Research paper / *Praca doświadczalna*

First published in Polish in 2018.

The main part of this analysis was presented at the 15th International Conference IPOEX2018, Ustroń Zawodzie June 11-13, 2018 in Poland.

Modification of HTPB (α,ω-dihydroxypolybutadiene) by esterification, silanization, epoxidation and hydrogenation
Modyfikowanie HTPB (α,ω-dihydroksypolibutadienu) w reakcjach estryfikacji, silanizacji, epoksydacji i uwodornienia

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Abstract: Hydroxyl-terminated polybutadiene (HTPB) is a co-monomer used in the production of polyurethanes. Its unique properties make it resistant to frost and give it excellent mechanical properties, especially at low temperatures. Polyurethanes obtained using this method are used in the production of propellants for space and military rocket propulsion systems, frost-resistant adhesives and insulation materials. Current research on the choice of binder indicates use of high-energy polymers or the modification of previously used polymers aimed at improving their properties. In modern rocket propulsion materials, the polymer binder may be replaced with a suitable high-energy compound, i.e. a polymer including energy groups, e.g. azide or nitro group.
The article presents the results of research on methods of modifying HTPB properties to widen its applicability.

Streszczenie: α,ω-Dihydroksypolibutadien (HTPB) jest cennym komonomerem do otrzymywania poliuretanów. Dzięki swoim specyficznym właściwościom, nadaje tym tworzywom mrozoodporność i świetne właściwości mechaniczne, szczególnie w niskich temperaturach. Tak otrzymywane poliuretany znajdują zastosowanie w produkcji stałych paliw rakietowych używanych w napędach rakiet kosmicznych i wojskowych, a także są podstawą mrozoodpornych klejów i lepiszcz oraz materiałów izolacyjnych. Współczesne badania nad doborem lepiszcza wskazują na zastosowanie polimerów wysokoenergetycznych lub modyfikacji dotychczas stosowanych polimerów polepszających ich właściwości. W nowoczesnych rakietowych materiałach pędnych polimerowe lepiszcze, może zostać zastąpione odpowiednim wysokoenergetycznym związkiem chemicznym, czyli polimerem z wbudowanymi grupami energetycznymi, takimi jak azydkowa lub nitrowa.
W prezentowanym artykule przedstawione zostaną wyniki badań nad takimi sposobami modyfikacji HTPB, które zapewnią jego rozszerzoną aplikację.

1. Introduction

Due to its properties, hydroxyl-terminated polybutadiene (HTPB) is widely used in the space, armaments and civil industries. In the latter, it is used in the production of adhesives and coatings, particularly products for low-temperature applications, as well as golf and tennis balls *etc.* [1]. In the armaments industry, HTPB is used as a heterogenous component of rocket fuels [2], a component of plastic explosive materials and a phlegmatizing agent. It is a liquid polymer with a relatively low molecular weight (M_n from 1,500 to 10,000 g/mol). Its polybutadiene chain may include three different monomeric units (Fig. 1): 1,4-*trans*, 1,4-*cis* and 1,2-*vinyl* [3]. The structure of the polybutadiene chain (individual monomeric units) and termination with hydroxyl groups gives it its specific and unique properties. HTPB is valued for its hydrophobic properties, resistance to aqueous acid and base solutions, good adhesion to different surfaces and insulating properties. Its main advantage is a low glass transition temperature (approximately −75 °C) providing excellent strength properties of HTPB-based polyurethanes at low temperature. HTPB is mostly used for obtaining polyurethanes (PU) as the product of the reaction with diisocyanates. Typical commercially available HTPB grades include approximately 20% 1,4-*cis*, 60% 1,4-*trans* and 20% 1,2-*vinyl* monomeric units.
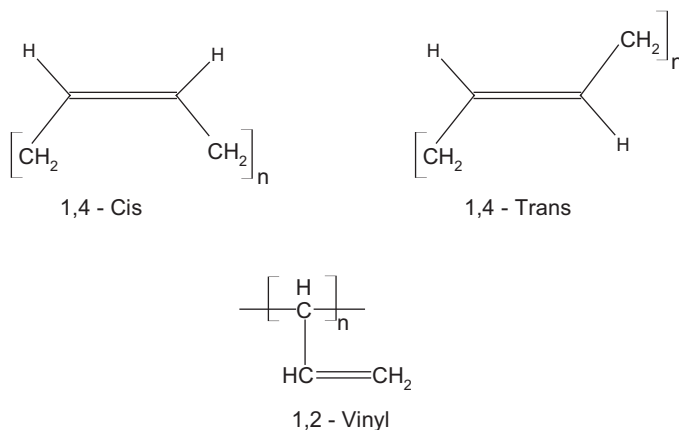

Figure 1. The isomers present in the polybutadiene chain

1,4-*cis* monomeric blocks provide the HTPB-based polyurethanes with high flexibility, tensile strength and low glass transition temperature $Tg = -45$ °C; 1,4-*trans* monomeric blocks provide mechanical strength; and 1,2-*vinyl* monomeric blocks provide relatively high adhesive properties. 1,2-*vinyl* isomer content also affects the viscosity of HTPB. Figure 2 shows the structure of standard commercially available HTPB grades. Commercially available polymers differ in the number of –OH groups and viscosity. Table 1 shows the commercially available HTPB grades used in the armament industry (R-45M) and civil industry (R-45HTLO).
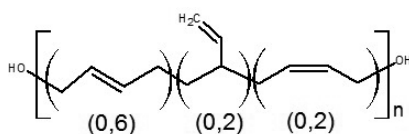

Figure 2. The structure of standard commercially available HTPB grades

Table 1.   Properties of commercially available HTPB grades [4-6]

Parameter	Unit	R-45HTLO	R-45M
Hydroxyl value	meq/g	0.84	0.72
Number-average molecular weight, M_n	g/mol	4046	4700
Weight-average molecular weight, M_w	g/mol	8189	11750
Polydispersity, D	–	2.01	2.5
Viscosity (23 °C, Brookfield)	mPa·s	8000	7000
Glass transition temperature, T_g(DSC)	°C	−75	−76

R-45M has a slightly higher molecular weight compared to R-45HTLO. R-45HTLO has more OH/g groups than R-45M; the difference is due to lower molecular weight or higher number of low-particle polyols. R-45M is a typical commercially available grade for military applications. The polymer properties significantly affect the end properties of fuel kernels. HTPB, with sufficiently long chains in the reaction with diisocyanate, forms a polyurethane matrix with an oxidant and additives dispersed within the matrix. The lower viscosity of R-45M compared to R-45HTLO and higher molecular weight (M_n) allows more fillers to be used (solid fuel components – oxidant and additives) compared to R-45HTLO. The higher molecular weight and lower –OH group content of R-45M yields polyurethane with a very high dispersion of fillers and excellent adhesion to them. A hydroxyl value of R-45M allows it to form polyurethanes showing the strength properties required in solid heterogeneous rocket fuels.

