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The Influence of Bonding Agents in Improving Interactions in Composite Propellants, Determined Using the FTIR Spectra

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Bonding agents synthesized in this research are 1, 3, 5-trisubstituted isocyanurates (substituents: 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl and 2, 3-epoxypropyl). All syntheses reactions were carried out according to a modified literature procedure.
All the synthesized isocyanurates were identified by their melting point and FTIR, ^{1}H NMR and UV spectroscopic data. The Fourier transform infrared spectrophotometry was also used to study the interaction between ammonium perchlorate, hydroxyl terminated poly(butadiene), carboxyl terminated poly(butadiene), cyclotetramethylenetetranitramine, tris[1-(2-methyl)aziridinyl]phosphine oxide and the compounds synthesized in this work. The results show that 1,3,5-tri(2-hydroxyethyl)isocyanurate is a universal bonding agent for the ammonium perchlorate/carboxyl terminated poly(butadiene)/cyclotetramethylenetetranitramine composite propellant system.

Key words: **composite propellant, rocket composite propellant, binder, isocyanurates.**

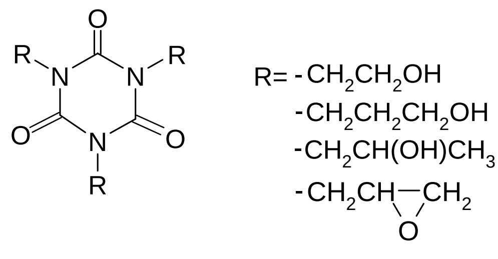
Introduction

THE isocyanurates are a class of bonding agents which provides an interaction of a filler with a resin to form a composite material. In the last ten years, 1,3,5-trisubstituted isocyanurates have been found to be suitable bonding agents in polymer chemistry [1,2]. They are also suitable for bonding an explosive substance, which is a special filler known as an oxidizer, in the resins in order to form a special type of a composite known as a composite propellant. [3,4].

Composite propellants are non-homogenous propellants which primarily comprise crystalline oxidizer and metal fuels uniformly suspended in a resin binder [5,6]. The crystalline oxidizers are usually inorganic compounds, such as ammonium perchlorate (AP) or potassium nitrate but can also be organic, for example cyclotrimethylenetrinitramine (RDX) or cyclotetramethylenetetramine (HMX). The metal fuels are powders of elemental metals, such as aluminum and magnesium. In contrast whit these components, the binders are organic polymers, such as urethanes, polyamides or vinyl polymers. Often as much as 80 weight percent of the propellant is an oxidizer along whit about 10 weight percent of a metal fuel, thus giving a solid loading of around 90 weight percent of the total composition. Poor binder and filler interaction is found mostly with the oxidizers and not with the metal fuels. The metals are not a problem because the metals have a more irregular surface and greater ease for chemical bonding with filler. On the other hand, oxidizers have surfaces which are very smooth, and in some cases, the oxidizers do not chemically bond with the binder. Attempts to improve the binder-filler interaction in composite propellants have included the addition of bonding agents. A bonding agent produces an interaction between the oxidizer crystal and the binder by forming either primary or secondary bonds with the oxidizer and a primary bond with the binder [7].

The strength of the bonds between the polymer matrix and the oxdizer determine the mechanical properties of composite propellants. One way of improving the mechanical properties of solid propellants is to add suitable bonding agents. There are many effective bonding agents for ammonium perchlorate. However, for nitramine fillers, for example cyclotrimethylenetrinitramine, there are only a few suitable bonding agents, but their effect in the RDX/AP system has been reported.

The presently used bonding agents are not universal bonding agents, [3] that is, they can only be used for one or a few binder-filler systems, but not for all binder-filler systems. Functionally substituted isocyanurates are universal bonding agents, [3] which form bonds with the surface of the crystalline oxidizers and binder of a propellant [8,9].



