



Cent. Eur. J. Energ. Mater. 2023, 20(2): 200-220; DOI 10.22211/cejem/169019

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Research paper

Isocyanate-free Carboxyl-terminated Polybutadiene and Epoxidised Hydroxyl-terminated Polybutadiene Cross-linking System as a Binder in Solid Heterogeneous Propellants

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Abstract: Propellants have found applications in many industries. They play an important role primarily in the armaments and space industries. Research and development of propellant technology has been ongoing for many years. The present authors have turned their attention to the aspect of compatibility of new components with isocyanates. As a result of the search for a solution to combine existing binders with new components, they propose using hydroxyl-terminated polybutadiene (HTPB) derivatives as the main binder components. In this way, the basic parameters of the HTPB binder, such as glass transition temperature, and compatibility with the solid components of propellants are retained. The use of an isocyanate-free binder system opens up possibilities for the use of new isocyanate-sensitive components. The authors have used two HTPB derivatives to create a new binder system. The combination of carboxyl-terminated polybutadiene (CTPB) and epoxidised HTPB, called EHTPB, allowed the elimination of isocyanates and the retention of good physicochemical properties of the binder. Here they present the method of synthesis of the components, the proportions of polymer and curing agent, and the pot-life. Heterogenic propellants based on CTPB, EHTPB, and ammonium perchlorate (AP) were prepared and the feasibility of such a system was confirmed. A study of the physical and chemical properties of

the produced propellants confirmed the possibility of using CTPB and HTPB as a new binder system.

Keywords: carboxyl-terminated polybutadiene, CTPB, epoxidised hydroxyl-terminated polybutadiene, EHTPB, isocyanate-free crosslinking, binder

Nomenclature

AO 2246	2,2'-Methylenebis(6- <i>tert</i> -butyl-4-methylphenol)
AP	Ammonium perchlorate, NH_4ClO_4
CTPB	Carboxyl-terminated polybutadiene
EHTPB	Epoxidised HTPB
HTPB	Hydroxyl-terminated polybutadiene
r	Burning rate [mm/cm]

1 Introduction

Propellants have found applications in many industries. They play an important role primarily in the armaments and space industries, but are also used in rocket launches, in aviation and to carry ailerons in shipbuilding. In the defence sector, they are used, among other things, as propulsion in the engines of artillery rocket shells and anti-tank guided missiles. In the space industry, on the other hand, they are used to power large space rockets as well as probes and artificial earth satellites [1-3]. Rocket propellants are defined as substances or mixtures of compounds having the ability to undergo an exothermic process of decomposition or combustion. During these transformations, significant amounts of high-temperature gases are released, which provide the energy source in a rocket engine [4].

The most widely used technology for producing heterogeneous propellants involves curing a prepolymer and creating a three-dimensional network of chemical bonds between the reactive groups or multiple bonds of the polymer and the crosslinking agent. The preferred crosslinking mechanism is polyaddition, which only results in a cured macromolecular compound. This ensures that no by-products are formed during the process, the presence of which could cause unfavorable cracks and/or gas bubbles in the finished propellant. During the course of the reaction, the viscosity of the mixture increases and, after a certain number of components have reacted, it reaches a point where the liquid mass takes on a rubbery form. The period of time between the addition of the crosslinking

agent to the fuel mixture and the attainment of a cross-linked form, which is practically impossible to process further, is called the pot life. It is a parameter that determines the usability of the crosslinking system used. A lifespan that is not long enough may prevent the casting of the resulting fuel mass, but a mixture that takes too long to cure results in prolonged occupancy of the apparatus and thus increased production costs [5-7].

2 The Binder and Its Purpose in Propellant Technology

2.1 The Binder

A binder is defined as the reaction product of a prepolymer with a suitable crosslinking agent. This binder makes up between 12% and 16% of the propellant mass. Its function is primarily to bind all the components of the mixture together. During the propellant mixing process, the binder is liquid most of the time, ensuring that all compounds are freely and thoroughly mixed together. When a crosslinking agent is added, this mixture solidifies after a certain time and a solid propellant is obtained. The binder used should meet a number of conditions, such as: this component should have a sufficiently low viscosity at the temperature at which mixing takes place so that all components are freely mixed together. For this to be possible, the value of this parameter must be between 1000 and 10000 mPa·s. The molar mass of the binder should be between 2500 and 5000 g/mol and its density between 0.8 and 1 g/cm³; it should be compatible with the other propellant components. It is required that the binder has a high ratio of hydrogen to carbon atoms, and, in addition, that the nitrogen or sulphur content is as low as possible [5, 8, 12, 13].

The properties of the resulting binder largely depend on the prepolymer used. The prerequisites for its usefulness are a low molar mass, in the range of 2500 to 5000 g/mol, the presence of at least two reactive functional groups, a polydispersity of between 1 and 2, and a low curing temperature, not exceeding 75 °C [5].

However, despite the high expectations placed on these components, there are a number of compounds that can act as a prepolymer. These include substances such as polybutadiene, polyvinyl chloride, polyacrylonitrile, polystyrene or compounds from the polyester group. However, three of them have played the most significant role in the history of heterogeneous propellants to date [5, 8]:

- HTPB (hydroxyl-terminated polybutadiene),
- CTPB (carboxyl-terminated polybutadiene), and
- PBAN (poly(butadiene-co-acrylic acid-co-acrylonitrile)).

With the development of propellant technology, the range of ingredients used as raw materials is increasing. This raises the issue of the compatibility of some components, or there are reports of harmful effects of some components on the environment or human health. For this reason, work is being done to find new propellant systems to eliminate harmful compounds or to change the system so that all components are compatible with each other.

One such component is isocyanates. They are used as a crosslinking component of polymers containing hydroxyl groups in the manufacture of polyurethanes. Isocyanates are an example of a compound that is both harmful to humans and a compound that is often becoming incompatible with new rocket propellant components. There are emerging reports of incompatibility with the oxidiser ADN (ammonium dinitramide) or nano-iron as a catalyst for the burning rate of propellants based on ammonium perchlorate (AP). Isocyanates are a group of highly toxic compounds. On direct contact, they irritate mucous membranes and cause severe allergic reactions. In addition, isocyanates react with a number of groups of compounds, including amines, aldehydes and peroxides, and release toxic gases such as HCN, CO, NO_x and SO_x [9, 10].

