

Long Term Investigation of Bonding Characteristics Between PVC Based Inhibitor and HTPB/IPDI Based Propellant

Jovan Radulović¹⁾
Aleksandar Milojković¹⁾

Bonding characteristics between extruded polyvinyl chloride (PVC) inhibitor and casted hydroxyl terminated polybutadiene/isophorone isocyanate (HTPB/IPDI) propellant, investigated in a long period of time, are topics of this paper. Basic statements about poly(vinyl) chloride, extrusion process and PVC tube (including compound formulation) are presented. There are, also, important considerations about propulsion systems, HTPB/IPDI propellant, plasticizer, casting technology and inhibitor. Specimens for investigation the properties of bond between inhibitor and external radial surface of solid propellant and specimens for determining the characteristics of bond between inhibitor and flat surface of solid propellant are shown.

Two kinds of characteristics of bond between PVC based inhibitor and external radial surface HTPB/IPDI based propellant were examined: strength properties and visual appearance. Strength characteristics include arithmetic mean value of bond strength and arithmetic mean value and standard deviation of bond strength. Mentioned properties, as indication of quantitative aspects of tested bond, were obtained using appropriate method of determination and specific tool, adjusted to geometry of propellant. Visual appearance of separated PVC parts and of remaining of PVC inhibitor-HTPB/IPDI propellant specimens, as indication of qualitative aspects of tested bond, were tested visually. Based on visual appearance of mentioned separated parts an assessment of way of separation was done. Strength characteristic of PVC inhibitor-HTPB/IPDI propellant specimens and visual appearance of separated parts were determined at the start of investigation procedure, after five years of ageing and after eleven years of weathering in warehouse conditions. Both mentioned properties were tested at temperature 20 °C and temperature 50 °C. Data obtained by testing PVC inhibitor-HTPB/IPDI propellant specimens are presented in Tables and in Figures.

Key words: polymeric materials, poly(vinyl chloride), inhibitor, hydroxyl terminated polybutadiene, isophorone diisocyanate, propellant, bond strength, quantitative aspects, visual appearance, qualitative aspects, ageing.

Introduction

MATERIALS are basic elements not only for natural structures, but also for all man-made structures. Development and introducing of new materials and continuous improvement of existing materials are two main factors of technological progress [1].

Materials are solid or liquid or gas matters that are used for a production of needed elements. Generally speaking, four basic engineering materials are metals (including alloys), ceramics (including glass), polymers (can be divided into

plastic materials and elastomeric materials) and composites (composed of two components: the matrix and the fibers).

Different materials can be used for a production of joint elements or assembly elements. These elements can be based at one of the mentioned four basic engineering materials or produced using other materials like wood, etc. [2].

Produced elements can be jointed in different ways: by permanent jointing processes (including adhesively bonded) and by mechanical fastening, as it is presented in Figure 1 [3]:

¹⁾ Military Technical Institute (VTI), Ratka Resanovića 1, 11132 Belgrade, SERBIA
Correspondence to: Jovan Radulović; e-mail: jovan.r.radulovic@gmail.com

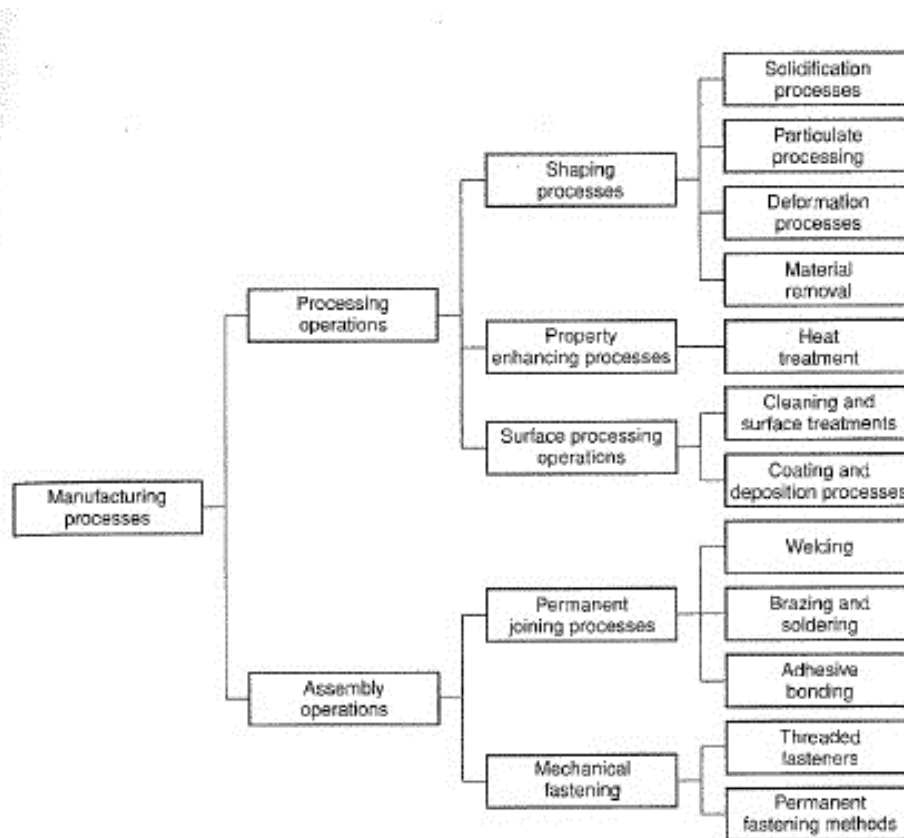


Figure 1. Classification of manufacturing processes

From many points of view, probably, the most important difference between plastic materials and other materials is a fact that characteristics of plastic materials are time dependent [4].

One of the important characteristics of plastic materials is changing of morphology with elapsing time, independent of any exposure. There are two reasons for this phenomenon: one is reduction of "free volume" in the plastic matrix and the other is enhancement of number of cross-links between macromolecules. Although one can suppose that two mentioned occurrences are beneficial, the consequences of plastic material ageing process are brittle-type fracture and reduction of impact resistance [5].

Polymeric based elements are widely used externally as well as internally. No matter where these parts are used it is an understandable concern connected with durability of the mentioned products from two points of view: one is relative newness of these materials and the second is need to plan their maintenance and replacement, if there is an estimation of their useful life [6].

Natural weathering as a process comprises all phenomena that lead to the degradation of materials and reduction of the life cycle of construction parts in shorter or longer period of time. This process, which can be named as weathering, ageing or degradation, depends on the way and extent to which materials interact with their surroundings [7].

This paper deals with bonding properties between one extruded plastic material (concretely thermoplastic polyvinyl chloride) and one casted elastomeric material (specifically hydroxyl-terminated polybutadiene). The basic idea of this investigation is to establish what happened with extruded polyvinyl chloride/casted cured hydroxyl-terminated polybutadiene bonding characteristics in a period of time longer than one decade.

Materials and technologies

Polyvinyl chloride, extrusion, pipes

Polyvinyl chloride (PVC), together with polyethylene (PE), polypropylene (PP), polystyrene (PS) and acrylonitrile butadiene styrene (ABS), are collectively referred to as the five general-purpose resins. Polyvinyl chloride is just behind polyethylene among the five kinds of general plastic materials by volume production [8].

This thermoplastic material was accidentally discovered twice in 19th century (first Regnault H.V. 1835 and second Baumann E. 1872), but the synthesis of polyvinyl chloride was patented by Russian chemist Ostromislensky I. in 1929 [9].

In shortest, polyvinyl chloride resin is a polymer compound formed by suspension polymerization of vinyl chloride monomer (VCM), and its structure unit is $[\text{CH}_2\text{-CHCl}]_n$. The polymerization degree (n) is usually from 590 to 1500 [10].

Polyvinyl chloride (PVC) is produced as white, amorphous, odorless powder which cannot be processed because it is too brittle. Owing to a high polarity of PVC and capability of this polymer to be mixed with some different additives, a lot of PVC-based compounds can be obtained. These compounds can be processed by different technologies.

Generally speaking, there are three main groups of PVC-based products:

1. rigid (unplasticized) PVC, which does not contain plasticizer,
2. flexible PVC, which contains up to 30 % of plasticizer and
3. foam PVC, which contains ingredients for making foam structure.

This thermoplastic polymer is widely used in industries

including construction, architecture, electronic, chemical engineering, packaging, transportation, daily life, public utilities, etc. [11].

PVC has the good mechanical properties at room temperature, flame retardancy, abrasion resistance, chemical resistance, electrical insulation and easy processing by appropriate technologies, including extrusion.

PVC compounds, prepared for pipe extrusion, are a mixture of PVC resin and a combination of stabilizers, fillers, lubricants, pigments and modifiers [12].

Compound formulation for PVC pipes extrusion [13]:

1. PVC K67 100 parts,
2. Tin merkpto ester 0,4 parts,
3. Calcium carbonate 4,0 parts,
4. Oxidized PE wax 0,25 parts,
5. Paraffin waxes 1,2 parts,
6. Calcium stearate 0,4 parts,
7. Titanium dioxide (rutile type) 2,5 parts,
8. Yellow quinophthalone pigment 0,5 parts,
9. Acrylic polymers 0,25 parts.

PVC resin is a suspension PVC whose K number is 67 (K is a defined mark of mean molecular weight and number 67 denotes that degree of polymerization is from 1000 to 1100).

Stabilizer is organotin merkpto ester. This ingredient protects heat and light sensitive PVC, prevents degradation of PVC compound during contact with metal surface of extruder and enables the manufacturing of extruded product. Stabilizer, also, enhances color stability, promotes fusion and reduces melt viscosity [9].

Filler is calcium carbonate coated with stearic acid (the coating reduces the abrasiveness of the mentioned ingredient and extruder barrel and screw). Generally speaking, metal carbonates lower the raw material cost and contribute to economic aspect of the finished compound [9].

Thermoplastics polymers (PVC among them) are made of long chains molecules which tend to be relatively viscous and sticky above their melting temperature.

The main purpose of using lubricants is to decrease frictional forces between polymeric chains (internal lubricants) and to decrease friction between polymer ingredients and metal surfaces of the process equipment (external lubricants). A lubricant combination, consisting of a paraffin wax, calcium stearate and oxidized PE wax, is well suited for PVC tube extrusion [9].

More precisely, internal lubricants lower the melt viscosity by reducing friction between the molecular chains of PVC. Internal lubricants are normally polar molecules (for example oxidized PE wax), which, also, promote fusion and have a low tendency for exudation. Oxidized polyethylene wax can improve the smoothness, evenness and yield of the finished products [13].