Sheme 1. The studied 1,3,5-trisubstituted isocyanurates

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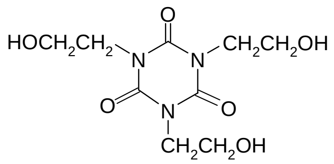
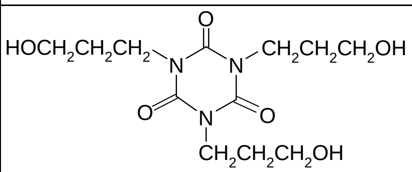
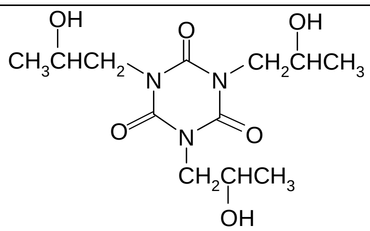
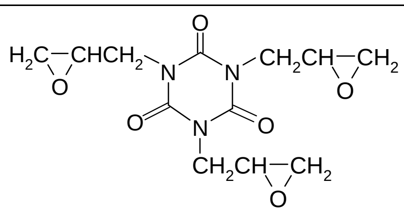
In our studies of the effect of bonding agents on the characteristics of composite propellants, in the present work, a series of 1,3,5-trisubstituted isocyanurates (Scheme 1) was synthesized. All the synthesized isocyanurates were identified by their melting point and FTIR, ^{1}H NMR and UV spectroscopic data.

The Fourier transform infrared spectrophotometar was also used to study the interaction between ammonium perchlorate, hydroxyl terminated poly(butadiene) (HTPB), carboxyl terminated poly(butadien) (CTPB), cyclotetramethylenetetranitramine (HMX) and the compounds synthesized in this work.

Results and discussion

A pratical appliciation of AP/HMX/Al/HTPB propellant systems has been one of the major problems in solid rocket technology in the relization of rocket motors having higher ballistic performance, especially for the upper stages. For this purpose, a great deal of effort has been spent to improve the poor adhesion between AP, HMX and HTPB. For the HTPB/AP combination, aziridine and alkylenepolyamine derivatives have been found to be effective and the usefulness of dimethylhydantoin derivatives for HMX/HTPB system was demonstrated recently [10, 11]. However, there is no report of a bonding agent which is effective for both AP/HTPB and HMX/HTPB, and bonding agents for AP/HTPB have no role for HMX/HTPB. Therefore, the use of combinations of bonding agent and new bonding agents for AP/HTPB and for HMX/HTPB is inevitable for the realization of AP/HMX/HTPB systems.

Table 1. Bonding agents used in the research

Bonding agent	Structural Formula	Abbreviation
1,3,5-Tri(2-hydroxyethyl) isocyanurate		BA_1
1,3,5-Tri(3-hydroxypropyl) isocyanurate		BA_2
1,3,5-Tri(2-hydroxypropyl) isocyanurate		BA_3
1,3,5-Tri(2,3-epoxypropil) isocyanurate		BA_4

Although several commercial bonding agents for AP/HTPB system have appeared, the adhesion mechanism has not been perfectly elucidated yet. It has already been shown that the adhesive force between AP and HTPB is determined by the wetting efficiency of the HTPB prepolymer on AP and the cohesive force of the binder-bulk. However, the interaction between AP and bonding agents is not clear [10, 12]. In the adhesion field, the FTIR spectroscopy has become a leading analytical method owing to its high sensitivity and a high signal to noise ratio [13, 14].

In this investigation the results of observations of the interaction between AP and four bonding agents by means of the FTIR spectroscopy are presented.

The bonding agents used in this research are summarized in Table 1. To simplify the text, these bonding agents are abbreviated as bonding agent BA_1, BA_2, BA_3 and BA_4.

The results of the study of the interactions between ammonium perchlorate and the different bonding agent, by means of the FTIR spectroscopic method, showed that the interfacial bonding force arises from the hydrogen bonding force in the case of BA_1 (Fig.1).