New crosslinking systems that do not use isocyanates as crosslinking agents are being sought, *e.g.* [11]. This is an extremely difficult task due to the mechanical properties of HTPB- and isocyanate-based polyurethanes. Therefore, the present authors have sought to solve this problem by proposing isocyanate-free systems based solely on HTPB derivatives. This solution preserves the positive characteristics of the polybutadiene chain and thus ensures good mechanical properties and a sufficiently low glass transition temperature. Modification of the polybutadiene chain can occur either through terminal hydroxyl groups or through double bond reactions. Using these two modification routes, the authors propose the use of CTPB, and epoxidised HTPB (EHTPB), as a binder system in solid heterogeneous rocket propellants.

CTPB, as a well-known polymer used for many years in the defence industry, has been displaced by HTPB. Methods of curing CTPB with compounds such as ERLA-0510, EPON X-801 or DER-332 (epoxy compounds) or MAPO, BITA or TEAT (aziridines) are known. In practice, mixtures of aziridines or epoxides with aziridines are most commonly used (Figure 1). The resulting binders are characterised by improved mechanical properties and increased strength at elevated temperatures [12, 13]. Using these motives, the authors propose the use of an epoxidised HTPB derivative (EHTPB), as a curing agent.

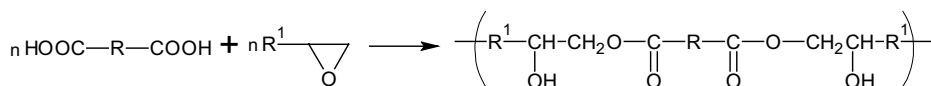


Figure 1. Schematic of the reaction of CTPB with an epoxy group [14]

2.2 CTPB

This polymer can be obtained by free-radical and anionic polymerisation of butadiene. However, an HTPB-based synthesis is used on an industrial scale. This method uses the reaction of hydroxyl groups from the polybutadiene with an anhydride, usually maleic anhydride. The commercial product of this reaction goes under the name Poly bd 45CT and is offered by the Cray Valley company. The structure and properties of the polymer so obtained are presented in Figure 2 and Table 1 [15].

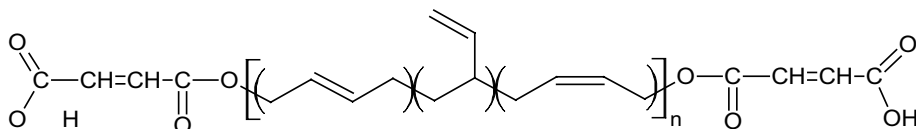


Figure 2. Structure of the commercial CTPB species [16]

Table 1. Physicochemical properties of the commercial grade CTPB Poly bd 45CT [15]

Property	Units	Value
Molar mass	g/mol	3050
Viscosity at 60 °C	mPa·s	4300
Density at 25 °C	g/cm ³	0.9
Acid value	meq/g	0.77

This product is characterised by a higher molar mass than the HTPB discussed in the previous section, but still within the acceptable limits for a prepolymer of 2500-5000 g/mol. Furthermore, Poly bd 45CT is characterised by low viscosity and the presence of reactive –COOH groups. All the above-mentioned characteristics make it suitable for successful use as a binder in rocket propellants. The reaction of HTPB with maleic anhydride is carried out in a reactor equipped with a magnetic stirrer. The process is carried out for 24 h at 80 °C under an inert gas atmosphere, which is usually argon or nitrogen. A schematic of the synthesis discussed is shown in Figure 3 [16].

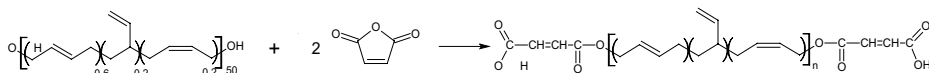


Figure 3. Reaction scheme for obtaining CTPB by reacting HTPB with maleic anhydride [16]

2.3 EHTPB

There are several methods for converting HTPB into its epoxidised form. One of these uses the reaction of HTPB with *meta*-chloroperbenzoic acid (*m*CPBA). In this method, *m*CPBA dissolved in toluene is added to HTPB placed in a reactor. The reaction is carried out at -10 to 5 °C using a nitrogen atmosphere in a darkened room. Some literature sources also describe syntheses using a stoichiometric mixture of the above-mentioned acid or peracetic acid with *tert*-butyl hydroperoxide acting as catalyst and vanadium(IV) acetylacetonate ($\text{VO}(\text{acac})_2$) having an oxidising capacity. These methods are characterised by the occurrence of many side reactions and the instability of the product obtained. For this reason, alternatives to the synthesis discussed above have been sought. One of these is the use of the Venturello-Ishii catalytic system, which uses tungsten and phosphoric ions. The most commonly used are sodium or ammonium tungstate and orthophosphoric(V) acid (H_3PO_4). These compounds are dissolved in a 30% solution of hydrogen peroxide (H_2O_2), which acts as an oxidant in the process, and this solution is then added to the HTPB dissolved in dichloromethane. Furthermore, in addition to the catalytic system discussed, the method uses the interfacial transfer catalyst Aliquat 336, a quaternary ammonium salt. This compound facilitates the transport of reactants between the phases [17-19].

Another method that does not use H_2O_2 is the use of the dimethyldioxirane (DMD)/*tert*-butylammonium bromide system. The DMD used in this process is generated *in situ*, *i.e.* directly in the reaction medium. The reaction is carried out at 25 °C and acetone and chloromethane are used as solvents. The product obtained is characterised by a high content of *cis*-mer and a low amount of vinylmer, making the presented reaction chemoselective [20].

