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Investigation of the interfacial bonding in composite propellants. 1,3,5-Trisubstituted isocyanurates as universal bonding agents

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Abstract: A series of 1,3,5-trisubstituted isocyanurates (substituents: CH_2CH_2OH, $CH_2CH{=}CH_2$ and CH_2CH_2COOH) was synthesized according to a modified literature procedure. Experimental investigations included modification of the synthetic procedure in terms of the starting materials, solvents, temperature, isolation techniques, as well as purification and identification of the products. All the synthesized isocyanurates were identified by their melting point and FTIR, ^{1}H NMR and UV spectroscopic data. Fourier transform infrared spectrophotometry was also used to study the interaction between ammonium perchlorate, hydroxyl terminated poly(butadiene), carboxyl terminated poly(butadiene), poly(butadiene-co-acrylonitrile), poly(propylene ether), cyclotrimethylenetrinitramine and the compounds synthesized in this work, which can serve as bonding agents. The results show that tris(2-hydroxyethyl)isocyanurate is a universal bonding agent for the ammonium perchlorate/carboxyl terminated poly(butadiene)/cyclotrimethylenetrinitramine composite propellant system.

Keywords: isocyanurates, binder, bonding agent, interactions, composite material, hydrogen bonding, FTIR.

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 oxidizers 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 cyclotrimethylenetri-

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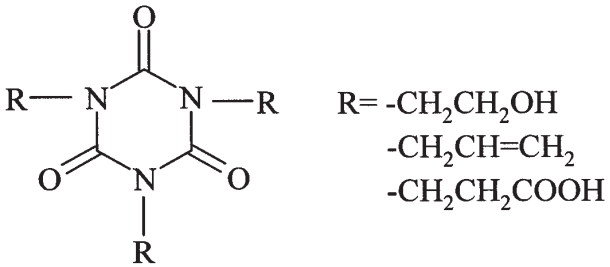
nitramine (RDX) or cyclotetramethylenetetramine (HMX). The metal fuels are powders of elemental metals, such as aluminum and magnesium. In contrast with these components, the binders are organic polymers, such as urethanes, polyamides or vinyl polymers. Often as much as 80 weight percent of the propellant is oxidizer along with about 10 weight percent of a metal fuel, thus, giving a solids 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 a 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 oxidizer 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 not 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.

In our studies of the effect of binding agents on the characteristics of composite propellant, 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.



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

Fourier transform infrared spectrophotometer was also used to study the interaction between ammonium perchlorate, hydroxyl terminated poly(butadiene) (HTPB), carboxyl terminated poly(butadiene) (CTPB), poly(butadiene–co–acrylonitrile) (PBAN), poly(propylene ether) (PPE), cyclotrimethylenetrinitramine and the compounds synthesized in this work.

RESULTS AND DISCUSSION

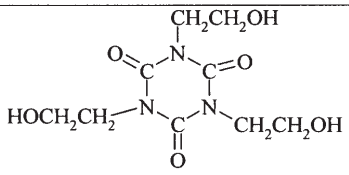
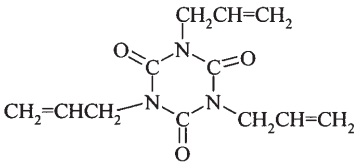
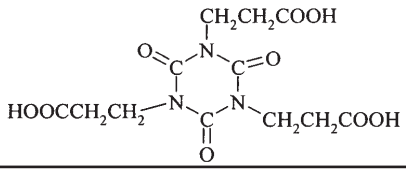
Practical appliciation of AP/RDX/Al/HTPB propellant systems has been one of the major problems in solid rocket technology in the realization of rocket motors having higher ballistic performance, especially for the upper stages. For this purpose, a great deal of effort has been spent to improve the poor adhesion between AP, RDX and HTPB. For the HTPB/AP combination, aziradine and alkylenepolyamine derivatives have been found to be effective and the usefulness of dimethylhydantoin derivatives for RDX/HTPB system was demonstrated recently.[8] However, there is no report of a bonding agent which is effective for both AP/HTPB and RDX/HTPB, and bonding agents for AP/HTPB have no role for RDX/HTPB. Therefore, the use of combinations of bonding agent and new bonding agents for AP/HTPB and for RDX/HTPB is inevitable for the realization of AP/RDX/HTPB systems.

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.[8,9] In adhesion field, FTIR spectroscopy has become a leading analytical method owing to its high sensitivity and high signal to noise ratio.[10,11]