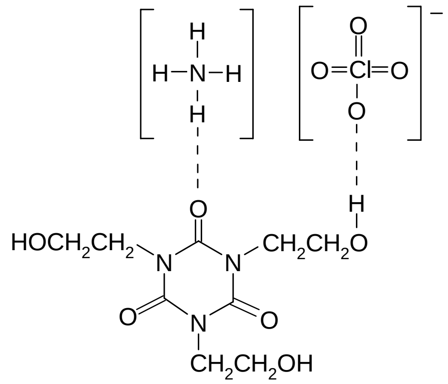
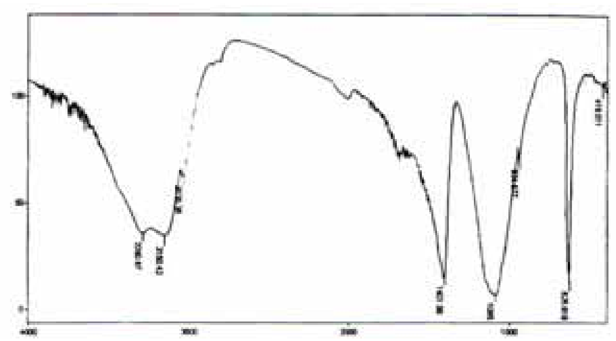
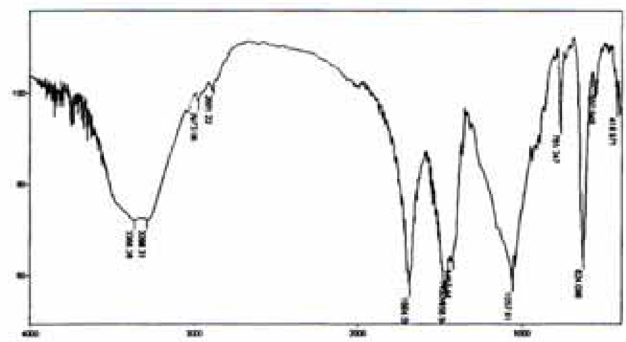


Figure 1. Hydrogen-bonded structure between AP and BA_1

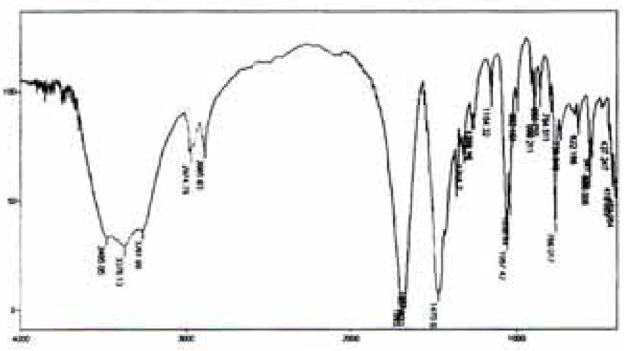
Fig.2. shows the spectra of AP, AP+BA_1 and BA_1. It is evident that spectral changes have occurred in the spectrum of AP+BA_1. The frequencies of OH stretching vibrations of BA_1 (3485.05 cm^{-1}, 33761.13 cm^{-1} and 3261.89 cm^{-1}) and N-H stretching vibration in AP (3290.67 cm^{-1} and 3150.42 cm^{-1}) changed. The band at 1401.98 cm^{-1} of AP disappeared and the frequency at 1076.28 cm^{-1} shifted to 1057.61 cm^{-1}. The frequency of the C=O stretching vibrations of BA_1 shifted downwards from 1693.19 cm^{-1} to 1684.59 cm^{-1} [15].



a)



b)



c)

Figure 2. Infrared spectra of AP (a), AP+BA_1 (b) and BA_1 (c)

These effects exist in the case of BA_2 and BA_4. The effect was very small when BA_3 was used as the bonding agent.

The results of observation of the interaction between HTPB, BA and AP, by means of the FTIR, suggested that spectrum changes have occurred in the spectrums of HTPB + BA_1 + AP and HTPB + BA_2 + AP. Very small spectrum changes have occurred in the spectrum of HTPB + BA_3 + AP and HTPB + BA_4 + AP.