External lubricant, added to the PVC compound, enables this mixture to be processed during the extrusion cycle. These normally non-polar molecules (usually paraffin waxes) prevent the sticking of PVC extrusion compound and the hot surfaces of the barrels, screws and dies. This kind of lubricants have positive effect on the gloss of extruded product surface [14].

Another external lubricant is calcium stearate. The role of this lubricant, in the form of white to yellowish-white powder, is decisive in rigid PVC, particularly in the production of PVC pipes without plasticizers [15].

Pigments for PVC (regardless organic or inorganic) must be thermally and light stable, have good dispersibility, and be compatible within the formulation. Usually, a mixture of titanium dioxide and another pigment are used. Rutile crystal

structure titanium dioxide (used due to high refractive index) gives "bright" whiteness and opacity. Used yellow quinophthalone pigment contributes to an appropriate color of extruded PVC pipes.

Acrylic polymers, as one of widely used impact modifiers, are required ingredient in production of extruded PVC pipes. It is mostly used in weatherable PVC products because this constituent enables good retention of properties (including color) and contribute to heat and impact resistance.

Maybe the shortest explanation of extrusion is following: that is compression process in which material is forced to flow through a die orifice to provide long continuous product whose cross-sectional shape is determined by the shape of the orifice [16].

Propellant, inhibitor, casting

In propulsion systems three terms are used: motor, engine and thruster. Word motor means solid propellant rocket propulsion system, engine is referred to liquid propellant rocket propulsion system and thruster is used in electric propulsion systems.

The solid propellant contains all the chemical elements for complete smooth burning at a predetermined rate on all the exposed internal surfaces, except inhibited ones. It is necessary that an inhibitor has good adhesive strength because it must stay bonded to the propellant. Chemical compatibility between propellant and inhibitor is very important in order to avoid migration and/or changes in material composition [17].

Migration, in this particular case, can be described as moving of mobile (liquid) chemical species in direction from the solid propellant to the inhibitor and the transfer of mentioned chemicals in direction from the inhibitor to the solid propellant.

This migratory process is happening very slowly but the consequences can be changes in physical properties, actually, the propellant next to the inhibitor may become brittle or weak [17].

Components for composite propellants, in the shortest, are a liquid phase and solid phase.

Liquid phase consists of two-components organic binder, plasticizer and bonding agent.

Solid phase contents antioxidant, inorganic oxidizer and metal fuel.

Two-components organic binder holds the composition together, acts as an auxiliary fuel and makes the propellant flexible. One component of organic binder is resin and another component of the mentioned system is curing agent.

Resin is prepolymer butadiene with end hydroxyl groups or commonly named hydroxyl terminated polybutadiene, shortly HTPB. It is considered that the first military grade HTPB was manufactured about sixty years ago (early 1960s) in Texas, USA. This synthesized product offered different possibilities owing to improved performance and enhanced mechanical properties. First experiments pointed out that reaction products of hydroxyl terminated polybutadiene and isocyanates had many desirable characteristics that cannot be achieved with other systems (excellent hydrolytic stability, compatibility with oil-type plasticizers, improved adhesion to substrates). It was concluded that HTPB/isocyanates system has potential utilization in commercial and military field, especially rockets [18,19].

Curing agent is isophorone diisocyanate, commonly called isophorone isocyanate, shortly IPDI. This curing agent is an organic compound (specifically, aliphatic diisocyanate) and is used in special applications. Isophorone isocyanate reacts with hydroxyl terminated polybutadiene and the product of

this reaction is organic binder.

A bonding agent is triethylenetetramine, shortly TETA. This colorless or yellowish color oily liquid, as a surface-active component makes contribution to the mechanical properties of propellants. This effect is based on the characteristic of mentioned ingredients to enable better adhesion between solid particles and the polymeric matrix. Mentioned TETA produces primary or secondary bonds with the oxidizer particles and a primary bond with a polymeric binder. Bonding agents are widely used in composite propellants in which basic binder is HTPB because mentioned polymer is weakly polar [9, 13].

Antioxidant is phenyl- β -naphthylamine, shortly P β NA. Mentioned stabilizer (widely used synonymous for antioxidant) in form of light tan or gray flake or powder prevent oxidative hardening of propellants [9].

Inorganic oxidizer is ammonium perchlorate, shortly AP. Having in mind weight and volume percent of the mentioned chemical, regarding percent of other constituents, it can be stated that AP is a major component in solid rocket propellant. Oxidizer produces the high energy on combustion and impact burn rate. Colorless or white solid ingredient is usually used as multimodal combination because this procedure enables optimum relation between exposed oxidizer surface area and packing fraction.

Metal fuel is aluminum (IUPAC chemical name for this ingredient), shortly Al. It is the most widespread metal on the Earth and is broadly used in solid propellants based on different polymeric binder. This component in the form of fine silvery white particles enhances the heat of combustion, propellant density and combustion temperature [20, 21].

Plasticizer is di-n-octyl adipate, shortly DOA. Dioctyl hexanedioate (IUPAC chemical name for dioctyl adipate) is relatively low-viscosity organic liquid which extends pot life of reaction mixture, improves the processing properties and flexibility at low temperatures of propellant [22].

Only liquid component of solid rocket propellant, which is not chemically bonded with other constituents, is plasticizer.

Generally speaking, plasticizers are the most broadly incorporated additive in plastic and elastomeric materials. Presence of this additive either in plastic materials or in elastomeric materials allows making products easier. Another positive consequence of using this kind of additive is that the products are softer and have better resistance to low temperatures. Plasticizers enhance the processability of polymeric composition by decreasing the viscosity and the melting temperature of processed mixture and have positive effects on the essential characteristics of finished products (improve the glass transition temperature (T_g) and the elastic modulus).

Considering the plasticization, there are two ways of this process: internal and external.

Internal plasticization implies copolymerization of the monomers of the chosen polymer (having high T_g) and of the plasticizer (having low T_g). Owing to this procedure, the plasticizer becomes an integral part of the polymer chain. Chemically modified internally plasticized copolymer is devoted for specified flexibility requirements. Internal plasticization is rarely used because reaction times are meaningfully longer (due to complexity of the reaction) and costs are increased. Polymeric materials plasticized at above-described manner are temperature dependent and dimensionally unstable at high temperatures.

External plasticization is a process in which the low-cost liquid plasticizers are added to reaction mixture, similar to the way the other constituents are used. The mentioned procedure

is the most commonly used method of plasticization.

It is of great importance that plasticization process does not change the basic chemical nature of plasticized polymeric material.

There are two kinds of external plasticizers: primary and secondary.

A primary plasticizer enables elongation, softness and flexibility of polymeric products. This kind of plasticizer is very compatible with basic polymer and can be used in great quantities.

A secondary plasticizer, usually, has limited compatibility with the polymer. Owing to this fact, this kind of plasticizer, mostly, is not added as the only plasticizer in a plasticized polymer. Non writing rule is to use the secondary plasticizer with the primary one [23].

Solid rocket propellants, based on HTPB/IPDI system, are almost entirely produced by casting technology. Generally speaking, casting is technology that can be used for production of thermosetting and thermoplastic based products.

This procedure involves pouring of a resin system in liquid state into an appropriate tool, whose cavity is filled by gravity, and enabling polymer to achieve the final state. Casted thermoplastic products are usually produced using polystyrene, polyamides, acrylic and vinyl polymers. The most suitable thermosetting polymer materials for casting technology are polyurethanes, unsaturated polyesters, phenolics and epoxy systems. There are few advantages of casting technology over similar procedures: a) mould is very simple and cheap, b) casted products possess low level of residual stresses and of viscoelastic memory. The casting procedure of liquid thermosetting systems includes pouring of components (necessary for production of desired final product) into a mould and allowing subsequently cross-linking of resin mixture. It is of great importance that chemical reactions of used thermosetting system is slow, in order to minimize the stresses in the produced part [3].

If one wants to describe the role of inhibitor, it should be stated that this material must have a whole set of characteristics, but some of them are difficult to be numerically expressed. An excellent bonding between inhibitor and the propellant is of essential significance because this characteristic is the most important for the reliability of the rocket motor. If it is not like that, any debonding between the inhibitor and the propellant will cause a failure of the rocket motor, because the pressure will rise without control. Inhibitor should have a sufficient bonding with propellant in the chosen temperature range in which the motor is planned to operate.

Although there is a great number of papers and books about adhesion (in other words bonding) in few past decades, the knowledge about basic relations is not large and unique theory that can explain the whole set of phenomena that does not exist [24, 25]. There are a lot of models trying to explain this multidisciplinary phenomenon (diffusion model by Russian researcher Voyutski, mechanical model by American expert MacBain, electrical model by Russian scientists Deriyagin and Krotova, wetting model by Zisman, model of the interfacial layer with weak cohesion by Bikerman, chemical model...) [26].

The other important characteristics of inhibitor are small level of rate of ablation, of thermal conductivity and of density, adequate compatibility (mechanical with deformation of propellant, pyrotechnic with propellant and ignition powder and chemical with present components) and good ageing characteristics. High specific heat, good gas permeability, small humidity absorption and adequate electric conductivity

to prevent electric charge are desirable characteristics of the inhibitor [26].

Reddy K.A. and others have studied the migration of chemical species in the hydroxyl terminated polybutadiene (HTPB) resin based solid propellants. They made specific specimens, which were very similar to the propellant of the main motor and exposed them to the influence of ambient temperature and accelerated ageing at elevated temperature. At regular intervals (for a period of 100 days) the specimen were taken and content of chemical species in insulation material and in propellant were determined by Soxhlet extraction. Migration of specific ingredients from solid propellant (taken from Agni motor) and from standard HTPB solid propellant were determined in a similar way. Although the main view was concentrated on plasticizer migration, data about the migration of other chemicals are presented in this paper [27].

Deuri S.A. and Bhowmick A.K. made a set of hydroxyl terminated polybutadiene (HTPB) specimens cured with different amount of toluene-di-isocyanate (TDI). Specimens were exposed to oxidative ageing and they concluded that higher proportion of TDI increased physical properties and also reflected in the morphology of the fracture surface. At specimens cured with higher quantity of mentioned curing agent more tear lines/tear deviations are observed on the fracture surface. After ageing there were no big differences in the fracture surfaces at almost all HTPB/TDI specimens [28].