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

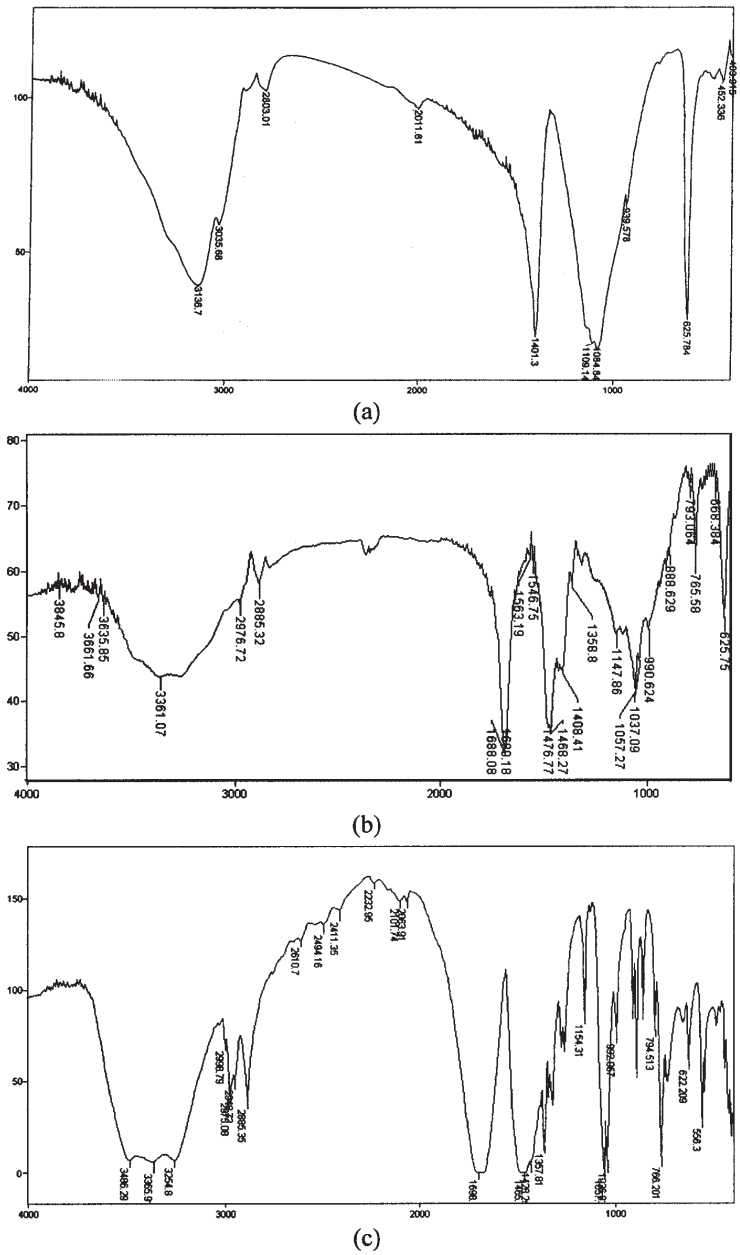
The bonding agents used in this research are summarized in Table I. To simplify the text, these bonding agents are abbreviated as bonding agent I, II and III.

TABLE I. Bonding agents used in the research

Bonding Agent	Structural Formula	Abbreviation
Tris(2-hydroxyethyl) isocyanurate		Bonding Agent I
Triallyl isocyanurate		Bonding Agent II
Tris(2-carboxyethyl) isocyanurate		Bonding Agent III

Interaction between ammonium perchlorate and bonding agents

The FTIR spectra of AP, AP + bonding agent I and bonding agent I are shown in Fig. 1. It is readily observable that fundamental spectral changes have occurred in the spectrum of AP + bonding agent I.



(a)

(b)

(c)

Fig. 1. Infrared specta of AP (a), AP + bonding agent I (b) and bonding agent I (c).

The frequency of the O–H stretching vibtrations of isocyanurate (3486 cm^{-1}, 3386 cm^{-1} and 3255 cm^{-1}) and the N–H stretching vibrations in ammonium perchlorate (3137 cm^{-1}) changed. The frequency of the C=O stretching vibrations of isocyanurate shifted downward from 1698 cm^{-1} to 1688 cm^{-1} which leads to the supposition of the formation of the hydrogen-bonded structure between AP and bonding agent I shown in Fig. 2.

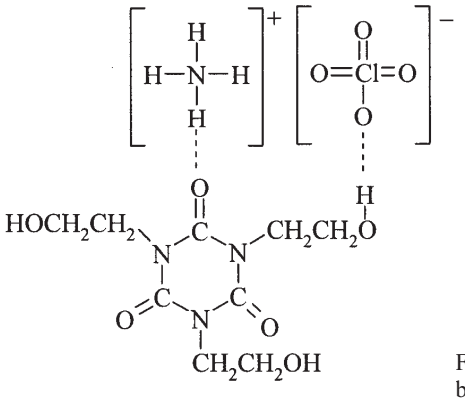


Fig. 2. Hydrogen-bonded structure between AP and bonding agent I.

New bonds are observed at 709 cm^{-1}, 699 cm^{-1}, 688 cm^{-1} and 678 cm^{-1}. These new bonds are assigned to hydrogen bonds with N–H group (Fig. 3).