The available pathways of chemical HTPB modifications and applications of modified HTPB derivatives and HTPB-based copolymers are presented below. Test results for derivatives intended for standard military applications: HTPB with nitro groups (NHTPB [29]) and HTPB with pendant ferrocenes (Butacene® [30]) were presented in the previous studies; this article discusses the methods of synthesizing HTPB and its derivatives with carboxyl groups (CTPB), alkoxide and epoxide groups and of synthesizing hydrogenated HTPBs. Physical and chemical properties, as well as applications of all derivatives, are presented.

2.   HTPB synthesis

HTPB can be synthesized using different pathways:
a)   initiated polymerization with organodilithium compounds [7-9],
b)   initiated polymerization with hydroxyl radicals from thermal hydrogen peroxide (H_2O_2) dissociation [10, 11],
c)   initiated polymerization with radicals containing groups hydrolysable to hydroxyl groups [12],
d)   free-radical polymerization of dienes using azo compounds as initiators [13].

Depending on the method used to synthesize HTPB, *i.e.* initiator, initiator/monomer ratio, solvent, reaction temperature, time and pressure, polymers with different molecular weight, polydispersity, and the number of hydroxyl groups and 1,4-*cis*, 1,4-*trans* and 1,2-*vinyl* isomers can be obtained [10, 11]. Each synthesis method has its pros and cons. The advantages of polymerization processes using lithium compounds or azo compounds as initiators are low process temperatures and the ability to carry out the reaction at atmospheric pressure. The biggest advantage of those methods is that they yield HTPBs only, however, they do have some disadvantages. The stages required to prepare the initiator, polymerize the butadiene and introduce the hydroxyl groups to the polymer chain are expensive and time-consuming. The finished product contains impurities and it is difficult to dispose of the effluents.

The disadvantages of the polymerization process using H_2O_2 as an initiator include the relatively high temperature and pressures required. The disadvantage is that the reaction product contains polyhydroxypolybutadienes. The reactants' properties are also disadvantageous – high concentration and toxicity of hydrogen peroxide and the flammability of 1,3-butadiene. The costs and availability of the reactants on the Polish market are their advantage, since the process uses cheap and readily available solvents, including 2-propanol and ethanol. The hourly yield of this method is also significantly higher. The economic factors (availability, raw material prices) and required product properties, mean that HTPB can be obtained on an industrial scale by polymerization of 1,3-butadiene with H_2O_2.

3. HTPB modification pathways

HTPB can undergo different reactions and form derivatives with new properties and applications. HTPB has suitable functional groups which can be used in its modification. In a polybutadiene chain those include double C=C bonds, and the second functional group −OH at both ends of the chain. The C=C bond can be oxidized or reduced, and the −OH group can react with alcohols, *e.g.* anhydrides, acids, acid chlorides or isocyanates. An ester bond is formed as a result of the reaction with acid anhydrides, acids or acid chlorides [5, 14, 15]. Two HTPB modification pathways allow multiple derivatives, showing different properties, to be obtained. The study will present the authors' own research on the synthesis of HTPB derivatives which can be used to extend the range or replace currently used polymers. The study included derivatives that can be obtained using widely available raw materials. This approach to the synthesis, modification and expansion of HTPB properties will not require significant expenditure in time, costs and energy. The derivatives are currently in high demand.

3.1. HTPB derivatives

3.1.1. CTPB

Hydroxyl groups at the end of a polybutadiene chain can undergo different reactions with anhydrides, *e.g.* acetylation with acid anhydride giving −O(CO)CH$_3$ terminated polybutadiene as a product. On an industrial scale, HTPB reaction with maleic anhydride is used to replace the −OH functional group with the carboxyl group. CTPB products of this reaction are widely available (*e.g.* Polybd® 45CT offered by Sartomer). A derivative based on Krasol 2000 (HTPB with 65% 1,2-*vinyl* isomer obtained in the anionic polymerization reaction) offered as Polybd® 2000CT, is also available. This product based on CTPB shows good strength, low temperature and hydrophobic properties [4].

3.1.2. Silanized HTPB

Polyurethanes are polymers characterized by urethane bonds formed by reacting isocyanates with alcohols. Due to their unique properties, they are widely used in the production of foams, elastomers, adhesives, fibres, paints and varnishes. The polyurethanes can be synthesized due to the high reactivity of hydroxyl groups which bond with isocyanates to form urethane bonds.

Standard applications of HTPB as a component of adhesives and paints, require the use of diisocyanates as cross-linking agents. After applying diol and diisocyanate to the surface, the components react to form a varnish, the diisocyanate is partially released into the environment and the user is exposed to this hazardous substance.

A viable alternative is to use HTPB modified with organofunctional silanes with O−R (R = −CH$_3$ or –C$_2$H$_5$) groups. The groups in contact with water vapour in air, form −Si−O−Si− oxygen bridges between the chains (Fig. 3). This cross-linking improves the mechanical strength, chemical resistance and gloss of the end product. The user is not exposed to isocyanates, since the reaction product releases significantly fewer hazardous alcohols [17].
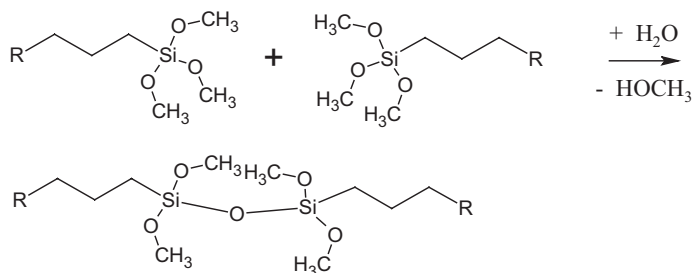

Figure 3. The diagram of −Si−O−R reaction with H$_2$O

Isocyanate silanes with propylene chains were introduced for commercial use by Wacker AG under the Geniosil® trade name. Using silanes for production of silanized HTPB derivatives, results in increased resistance to scratching, non-toxic cross-linking and significantly reduced curing time [18]. The substituents of a silicon atom include methoxy-, ethoxy- or propoxy- substituents. The use of silane with ethoxy substituents is preferred. Ethanol is released as a result of the synthesis, however, despite its flammable and toxic properties, it is a much safer alternative to methanol and propanol.