Selvakumar S. et al. developed solid propellants based on hydroxyl terminated polybutadiene resin (HTPB) blended with the hydrocarbon oil (named Extol-21) trying to overrun the difficulties existing in processing of standard HTPB solid rocket propellants (firstly pot life of the propellant mixture). They produced an appropriate number of propellant specimens based on standard HTPB and on HTPB mixed with low and high viscosity oils. Mentioned specimens (similar to propellant of the main motor) were exposed to the influence of ambient temperature and of high temperature for different periods of time. After this treatment, the content of labile chemicals in insulation rubber and in propellant of specimens (aged at room and high temperature) were determined by analytical extraction method. These data were analyzed with data obtained using standard HTPB specimens. One of their observations was that diffusion of plasticizer and other chemicals took place. They, also, investigated the movement of solid ingredient (named Nonax-D) and observed migration of this constituent because of dissolving it in propellant matrix (not for physical movement of this particle). Chemicals from propellant moved into insulation and consequence of this process is a fact that initial concentration of mentioned ingredients in propellant regions near insulation surface is significantly reduced. Temperature and time have influence on the migration of the chemically unbound species. Viscosity data and data obtained by testing mechanical, interfacial and ballistic characteristics of specimens based on standard HTPB and on mixture HTPB/ Extol-21 were presented [29].

Experimental part

The experimental part was planned and realized in an attempt to establish the influence of time on quantitative and qualitative aspects of bond between extruded polyvinyl

chloride (PVC) inhibitor and casted hydroxyl terminated polybutadiene/isophorone isocyanate (HTPB/IPDI) propellant, after weathering in warehouse conditions. In order to obtain the mentioned goal, four activities were done at the beginning of the experimental part.

The first activity in the production of extruded PVC pipe/casted HTPB/IPDI propellant specimen was extrusion of non-plasticized PVC pipe. The extrusion of PVC compound, whose formulation is described previously in this paper, and production of rigid PVC pipe was performed using equipment produced by Cincinnati-Milacron, Wien, Austria (twin screw counter rotating extruder with cooling system with vacuum bath RWN 1).

The second activity in the production of the mentioned specimen was mixing of liquid and solid components of HTPB/IPDI propellant, whose content is noted elsewhere [30]. A one-gallon Baker-Perkins planetary mixer was used for homogenizing of all the components of the mentioned propellant.

The third part of the experimental procedure in production of PVC pipe/HTPB/IPDI propellant specimen was casting, i.e. pouring of homogenized liquid HTPB/IPDI mixture into extruded PVC pipe, whose internal surface was previously prepared in an appropriate manner. The subsequent, integral action of the mentioned third part was curing of casted propellant. The curing procedure was determined by composition of used and casted propellant, primarily by characteristics of HTPB/IPDI system [30].

The fourth activity was removing of certain parts of rigid PVC pipe from the surface of the cured HTPB/IPDI propellant by machining procedure. In this way specimens, intended for investigation of the bonding characteristics between extruded thermoplastic PVC inhibitor and casted thermosetting HTPB/IPDI propellant were made.

Three groups of extruded PVC inhibitor-casted HTPB/IPDI solid propellant specimens were produced.

One group was used for determining the characteristics of bond between extruded PVC inhibitor and casted HTPB/IPDI solid propellant immediately after production. These samples were denoted as Start samples.

The second group of extruded PVC inhibitor- casted HTPB/IPDI solid propellant specimens was aged for a period of five years in warehouse, and then tested. Samples of the second group were marked as A5.

The third group of the mentioned specimens was exposed to the ageing for a period of eleven years, also, in warehouse. These samples of extruded PVC inhibitor-casted HTPB/IPDI solid propellant specimens have designation A11.

Testing of the mentioned three groups of PVC inhibitor-HTPB/IPDI propellant specimens were done at ambient, i.e. laboratory temperature (20 °C) and at high temperature (50 °C).

Results

Rocket motor, i.e. solid propellant propulsion system, generally speaking, can contain radial inhibited surface and flat inhibited surface.

Specimen for investigation the properties of bond between inhibitor and external radial surface of solid propellant is presented in Figure 2.

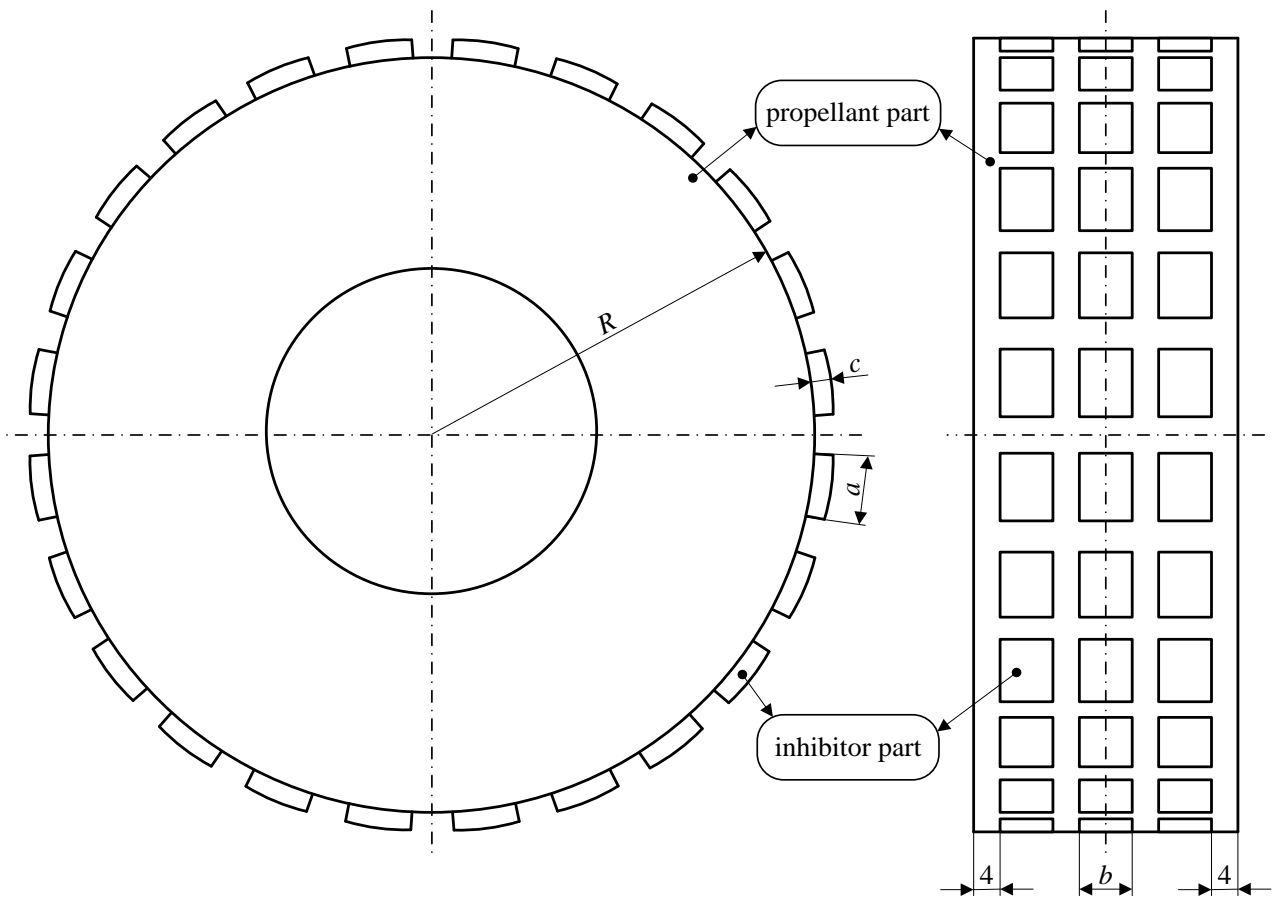


Figure 2. Specimen for investigation of the properties of bond between inhibitor and external radial surface of solid propellant

Specimen for determination of the bond features between inhibitor and internal radial surface of solid propellant is similar to the specimen presented in Figure 2.

In Figure 3 a specimen is presented intended for investigation of the characteristics of bond between inhibitor and flat surface of solid propellant.

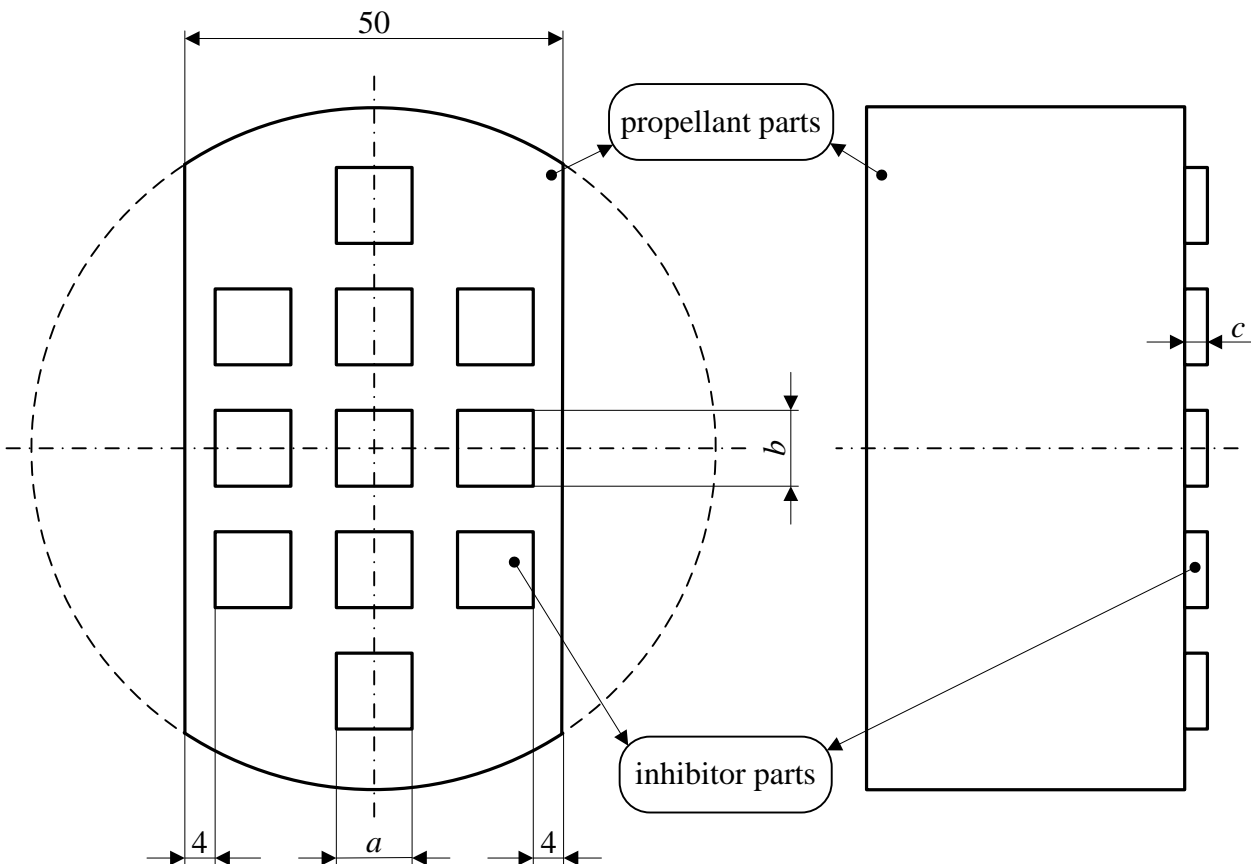


Figure 3. Specimen for investigation of the characteristics of bond between inhibitor and flat surface of solid propellant

Specimens PVC inhibitor/HTPB/IPDI propellant, whose production is described in this paper, are intended for investigation of the properties of bond between mentioned inhibitor and external radial surface of solid propellant. For realization of planned experiments, it is necessary to use specific pusher, whose geometry directly depends on dimensions of solid propellant and dimensions of inhibitor. Specific pusher for determination of the features of bond between external radial surface of solid propellant and inhibitor is presented in Figure 4.