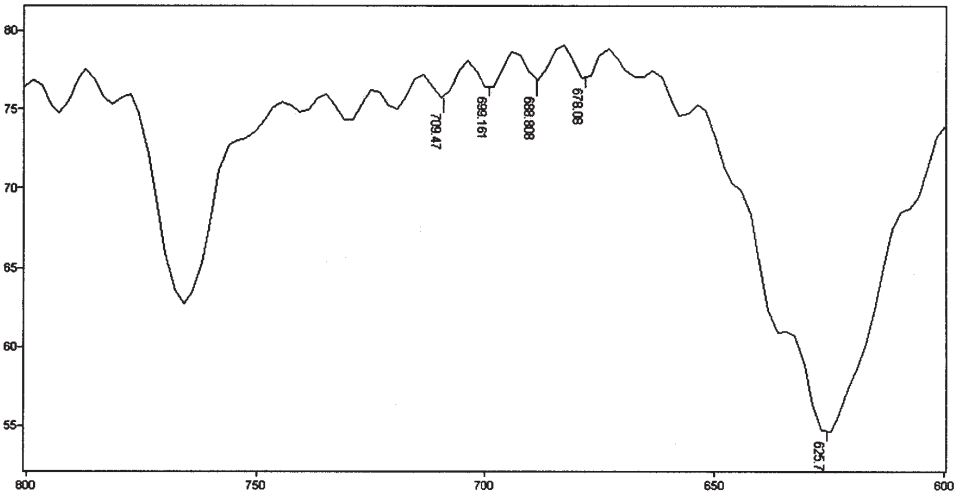


Fig. 3. Infrared spectrum of AP + bonding agent I.

The results of the observation of the interaction between AP and bonding agent II by means of FTIR spectroscopy suggested that fundamental spectrum changes occurred in the spectrum of AP + bonding agent II. The frequency of the N–H group in AP (3137 cm^{-1}) was changed. The frequency of the C=O group of

isocyanurate shifted from 1692 cm^{-1} to 1686 cm^{-1}. New bands appeared at 1560 cm^{-1}, 1542 cm^{-1} and 1508 cm^{-1} and the band at 1401 cm^{-1} of AP disappeared. The frequency at 1085 cm^{-1} of AP shifted to 1075 cm^{-1}.

The results of the study of the interaction between AP and bonding agent III show that no change was observed in the spectrum of AP + bonding agent III. These results indicate the strong intramolecular hydrogen bond in tris(2-carboxyethyl) isocyanurate, as shown in Fig. 4.

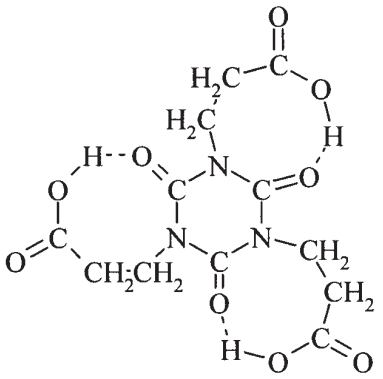


Fig. 4. Intramolecular hydrogen bond in tris(2-carboxyethyl) isocyanurate.

Interaction between different binders and bonding agents

Fourier transform infrared spectroscopy was used to study the binder/bonding agent interface. The binders used in this work were: hydroxyl terminated poly(butadiene) (HTPB), carboxyl terminated poly(butadiene) (CTPB), poly(butadiene–co–acrylonitrile) (PBAN) and poly(propylene ether) (PPE).

The results of observation of the interaction between the bonding agents and the corresponding binders by means of FTIR spectrocopy suggested that fundamental spectrum changes occurred in the spectra of CTPB + bonding agent I and CTPB + bonding agent II in the region of carbonyl group, as shown in Figs. 5 and 6, respectively. It is shown that the solidification of the composite mixtures and the change of the intensity of the carbonyl band are due to copolymerization of CTPB and bonding agents I and II, followed by decarboxylation of the obtained composite materials. Very small spectrum changes occurred in the spectra of HTPB + bonding agent II and PBAN + bonding agent II. No change was observed in the spectra of HTPB + bonding agent I (Fig. 7) and PPE and the bonding agents used in this investigation.

Interactions between cyclotrimethylenetrinitramine and the bonding agents

The results of the study of the interaction between RDX and the bonding agents synthesized in this work, by means of FTIR spectroscopy, suggested that changes in the spectrum occurred only in the spectrum of RDX + bonding agent I in the region of the carbonyl group band, as shown in Figs. 8 and 9.

The results of the study of the interaction of RDX with the bonding agents show that interactions occurred in the case of tris(2-hydroxyethyl) isocyanurate.