The advantages of polymers terminated with alkoxysilane groups include low toxicity and high corrosion resistance of the end products. Despite the many advantages of silanization, there are also many disadvantages. The main disadvantages of using silanes as cross-linking agents is that the reaction must be carried out in anhydrous conditions. In industrial practice, providing such conditions translates into high process complexity and thus high production costs [19]. Two methods of synthetizing the derivative are known. The first method (A) (Fig. 4) is a single stage reaction of diol (HTPB) with silane with −NCO group and –OR groups, producing a polymer terminated with −Si−(OR)$_x$ groups. The second method (B) (Fig. 5) is a two-stage synthesis. In the first stage, as a result of the reaction between the diol and the excess diisocyanate, a pre-polymer terminated with –NCO group is formed which reacts in the second stage with amino silane containing an –OR group. An −Si−(OR)$_x$ terminated polymer is the product of the reaction.
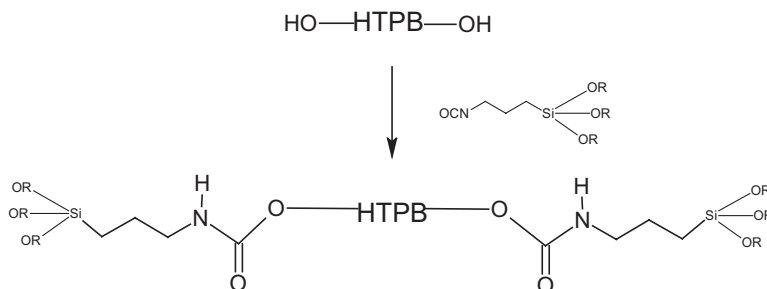

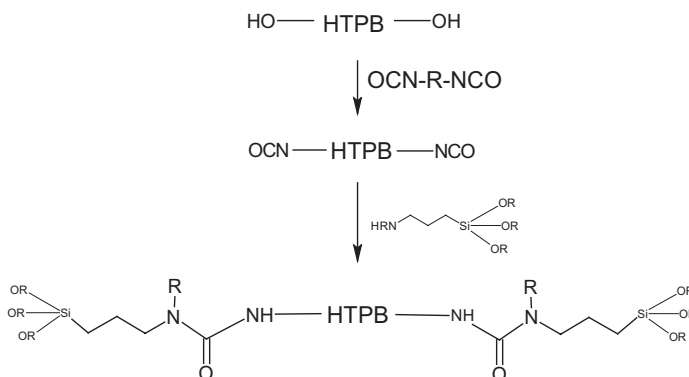**Figure 4.** The synthesis of –Si−(OR)$_x$-terminated polymer – method A

Figure 5. The synthesis of –Si−(OR)$_x$-terminated polymer – method B

The catalysts used in diol silanization reactions are dialkyltin(IV) derivatives, metal complex compounds (chelates and carboxylates), *e.g.* titanium, zirconium, bismuth, amines and their salts and other acid and base catalysts. Examples include dibutyltin dilaurate, dibutyltin diacetate and tin(II) octanoate. A common disadvantage of the silanization catalysts is that they take part in the silane condensation reaction, *e.g.* toxic dialkyltin(IV) derivatives. Metal derivatives (compounds) and complex compounds: bismuth, zinc or tertiary amines show lower toxicity [19].

The polyurethanes so obtained can be used to replace the polyurethanes obtained in the reaction of HTPB with diisocyanates, where the urethane bond is formed after the varnish is applied to a surface. Using polyurethanes with silane as cross-linking agent is less hazardous than using isocyanate-based polyurethanes. In a currently used method [20], the isocyanates are released immediately whereas in the proposed method the alcohols are released during cross-linking.

3.1.3. Epoxidized HTPB

Another commercially available HTPB derivative is its epoxidized form (EHTPB) often used as an intermediate product in the synthesis of nitrated HTPB derivative (NHTPB). The required maximum epoxidation rate should not exceed 13%. The authors' own studies, presented in the article, were aimed at achieving the epoxidation rate required for the next NHTPB synthesis stage. Based on the literature, EHTPB can be obtained by reaction with peroxy acids: H_2O_2/CH_3COOH [21]. The epoxidation due to low efficiency of the epoxidizing system results in the epoxidation of ~10% of dual C=C bonds. Other epoxidizing systems, containing sodium tungstate dehydrate (Na_2WO_4) or tungsten heteropolyacids, can be used, thereby removing the need for acetic acid. With the use of solid catalysts, the epoxy groups can be introduced at an efficiency of up to 60% [22]. The efficient HTPB epoxidation reactions are carried out using phase transfer catalysts and many reactants, *e.g.* H_2O_2 (Fig. 6) or *meta*-perchlorobenzoic acid as an oxidizer or tungsten acid or its salts, orthophosphoric acid or its salts. The epoxidation of unsaturated polymer can be carried out at 0 to 100 °C (preferably from room temperature to 70 °C) since H_2O_2 may undergo spontaneous decomposition above that temperature range. The reactions proceed quicker and more efficiently at higher temperatures [23]. The epoxidation reaction is exothermic and require temperature control when adding the peroxide. The reaction may be carried out with a solvent, however, the system's viscosity is reduced in this case. Suitable solvents include toluene, chlorobenzene, chloroform and methylene chloride.
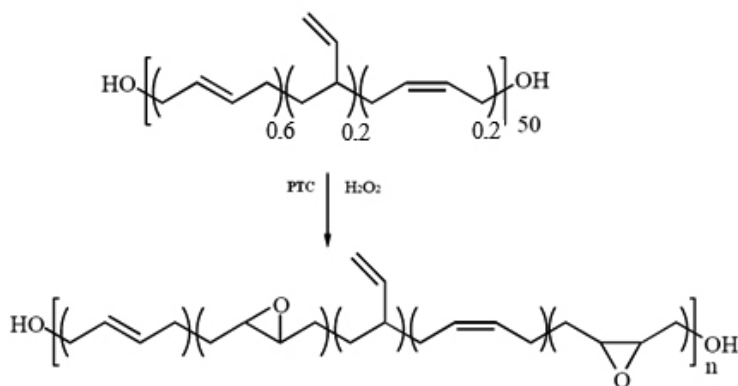