Commercially, EHTPB (Figure 4) is offered by both Sigma Aldrich, and Cray Valley. The latter company offers two grades of EHTPB – Poly bd 605E and Poly bd 600E. The properties of both samples are summarised in Table 2. From the table, it can be seen that the two species have similar molar mass and acid number, but significantly different viscosity and epoxide number values.

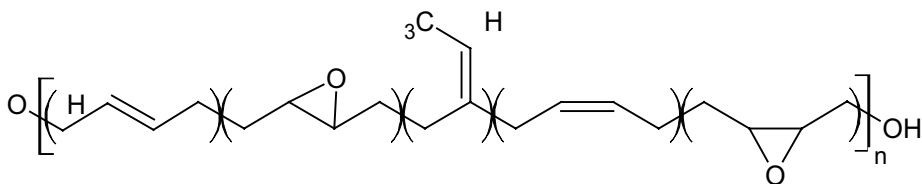


Figure 4. Structure of the epoxidised derivative of HTPB (EHTPB) [15]

Table 2. Comparison of physicochemical properties of EHTPB commercial grades – 600E and 605E [15]

Property	Units	600E	605E
Molar mass	g/mol	1300	1300
Viscosity at 30 °C	mPa·s	7000	22000
Epoxide number	meq/g	2.2	3.5
Acid value	meq/g	1.7	1.74

3 Materials and Test Methods

HTPB R45 HTLO: –LOH – 48 mgKOH/g, – viscosity at 30 °C – 5100 mPas, – M_n – 2800 g/mol (Cray Valley). Maleic anhydride – 99%, and tetra-butylammonium bromide – 99% (both from Pol-Aura, Poland). Toluene – p.f.a, and acetic acid – 85% (both from Chempur, Poland). H_2O_2 – 30% (POCH, Poland).

Viscosity: These tests were performed on a Brookfield DV2T rotational viscosity meter with a small-volume sample measurement attachment, connected to a WSL brand thermostat. RheocalcT computer software compatible with the viscometer was also used during the measurements. Measurements were carried out by placing the test compound in the measuring vessel and then running the spindle rotation. The vessel was thermostated at a given temperature for a few minutes, the temperature and viscosity values obtained were recorded, and the thermostat temperature was then increased by 10 °C. Measurements were carried out in the temperature range from 25 to 65 °C. During the measurements, a SC4-21 type spindle was used.

FT-IR: Infrared analysis of the polymers was performed on an FT-IR NICOLET 6700 spectrophotometer using the ATR technique. Infrared spectra were obtained: 600-4000 cm^{-1} .

1H NMR: The use of proton nuclear magnetic resonance spectroscopy allows the calculation of the amount of epoxidised HTPB double bonds during the synthesis of EHTPB. The study was carried out using a Varian 500 MHz spectrometer and deuterated chloroform was used as solvent.

Mechanical properties: These tests were carried out using an Instron 3366 testing machine and Bluehill computer software compatible with the machine. The specimens were prepared by placing the prepolymer and crosslinking agent in silicone containers, vigorously stirred, then placed in a laboratory dryer and left for 24 h at 65 °C. After this time, the cured systems were removed from the containers and rectangular specimens were cut to size. Specimens with a thickness of 3 mm, a length of 64 mm and a width in the range of 5.5-7.0 mm were placed in the specimen jaws of the testing machine and then the measurement was started using the software. Stretching of the specimen continued until the specimen broke.

Pot life: The pot life of the propellant mixture is an important parameter in the propellant manufacturing process, as it determines at what time after the addition of the crosslinking agent the final mixing step and casting of the finished mass should be carried out. Once a certain propellant-specific time has been exceeded, the mixture takes a form in which no further modification of the product is possible. A life time that is too short may be the reason why the fuel mass cannot be cast. On the other hand, too long a life results in prolonged occupancy of the apparatus and increased production costs.

An appropriate amount of prepolymer and crosslinking agent were placed separately in two plastic containers. Both samples were then placed in a laboratory dryer and left for 30 min at 65 °C. After this time, the two components were mixed together using a wooden spatula and then transferred to the measuring vessel of the viscometer and the spindle rotation was started. The viscosity of the mixture was recorded every 5 min. A temperature of 65 °C was used during the measurements, as this is the temperature at which the mixing and curing of the fuel mass is most often carried out. The spindle speed was selected so that the resistance value did not exceed 80%.

Density: These tests were carried out on a Micromeritics AccuPyc II pycnometer. Before measuring the density, the propellant sample was weighed and then placed in the measuring chamber of the pycnometer. During the measurement, an inert gas flows through the measuring chamber, which then enters the empty chamber. The change in pressure during filling of the measuring chamber and emptying the gas from the measuring chamber allows the volume of the sample to be determined.

Hardness: Measurements were carried out using a Shore HBA 100-0 analogue durometer from CAL TOOLS. The propellant sample prepared for the test was placed on a flat surface, and the hardness tester was then applied perpendicularly to the test material. The instrument pressed smoothly. The result was read out based on the deflection of the passive pointer.

Ballistic properties: Samples of each propellant were prepared as a non-inhibited cylindrical charge (Figure 5), for each of the propellant mixtures produced. Combustion was carried out in a laboratory rocket engine. The engine consisted of a nozzle section with an interchangeable nozzle, a cylinder-shaped combustion chamber, a propellant charge and an igniter and chamber closure. A pressure sensor, an amplifier and a computer set were connected to the system. Software to control and record the burning time characteristics and combustion chamber pressure was employed. A nozzle with a diameter of 2.2 to 3.5 mm was fitted to the system. A cylindrical propellant charge was then placed in the chamber. An igniter, consisting of a 0.2 A electric igniter unit initiating a mass of 6×2 mm black powder lozenge weighing 0.2 g, was constructed. The igniter was placed behind the propellant. Combustion was started and the chamber pressure recorded while the propellant was burning. This determined the maximum pressure in the chamber during propellant burning and the rate of propellant burning (r).