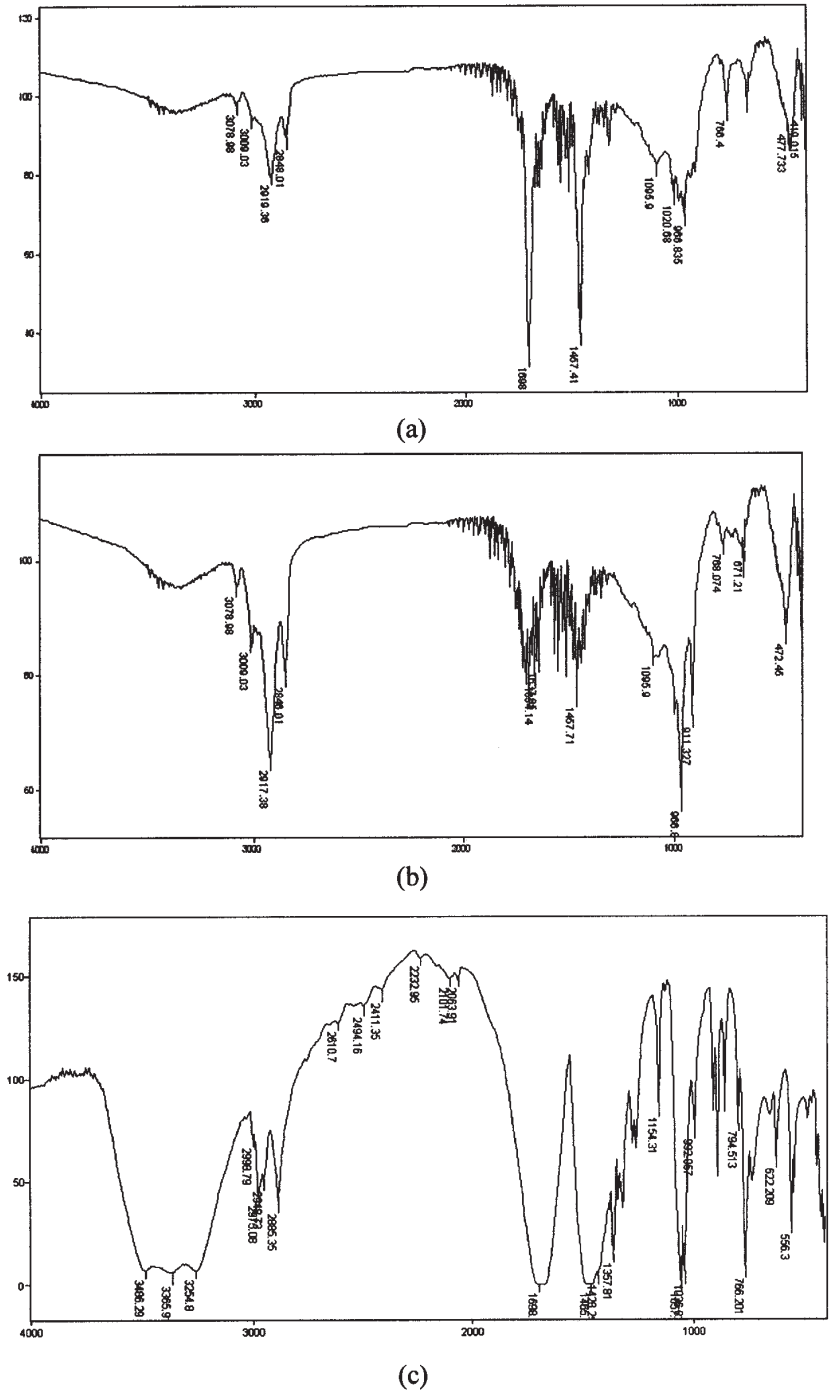


Fig. 5. Infrared spectra of CTPB (a) and CTPB + bonding agent I (b) and bonding agent I (c).