Figure 6. EHTPB synthesis

3.1.4. Hydrogenated HTPB

Due to the presence of double bonds in the polymer chain, HTPB is susceptible to chemical and ambient factors. Reduced polymer stability has been observed at increased temperatures or UV radiation [4]. To eliminate or reduce the effect of these, the double bonds in the polymer chain must be hydrogenated (Fig. 7). The hydrogenated HTPB can be used as a component of chemical and thermal resistant polyurethanes. The key HTPB property, *i.e.* flexibility at low temperatures, is maintained. The literature discusses several types of catalysts which can be used in hydrogenation and include, Raney nickel [24]; Ziegler-Natta catalysts [25] and Pd or Rh catalysts [26] on activated charcoal.
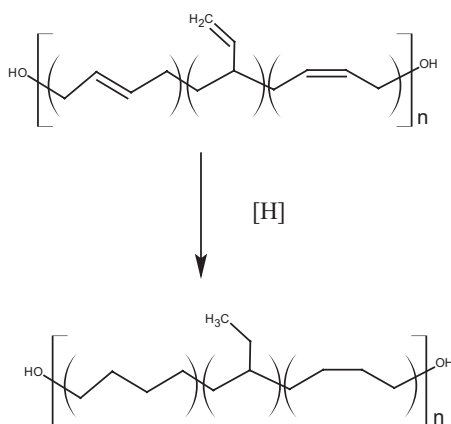
Figure 7. HTPB hydrogenation diagram

4. Authors' own research

4.1. Raw materials and analysis methods

The authors' own research included the following raw materials: HTPB R-45HTLO (Cray Valley), toluene (analytically pure, Avantor), H_2O_2 (60%, Chempur), phthalic (acid) anhydride (>99%, Sigma-Aldrich), succinic anhydride (for synthesis, Sigma-Aldrich), glutaric anhydride (95%, Sigma-Aldrich), acetic acid (80%, Avantor), Na_2WO_4 (>99%, Sigma-Aldrich), cyclohexane (pure, Avantor), methylene chloride (pure, Avantor), nickel acetylacetonate (95%, Sigma-Aldrich), cobalt acetylacetonate (for synthesis, Sigma-Aldrich), 0.5%Pd/C (Rutgerswerke AG), 1%Pd/C (prepared in the laboratory), H_2WO_4 (99%, Sigma-Aldrich), Aliquat 336 (Sigma-Aldrich).

The analysis of ^{1}H NMR was carried out using Varian NMR System 500 MHz at 25 °C with CDCl$_3$ as the solvent. FTIR analysis was carried out using ThermoScientificNicolet 6700 with ATR attachment.

4.2. Modification of HTPB using −OH groups

4.2.1. CTPB

As shown by the reactions of maleic anhydride with HTPB, the reaction efficiency is less than 100% and the end product contains a small amount of unreacted HTPB. However, the product can be used to obtain polyesters and other derivatives in the carboxyl group reaction [27]. The authors' own research included investigation of HTPB reactions with anhydrides other than maleic anhydride. A wide range of acid anhydrides which can be used to obtain esters is available. The type of acid or anhydride used determines the mechanical properties of the polyesters. Flexibility is affected by the chain structure of HTPB, whereas the rigid polyester bonds are interleaved with long and flexible polybutadiene chains. Diols (or polyols) with a short carbon chain are currently used for obtaining hard and brittle polyesters. Using anhydrides with different structures in CTPB synthesis will improve the mechanical properties and weather resistance of the end products based on the obtained polymers [16, 28].

The reactions of HTPB with different anhydrides were analysed. The anhydrides used included an aromatic nucleus, an aliphatic nucleus or an aliphatic chain. The ability of obtaining CTPB using succinic, phthalic and glutaric anhydride was analysed. The characteristic signals from fading –OH groups and formed –COOH terminal groups in the polymer were observed. The reactions were carried out in a dried argon atmosphere. 30 g of dried HTPB was added to a three-necked round-bottomed flask, heated in an oil bath to a pre-determined temperature and stirred with a magnetic stirrer. After reaching the set polymer temperature, dried anhydride was added.

The reaction was carried out in a dried argon atmosphere. To avoid the potential addition of moisture, no solvents were used. The mixture was heated at a pre-determined temperature for a specified time (the synthesis conditions are shown below). Any unreacted anhydride was removed from the reaction mixture by dissolving the HTPB and CTPB, filtering and rinsing out the anhydride.

Depending on the ratio of anhydride to the number of –OH groups, a mixture of HTPB and CTPB (anhydride/OH ratio <1), pure CTPB (anhydride/OH ratio = 1) or CTPB and unreacted anhydride (anhydride/OH ratio >1) was expected. Assuming a stoichiometric ratio of anhydride to –OH groups in the polymer, the reaction yield was determined based on the amount of unreacted anhydride. In the reactions, the stoichiometric ratio of anhydride to –OH groups in HTPB was selected and the fading of the –OH group signal was observed using FTIR analysis to monitor the progress of the reaction. In all cases, the analysis diagram was similar with the FTIR spectrum showing partial fading of the band at 3300 cm^{-1}, corresponding to the presence of the –OH group in HTPB. The bands corresponding to ester and acid groups forming (C=O valence vibrations) were observed at 1650-1780 cm^{-1}. A wide band at 2500-3300 cm^{-1}, partially corresponding to the HTPB spectrum, indicated the valence vibrations of the acid's –OH group.

Figures 8-10 show the HTPB reactions with different anhydrides. HTPB reactions with succinic anhydride and phthalic anhydride were carried out at 130-160 °C for 3 h in an argon atmosphere. The reactions with glutaric anhydride were carried out at 60-110 °C for 3 to 6 h in an argon atmosphere. The following HTPB and anhydride reaction yields were observed:

a)   succinic − 85%,
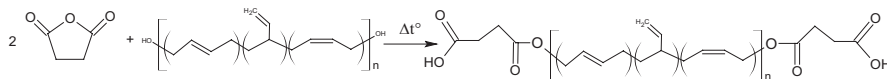b)   phthalic − 90% (at 160 °C),
c)   glutaric − 95%.