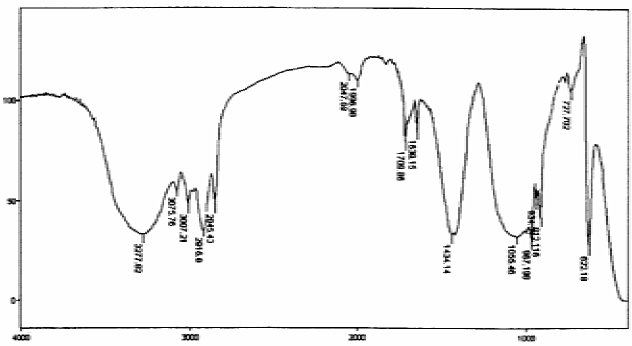


Figure 3. Infrared spectra of the mixture CTPB +BA_1+AP

The results of observation of the interaction between CTPB, BA and AP suggested that fundamental spectrum changes have occurred in all spectrums (Figures 3 and 4). It is shown that the solidification of the composite mixture and the change of the intensity of carbonyl bond are due to copolymerization of CTPB and bonding agents followed by the decarboxylation of the obtained composite propellants.

Fig.3 shows spectra of CTPB +BA_1+AP. It is evident that spectral changes have occurred in the region of OH, NH and C=O frequencies. The bands of AP at 1401.98 cm^{-1} and 1693.19 cm^{-1} of BA_1 disappeared. The results show strong interactions between CTPB and BA_1 in the presence of AP and fundamental change in the structure of BA_1 occurred (Fig.2(c)).

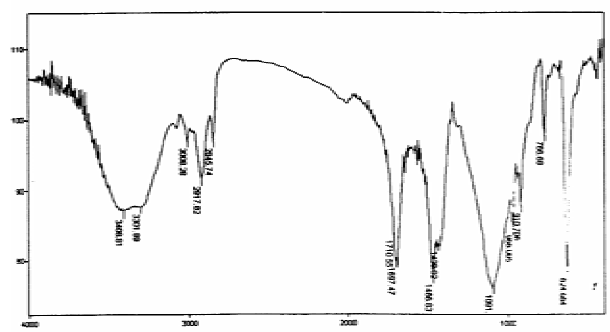


Figure 4. Infrared spectra of the mixture CTPB + BA_4 +AP

Fig.4. shows the spectra of CTPB + BA_4 +AP. The frequency of OH vibrations changes from 3507 cm^{-1} to 3408 cm^{-1}. The band at 1402 cm^{-1} in AP disappeared and the frequency at 1076 cm^{-1} shifted to 1091 cm^{-1}. It is evident that strong interactions between CTPB, BA_4 and AP have occurred.

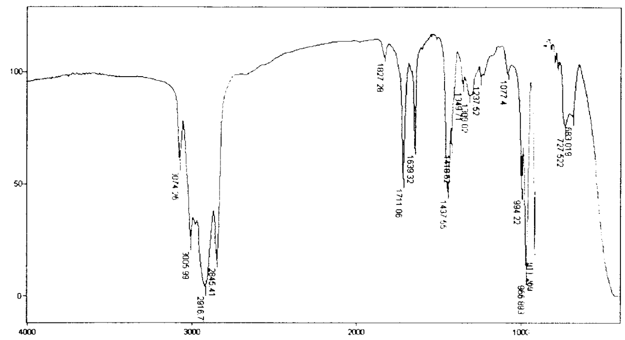


Figure 5. Infrared spectra of CTPB

Fig.6 shows the spectra of BA_1+AP+HTPB+MAPO. It is readily observable that fundamental spectral changes have occurred in the frequencies of Ap and BA_1. The frequency of C=O stretching vibrations of BA_1 shifted from 1743.01 cm^{-1} to 1723.38 cm^{-1}. The intensity of this frequency in the mixture was very small. The frequencies at 14401.96 cm^{-1} in MAPO and 1400.97 cm^{-1} in AP disappeared. It is evident that strong intermolecular interactions between AP, BA_1, and MAPO have occurred. [15]