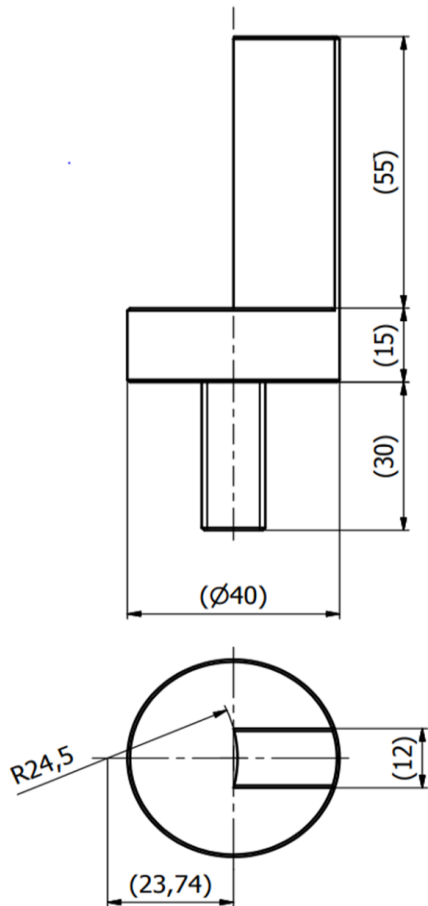


Figure 4. Specific pusher for testing the bond of external radial surface of solid propellant and inhibitor

Results after eleven years of ageing

Visual appearance of PVC-HTPB/IPDI specimens, marked A11-1, A11-2 and A11-3, after ageing for a period of eleven years and before testing, are presented in Figure 5.

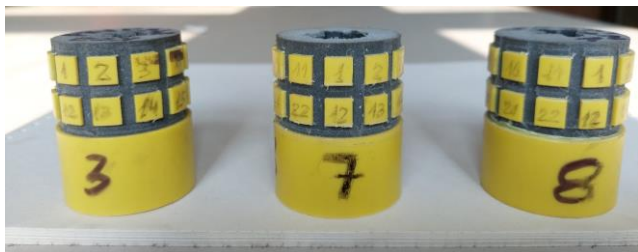


Figure 5. Visual appearance of specimens A11-1, A11-2 and A11-3 before testing

In order to obtain exact and reliable results of testing characteristics of PVC-HTPB/IPDI specimens, it is of the highest importance to properly adjust the position between special pusher (which has internal radial surface and lower flat surface), external radial surface of solid propellant and flat upper surface of PVC inhibitor. The internal radial surface of pusher, which is in direct contact with the external radial surface of HTPB/IPDI propellant, has a radius which is equal to the external radius of the mentioned propellant. Lower flat area of the pusher is in direct contact with an upper flat area of the PVC inhibitor. Pusher, in described manner, is acting on PVC-HTPB/IPDI propellant bond under the influence of compressive stress from the upper side. Described testing parameters are almost the same as ones in standard for investigation of shear properties of bond [31].

The mutual position of three mentioned parts on the PVC inhibitor-HTPB/IPDI propellant specimen A11-1, just before the start of testing, is presented in Figure 6.



Figure 6. Adjusting position of the pusher on the PVC inhibitor-HTPB/IPDI propellant specimen A11-1 just before the start of testing

The PVC inhibitor-HTPB/IPDI propellant specimen A11-1, which had 22 bond samples, was tested at ambient temperature. Mentioned specimen at the beginning of testing is presented in Figure 7.



Figure 7. The PVC inhibitor-HTPB/IPDI propellant specimen A11-1 at the beginning of testing at ambient temperature

Separated PVC parts with propellant layer and rest of PVC inhibitor-HTPB/IPDI propellant specimen A11-1 in the middle of testing at ambient temperature are presented in Figure 8.



Figure 8. Separated PVC parts with propellant layer and rest of specimen A11-1 in the middle of testing at ambient temperature

Figure 9 presents the parts of PVC inhibitor-HTPB/IPDI propellant specimen A11-1 after testing at ambient temperature, i.e. PVC parts (all with propellant layer) and the rest of specimen A11-1 (without PVC parts).

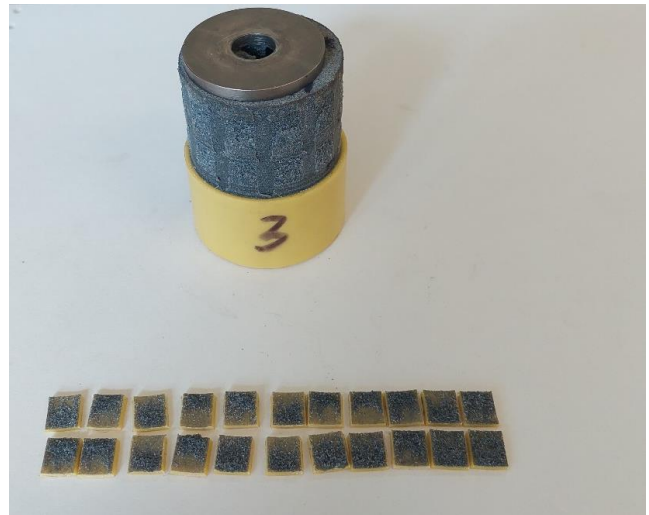


Figure 9. Separated PVC parts (all with the propellant layer) and the rest of the PVC inhibitor-HTPB/IPDI propellant specimen A11-1 (without PVC parts) after testing at ambient temperature

Table 1 presents bond mark (BM), single values for all 22 samples (x_i) and arithmetic mean value with standard deviations ($\bar{x} \pm \delta$) of the bond strength of the PVC inhibitor-HTPB/IPDI propellant specimen A11-1, determined at temperature 20 °C.

Table 1. Bond strength of the 22 samples of the PVC inhibitor-HTPB/IPDI propellant specimen A11-1 determined at temperature 20 °C

BM	1	2	3	4	5	6	7	8	9	10	11
(x_i) (N)	70.02	70.04	72.76	69.99	72.67	72.56	72.39	71.75	69.69	71.70	71.99
$(\bar{x} \pm \delta)$ (N)	71.18 ± 1.90										

Table 1. Continued

BM	12	13	14	15	16	17	18	19	20	21	22
(x_i) (N)	71.10	68.27	70.43	68.27	74.12	74.76	70.67	73.96	72.44	69.26	67.94
$(\bar{x} \pm \delta)$ (N)	71.18 ± 1.90										

Specimen A11-2 contents 22 bond samples. One half of the mentioned samples was tested at ambient temperature. Bond mark (BM), single values for 11 single samples (x_i) and arithmetic mean value with standard deviations ($\bar{x} \pm \delta$) of the

PVC inhibitor-HTPB/IPDI propellant bond strength for sample A11-2, determined at temperature 20 °C, are shown in Table 2.

Table 2. Bond strength of the 11 samples of the PVC inhibitor-HTPB/IPDI propellant specimen A11-2 determined at 20 °C

BM	1	2	3	4	5	6	7	8	9	10	11
(x_i) (N)	66.55	66.77	66.08	66.13	70.88	65.34	66.45	70.64	68.80	67.56	66.97
$(\bar{x} \pm \delta)$ (N)	67.47 ± 1.85										

Figure 10 presents a PVC part with propellant layer and the remaining part of PVC inhibitor-HTPB/IPDI specimen A11-2 just after the start of testing at ambient temperature.

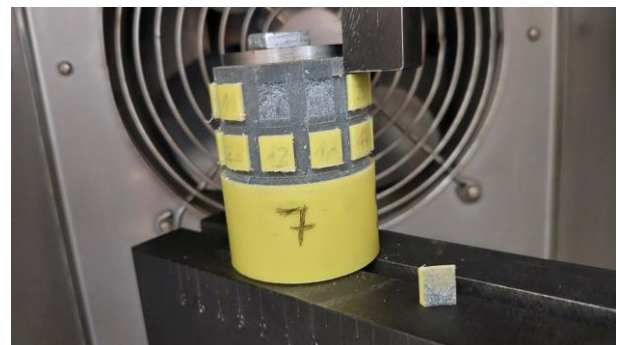


Figure 10. Separated PVC part with propellant layer and rest of PVC inhibitor-HTPB/IPDI specimen A11-2 just after the start of testing at ambient temperature

Arithmetic mean values of bond strength of samples of PVC inhibitor-HTPB/IPDI propellant specimen A11-1 and of specimen A11-2, determined at temperature 20 °C, are relatively close (71.18 N and 67.47 N, respectively).

If one takes a good look at Figure 8 and Figure 9 (concerning visual appearance of separated parts of PVC inhibitor-HTPB/IPDI propellant specimen A11-1 after testing at ambient temperature) and Figure 10 (at which the visual appearance of separated parts of PVC inhibitor-HTPB/IPDI propellant specimen A11-2 after testing at same temperature is presented), it can be seen that separated PVC parts contain a layer of solid propellant, in both cases. This fact is a proof of so-called cohesive way of part separation, i.e. adhesive energy between PVC inhibitor and HTPB/IPDI propellant is higher than cohesive energy of the mentioned propellant. The opposite situation of the mentioned is so-called adhesive way of part separation, where cohesive energies of both bonded materials are higher than adhesive force between bonded materials. Practically, in adhesive way of part separation, bonded parts are separated at interphase, i.e. at surface at which bonded and separated parts remained compact.