Figure 8. HTPB reaction with succinic anhydride
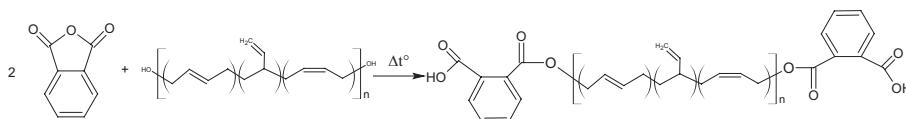

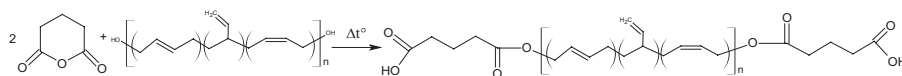**Figure 9.** HTPB reaction with phthalic anhydride

Figure 10. HTPB reaction with glutaric anhydride

4.2.1.1.   *CTPB synthesis – conclusions*

The ability to obtain CTPB in reaction with anhydrides was verified. The reaction and synthesis conditions were determined. The authors observed that the reaction requires temperatures which are higher than the melting points of the anhydrides. A low reaction temperature resulted in unreacted reagents and the presence of anhydride sediments in the reaction mixture. In each reaction, a stoichiometric ratio of anhydride to the number of –OH groups was used to observe the effect of synthesis conditions on the reaction's progress and the appearance of the end product.
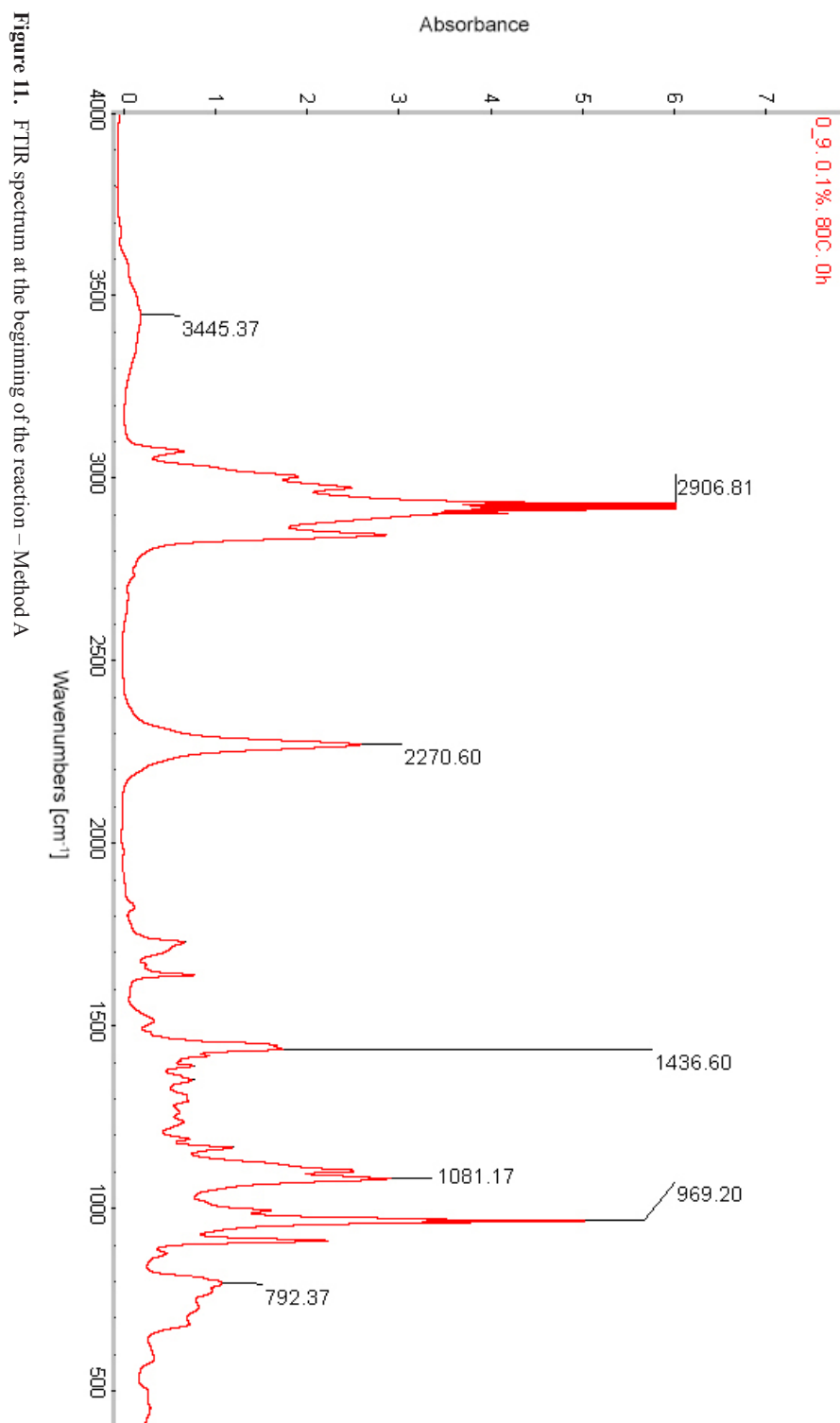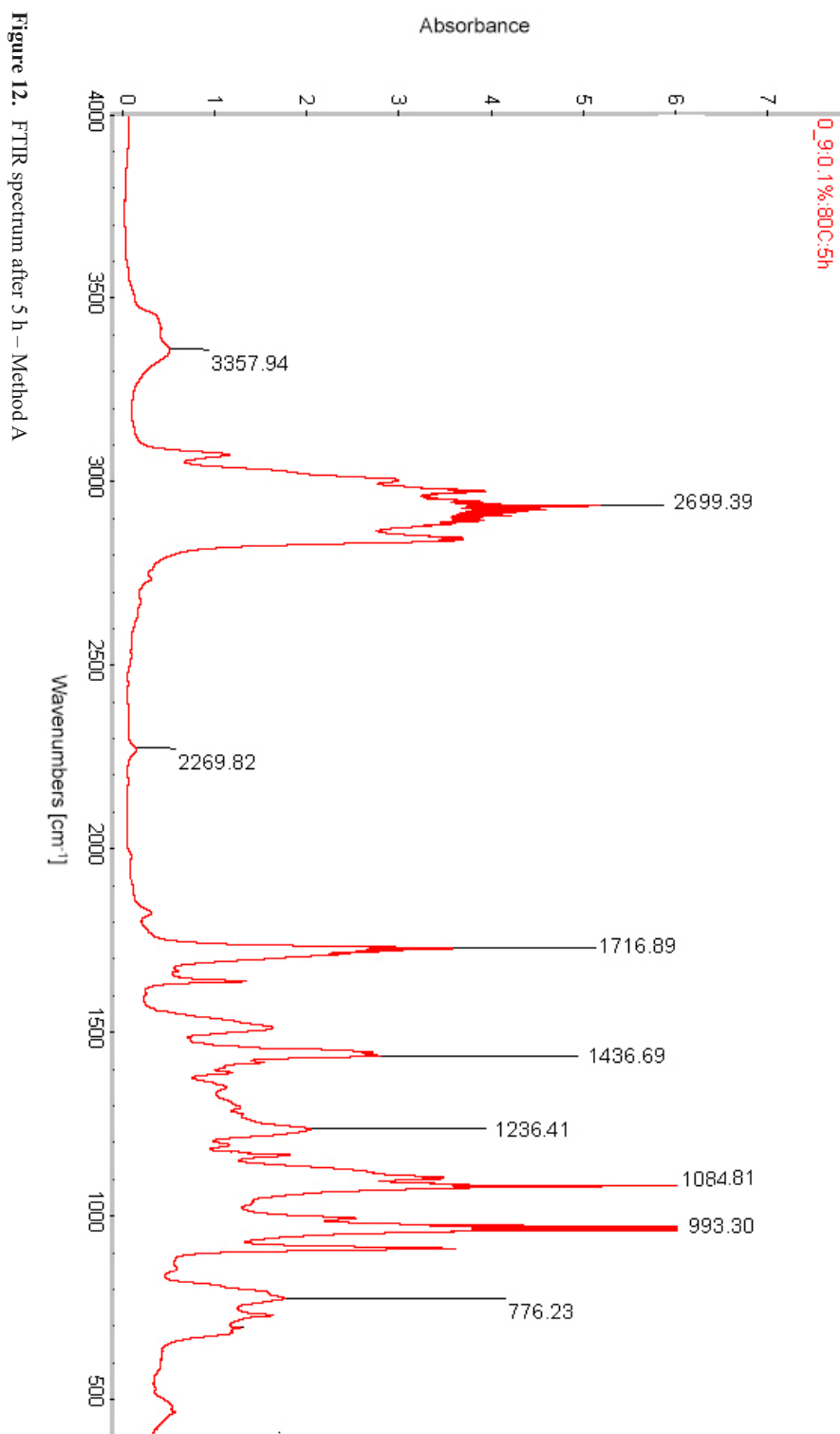
4.2.1.2. *CTPB properties and applications*