Figure 5. Cylindrical charge prepared for the burning test

4 Synthesis of CTPB

The reaction of HTPB with maleic anhydride following the scheme shown above was used to obtain CTPB. The reaction set-up consisted of a two-neck round-

bottomed flask fitted with a magnetic stirrer, which was placed in a thermostated water bath. In the first step of the synthesis, HTPB was thoroughly dried at a temperature close to 90 °C under reduced pressure. In the next step of the process, maleic anhydride was added to the dried HTPB. The reaction was carried out at 70-80 °C for approx. 24 h using a dry argon atmosphere. CTPB was obtained using stoichiometric amounts of HTPB and maleic anhydride.

5 Synthesis of EHTPB

An epoxidation system based on a mixture of H₂O₂ and acetic acid solution was used to carry out the reaction. The interfacial transfer catalyst *tert*-butylammonium bromide was also used. A schematic of the synthesis discussed is shown in Figure 6.

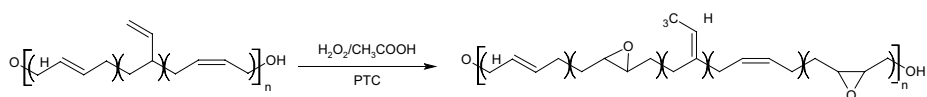


Figure 6. Reaction scheme for obtaining EHTPB

The reaction was carried out in a three-necked round-bottomed flask fitted with a magnetic stirrer and thermometer and placed in a thermostated water bath. In the first step of the synthesis, HTPB was placed in the flask and toluene was added. The magnetic stirrer was started and the solution was heated to 60 °C. Once the desired temperature was attained, the catalyst was added. A dropping funnel containing a mixture of 30% H₂O₂ solution and acetic acid was placed in the side neck of the flask, and the addition lasting 45 min was commenced. After the entire amount of epoxidising mixture had been added, the funnel was removed, and was replaced by a Liebig condenser. The free holes in the necks of the flask were stoppered. The solution was stirred in the flask for 4 h at 60 °C. After this time, the reaction mixture was transferred to a separatory funnel, the aqueous phase was separated and the organic phase was washed three times with 300 mL of distilled water (3 x 300 mL). After washing, the organic phase was concentrated on a rotary evaporator to furnish the product. Depending on the amounts of H₂O₂, acetic acid and catalyst used in relation to the HTPB, several types of EHTPB were obtained, differing in the amount of epoxidised double bonds in the polybutadiene chain.

Table 3. Quantities of the components used for the synthesis of EHTPB

Component	EHTPB I	EHTPB II	EHTPB III
HTPB R45 HTLO [g]	75	100	50
Toluene [cm ³]	225	300	150
Catalyst [g]	6	8	2
30% H ₂ O ₂ [cm ³]	409	546	210
Acetic acid [g]	185	260	100

6 Propellants with the Selected Cross-linking System

Mixing was carried out in a 1 L Retsh PML1 planetary mixer from NETZSCH fitted with a planetary mechanical stirrer and connected to a vacuum pump. The mixer was thermostated at 65 °C before dosing the ingredients. The prepolymer, dioctyl adipate (DOA) and 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) (AO 2246) were then added to the reactor. The mixer was closed, the mechanical stirrer was started and the contents stirred for 5 min. The vacuum pump was then activated and stirred for a further 15 min. After this time, the system was aerated, the stirrer was turned off, the mixer was opened and coarse AP was added. The mixer was then closed again, the stirrer was started and the contents stirred for 15 min. After this time, the stirrer was turned off, the mixer was opened, and the first portion of fine AP was added. The mixer was closed again, the stirrer was started and the contents stirred for 15 min. These operations were repeated with the addition of the second portion of fine AP. After 15 min of stirring, the vacuum pump was started and the contents stirred for a further 30 min. After this time, the system was aerated, the mixer was turned off, the mixer was opened and the crosslinking agent was added. The mixer was closed again, the agitator started and the contents mixed for 5 min. After this time, the pump was started and the ingredients were mixed for a further 10 min. The system was then aerated, the stirrer was turned off and the mixer opened, and the resulting mass was poured into a mould, which was placed in a laboratory dryer for 24 h at 65 °C. To test the selected crosslinking system, a propellant consisting only of an oxidiser, the CTPB-EHTPB system, a plasticiser and an antioxidant was prepared. The compositions of the propellants made are listed in Table 4.

Table 4. Quantities of ingredients used in the production of propellants P-II and P-III

Component	Content [%] in propellant	
	P-II	P-III
CTPB	10.63	
EHTPB II	1.6	–
EHTPB III	–	1.6
DOA	2.5	
AO 2246	0.2	
AP:		
– coarse-grained	63.8	
– fine-grained	21.27	

7 Results

By analysing the graph (Figure 7) showing a comparison of the viscosity changes of the two prepolymers, it can be seen that the compounds differ significantly in their viscosity values at 25 °C. However, this difference decreases with increasing temperature, and at 65 °C the viscosity of HTPB is 1020 mPa·s and that of CTPB 2600 mPa·s. The temperature of 65 °C is the most relevant temperature in the range shown, as mixing of the fuel mass is most often carried out under these conditions. The acceptable viscosity range of the prepolymer at 65 °C is 1000-10000 mPa·s. Therefore, the analysis of both components indicates that they can be successfully used as prepolymers in the binders of heterogeneous solid rocket propellants. Viscosity of the EHTPB cross-linking agent in the new system are shown in Figure 8. When EHTPB I and II were tested, it was noted that these compounds exhibit high viscosity at both 25 and 65 °C. By contrast, the viscosity of EHTPB III is significantly lower than the values of the other two substances at both temperatures. These differences are illustrated by the relationships shown in Figure 8. The high viscosity values of EHTPB I and II are probably due to the high molecular weights of the compounds, which result from a significant degree of epoxidation of the HTPB double bonds.