Arithmetic mean value and standard deviations ($\bar{x} \pm \delta$) of bond strength of all samples tested at temperature 20 °C (22 samples of PVC inhibitor-HTPB/IPDI propellant specimen A11-1 in Table 1 and 11 samples of PVC inhibitor-HTPB/IPDI propellant specimen A11-2 in Table 2) is 69.94 ± 2.60 N.

The second half of the samples of PVC inhibitor-HTPB/IPDI propellant specimen A11-2 was tested at high temperature. Separated 11 PVC pieces and remaining PVC inhibitor-HTPB/IPDI solid propellant of the above cited specimen, after testing at temperature 50 °C, are presented in Figure 11.

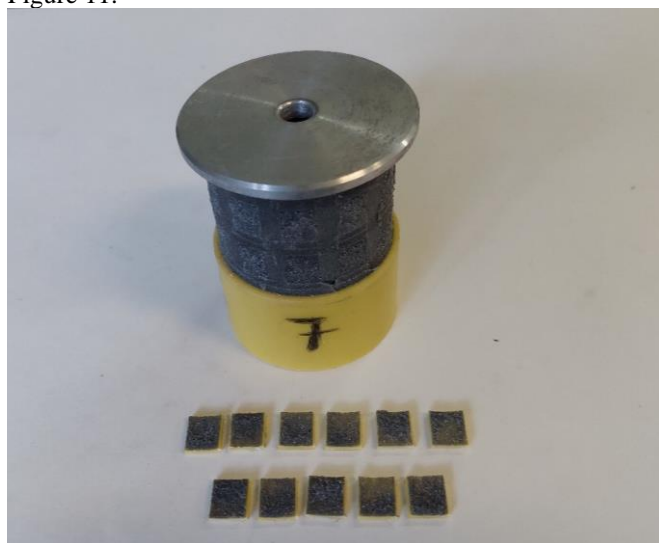


Figure 11. Separated PVC parts (11 pieces) with propellant layer and rest of PVC inhibitor-HTPB/IPDI specimen A11-2 after testing at temperature 50 °C

Figure 12 presents six PVC pieces separated from PVC inhibitor-HTPB/IPDI propellant specimen A11-2. Three PVC pieces at the left side were separated from the mentioned specimen at temperature 20 °C and three PVC pieces at the right side were separated from the above cited specimen at temperature 50 °C.

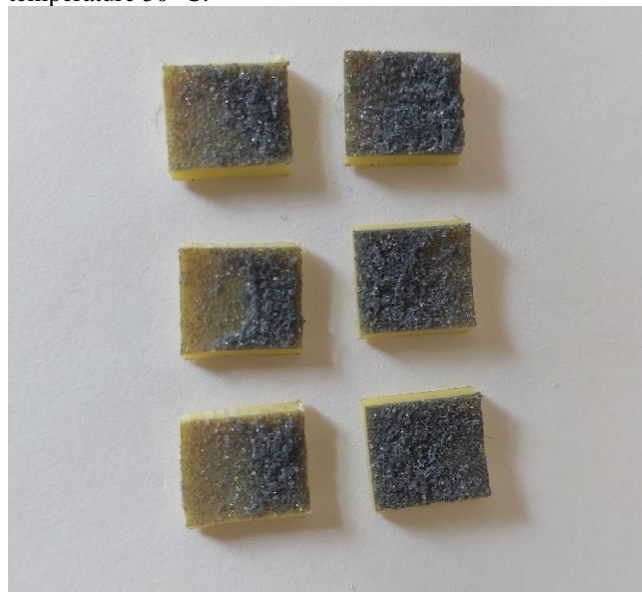


Figure 12. PVC parts with propellant layer separated from specimen A11-2 at temperature 20 °C (three pieces at the left side) and PVC parts with propellant layer separated from the same specimen A11-2 at temperature 50 °C (three pieces at the right side)

As it can be seen in Figure 12, all six PVC pieces contain a layer of solid propellant. This is an indication that cohesive way of parts separation, also, happened at specimen A11-2.

Bond mark (BM), single values (x_i) and arithmetic mean value with standard deviations ($\bar{x} \pm \delta$) of bond strength for 11 samples of the PVC inhibitor-HTPB/IPDI propellant specimen A11-2, determined at temperature 50 °C, are shown in Table 3.

Table 3. Bond strength of the 11 samples of the PVC inhibitor-HTPB/IPDI propellant specimen A11-2 determined at high temperature (50 °C)

BM	1	2	3	4	5	6	7	8	9	10	11
(x_i) (N)	62.60	61.66	60.96	62.02	62.73	62.66	63.72	62.39	62.25	62.38	62.97
$(\bar{x} \pm \delta)$ (N)	62.39 ± 0.71										

Arithmetic mean value of bond strength of PVC inhibitor-HTPB/IPDI propellant specimen A11-2, determined at temperature 50 °C, is 62.39 N.

By comparison of data obtained for the bond strength

regarding the same sample (PVC inhibitor-HTPB/IPDI propellant specimen A11-2) determined at temperature 20 °C and temperature 50 °C, it can be seen that this parameter decreases with increasing temperature. The reduction of bond

strength with increasing temperature from temperature 20 °C to temperature 50 °C, concerning the mentioned specimen, is a little bit smaller than 10 %.

PVC inhibitor-HTPB/IPDI propellant specimen A11-3 had 22 bond samples and was tested at high temperature. Figure 13 presents all separated 22 PVC parts and remaining part of the mentioned solid propellant specimen.

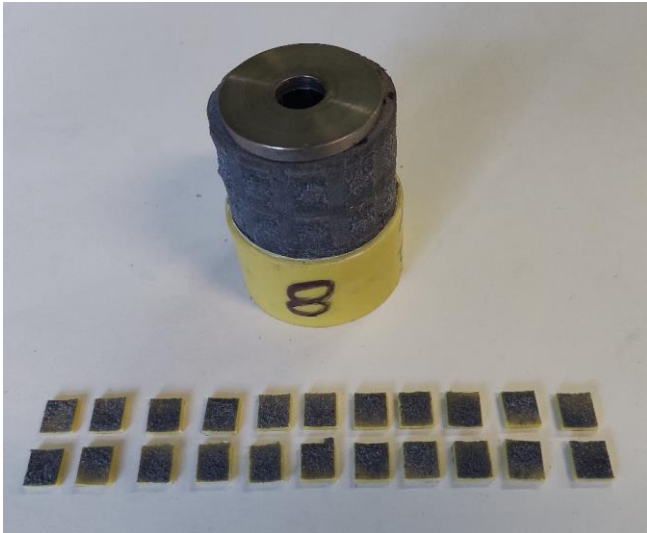


Figure 13. Separated PVC parts (22 pieces) with propellant layer and rest of PVC inhibitor-HTPB/IPDI propellant specimen A11-3 after testing at temperature 50 °C

All separated PVC pieces, presented in Figure 13, contain a layer of propellant, which is an evidence of cohesive way of separation.

The most interesting of all presented samples is a sample in the middle of the first row (from the bottom) because surface of the propellant layer on the separated PVC part is bigger than surface of PVC piece itself. This observation, firstly noted at PVC inhibitor-HTPB/IPDI propellant specimen after ageing for a period of eleven years, is an indication that inside the propellant, near the inter surface with a PVC part, happened a change in physical characteristics of propellant. This occurrence is, most probably, caused by moving of plasticizer (only liquid non-chemically bonded component in

cured propellant) toward the inhibitor. The consequence of this migratory process is that the propellant near to the inhibitor becomes brittle or weak.

In Figure 14 an enlarged detailed visual appearance of separated PVC part with a piece of the propellant (which is bigger than mentioned thermoplastic part) can be seen and, also, an enlarged place at remaining solid propellant, after testing at temperature 50 °C. The piece of propellant, which is at PVC part, and piece of propellant, which is missing at remaining solid propellant, are practically the same, especially after a detailed analysis of size and configuration of the mentioned piece.

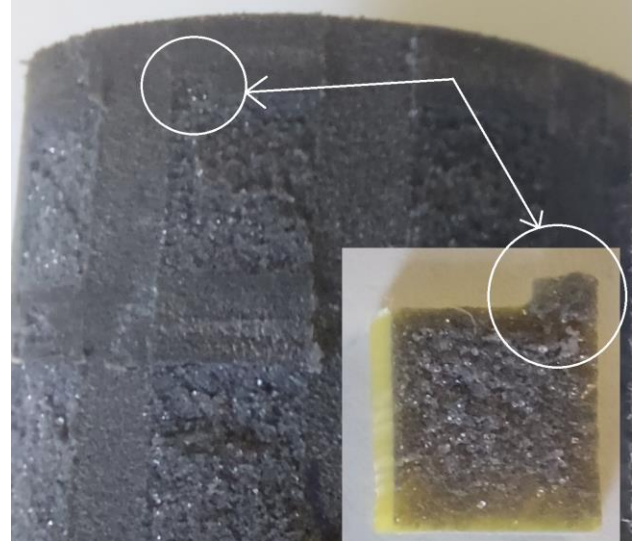


Figure 14. Detailed insight in separated PVC part with bigger propellant layer and place of the specimen A11-3 from which is separated propellant part (which is on PVC part), after testing at temperature 50 °C

Bond mark (BM), single values for all 22 samples (x_i) and arithmetic mean value with standard deviations ($\bar{x} \pm \delta$) of the bond strength of the PVC inhibitor-HTPB/IPDI propellant specimen A11-3, determined at temperature 50 °C, are presented in Table 4.

Table 4. Bond strength of the 22 samples of the PVC inhibitor-HTPB/IPDI propellant specimen A11-3 determined at 50 °C

BM	1	2	3	4	5	6	7	8	9	10	11
(x_i) (N)	62.53	63.25	61.05	63.70	64.25	71.01	60.99	59.85	60.32	65.80	63.81
$(\bar{x} \pm \delta)$ (N)	63.46 ± 2.57										

Table 4. Continued

BM	12	13	14	15	16	17	18	19	20	21	22
(x_i) (N)	65.09	62.64	63.32	65.21	66.77	62.74	61.04	60.37	63.63	63.06	66.04
$(\bar{x} \pm \delta)$ (N)	63.46 ± 2.57										

Based on data for 22 samples of PVC inhibitor-HTPB/IPDI propellant specimen A11-3 in Table 4 and based on data for 11 samples of PVC inhibitor-HTPB/IPDI propellant specimen A11-2 in Table 3, all tested at high temperature (50 °C), it can be stated that arithmetic mean value and standard deviation ($\bar{x} \pm \delta$) of bond strength, determined at temperature 50 °C, is 63.11 ± 2.19 N.