HTPB derivative terminated with carboxyl groups can be used as a modifier of thermoplastic polymers (polyamides, PET, PBT and other) and as a modifier of epoxy resins, adhesive additives or coatings. The derivatives can also be used as cover coatings in laminated printed circuit boards. Due to its chemical resistance, it is also as a component of sealants and putties. In military applications, it is used as a component of heterogenous solid rocket fuels (space rockets) or as a component of solid fuel in gas generators.

4.2.2. Silanized HTPB

As part of the research, the possibilities of synthesizing silanized HTPB in a reaction of HTPB with (3-isocyanatopropyl)triethoxysilane using different process conditions, were analysed. The temperature, catalyst to silane ratio and −NCO/−OH group ratio were modified to determine optimum reaction conditions. In theory, the −NCO/−OH = 1 ratio is optimal, however, due to possible errors in allocating the number of −OH groups there is a risk that the reaction mixture will contain unreacted –NCO groups. This is undesirable in the production of silanized HTPB-based adhesives and sealants. Free NCO groups will react with other adhesive components and affect the production and overall adhesive performance. A lower −NCO/−OH ratio was used in the synthesis. The reactions were carried out until all −NCO group signals had disappeared. The analysis was carried out using FTIR to observe the reaction progress – disappearance of the −NCO and −OH group signals and presence of the urethane bond signals. The reaction progress observations were qualitative and aimed to estimate the required reaction time. By observing the loss of the –NCO group signal, the effect of temperature and catalyst amount on the reaction time, was estimated. To verify a complete absence of the –NCO groups, the concentration of free –NCO groups was determined using the amine hydrogen equivalent weight method.

The optimum reaction conditions are 80 °C with a catalyst content of over 0.05% in relation to the silane content. Those conditions guarantee complete reaction of all reagents within 5 h. The ability to obtain silanized HTPB without solvents has been verified. Using only the raw materials and the catalyst allowed the elimination of the stages involving removal of the solvent from the reaction mixture and prevented adding impurities to the system with the solvent. The example reaction for NCO/OH = 0.9 ratio at 80 °C and 0.1% catalyst content (by silane weight) is shown below. Figures 11 and 12 show the FTIR spectra of the reaction mixture at the beginning of the reaction and after 5 h (Method A). Figure 11 shows the spectrum with strong –NCO group signal at 2270.60 cm^{-1}. A hydroxyl group band can be observed at 3445.97 cm^{-1}. After 5 h, a practically complete lack of a –NCO group signal can be observed (Fig. 12). A low-intensity band can be observed at 2269.82 cm^{-1}. Fading of the hydroxyl group band can also be observed. An –NH group signal from the urethane bond can be observed at 3357.94 cm^{-1} and a C=O group signal can be observed at 1716 cm^{-1}.

Figure 11. FTIR spectrum at the beginning of the reaction – Method A

Figure 12. FTIR spectrum after 5 h – Method A

4.2.2.1. Silanized HTPB properties and applications

Silanized HTPB derivatives can be used in the production of adhesives, sealants, coatings, in particular floor varnishes which are safer for the person applying the adhesive or varnish. The user won't notice any difference in the end product. HTPB and silanized HTPB-based products show similar mechanical properties [21].

4.3. Modification of HTPB using C=C bonds

4.3.1. Epoxidized HTPB

As part of the authors' own research, the usability of different epoxidizing systems was verified. H_2O_2 and *meta*-perchlorobenzoic acid were used as an oxidizer; toluene and tetrahydrofuran were used as a solvent and sodium tungstate dihydrate, tungsten acid, Aliquat 336, acetic acid, orthophosphoric acid and methylammonium chloride were used as the catalyst components. Use of *meta*-perchlorobenzoic acid did not bring the expected results. Despite reaching 7-8% of double epoxy bonds in the polymer, the main problem was the removal of *meta*-perchlorobenzoic acid from the product. The reaction was carried out using constant solvent volume (100 cm^3) by modifying the reaction time, the temperature and the oxidizer amount. H_2O_2 and acetic acid solution was added dropwise to the polymer solution in toluene, while stirring. The reaction was carried out at a given temperature for a given time.

While the different epoxidizing combinations were carried out, the effects of oxidizer and catalyst quantity, reaction times and temperatures were determined. The degree of epoxidation was determined based on the analysis of ^{1}H NMR spectra. The following epoxidizing systems were analysed:

a) **CH_3COOH/H_2O_2/toluene** – The reactions were carried out at 0-60 °C for 4 to 8 h. Up to 13.6% of double bonds in the polymer were oxidized.

b) **$H_2WO_4/CH_3NH_2Cl/H_2O_2/H_3PO_4$/toluene** – The reactions were carried out at 25-65 °C for 4 to 6 h. Up to 8.3% of double bonds in the polymer were oxidized.

c) **H_2WO_4/H_2O_2/toluene** – The reactions were carried out at 40-60 °C for 4 to 8 h. Up to 9.6% of double bonds in the polymer were oxidized.

d) **Na_2WO_4/H_3PO_4/Aliquat 336/H_2O_2/toluene** – The reactions were carried out at 25 °C for 15 to 45 min. Up to 14.5% of double bonds in the polymer were oxidized.