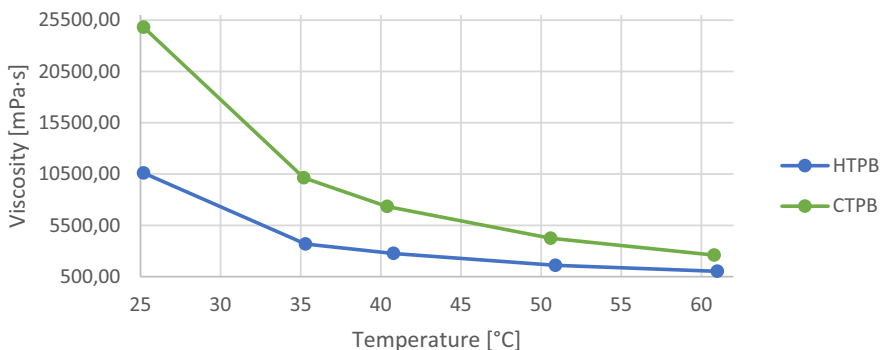


Figure 7. Plot of viscosity variation as a function of temperature for CTPB and HTPB

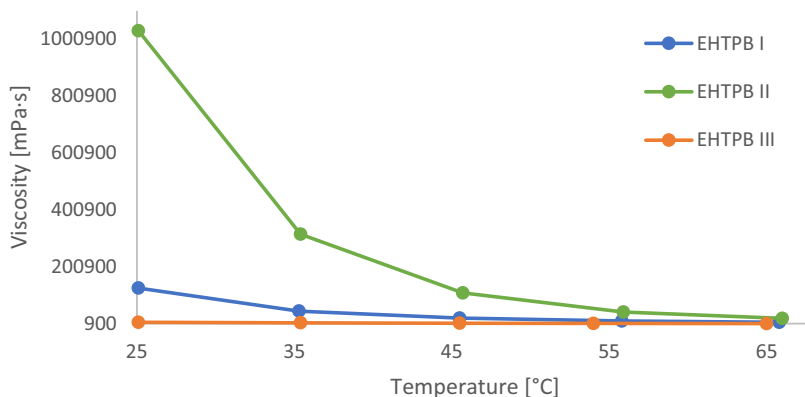


Figure 8. Summary of changes in viscosity as a function of temperature for EHTPB I, II and III

The HTPB FT-IR spectrum is characterised by bands at 3300 and 2900 cm^{-1} derived from the -OH group stretching vibrations, and a band at 1750 cm^{-1} derived from the C=C bond stretching vibrations. Comparing the spectrum obtained for the CTPB polymer (Figure 9), it is possible to see the disappearance of a band originating from the stretching vibrations of the hydroxyl group in the range $3100\text{-}3500\text{ cm}^{-1}$. However, bands originating from the stretching vibrations of the C=O bond (1640 cm^{-1}) and from the stretching vibrations of the C-O bond (1150 cm^{-1}) can be observed, which indicates the presence of ester and carboxyl groups. All of the observations mentioned above demonstrated that the synthesis of CTPB had been successful.