Comparing an arithmetic mean value of samples of PVC inhibitor-HTPB/IPDI propellant specimen A11 tested at ambient temperature and an arithmetic mean value of samples of mentioned specimen A11 but determined at high

temperature, it can be observed that increasing temperature from 20 °C to 50 °C cause decreasing of bond strength for about 10 %.

Results obtained by testing start specimens, specimens aged for five years and specimens after eleven years of ageing

PVC inhibitor-HTPB/IPDI propellant specimens tested at the start of this investigation are so-called S specimens.

Figure 15 presents a visual appearance of samples of PVC inhibitor-HTPB/IPDI propellant specimen S-1, after testing at temperature 20 °C.

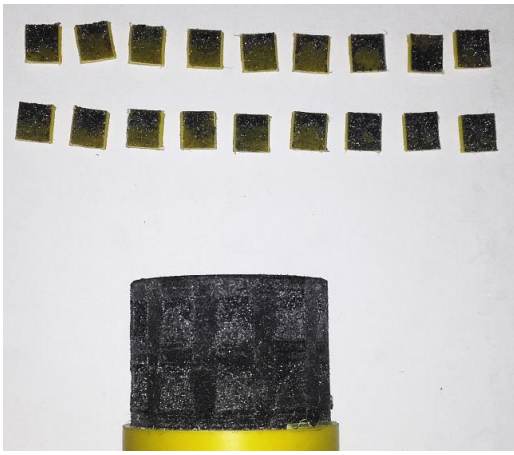


Figure 15. Visual appearance of PVC inhibitor-HTPB/IPDI propellant specimen S-1 samples, after testing at temperature 20 °C

Separated PVC parts and the remaining piece of PVC inhibitor-HTPB/IPDI propellant specimen S-2 after testing at temperature 50 °C are shown in Figure 16.

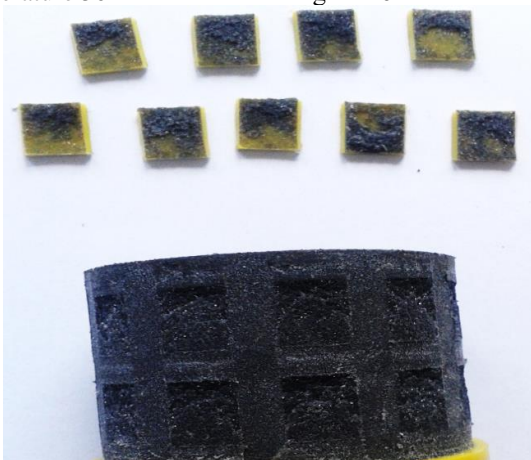


Figure 16. Separated PVC parts and the remaining piece of PVC inhibitor-HTPB/IPDI propellant specimen S-2 after testing at temperature 50 °C

Detailed analysis of visual appearance of separated PVC parts of Start specimen, tested at temperature 20 °C and at temperature 50 °C (presented in Figures 15 and 16, respectively), clearly shows that cohesive way of separation between PVC inhibitor and HTPB/IPDI propellant is present.

Arithmetic mean value and standard deviations ($\bar{x} \pm \delta$) of bond strength of PVC inhibitor-HTPB/IPDI propellant specimen tested immediately after production (Start samples), at temperature 20 °C, is 76.0 ± 6.36 N.

The value of 64.0 ± 4.4 N is arithmetic mean value and standard deviations ($\bar{x} \pm \delta$) of bond strength obtained by investigation of so-called Start PVC inhibitor-HTPB/IPDI propellant specimen, at temperature 50 °C.

The thickness of propellant fragments on separated PVC parts of the Start samples, after testing at temperature 20 °C and temperature 50 °C, is from about 0.4 mm to about 1.8 mm [13].

Visual appearances of separated elements of PVC inhibitor-HTPB/IPDI propellant specimen, tested after ageing for a period of five years (so-called A5 specimen) are presented in Figures 17 and 18. Figure 17 presents the mentioned separated elements of PVC inhibitor and HTPB/IPDI propellant after testing at temperature of 20 °C.

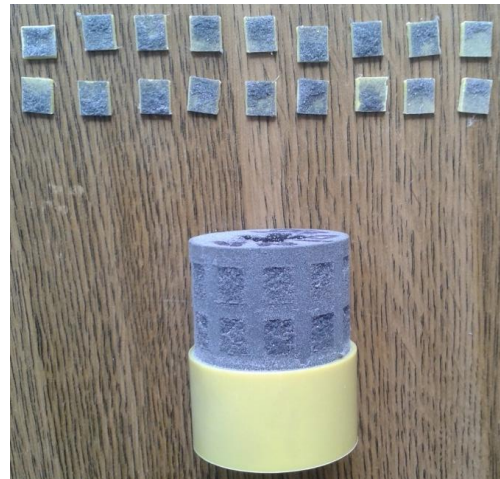


Figure 17. Visual appearance of separated elements of PVC inhibitor-HTPB/IPDI propellant specimen A5-1 after ageing for a period of five years, tested at temperature 20 °C

PVC inhibitor-HTPB/IPDI propellant specimen, after ageing for a period of five years was tested at temperature of 50 °C. Visual appearance of obtained PVC parts and remaining part of solid propellant of specimen A5-2 are presented in Figure 18.



Figure 18. PVC parts and rest of solid HTPB/IPDI propellant obtained by testing PVC inhibitor-HTPB/IPDI propellant specimen A5-2 at temperature 50 °C

Layers of solid HTPB/IPDI propellant presented at separated PVC parts, after testing specimen A5-1 at temperature 20 °C and after testing specimen A5-2 at temperature 50 °C, are evidences of cohesive way of separation between mentioned thermoplastic inhibitor and thermoreactive propellant.

Arithmetic mean value and standard deviations ($\bar{x} \pm \delta$) of bond strength of PVC inhibitor-HTPB/IPDI propellant specimen A5-1, after ageing for a period of five years, tested at temperature 20 °C, is 78.2 ± 2.78 N.

PVC inhibitor-HTPB/IPDI propellant specimen A5-2, aged for a period of five years, was tested at temperature 50 °C and arithmetic mean value and standard deviation ($\bar{x} \pm \delta$) of bond strength is 66.9 ± 2.04 N.

The thickness of propellant fragments on PVC parts of the A5 samples, after testing at temperatures 20 °C and 50 °C, is from about 0.4 mm to about 1.7 mm [9].

The characteristics of bond between thermoplastic PVC inhibitor and thermoreactive HTPB/IPDI propellant were determined in quantitative and qualitative matter. The quantitative properties imply numerical parameters obtained by testing bond strength between two mentioned parts. The qualitative characteristic is related with visual appearance of

separated PVC parts and remaining HTPB/IPDI propellant.

The basic quantitative property, i.e. numerical parameter is arithmetic mean value of bond strength of PVC inhibitor-HTPB/IPDI propellant specimens. Dependence of arithmetic mean value of bond strength of PVC inhibitor-HTPB/IPDI propellant specimens with elapsed time, tested at temperature 20 °C, is presented in Figure 19.

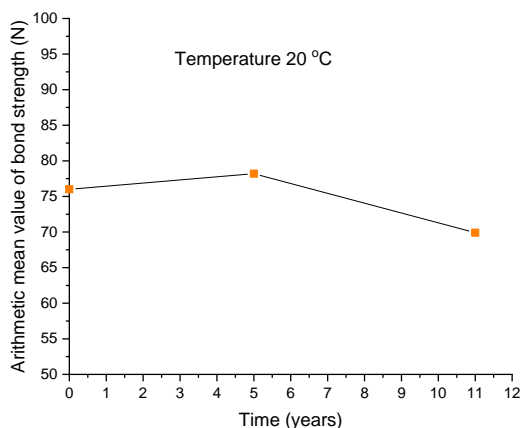


Figure 19. Dependence of arithmetic mean value of bond strength of PVC inhibitor-HTPB/IPDI propellant specimens with elapsed time, tested at temperature 20 °C

Figure 20 shows how arithmetic mean value of bond strength of PVC inhibitor-HTPB/IPDI propellant specimens was changing in specified periods of time, tested at temperature 50 °C.

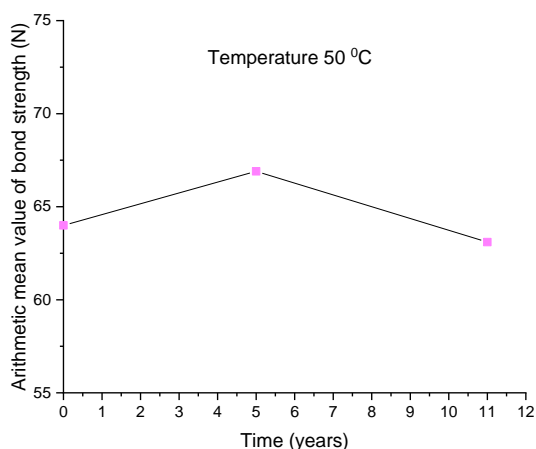


Table 5. Arithmetic mean values and standard deviations of bond strength of the PVC inhibitor-HTPB/IPDI propellant specimens at the start of investigation, after five years of ageing and after eleven years of weathering, tested at temperatures 20 °C and 50 °C

Test temperature (°C)	Arithmetic mean values and standard deviations of bond strength (N)		
	Time of investigation		
	Start (zero year)	After five years	After eleven years
20	76.0 ± 6.36	78.2 ± 2.78	69.94 ± 2.60
50	64.0 ± 4.40	66.9 ± 2.10	63.11 ± 2.18

From data, presented in Table 5, it is visible that standard deviations of bond strength of the PVC inhibitor-HTPB/IPDI propellant specimens at the start are bigger than standard deviations of the mentioned characteristic after five years and after eleven years of ageing at both listed temperatures. This is an indication that single values of bond strength after two mentioned periods of investigation are more uniform than at

Figure 20. Changing of arithmetic mean value of bond strength of PVC inhibitor-HTPB/IPDI propellant specimens in specified periods of time, tested at temperature 50 °C

In Figure 19 and Figure 20 it can be seen that the way of change of arithmetic mean value of bond strength of PVC inhibitor-HTPB/IPDI propellant specimens with time, tested at temperature 20 °C, is very alike to the change of the same characteristic of the mentioned specimens tested at temperature 50 °C.