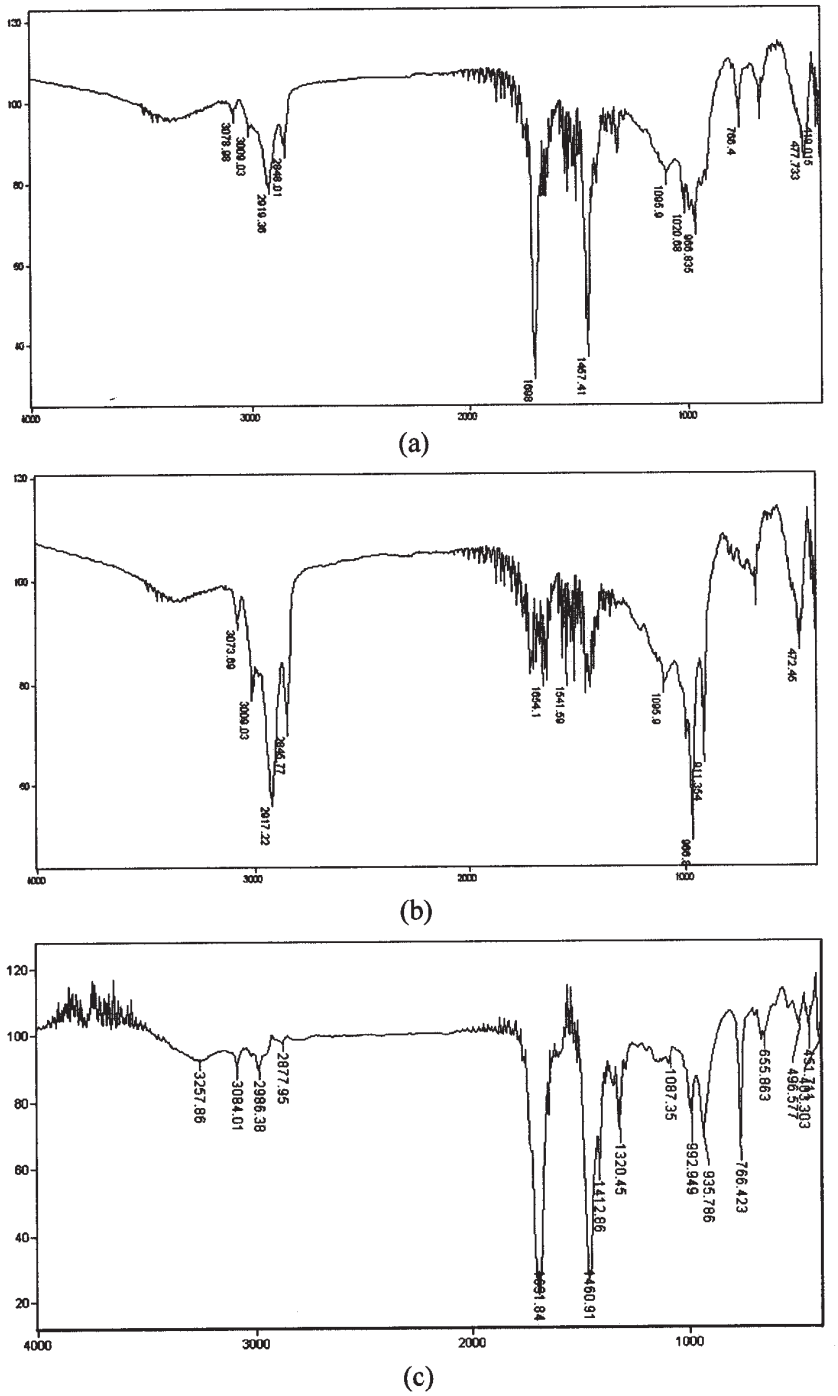


Fig. 6. Infrared spectra of CTPB (a), CTPB + bonding agent II (b) and bonding agent II (c).

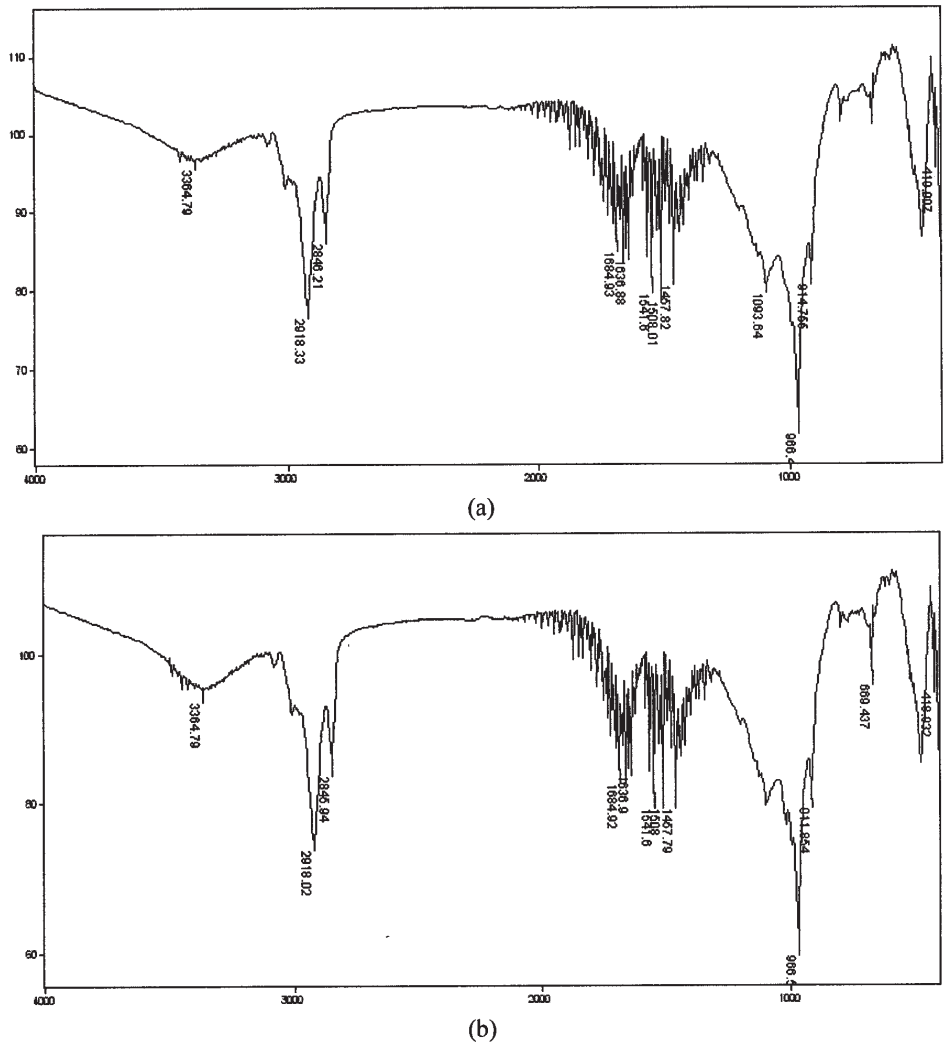


Fig. 7. Infrared spectra of HTPB (a) and HTPB + bonding agent I (b).