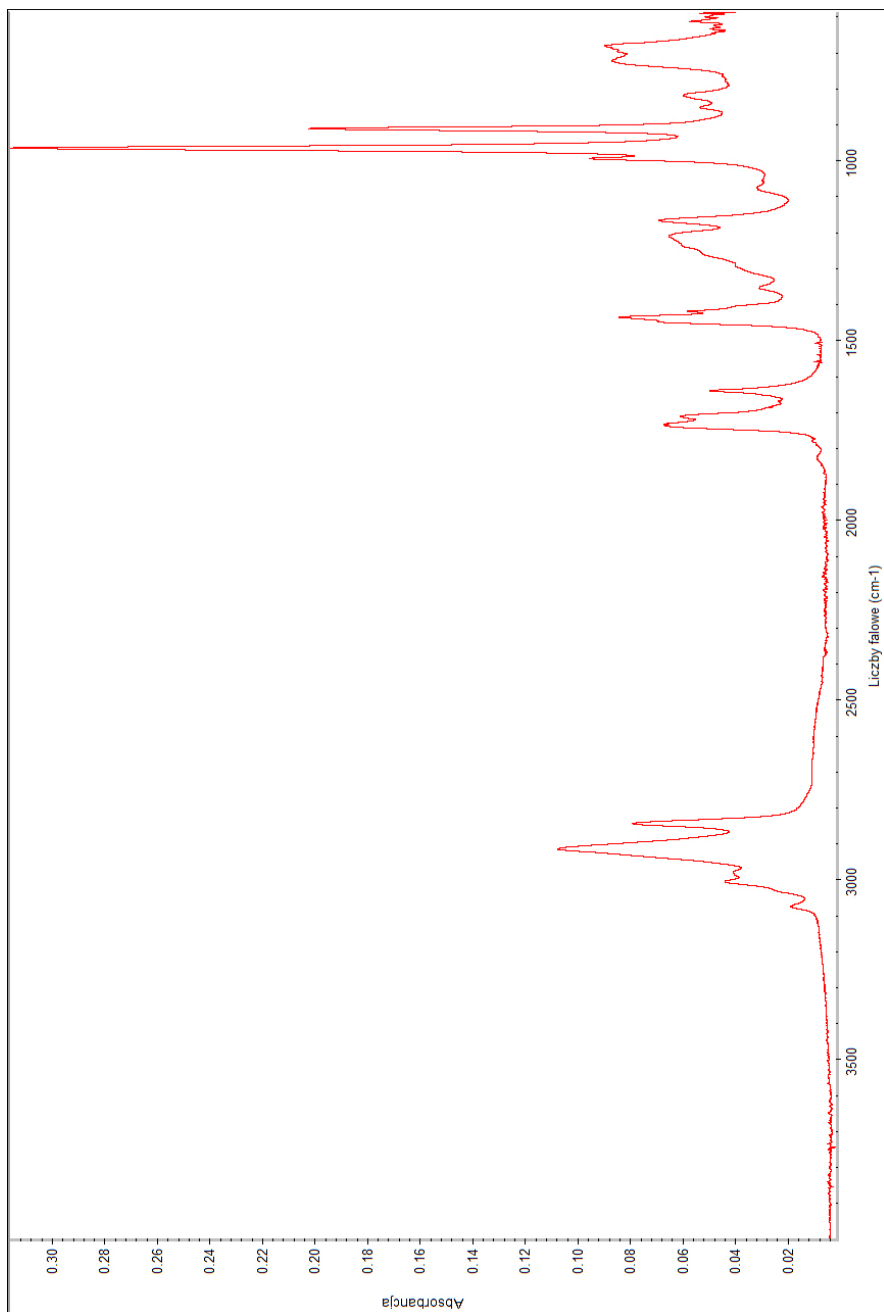


Figure 9. FT-IR spectrum obtained for the CTPB prepolymer

A comparative analysis of the HTPB and EHTPB ^1H NMR spectra (Figures 10-12) indicated the appearance in the EHTPB spectra of signals originating from protons bound to the carbons of the epoxy groups at 2.8 and 3.0 ppm, and the partial disappearance of signals originating from protons of the $\text{C}=\text{C}$ double bonds in the range 5.0-5.6 ppm. At the same time, by comparing the spectra of EHTPB II and EHTPB III, it can be seen that these signals appear in the spectra with different intensities, due to differences in the degree of epoxidation of the double bonds of the HTPB chain. The degree of epoxidised double bonds was calculated from the areas under the relevant signals (Table 5).