Slightly higher arithmetic mean values of bond strength of PVC inhibitor-HTPB/IPDI propellant specimens after 5 years of ageing at both tested temperature (regarding start values) can be ascribed to the process of subsequent curing between hydroxyl-terminated polybutadiene (HTPB) and isophorone diisocyanate (IPDI) and achieving the final three-dimensional spatial network in propellant.

Certain lower arithmetic mean values of bond strength between mentioned two parts after 11 years of ageing, tested at temperatures 20 °C and 50 °C (in comparison to the initial values), can be the consequence of the influence of overpassed time and migration of plasticizer inside propellant toward inhibitor. The influence of these two processes led to weakening of mechanical characteristics of the propellant near the inhibitor-propellant bond.

In order to obtain more reliable data about tested specimens, mathematic analysis of single values of bond strength of the PVC inhibitor-HTPB/IPDI propellant specimens were done and arithmetic mean value with standard deviations were calculated. These calculation procedures were done for specimens at the start of investigation, after five years of ageing and after eleven years of weathering, at both mentioned temperatures. Arithmetic mean values and standard deviations of bond strength of the PVC inhibitor-HTPB/IPDI propellant specimens at the start of investigation, after five years of ageing and after eleven years of weathering, tested at temperatures 20 °C and 50 °C, are presented in Table 5 [9, 13].

the beginning of investigation.

Arithmetic mean values and standard deviations of bond strength are intervals of bond strength for specified period of time at appropriate testing temperature.

Figure 21 presents a dependence of this calculated quantitative parameter (arithmetic mean value with standard deviations of bond strength) versus time of investigation, for the tests done at temperature 20 °C.

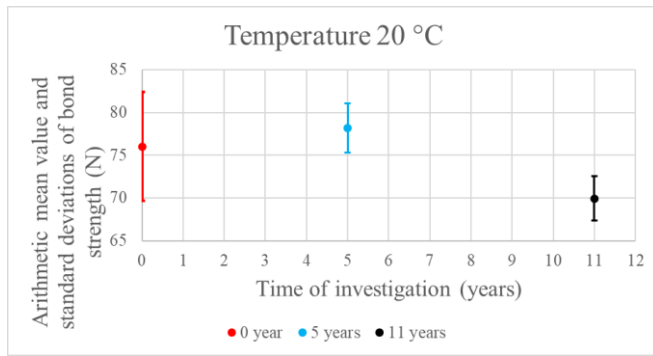


Figure 21. Dependence of arithmetic mean value with standard deviations of bond strength of the PVC inhibitor-HTPB/IPDI propellant specimens versus time of investigation, for the tests done at temperature 20 °C

From Figure 21 it can be seen that the initial interval of bond strength includes an interval of bond strength after five years (completely) and an interval of bond strength after eleven years (partially). The interval of bond strength after five years is in upper half of the initial interval, while the interval of bond strength after eleven years is partially in a lower half of the initial interval and partially under the low limit of start interval.

Time dependence of arithmetic mean value with standard deviations of bond strength of the PVC inhibitor-HTPB/IPDI propellant specimens in specified periods, tested at temperature 50 °C, are presented in Figure 22.

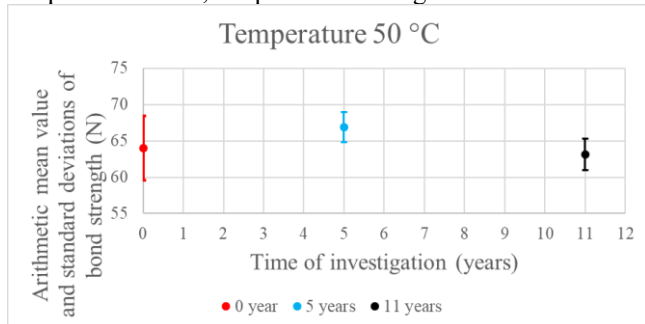


Figure 22. Time dependence of arithmetic mean value with standard deviations of bond strength of the PVC inhibitor-HTPB/IPDI propellant specimens in specified periods, tested at temperature 50 °C

Figure 22 shows that inside the initial interval of bond strength is an interval of bond strength after five years (almost completely) and an interval of bond strength after eleven years (completely). A great part of the interval of bond strength after five years is in upper half of the initial interval and only small part is above the upper limit of the start interval. The interval of bond strength after eleven years is mostly in lower half of the initial interval of bond strength.

The visual appearance of separated PVC parts and remaining HTPB/IPDI propellant is qualitative characteristic of the mentioned bond.

All separated PVC parts, obtained by testing at ambient temperature and at temperature 50 °C, just after the production, contain a layer of propellant (Figure 15 and Figure 16).

The visual appearance of separated PVC parts, tested at ambient temperature and at temperature 50 °C, after five years of ageing, is almost the same as visual look of separated PVC parts, examined immediately after the production (Figure 17 and Figure 18).

At all separated PVC parts, obtained by examination of PVC inhibitor-HTPB/IPDI propellant specimen, at ambient temperature and at temperature 50 °C, after eleven years of weathering in warehouse conditions, a layer of propellant is visible (Figure 9, Figure 11 and Figure 13).

Visual appearances of separated PVC parts (initial

specimens, specimens after five years of ageing and specimens after eleven year of weathering) are evidences that so-called cohesive way of separation happened. This way of separation is especially visible at separated PVC part, aged eleven years and tested at temperature 50 °C, which contain a piece of propellant, bigger than PVC part itself (Figure 14).

All start specimens, aged five years specimens and aged eleven years specimens were tested using the same testing machine (810 Material Testing Systems), the same pusher and the same auxiliary equipment.

Data obtained during testing start specimen (bond strength 76,2 N), five years aged specimen (bond strength 78,7 N) and eleven years aged specimen (Table 1, sample 17, bond strength 74,7 N) at temperature 20 °C are presented at Figure 23, as force-time graphic dependence [9].

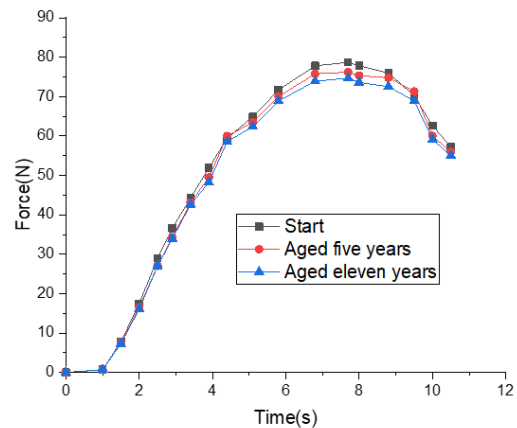


Figure 23. Graphic dependence force-time for start, aged five years and aged eleven years specimens tested at temperature 20 °C

The processes of testing the three mentioned kind of specimens at temperature 20 °C, are mutually almost the same, as it can be concluded from Figure 23.

Force-time graphic dependence for start specimen (bond strength 64,4 N), five years aged specimen (bond strength 67,9 N) and eleven years aged specimen (Table 4, sample 14, bond strength 63,3 N), obtained by testing at temperature 50 °C, are presented in Figure 24 [9].

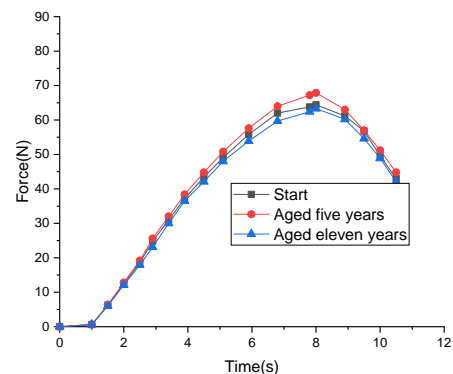


Figure 24. Graphic dependence force-time for start, aged five years and aged eleven years specimens tested at temperature 50 °C

From Figure 24 it can be pointed out that there are great similitudes between force-time graphic dependences of start specimens, aged five years specimens and aged eleven years specimens, tested at temperature 50 °C.

Conclusion

1. Regarding quantitative parameters of PVC inhibitor-HTPB/IPDI propellant bond, it can be stated:

- arithmetic mean value of bond strength after five years of ageing is a little bit higher than starting mentioned property owing to formation of completely cured HTPB/IPDI network,
- arithmetic mean value of bond strength after eleven years of weathering is lower, in comparison to the initial characteristic, due to the influence of investigation time and migration of plasticizer inside the propellant in inhibitor direction,
- trend of changing of arithmetic mean value of bond strength at temperature 20 °C is very similar to the route of transition of the mentioned property at temperature 50 °C for specimens tested shortly after the production, after five years of ageing and after eleven years of weathering,
- initial interval of bond strength (arithmetic mean value and standard deviations of bond strength at start) includes an interval of bond strength after five years of ageing (completely) and an interval of bond strength after eleven years of weathering (partially), having in mind data obtained at temperature 20 °C,
- for bond strength data determined at temperature 50 °C the facts are almost the same because inside the initial interval is almost completely the interval of bond strength after five years of ageing and the whole interval of bond strength after eleven years of weathering.

2. From qualitative point of view, for PVC inhibitor-HTPB/IPDI propellant bond, one can observe:

- a layer of propellant can be seen at all separated PVC parts, obtained by testing start specimens, specimens after five years of ageing and specimens after eleven years of weathering, at temperatures 20 °C and 50 °C,
- the presence of a layer of propellant at all separated PVC parts is a proof that cohesive way of separation of PVC inhibitor-HTPB/IPDI propellant bond happened, no matter time and temperature of investigation,
- cohesive way of separation is an evidence that adhesive force of extruded PVC inhibitor –casted HTPB/IPDI propellant bond is higher than the cohesive energy of tested solid propellant.

3. The processes of investigation force versus time of start specimens, five years aged specimens and eleven years aged specimens, tested at temperatures 20 °C and 50 °C, are mutually very similar.

4. The visual appearance of specimen aged eleven years and tested at temperature 50 °C (the piece of propellant on separated PVC inhibitor is bigger than PVC part itself) is an indication that diffusion process of plasticizer inside HTPB/IPDI propellant toward PVC inhibitor happened during this long period of time. This migratory process caused the weakening of mechanical characteristics of propellant near the inhibitor-propellant bond.

5. There was no separation between PVC based inhibitor and HTPB/IPDI based propellant at any sample, not even at any specimen after eleven years of storage in non climatized conditions.

