The crucial fact is that most of those works can not be realized with other explosives, whereas, if there is such a possibility, it turns to be less economically profitable. For a long time, the disadvantage of linear shaped charges was that they have been characterized by high stiffness, what made their application difficult. The occurrence of flexible linear shaped charges significantly improved the work comfort, and also created an opportunity of their application in completely different objectives. Charges of this type are readily used by counter-terrorist (e.g. S.W.A.T.) in elimination of solid obstacles like doors or bars.

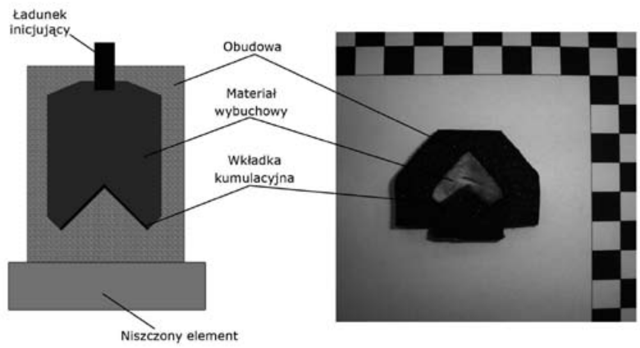

Fig. 4. Scheme of a flexible linear shaped charge (left) and a photo of a flexible linear shaped charge „BLADE" (right)

Shaped charges, both linear and axial, are generally constructed of three elements, there are: explosive, liner and casing, Fig. 4. Each of those components can be prepared on the basis of olefin polymers. The biggest problem in the material selection is that flexible linear shaped charge is going to be deformed, it means formed in such a way, that it sticks to the obstacle despite its shape. In this case, essential is to preserve, in a great range, the geometry of the charge and especially of the liner during its formation, [11-13].

Explosive

Its task is the production of relatively large pressure, which acts on the liner the jet. In connection to that, use to create explosives with relatively high detonation velocity is favored. Elaborated flexible shaped charges are plastic bonded explosives relatively resistant to expansion forces. In this element polyolefins are applied as binders for plastic bonded explosive.

Liner

At the beginning liner was used to secure shape from deformation. However, in practice it turned out, that appropriate material and liner selection positively affects the shaped charge effectiveness, causing increase of penetration or cutting effect. Liners with high density, with respect to their light equivalents, allows for higher detonation front wave pressure in the area of explosive and liner contact. As a result shaped charges with high density liners are more effective. As the material for liners most often are used heavy metals such as lead, copper, tungsten, beryllium, or even impoverished uranium. Flexible liners are polymer materials filled to a high degree with metal dusts. These composites, in relation to their consistency, can be divided into two groups, it is pastas and solids. In both groups are well known solutions based on olefin polymers. As an example can be used pastas containing copper dust and polyisobutylene. Whereas, liners of solid consistency often contain polyethylene and its copolymers as well as their mixtures. Properly chosen olefin polymers become matrix, which can be filled with metal dust up to 95 cg/g and at the same time maintain good durability and operational properties [14-15].

Casing

Basic task of the casing is the protection of explosive and liner against mechanical damage. This way casing in a large measure is responsible for shaped charge shape. Casing can also function as a distance kept between shaped charge and destroyed target. The best results of penetration or cutting are achieved, when the obstacle is in such a distance, that energy concentration of the jet with respect to its cross-section is the biggest. Some patent solutions describe also the use of casing for the purpose of attaching shaped charge to destroyed target. Very often casing is made of the same materials as an liner [16-18]. There are also known solutions, in which casing of flexible shaped charge is made of foamed polyethylene. This solution, among others, is used by respected in the explosives branch company „Explosia".

Proper selection of polyolefin materials in the main constructional elements of flexible shaped charges allows for a good operational parameters, especially preservation of flexibility in a wide temperature range. Application of polyolefins in comparison to other types of polymers is often economically profitable.

Shields against harmful battlefield factors

Above were introduced applications of olefin polymers in 'sword' elements. However, olefin polymers also found applications in 'shield' components, among others, in the production of ballistic shields [19]. Bulletproof shields may by made on the basis of polymer-ceramic composites, this is ceramic plate immersed in polymer. As a polymer most often, for this purpose, is used high density polyethylene. In ballistic shields weight is as much important parameter as resistance to penetration. Increasing durability with minimum change of mass can be obtained by the use of polyethylene matrix filed with polypropylene fibers. Polyolefins are also used in elements of bulletproof vests, but in a limited way. In this field prevail aramid materials, such as e.g. Kevlar, which despite higher price have better usage parameters.

Polyolefin composites are also used in the production of shields against neutron radiation, on which can be exposed tank or bunker crew during nuclear attack. Even though, penetrating radiation (neutron and gamma) is emitted only over 10 to 15 seconds and 5 % of explosion energy falls on it, it presents the most dangerous agent. Gamma radiation in a high degree is reduced by construction metal elements, e.g. tanks armor [20]. Neutron radiation is a penetrable radiation, which carries a large mass. Neutrons as a particles, which do not posses a charge, have simplified access to atomic nucleus. As a result of neutrons collision with nuclei, atom ionization can occurs, and depending on their energy, even nuclei can be split, what in the effect can cause secondary radiation [21]. Depending on energy neutrons are divided into:

- thermal $<0,1$ eV,
- small 0,1-100 eV,
- medium 0,1-100 keV,
- fast >100 keV.

As the high energy neutrons capture is not possible, their energy should be decreased and thermal neutrons should be created, that is why radiation shield act two-stages.

At the first, stage neutrons energy occurs and thermal neutrons are created. In the slowing down process are used moderators. Neutrons, by collisions with their particles lose energy, but are not absorbed. The best in this role are materials with high concentration of light elements and the best is hydrogen. Often for this purpose are used water, heavy water, beryllium, carbon in the form of graphite, hydrides e.g. zirconium hydride, lithium compounds, and also organic compounds, like waxes and polymers. Polymer matrix in radiation shields, not only lowers neutrons energy but also in a great manner affects mechanical properties. As a matrices it is profitable to use olefin polymers. They are characterized by high hydrogen atoms concentration, understood as an amount of hydrogen in the volume unit, better than in other groups and similar to popular inorganic moderators, such as: lithium or sodium borohydride.

The second stage of radiation shield action is thermal neutrons capturing. This task is fulfilled by compounds containing gadolinium and impoverished uranium, but the best results give boron compounds [21], and to be more specific isotope ^{10}B.

Known from the literature polyolefin composites designed as materials for production of shields against neutron radiation are for example: India-rubber/boron carbide [22], India-rubber/boric acid [23], terpolymer ethylene-propylene-dien/LDPE/boron carbide [24], HDPE/LDPE/boric acid [25]. It should be pointed out, that composites based on boric acid are significantly cheaper, than those in which absorbing agent is boron carbide.

Summary

Polyolefin materials are used in specialist constructional solutions in military industry. Due to their wide variety, they are used not only in striking agents, but also in shields against harmful agents on the battlefield. At present polyolefins are especially applied as:

- binders for plastic bonded explosives,
- binders for propellants, powders and rocket fuels,
- flexible liners,
- elements of ballistic shields,
- elements of shields against penetrating radiation.

Selected applications show high potential of this polymer group and materials based on them.

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