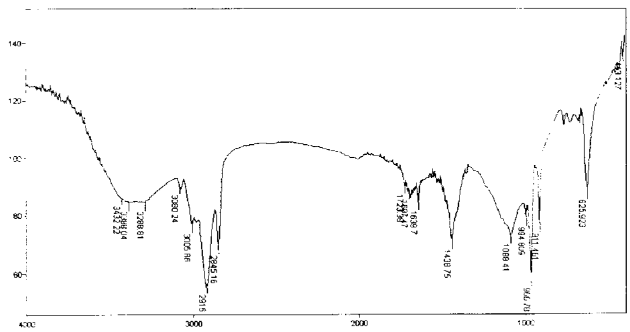


Figure 6. Infrared spectra of the mixture BA, AP, HTPB and MAPO

The results of the study of the interactions between bonding agents synthesized in this work and ammonium perclorate, different binders and HMX, showed the strongest hydrogen-bonding force in the case of 1,3,5-tri(2-hydroxyethyl) isocyanurate.

These resulte suggest that 1,3,5-tri(2-hydroxyethyl) isoczanurate is a universal bonding agent for AP/CTPB/HMX composite propellant system.

Experimental

Synthesis of 1,3,5-trisubstituted isocyanurates

The experimental investigation comprised a complete synthetic procedure by the definition of the starting materials, temperature, solvents, isolation techniques as well as purification and identification of the products.

1,3,5-Tri(2-hydroxyethyl)isocyanurate was prepared according to the literature [16] by the reaction of cyanuric acid and 2-chloroethanol in basic medium.

1,3,5-Tri(3-hydroxypropyl)isocyanurate was prepared according to the modified literature procedure for the 1,3,5-tri(2-hydroxyethyl)isocyanurate [16] by the reaction of cyanuric acid and 3-chloropropanol in basic medium.

1,3,5-Tri(2-hydroxylpropyl)isocyanurate was prepared according to the modified literature procedure [17] using the mol excess of propen oxide.

1,3,5-Tri(2,3-epoxypropyl)isocyanurate was prepared according to the literature [18] bu the reaction of cyanuric acid and epichlorohydrin.

All the synthesized 1,3,5-trisubstituted isocyanurates were identified by the melting point, FTIR, UV and ^{1}HNMR spectroscopic data.

The experimental metod for determining interaction between a bonding agent and different constituents of composite propellants

Sufficiently dried ammonium perchlorate was mixed with a bonding agent in the ratio of 1:1 (by weight), and maintained at 60°C for 48 hours. Each of these samples were mixed with preground potassium bromide powder of spectroscopic grade and ground for several minutes. The potassium bromide sample mixure was then placed in a press under a pressure of 10 MPa for 1 min to obtain a potassium bromide sample pellet after which the pellet was placed in the FTIR spectrophotometer and scanned 4 cm^{-1} resolution over the range 4000-400 cm^{-1} by the transmission technique.

The Fourier transform infrared spectrophotometer was used, also, to study the binder/bonding agent interface. Binders used in this work were: hydroxyl terminated poly(butadiene) (HTPB), and carboxyl terminated poly(butadiene) (CTPB).

Sufficiently dried bonding agents were mixed with a binder in the ratio 1:1 (by weight) and maintained at 60°C for 48 hr. After that the FRIT spectra were recorded from each of these samples in the form of KBr pellets.

The infrared spectra were recorded, also, on a Bomem FTIR spectrophotometer, in the form of KBr pellets, for two samples of HMX/ bonding agennts mixture.

Sufficiently dried bonding agents were mixed with binders and ammonium perchlorate in the ratio 1:2:7 (by weight) and maintained at 60°C for 48 hr. Also, two samples from bonding agents (hydroxyethyl and hydroxypropyl) mixed with binders, ammonium perchlorate and MAPO in the ratio 1:2:6:1 (by weight) and maintained at 60°C for 48 hr. After that the FTIR spectra were recorded from each of these samples in the form of KBr pellets.

Conclusion

The results of the study of the interactions between ammonium perhlorate and a different bonding agent, by means of the FTIR spectroscopic method, showed that the interfacial bonding force arises from the hydrogen bonding force in the case of 1,3,5-tri(2-hydroxyethyl)isocyanurate.

The results of observation of the interaction between carboxy terminated poly(butadiene) and different bonding agents with hydroxyalkyl substituents in the presence of ammonium perhlorate suggested that fundamental spectrum changes have occurred in all spectrums. It is shown that the solidification of composite mixture and the change of the intensity of carbonyl bond are due to copolimerization of CTPB and bonding agents followed by decarboxylation of obtained composite propellants.