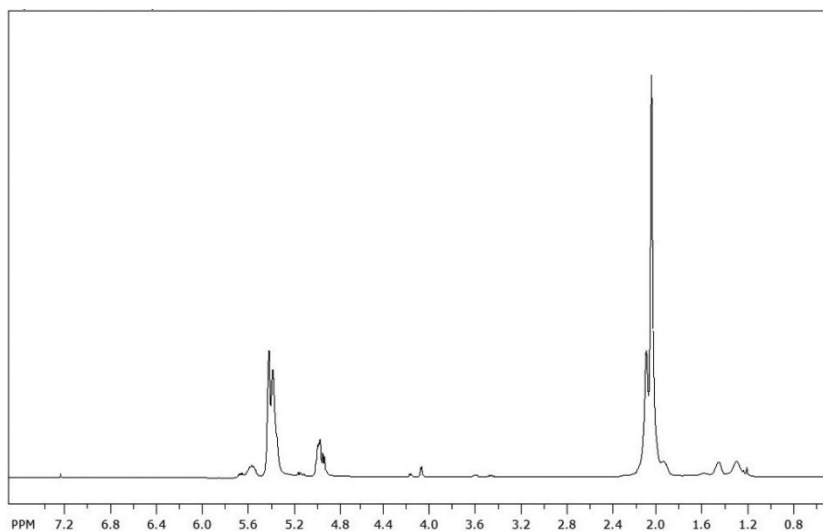


Figure 10. ^1H NMR spectrum of the HTPB prepolymer

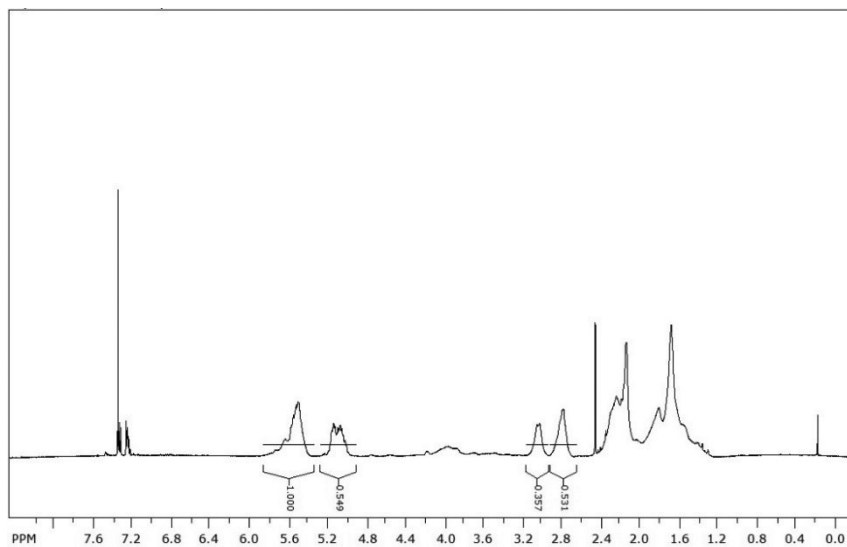


Figure 11. ¹H NMR spectrum of EHTPB II

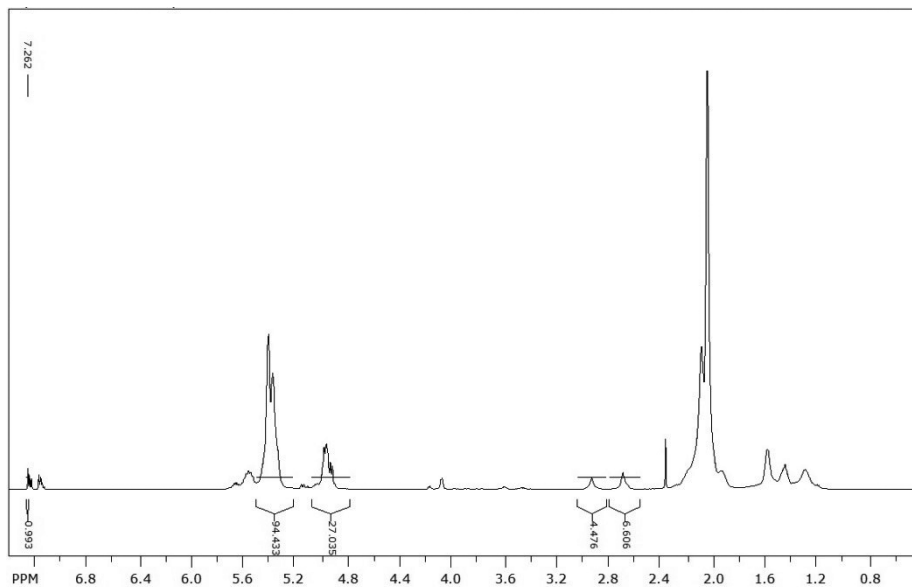


Figure 12. ¹H NMR spectrum of EHTPB III

Table 5. Summary of the degree of epoxidised double bonds in EHTPB I, II and III

EHTPB	Amount of epoxidised double bonds [%]
I	35
II	41
III	9.5

The proportion of the crosslinking agent (EHTPB) for curing ranged from 10 to 15% relative to the amount of CTPB (Table 6). A lower amount of EHTPB did not ensure complete curing of the CTPB-EHTPB system. In each of the systems, the type and content of the crosslinking agent significantly influenced the results obtained. The system containing 15% EHTPB III had the highest tensile strength and maximum tensile force values. However, the same system had the lowest value of strain at break. However, the lowest values of R_m and F_{max} were obtained for the system containing 9.97% EHTPB I.

Table 6. Summary of the averaged values obtained for CTPB-based systems

Cross linking agent	Content of crosslinking agent [%]	R_m [MPa]	F_{max} [N]	A [%]
EHTPB I	10	0.12	2.47	28.22
	15	0.18	3.72	24.36
EHTPB II	15	0.20	4.14	34.56
EHTPB III	10	0.20	4.03	7.60
	15	0.31	6.49	6.86

Pot life of selected systems containing 15% crosslinking agent is shown in Figure 13. An analysis of the graph in Figure 13 allowed us to conclude that the pot life of the tested mixtures is highly dependent on the crosslinking agent used. The use of compounds with a high content of epoxidised double bonds (EHTPB I and EHTPB II) results in a much shorter pot life than in the case of substances with a low content of epoxy bonds (EHTPB III). If a crosslinking agent content of 10% is used, an increase in the pot life of the mixture is to be expected.

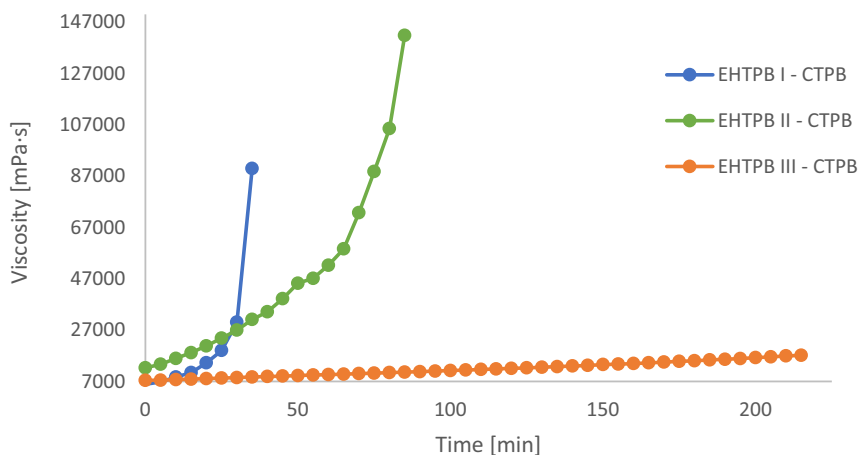


Figure 13. Summary of viscosity changes over time for CTPB and 15% EHTPB-based systems I, II, III

Propellants P-II and P-III have similar densities. This value is similar to the density of HTPB-based propellants (1.66 g/cm^3) and lower than poly(glycidyl azide) (GAP)-based propellants. The difference in density between the resulting propellants and those based on GAP is due to differences in the density of the prepolymers themselves – the density of HTPB/CTPB is 0.9 g/cm^3 , while that of GAP is 1.3 g/cm^3 [21].

Propellants based on the HTPB-DDI system have a hardness of 75 Shore A [22, 23], while those based on the GAP-N-100 system have a hardness of 90 Shore A. Comparing these values with results presented in Table 7, propellants P-II and P-III have a hardness very close to that of HTPB-DDI, but lower than that of the GAP-N-100 system.

Table 7. Densities and hardness of the prepared propellants

Propellant	Density [g/cm^3]	Hardness [Shore A]
P-II	1.6798	75
P-III	1.6791	65

Propellants P-II and P-III exhibited typical characteristics like those of HTPB-based propellants (Table 8). As the nozzle is reduced, the pressure in the combustion chamber is increased and the fuels have a higher r . The same relationship was observed for both propellants. Further research should determine the applicability of known r catalysts for solid propellants in this binder system.

Table 8. Ballistic properties of the propellants P-II and P-III

Propellant	Nozzle [mm]					
	2.2		3.0		3.5	
	r [mm/cm]	P_{\max} [MPa]	r [mm/cm]	P_{\max} [MPa]	r [mm/cm]	P_{\max} [MPa]
P-II	6.11	3.9	4.9	2.1	3.2	0.6
P-III	5.9	3.8	4.8	2.0	3.6	0.7

8 Summary and Conclusions

- ◆ The tests carried out for the individual components and crosslinking systems allowed the selection of systems with the best physicochemical and mechanical properties. On the basis of the results obtained, heterogeneous solid propellants were prepared and the hardness and density of the products obtained were measured.
- ◆ Depending on the type and content of the crosslinking agent, materials with different degrees of hardening, as well as different physico-chemical and mechanical properties, can be obtained. Systems based on epoxidised HTPB derivatives (EHTPB I, II and III) have significant differences in both pot life and mechanical properties. A high viscosity value (and high degree of epoxidation) of the crosslinking agent results in a shorter mixture pot life compared to a system containing a lower viscosity compound. The properties of the components used significantly affect the properties of the cross-linked systems based on them and, consequently, of the rocket propellants.
- ◆ The advantage of the proposed methods for crosslinking prepolymers is that these methods do not use harmful compounds, as is the case with the way HTPB is crosslinked with isocyanate compounds. Moreover, in the case of the CTPB-EHTPB system, both the prepolymer and the crosslinking agent are obtained by modifying the HTPB chain, which is a common and widely available raw material in the rocket propellant sector.
- ◆ The authors' future research aims are to explore the broadest possible application aspects of the proposed crosslinking system. Exploring the use of burn rate catalysts, for example nano-iron, or the isocyanate incompatible oxidant ADN.