It was confirmed that acetic acid can be replaced by tungstic acid or its salt. Application of more complex epoxidizing systems tested allowed a reduced reaction time as well as a decrease in the process temperature. From the above-mentioned data, especially that related to the reaction conditions and to the facility for product purification, it can concluded that the simplest epoxidation of HTPB (without using of acetic acid) is by applying the H_2WO_4/H_2O_2/toluene system. When EHTPB is applied as an intermediate in the NHTPB synthesis, the level of double bond epoxidation cannot exceed 13%. Application of both the H_2WO_4/H_2O_2/toluene system and slightly extending the reaction time over 4 h, allowed the required maximal epoxidation degree to be achieved. Such an uncomplicated arrangement allows easy purification of the product. The post-reaction mixture only requires the removal of remaining acid, flushing with water with the aim of removing the peroxide and distilling off the solvent.

4.3.1.1. Epoxidized HTPB properties and applications

The epoxy HTPB derivatives obtained in the reactions can be used as a component of adhesives, electronics coatings or as a plasticizer for commonly used epoxy systems. It can also be used as a component of flexible and impact resistant sealants [4].

4.3.2. Hydrogenated HTPB

The authors have carried out own research to verify the ability of obtaining hydrogenated HTPB derivatives. Attempts to hydrogenate HTPB were made using:

a) **Ni(acac)₂/(C₂H₅)Al) or Co(acac)₂/(C₂H₅)Al) based catalysts** – The reactions were carried out in toluene at 40-80 °C and 0.5-1.5 MPa H$_2$ pressure. The degree of hydrogenation was 9%.

b) **1%Pd catalyst on activated charcoal (dust)** – The reactions were carried out in toluene at 40-80 °C and 3-4 MPa H$_2$ pressure. The degree of hydrogenation was 95%.

c) **0.5%Pd catalyst on activated charcoal (3 mm particles)** – The reactions were carried out in toluene at 40-80 °C and 3-4 MPa H$_2$ pressure. The degree of hydrogenation was 36%.

An AutoclaveEngineers 100 cm^3 mini-autoclave was used. The reactor is fitted with an adjustable turbine mechanical stirrer with magnetic coupling. Due to the viscosity of HTPB and good contact between the polymer, catalyst and hydrogen, the reaction was carried out in a solvent. The solvent was dessicated and distilled over calcium hydride in all cases. The reactor was completely filled with hydrogen and pressurised to the required amount. The stirrer was activated and the reactor mixture heated. Hydrogen pressure losses were compensated. The reaction was carried out for a pre-determined time.

An H^1 NMR method was used to determine the state of C=C bond hydrogenation in the HTPB chain. In the spectrum, the signals from 5.25 to 6.2 ppm correspond to the HC=CH bonds of 1,4-*cis/trans* isomers, and the signals from 4.8 to 5.05 ppm correspond to the methine group HC=CH$_2$ of 1,2-*vinyl* isomer (Fig. 13).
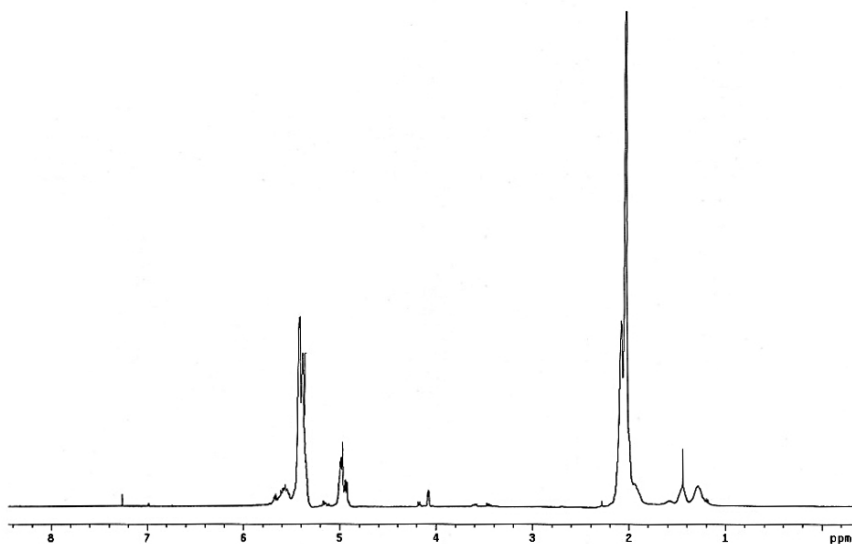

Figure 13. ^{1}H NMR HTPB R-45HTLO spectrum

After the hydrogenation of the double bonds in the polybutadiene chain, a decrease in signal intensity of individual isomers and an increase in intensity of peak values of –CH$_2$– group protons was observed. Figure 14 shows the selected ranges of ^{1}H NMR spectra of hydrogenated HTPB.
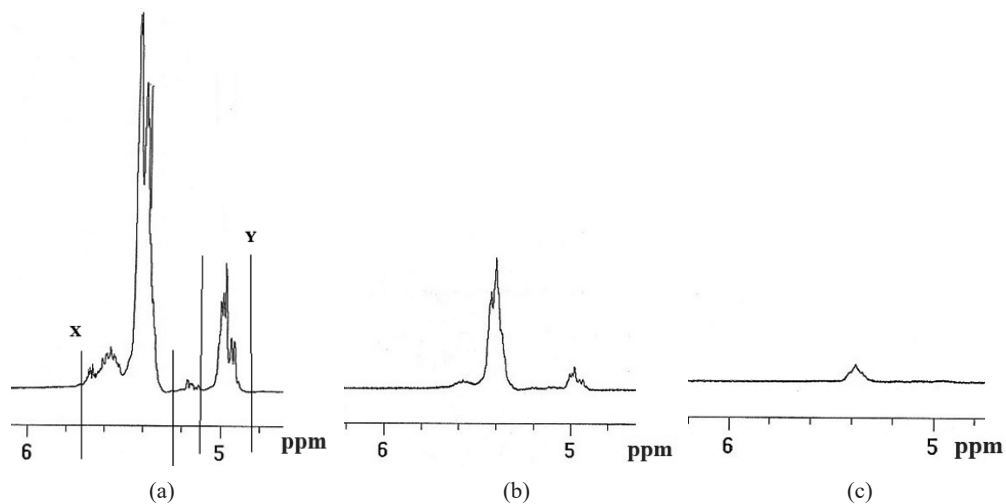
Figure 14. Changes in the signal intensity corresponding to the 1,4-*cis/trans* isomer protons (X) at over 5.25 ppm and 1,2-*vinyl* isomer protons (Y) at a 4.8 to 5.05 ppm range (a) in the ^{1}H NMR spectrum of HTPB polymer after (b) 25% and (c) 95% hydrogenation of double bonds