EXPERIMENTAL

Synthesis of 1,3,5-trisubstituted isocyanurates

Tris(2-hydroxyethyl) isocyanurate was prepared by the reaction of cyanuric acid and 2-chloroethanol in alkaline medium, according to a literature method.[12] The synthesis was found to be convenient and reproducible (Table II). An attempt to synthesize tris(2-hydroxyethyl) isocyanurate using an excess of sodium hydroxide (molar ratio of cyanuric acid and sodium hydroxide 1:3) was not successful.

Triallyl isocyanurate has previously been prepared in a variety of ways, which are generally characterized by the reaction of a metal salt of cyanuric acid with an alkylating agent, most commonly an alkyl sulfate or halide.[13] Other methods of preparation of trialkyl isocyanurates included the trimerization of a variety of cyanates and isocyanates.[14] All of these methods are accompanied by various disadvantages, such as requiring the use of expensive starting materials or of superatmospheric pressure, having a long reaction time, or poor yields of product.

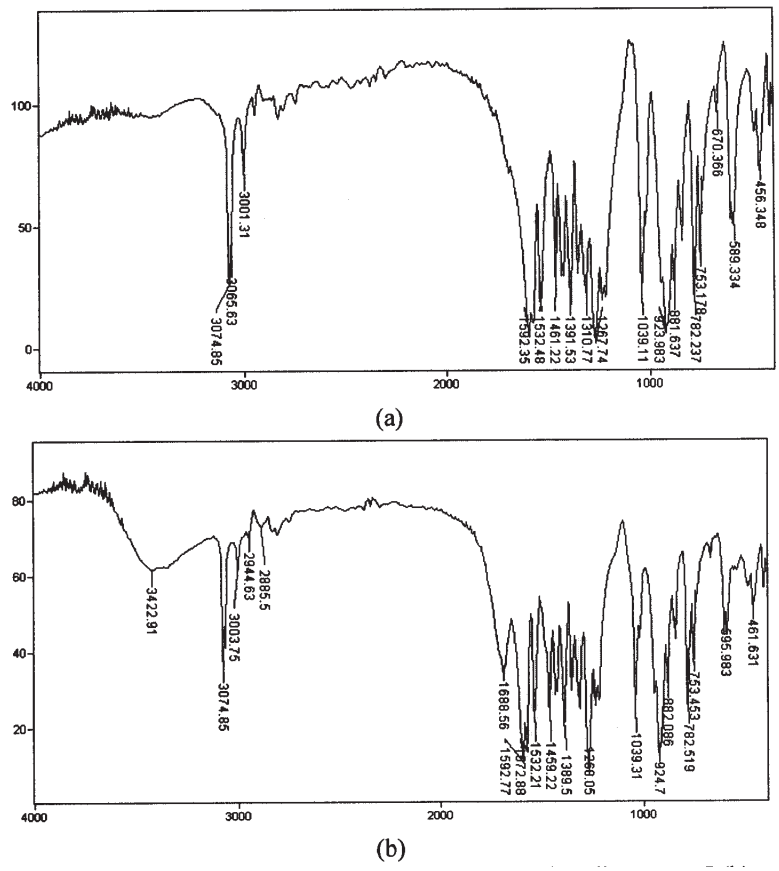


Fig. 8. Infrared spectra of RDX (a) and RDX + bonding agent I (b).

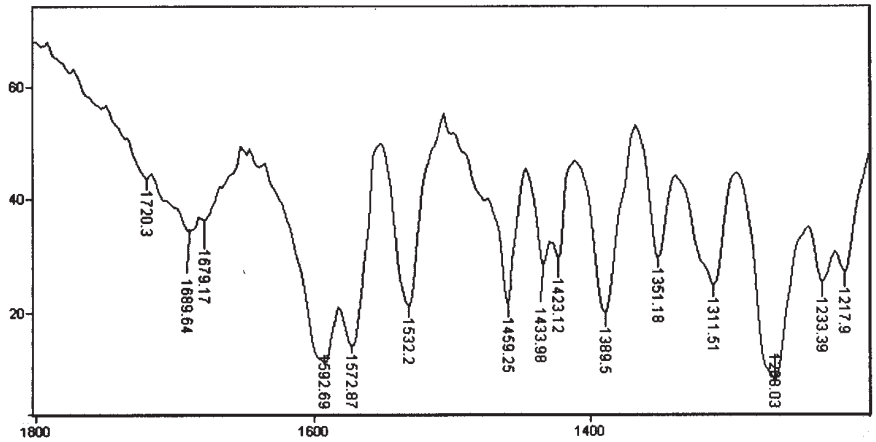


Fig. 9. Infrared spectrum of RDX + bonding agent I (region 1800–1200 cm^{-1}).

In this work triallyl isocyanurate was prepared by the reaction of potassium cyanate and allyl bromide in an aprotic solvent (dimethylformamide).[14] In this process it is assumed that allyl

isocyanurate is formed *via* allyl isocyanate, as shown in the following reaction (1), which then trimerizes in the reaction system to form triallyl isocyanurate (2).

$$CH_2{=}CHCH_2Br + KOCN \rightarrow CH_2{=}CHCH_2NCO + KBr \quad (1)$$

$$3CH_2{=}CHCH_2NCO \rightarrow (CH_2{=}CHCH_2NCO)_3 \quad (2)$$

The isolation of this product and the purification process were modified. They involved first distillation to remove the solvent from the solution after completion of the reaction and the addition of water or an aqueous solution of hydrogen chloride to the resulting reaction mixture containing triallyl isocyanurate. The aqueous layer was then removed and the layer containing triallyl isocyanurate was washed with trichloroethylene and distilled.