The results of the study of the interactions between bonding agents synthesized in this work and ammonium perchlorate, different binders and HMX, showed the strongest hydrogen bonding force occurred in the case of 1,3,5-tri(2-hydroxyethyl)isocyanurate. These results suggest that 1,3,5-tri(2-hydroxyethyl)isocyanurate is a uiversal bonding agent for the AP/CTPB/HMX composite propellant system.

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Uticaj vezujućih agenasa na poboljšanje interakcija u kompozitnim gorivima utvrđen korišćenjem FTIR spektara

Vezujući agensi sintetizovani u ovom radu predstavljaju 1,3,5-trisupstituisane izocijanurate (supstituenti: 2-hidroksietil, 3-hidroksipropil, 2-hidroksipropil i 2,3-epoksipropil). Sve sintetske reakcije su izvedene koristeći modifikovane literaturne postupke.

Svi dobijeni izocijanurati su okarakterisani temperaturama topljenja, FTIR, ^{1}H NMR, i UV spektroskopskim podacima.

FTIR je takođe korišćen za proučavanje interakcija između amonijum-perhlorata (AP), poli(butadiena) sa hidroksi i karboksi krajnim grupama (HTPB i CTPB), tetrametilentetranitramina (HMX) i jedinjenja sintetizovanih u ovom radu. Rezultati su pokazali da se 1,3,5-tri(2-hidroksietil)izocijanurat može koristiti kao univerzalni vezujući agens za AP/CTPB/HMX sistem kompozitnih goriva.

Ključne reči: **kompozitno gorivo, raketno kompozitno gorivo, vezivo, izocijanourat.**

Изучение взаимных связей составляющих в HMX/AP системе композитных топлив

Соединительные средства (вещества) синтетизованы в настоящей работе являются 1,3,5-трёхзаместителями изоциануратами (заместители: 2-гидроксиэтил, 3-гидроксипропил, 2-гидроксипропил и 2,3-эпоксипропил). Все синтетические реакции выполнены при помощи видоизменяющих поступков из справочной литературы. Все полученые изоцианураты охарактеризованы температурой плавления, FTIR, 1H NMR и UV спектроскопическими данными.
FTIR тоже использован для изучения взаимодействий между аммоний-перхлоратом (AP), поли(бутадиеном) с гидрокси и карбокси крайними группами (HTPB и CTPB), четырёхметилентетранитрамина (HMX) и смесь (соединений) синтетизованных в настоящей работе. Результаты показали, что 1,3,5-трёх(2-гидроксиэтил) изоциануратом возможно пользоваться в роли универсального соединительного средства (вещества) для AP/ CTPB /HMX системы композитного ракетного топлива.

Kly~evwe slova: **композитное топливо, ракетное композитное топливо, соединительное средство (вещество), изоцианурат.**

L'influence des agents liants sur l'amélioration des interactions chez les propergols composites déterminée par l'emploi du spectre FTIR

Les agents liants, synthétisés dans le cadre de ce travail, représentent 1,3,5 Isocianurates trisubstitués (substituants : 2-hydroxyéthyl, 3-hydroxypropyl 2-hydroxypropyl et 2,3 époxypropyl. Toutes les réactions de synthèse ont été réalisées par des procédés modifiés de littérature. Tous les isocyanurates obtenus se caractérisent par les températures de fonte, FTIR, H NMR et UV données spectroscopiques.FTIR est utilisé aussi pour l'étude des interactions entre l'ammonium perchlorate (AP), poly(butadiène) avec les groupes finals hydroxyle et carboxyle (HTPB et CTPB) tétraméthylentetranitramine(HMX) et les composés synthétisés dans ce travail. Les résultats ont démontré que le 1,3,5-tri(2 hydroxyéthyl) isocianurate peut être employé comme agent de liage universel pour AP/CTPB/HMX système des propergols composites.

Mots clés: **propergol composite, propulsion composite de fusée, liant, isocianurate.**