Compared to Figure 14(a), a partial decline in signals from 1,4-*cis/trans* isomers at over 5.25 ppm and 1,2-*vinyl* isomer at a 4.8 to 5.05 ppm range at partial hydrogenation (Fig. 14(b)) and almost complete lack of signals from 1,4-*cis*/*trans* isomers at over 5.25 ppm and 1,2-*vinyl* isomers at a 4.8 to 5.05 ppm range at 95% hydrogenation (Fig. 14(c)). Figure 15 shows changes in signal intensity corresponding to the –CH$_2$– groups at 1.2 ppm of a formed aliphatic chain and the declining signals from the protons in double bonds at ~2 ppm.
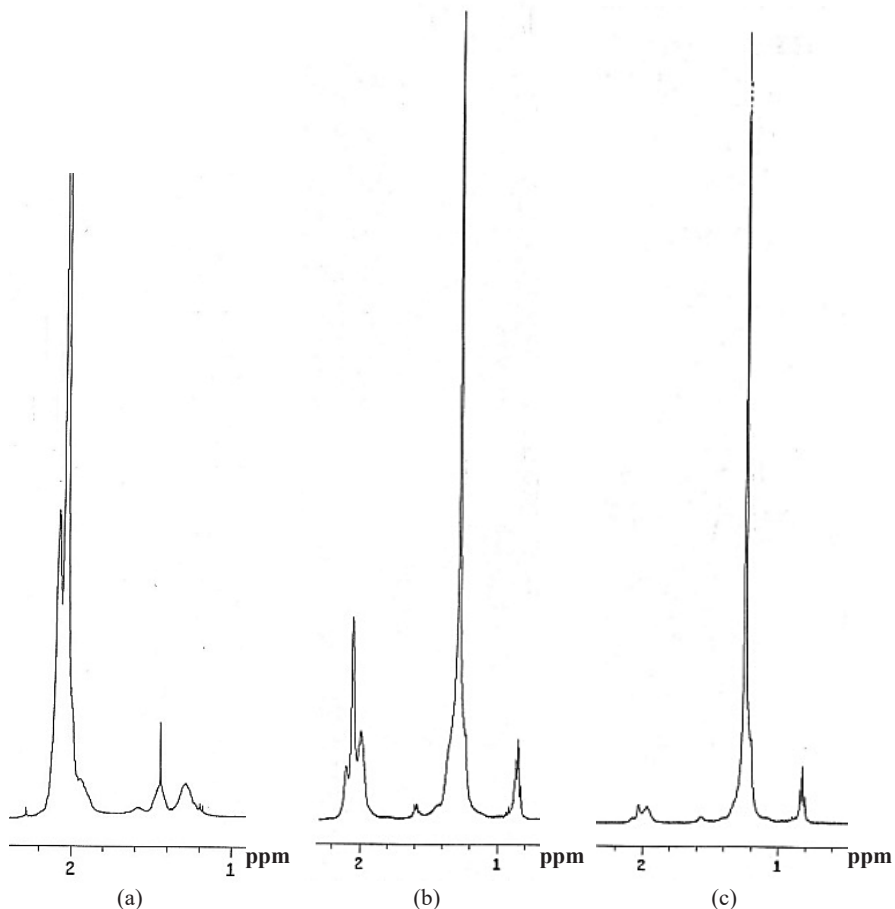
Figure 15. The signals from the protons of –CH$_2$– groups at a 1-1.2 ppm range and a 1.7-2.2 ppm range of the ^{1}H NMR HTPB spectrum (a) after (b) 25% and (c) 95% hydrogenation of double bonds

Compared to Figure 15(a), an increase in intensity was observed for signals corresponding to –CH$_2$– groups at a 1-1.2 ppm range and a 1.7-2.2 ppm range after partial (25%) hydrogenation (Fig. 15(b)) and significant increase in intensity of signals from –CH$_2$– groups at a 1-1.2 ppm range at 95% hydrogenation of double bonds (Fig. 15(c)).

4.3.2.1. HHTPB synthesis – conclusions

All the catalysts used showed activity in the hydrogenation reaction. The requirements for the end product (degree of HTPB hydrogenation) determined the synthesis conditions, in particular hydrogen pressure and catalyst type. Use of PD/C is preferred due to ease of preparation of the catalyst (drying) and ease of separation of the product from the catalyst. The disadvantage of using Ni(acac)$_2$ or Co(acac)$_2$ based catalysts is that they require the use of organometallic compounds – anhydrous catalyst synthesis conditions. Separating the catalyst from the reaction mixture is also a problem. Using Pd/C (dust) under hydrogen pressure of approximately 4 MPa and the reaction temperature over 70 °C allows a high degree of polybutadiene chain hydrogenation to be reached.

4.3.2.2. HHTPB properties and applications

The hydrogenated HTPB derivative shows very good thermal and weathering stability. It maintains its hydrophobic properties, low glass transition temperature and reactive hydroxyl groups. It can be used in the production of adhesives, sealants and coatings. It can also be used as a component of thermoplastic polymers for coating and isolating electronic components and as an additive to asphalts [4].

5. Summary

Research of the methods of obtaining HTPB derivatives allows an expansion of the range of HTPB-based products for commercial use. A series of syntheses was carried out to determine the reaction conditions, yielding the following products:

a) derivatives containing an epoxy group (EHTPB) using CH_3COOH/H_2O_2/toluene system in an 8 h reaction at 40 °C results in a 13.6% epoxidation of double polymer bonds; changing the epoxidizing system to H_2WO_4/H_2O_2/toluene allows a similar degree of epoxidation of the double bonds to be achieved and eliminates the use of acetic acid,

b) hydrogenated (HHTPB) derivatives in a reaction catalysed by 1% Pd on activated carbon (dust) in toluene at 80 °C and H_2 pressure of 4 MPa result in a 95% hydrogenation,

c) carboxyl-terminated (CTPB) derivatives in HTPB reaction with different anhydrides at 6 to 160 °C for 8 h result in a 95% yield of reaction,

d) $-Si(OR)_x$ terminated HTPB derivatives obtained in a 5 h reaction of HTPB and (3-isocyanatopropyl) triethoxysilane where the NCO/OH ratio was 0.9, the reaction temperature was 80 °C, and the amount of catalyst was 0.1% (in relation to silane mass).

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