This paper represents a contribution to the understanding of processes, which have been happening between bonded extruded PVC inhibitor and casted HTPB/IPDI solid propellant during weathering period of eleven years. The great importance of this paper lies in a fact that data regarding start, aged five years and aged eleven years samples, presented in Tables and Figures, are obtained in appropriately conducted testing procedures.

This multi-year investigation and unique results pointed

out which are the consequences of mentioned weathering period on the characteristics of the bond between two basically polymeric materials.

In this paper and in closely related references a specialist dealing with plastic materials and solid propellant and experts designing rocket motors can find useful data for considering their professional challenges and for planning their activities.

Data in this paper, especially the statements in conclusions, can be useful for personnel concerning maintenance and use of the rocket with PVC inhibitor and HTPB/IPDI solid propellant.

Literature

- [1] Vasilev V. and Morozov E., *Advanced Mechanics of Composite Materials and Composite Elements*, 2013, Third Edition, Elsevier Limited.
- [2] Čitaković S. and Radulović J., *The Strength Investigation of Specific Polymeric Composite Elements/Metalic Element Realized by Pins*, Proceedings of Seventh International Scientific Conference of Defensive Technologies, Belgrade, October 6-7, 2016, Belgrade, Serbia.
- [3] Groover M.P., *Fundamentals of Modern Manufacturing, Materials, Processes and Systems*, John Wiley & Sons Inc, Hoboken, 2010.
- [4] Rachid A., Goren A., Beccera V., Radulovic Jovana and Khanna S., *Solar Energy Engineering and Applications, Power Systems*, Spinger Nature Switzerland AG, 2023.
- [5] www.vinindex.com.au/technical-resources/technical-notes/weathering-and-aging-of-pvc-pipes-vx-tn-6b.
- [6] Davis A. and Sims D., *Weathering of Polymers*, Applied Science Publishers Limited, 1983, Barking, England.
- [7] Radulović J., *Investigation of the Influence of Natural Weathering Factors on the Properties of Polyamide Thermoplastic Materials*, Scientific Technical Review, 2005, Vol. 55, No 3-4, pp. 21-28, UDK: 678.675-620.193.91 COSATI: 07-04,11-09,14-07.
- [8] *PVC Resins Market Size, Production, Price, Import, Export*, volume 2023-2029 ([linkedin.com](https://www.linkedin.com)), Published May 2nd, 2023.
- [9] Radulović J. and Milojković A., *Influence of Time on Bond Characteristics Between Extruded PVC Tube and Cast HTPB/IPDI Rocket Propellant*, Scientific Technical Review, 2017, Vol. 67, No 2, pp. 27-36, UDK: 666.678:658, COSATI: 07-04, 11-09.
- [10] *PVC Resin SG8, China PVC Resin SG8 Manufacturers, Suppliers, Factory - XINJIANG ZHONGTAI IMPORT & EXPORT CO., LTD* (zhongtaiint.com).
- [11] Huijing Tan, Xiuhua Zheng, Long Chen, Kang Liu, Wenxi Zhu and Bairu Xia, *The Self-Degradation Mechanism of Polyvinyl Chloride-Modified Slag/Fly Ash Binder for Geothermal Wells*, Energies 2019, 12, 2821-2837; doi:10.3390/en12142821, Published May 2nd, 2023.
- [12] *Handbook of PVC Pipe Design and Construction*, Fifth Edition, December 2012, Published by INDUSTRIAL PRESS, INC. 989 Avenue of the Americas New York, NY 10018.
- [13] *Oxidized PE wax | Manufacturer in China [Tianshiwax]* (tianswax.com).
- [14] RADULOVIĆ J.: *Qualitative and Quantitative Assessment of Bond Strength of Solid Rocket Propellant and Thermoplastic Material for Cartridge Loaded Grain*, 7th International Scientific Conference on Defensive Technologies OTEH 2016, October 6-7, 2016, Belgrade SERBIA, Proceedings, ISBN 978-86-81123-82-9, pp. 659-664.
- [15] [www.faithind.com/why-is-calcium-stearate-so-significant-in-pvc/#:~:text="](http://www.faithind.com/why-is-calcium-stearate-so-significant-in-pvc/#:~:text=)
- [16] OE, JFD, HHL and RH] Oberg E., Jones Franklin D.; Horton Holbrook L.; Ryffel Henry H. (2012), *Machinery's Handbook*, (29th ed.), New York: Industrial Press, ISBN 0-8311-2635-3.
- [17] Sutton G.P. and Biblarz O., *Rocket Propulsion Elements*, Ninth Edition, John Wiley & Sons, Inc., 2017, Hoboken, New Jersey.
- [18] Hunley J. D., "The History of Solid-Propellant Rocketry: What We Do and Do Not Know." AIAA 99-2925, Invited Paper at the 35th AIAA, ASME, SAE, ASEE Joint Propulsion Conference and Exhibit, Los Angeles, CA, June20-24, 1999.
- [19] dsiac.org/articles/historical-overview-of-htpb-the-militarys-preferred-solid-propellant-binder-for-a-half-century/, Historical Overview of HTPB The Military's Preferred Solid Propellant Binder for a Half Century, Fall 2016: Volume 3, Number 4.

- [20] Chaturvedi S. and Dave, P.N.: Solid propellants: AP/HTPB composite propellants. *Arabian Journal of Chemistry* (2015), <http://dx.doi.org/10.1016/j.arabjc.2014.12.033>.
- [21] www.aluminiumleader.com/about_aluminium/what_is_aluminum.
- [22] <https://pubchem.ncbi.nlm.nih.gov/compound/Dioctyl-adipate>.
- [23] KANADE YASHODHAN, ROLE OF DIFFERENT PLASTICIZERS IN PVC PRODUCTS, Published Jan 22, 2019, ([linkedin.com](https://www.linkedin.com)).
- [24] SCHULTZ, R., Actes du colloque "Adhesion". Universite de Bordeaux I. Universite du Haut-Rhin, France, 1979.
- [25] KAEBLE, M., Physical Chemistry of Adhesion. North American Rockwell Corporation — Science center, Thousand Oaks, California; Van Nostrand, 1967.
- [26] Davenas A., SOLID ROCKET PROPULSION TECHNOLOGY, First edition, Pergamon Press Ltd, Headington Hill Hall, Oxford OX3 0BW, England, 1993.
- [27] Reddy K.A., Mohana Rao K., Sreenivasa Rao G. and Athifhan S.K., MIGRATION OF CHEMICAL SPECIES IN HTPB-XT PROPELLANTS, INTERNATIONAL SEMINAR ON HIGH ENERGY MATERIALS (HEM), 19-21 NOVEMBER 1996, Sutar wadi, Pune, INDIA, Proceedings.
- [28] Deuri S.A. and Bhowmick A.K., Influence of ageing on strength properties and morphology of fracture surface of hydroxy terminated polybutadiene rubber, *Materials Chemistry and Physics*, Volume 18, Issues 1–2, October 1987, pp. 35-48.
- [29] Selvakumar S., Sreenivasa Rao G. and Audishesha Reddy K., Diffusion of Labile Chemical Species in HTPB and HTPB-XT Solid Propellants and Its Effect over Solid Rocket Motor Properties on Aging – A Study, First published: 01 March 2021,, <https://doi.org/10.1002/prep.202000253>, *Propellants, Explosives, Pyrotechnics*, Volume 46, Issue 5, May 2021, pp. 782-790.
- [30] Brzić S., Radulović J.: Dynamic-Mechanical Investigation of the Cured Filled Polymeric System of Hydroxyl Terminated Poly (Butadiene)/Isophorone Diisocyanate, *Scientific Technical Review*, ISSN 1820-0206, 2013, Vol. 63, No 4, pp. 32-39.
- [31] ASTM D 905, Standard Test Method for Strength Property of Adhesive Bond in Shear by Compression Loading, ASTM Committee of Standards, Philadelphia, 2013.

Received: 17.06.2024.

Accepted: 11.09.2024.

Dugotrajno ispitivanje spojnih karakteristika između inhibitora na bazi PVC-a i goriva na osnovu HTPB/IPDI

Karakteristike spajanja između ekstrudiranog PVC inhibitora i izlivenog HTPB/IPDI goriva, ispitivane u dugačkom periodu vremena, jesu tema ovog rada. Osnovni stavovi o polivinil-hloridu, procesu ekstruzije i PVC cevima (uključujući sastav jedinjenja) su prikazani. Navedena su, takode, značajna razmatranja o sistemima propulzije, HTPB/IPDI gorivu, plastifikatoru, tehnologiji izlivanja i inhibitorima. Epruvete za ispitivanje karakteristika veze između inhibitora i spoljne radijalne površine čvrstog goriva i epruvete za određivanje svojstava spoja između inhibitora i ravne površine čvrstog goriva su prikazane.

Dve vrste karakteristike veze između inhibitora na bazi PVC-a i spoljne radijalne površine goriva na bazi HTPB/IPDI goriva su ispitivane: karakteristika čvrstoće i vizuelan izgled. Karakteristike čvrstoće obuhvataju aritmetičku srednju vrednost i aritmetičku srednju vrednost i standardnu devijaciju jačine veze. Pomenute karakteristike, kao indikacija kvantitativnog aspekta ispitivane veze, dobijene su koristeći specifičan metod određivanja i alat, koji je podešen prema geometriji goriva. Vizuelan izgled razdvojenih PVC delova i preostalih delova epruveta PVC inhibitor-HTPB/IPDI gorivo, kao indikacija kvalitativnog aspekta ispitivane veze, ispitivan je običnim vizuelnim pregledom. Na osnovu vizuelnog izgleda pomenutih razdvojenih delova, izvršena je procena načina razdvajanja. Karakteristike čvrstoće epruveta PVC inhibitor-HTPB/IPDI gorivo i vizuelan izgled razdvojenih delova su ispitivani na početku procesa ispitivanja, posle pet godina starenja i posle jedanaest godina starenja u uslovima skladištenja. Obe pomenute karakteristike ispitivane su na temperaturi 20oS i temperaturi 50oS. Podaci, dobijeni ispitivanjem uzoraka PVC inhibitor-HTPB/IPDI gorivo, prikazani su u vidu tabela i dijagrama.

Ključne reči: polimerni materijali, polivinil-hlorid, inhibitor, hidroksi terminirani polibutadien, izoforon diizocijanat, jačina veze, kvantitativni aspekt, vizuelni izgled, kvalitativni aspekt, starenje.