TABLE II. Physicochemical data of the synthesized 1,3,5-trisubstituted isocyanurates

Substituent	Melting or boiling point/ºC		Yield/%		Solvent for purification
	Observed	Literature	Observed	Literature	
CH_2CH_2OH	125–135	135[a]	85	83[a]	Methanol
$CH_2CH{=}CH_2$	114–114/0.8 mmHg	113–115/1.0 mmHg[b]	80	80[b]	
CH_2CH_2COOH	224–228	227–230[e]	34	30[c]	Water

[a]Ref 6; [b]Ref 8; [c]Ref 9.

Tris(2-carboxyethyl) isocyanurate was obtained by reacting cyanuric acid with a molar excess of acrylonitrile in the presence of a strongly alkaline catalyst, trimethylphenylammonium hydroxide, in a reaction medium containing a suitable solvent (dimethylformamide) for the reactants and the formed intermediate product tris(2-cyanoethyl) isocyanurate. The tris(2-cyanoethyl) isocyanurate product may then be reacted in the conventional manner to obtain tris(2-carboxyethyl) isocyanurate. The yield of tris(2-cyanoethyl) isocyanurate in this reaction was 38 % (literature data 33 %)[15] and the yield of tris(2-carboxyethyl) isocyanurate was 90 %.

Acrylonitrile in this reaction was added to a solution of cyanuric acid in a solvent containing a small amount of a strongly alkaline material which functions as a catalyst. It is preferable to add the acrylonitrile in small portions under stirring at room temperature to avoid polymerization of the acrylonitrile. The resulting mixture was then heated under reflux to complete the cyanoethylation. The tris(2-cyanoethyl) isocyanurate can be hydrolized to the corresponding tris(2-carboxyethyl) isocyanurate by heating to boiling with aqueous mineral acid. Upon cooling to room temperature a solid formed which was filtered off and dried. The obtained white solid had a melting point of 226 – 228 ºC.

All other material were obtained from Fluka or Arco Chemicals.

Physicochemical and spectroscopic data of the 1,3,5-trisubstituted isocyanurates

The melting points were measured using an electrothermal melting point apparatus and are not correctred. The physicochemical data for all the synthesized isocyanurates are presented in Table II.

The infrared spectra of all the synthesized 1,3,5-trisubstituted isocyanurates were recorded on a FTIR model BOMEM 100 MB spectrophotometer in the form of KBr pellets or neat (Table III).

TABLE III. FTIR spectroscopic data for the 1,3,5-trisubstitued isocyanurates

Substituent	ν_{max} cm^{-1}
CH_2CH_2OH	3486, 3367, 3253, 2975, 2885, 1693, 1469, 1359, 1036, 766
$CH_2CH{=}CH_2$	3085, 2924, 2853, 1692, 1459, 1319, 993, 933, 766
CH_2CH_2COOH	3486, 2942, 2834, 1749, 1702, 1482, 1464, 1220, 767

The ^{1}H NMR spectra of the 1,3,5-trisubstituted isocyanurates were determined as solutions in dimethyl sulfoxide (DMSO-d_6) using a 90 MHz Varian ^{1}H NMR spectrometer with tetramethylsilane as the internal standard (Table IV).

TABLE IV. ^{1}H NMR data for the synthesized 1,3,5-trisubstituted isocyanurates

Substituent	^{1}H NMR (DMSO-d_6), δ/ppm
CH_2CH_2OH	3.60 (2H, *t*, CH_2–N), 3.80 (2H, *t*, $\underline{CH_2}$–CH_2–N), 4.75 (1H, s, H–O),
$CH_2CH{=}CH_2$	4.50 (2H, *d*, CH_2–N), 5.40 (1H, *t*, HC=CH_2), 5.80 (2H, *m*, $\underline{CH_2}CH{=}CH_2$)
CH_2CH_2COOH	2.50 (2H, *t*, CH_2–N), 4.00 (2H, *t*, $\underline{CH_2}$–CH_2–N), 11.00 (1H, *s*, H–OOC)

The ultraviolet absorption spectra of the synthesized 1,3,5-trisubstituted isocyanurates, in the region 200–400 nm, were recorded on a Shimadzu UV-160 A spectrophotometer. The spectra were run in spectraquality solvent using a concentration of 5×10^{-4} M (Table V).