References

- [1] Florczak, B.; Witkowski, W. Prospects for the Development of Solid Heterogeneous Rocket Fuels. (in Polish) *Issues of Armament Technology* **2006**, 98: 67-78.
- [2] Chmielarek, M.; Szejter, B.; Kasprzak, P.; Prasula, P. Effects of Azide-Hydroxyl-Terminated Polybutadiene on the Properties of Solid Heterogeneous Rocket Propellants. *Cent. Eur. J. Energ. Mater.* **2022**, 19(4): 393-408; DOI: 10.22211/cejem/158247.
- [3] Heger, L. *Encyclopedia of Explosives*. (in Polish) 1st Ed., Warsaw, Warsaw University of Technology Publishing House, **1979**, pp. 159.
- [4] Okniński, A. HTPB-based Binder Surrogates and their Effects on Preliminary Rocket Motor Analyses. *Cent. Eur. J. Energ. Mater.* **2022**, 19(3): 209-230; DOI: 10.22211/cejem/154720.
- [5] Sutton, G.P.; Biblarz, O. *Rocket Propulsion Elements*. 8th Ed., New Jersey, John Wiley & Sons, Inc., **2010**, pp. 755; ISBN 978-0-470-08024-5.
- [6] Davenas, A. *Solid Rocket Propulsion Technology*. Pergamon Press, **1993**, pp. 619; ISBN 0-08-040999-7.
- [7] Florjańczyk, Z.; Penczek, S. *Chemistry of Polymers, Basic Synthetic Polymers and Their Applications*. (in Polish), Vol. II, Warsaw, Publishing House of the Warsaw University of Technology, **2002**, pp. 265-275; ISBN: 83-7207-368-6.
- [8] Krowicki, K.; Syczewski, M. *Solid Rocket Fuels*. (in Polish) Warsaw, MON, **1964**, pp. 297.
- [9] *Solid and Liquid Fuel Rockets*. The European Space Agency, https://www.esa.int/Education/Solid_and_liquid_fuel_rockets4 [Accessed 1 December **2022**].
- [10] Ruffin, A. *Study and Development of Throttleable Hybrid Rocket Motors*. Ph.D. School STMS, Padova, **2018**.
- [11] Singh, S.; Raveendran, S.; Kshirsagar, D.R.; Gupta, M.; Bhongale, C.J. Studies on Curing of an Aluminized Ammonium Perchlorate Composite Propellant Based on Nitrile Butadiene Rubber Using a Quinol Ether of 1,4-Benzoquinone Dioxime. *Cent. Eur. J. Energ. Mater.* **2022**, 19(1): 18-38; DOI: 10.22211/cejem/147553.
- [12] Mastrolia, E.J.; Klager, K. *Solid Propellants Based on Polybutadiene Binders*. Sacramento, Aerojet-General Corp., Propulsion Division, Advances in Chemistry, **1969**, pp. 43; ISBN 9780841200890.
- [13] Crimmins, P.; Cousineau, M.; Rogers, C. *The 260 – the Largest Solid Rocket Motor Ever Tested*. Gencorp Aerojet, Los Angeles, **1999**, pp. 11.
- [14] Rarata, G.; Surmacz, P. Modern Solid Rocket Propellants. (in Polish) *The Papers of the Institute of Aviation* **2009**, 7: 112-124.
- [15] *Hydroxyl Terminated Polybutadiene Resins and Derivatives – Poly bd and Krasol*. Cray Valley, Total, **2022**. pp. 44.
- [16] Gonçalves, V.; Barcia, F.L.; Soares B.G. Composite Materials Based on Modified Epoxy Resin and Carbon Fiber. *J. Brazilian Chem. Soc.* **2006**, 17(6): 1117-1123; DOI: 10.1590/S0103-50532006000600008.
- [17] Aguiar, M.; Menezes, S.C.; Akcelrud, L. Configurational Double Bond Selectivity

- in the Epoxidation of Hydroxy-terminated Polybutadiene with *m*-Chloroperbenzoic Acid. *Macromol. Chem. Phys.* **1994**, *195*(12): 3937-3948; DOI: 10.1002/macp.1994.021951219.
- [18] Zhang, Q. Hydroxyl Terminated Polybutadiene: Chemical Modification and Application of these Modifiers in Propellants and Explosives. *Cent. Eur. J. Energ. Mater.* **2019**, *16*(2): 153-193; DOI: 10.22211/cejem/109806.
- [19] Wang, G. Kinetics of Epoxidation of Hydroxyl-Terminated Polybutadiene with Hydrogen Peroxide under Phase Transfer Catalysis. *Ind. Eng. Chem. Res.* **2008**, *48*(3): 1364-1371; DOI: 10.1021/ie800875h.
- [20] Nikje, M.M.A.; Mozaffari, Z. Chemoselective Epoxidation of Hydroxylterminated Polybutadiene (HTPB) Using *in-situ* Generated Dimethyl Dioxirane (DMD). *Des. Monomers Polym.* **2007**, *10*(1): 67-77; DOI: 10.1163/156855507779763630.
- [21] Mason, B.P.; Roland, C.M. Solid Propellants. *Rubber Chem. Technol.* **2019**, *92*(1): 24; DOI: 10.5254/rct.19.80456.
- [22] Chai, T. Rheokinetic Analysis on the Curing Process of HTPB-DOA/MDI Binder System. *IOP Conf. Ser.: Mater. Sci. Eng.* **2016**, *137*: DOI: 10.1088/1757-899X/137/1/012069.
- [23] *Isocyanates and Isothiocyanates*. CAMEO Chemicals, <https://cameochemicals.noaa.gov/react/18> [Retrieved 1 Dec. **2022**].

Received: December 11, 2022

Revised: June 29, 2023

First published online: June 30, 2023