TABLE V. UV spectroscopic data for the synthesized 1,3,5-trisubstituted isocyanurates

Substituent	Methanol		Ethanol (96 %)		Acetonitrile	
	λ/nm	ε	λ/nm	ε	λ/nm	ε
CH_2CH_2OH	218.4	17930	218.0	18190	210.4	17360
$CH_2CH{=}CH_2$	216.6	17220	216.2	17840	209.8	17610
CH_2CH_2COOH	215.0	16820	214.2	15040	206.8	16420

The experimental method for the determination of the interactions between the bonding agents and the different constituents of composite propellants[16]

Sufficiently dried ammonium perchlorate (0.5 g) was mixed with a bonding agent (0.5 g) in the ratio of 1:1 (by weight), and maintained at 60 ºC for 48 h. Each of these samples were mixed with approximately 500 mg of preground potasium bromide powder of spectroscopic grade and ground for several minutes. The potassium bromide sample mixture was then placed in a press under a pressure of 20 MPa for 1 min to obtain a potassium bromide sample pellet which was subsequently placed in the FTIR spectrophotometer and scanned at 4 cm^{-1} resolution over the range 4000–400 cm^{-1} in the transmission mode.

The Fourier transform infrared spectrophotometer was also used to study the binder (HTPB, CTPB, PBAN, PPE)/bonding agent interface in the form of KBr pellets, using the same procedure as described for the AP/bonding agents mixtures.

The infrared spectra were recorded on a Bomem FTIR spectrophotometer, in the form of KBr pellets, for three samples of cyclotrimethylenetrinitramine (RDX)/bonding agents mixtures, using the same procedure as described above.

CONCLUSION

The results of the study of the interactions between ammonium perchlorate and the different bonding agents, by means of the FTIR spectroscopic method, showed that interfacial bonding force arises from hydrogen bonding in the case of tris(2-hydroxyethyl) isocyanurate and triallyl isocyanurate. This effect was not observed when tris(2-carboxyethyl) isocyanurate was used as the bonding agent.

The results of the study of the interactions between different binders and the bonding agents synthesized in this work also showed that the interfacial bonding

force arises from hydrogen bonding in the case of tris(2-hydroxyethyl) isocyanurate and triallyl isocyanurate. This effect was not observed when tris(2-carboxyethyl) isocyanurate was used as the bonding agent.

The results of the study of the interactions between RDX and bonding agents I, II and III show that these interactions exist only in the case of tris(2-hydroxyethyl) isocyanurate.

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

Acknowledgment: The authors are grateful to the Ministry of Science and Environmental Protection of Serbia for financial support (Project 142063).

ABBREVIATIONS

AP – ammonium perchlorate
CTPB – carboxyl terminated poly(butadiene)
HMX – cyclotetramethylenetetramine
HTPB – hydroxyl terminated poly(butadiene)
PBAN – poly(butadiene–co–acrylonitrile)
PPE – poly(propylene ether)
RDX – cyclotrimethylenetrinitramine

ИЗВОД

ПРОУЧАВАЊЕ МЕЂУСОБНИХ ВЕЗА КОМПОНЕНАТА У КОМПОЗИТНИМ ГОРИВИМА. 1,3,5-ТРИСУПСТИТУИСАНИ ИЗОЦИЈАНУРАТИ КАО УНИВЕРЗАЛНИ ВЕЗИВНИ АГЕНСИ

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1,3,5-Трисупституисани изоцијанурати (супституенти: CH_2CH_2OH, $CH_2CH{=}CH_2$ и CH_2CH_2COOH) су синтетизовани користећи модификоване литературне поступке. При томе су мењани реактанти, растварачи, температура, начин изоловања као и начин пречишћавања производа. Сви добијени изоцијанурати су окарактерисани температурама топљења, FTIR, ^{1}H NMR и UV подацима. FTIR је такође коришћен за проучавање интеракција између амонијумперхлората, поли(бутадиена) са хидрокси и карбокси крајњим групама, поли(бутадиен–ко–акрилонитрила), поли(пропиленетра), циклотриметиленнитрамина и једињења синтетизованих у овом раду који могу послужити као везивни агенси.

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REFERENCES

1. K. Hutchmacher, D. Most, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2003, p. 234
2. D. Vanloye, P. Grosius, US 5,256,748 (1993) (ATOCHEM)

3. J. P. Consaga, US 4,944,815 (1990) (US Navy)
4. A. Davenas, *Solid Rocket Propulsion Technology*, Pergamon Press, Oxford, 1993
5. P. K. Amtower, US 2004200553 (2004)
6. M. L. Chan, A. D. Turner, US 2003047260 (2003) US Navy)
7. G. P. Sutton, *Pocket propulsion elements*, Wiley, New York, 1996
8. H. Ishida, L. Koenig, *J. Polym. Sci. Phy. Ed.* **18** (1980) 1931
9. H. G. Linde, *J. Polym. Sci. Chem. Ed.* **20** (1982) 1031
10. S. R. Galler, H. Ishida, L. Koenig, *J. Colloid Interface Sci.* **1** (1986) 109
11. K. Hori, A. Iwama, T, Kukada, *Propellants, Explosives, Pyrotechnics* **10** (1985) 176
12. A. A. Suyigh, H. Ubrich, *J. Chem. Soc.* (1961) 3148
13. J. J. Tazuma, R. Miller, US 3,075,979 (1963) (FMC Corp.)
14. GB 961,624 (1964) (Spencer Chem. Co.)
15. A. Sadle, US 3,485,833 (1969)
16. K. Hori, *PhD Thesis*, The Institute of Space and Astronautical Science, Tokyo, 1987.