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PREPARATION AND INVESTIGATION OF AZIDO HYDROXY TERMINATED POLYBUTADIENE

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ABSTRACT

Composite solid rocket propellants based on hydroxy terminated polybutadiene (HTPB) have become the workhorse propellants in solid rocket motors world-wide. It was reported that polymers containing azide groups exhibit an interesting feature. On pyrolysis or combustion they liberate extra heat due to the scission of the azide bond which is highly exothermic. In this paper energetic polymeric binder based on azido hydroxy terminated polybutadiene (AHTPB) was proposed, prepared and characterized. The synthesis was started by brominating the commercial hydroxy terminated polybutadiene (HTPB), followed by its refluxing with sodium azide for about 30 hours. The investigated propellant formulations were based on mixtures of the prepared energetic binder (AHTPB) (13%) with different nitrogen content, ammonium perchlorate (71%) and Aluminum (16%).The performance of these propellant formulations was deduced through a computer program. Also, the effect of nitrogen content variation of the polymeric fuel binder on the specific impulse and the adiabatic flame temperature was investigated.

KEY WORDS

HTPB, AHTPB, bromination, azidation, energetic polymeric binder, specific impulse and adiabatic flame temperature.

INTRODUCTION

In the field of rocket propellant devolopment, many research programs have been directed to the selection and investigation of rocket propellant based on new polymeric materials in order to improve the performance of these propellants. The polymeric binder in a composite propellant usually represent 10-15 percent by weight[1] of the composition. This polymeric binder has great effects on the mechanical properties of the final material perhaps the most important of these properties is the elastomeric behaviour and dimensional stability [2] in addition to improving the mechanical properties. The research was also directed to make it highly energetic. In this respect, polymeric materials carrying energetic groups

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as: nitro ($-NO_2$), nitrato ($-ONO_2$), nitramino ($-N-NO_2$) and azide ($-N_3$) in their molecules [3,4] were prepared and some of them are still under research. On pyrolsis or combustion, these groups liberate extra heat due to the scission on certain chemical bonds which are highly exothermic. In the last few years [5], new types of binder systems have been developed containing azido--, azido methyl-groups as energetic materials [6]. Hydroxy terminated polybutadiene (HTPB) is an important polymeric fuel binder in modern solid rocket propellants, therefore it is necessary to improve the propellant performance. HTPB in contact with air (which is unavoidable) exhibits viscosity build-up and sometimes gelling. In order to prevent this problem antioxidants are often added to the resin.The residual double bonds located on the polymeric backbone are the active centers responsible for such gelling characteristics, so it was suggested to be replaced by the azide groups to reduce this viscosity build-up and to increase the liberated heat on combustion.

EXPERIMENTAL

Material

The chemicals used are of pure grades normally used in chemical laboratories. They were used without further purification, these chemicals are: Bromine (Br) (Aldrich), n-Hexane (C_6H_{14}) (Fisher), Ethanol-C_2H_5OH-(Prolabo), Formamide ($HCONH_2$) (Aldrich), p-xylene(El-Naser), Acetone (Colinbrook). sodium azide NaN_3 (BDH) and HTPB (LTM).

HTPB specification

Chemical formula : $HO-(CH_2-CH=CH-CH_2-)_n-OH$
Hydroxyl number:1.05 mg equivallent (OH) / g HTPB
Heat of formation of HTPB (Δu_f) =- 138 cal/g.
Density(g/c.c): 0.9032
Composition Of HTPB: Cis 19%,Trans 58%, Vinyl 23%

Testing of bromine and HTPB solubility in different solvents

In order to find the best solvent for both bromine and HTPB, several organic solvents were used. n-Hexane was the most suitable for both reactants as 20 g of bromine were dissolved in 500ml n-hexane and 10g of HTPB were dissolved in 125ml n-hexane. These represent the starting concentration of both reactants used in the synthesis.

Preparation of azido hydroxy terminated polybutadiene

Bromine solution (7g bromine in 175ml n-hexane) was added dropwisely in a controlled rate of about one drop/two seconds to HTPB solution (40g HTPB in 500 ml) in a 2-liter beaker at room temperature .The color of bromine solution disappears after each addition due to its reaction with the polymeric double bonds. The resultant colourless solution was transffered to a suitable conical flask and to which sodium azide (4.75g) was added. The mixture was then refluxed on a water bath for 30 hours at a temperature of 50-65 ^{0}c . The reaction mixture was cooled and the solvent was partially evaporated using a rotary evaporator. The precipitated sodium bromide was then filtered and the residual solvent in the filterate was completely evaporated to obtain the crude azido hydroxy terminated polybutadiene, which is directly used in the formulations.

Characterization of the prepared energetic polymeric binder

The prepared bromo-, and azido-polymeric binders were analyzed by infrared spectroscopy and elemental microanalysis of Br and N, IR analysis was determined by-a Perkin-Elmer model 3087 spectrophotometer .The results of these analysis were shown in fig1,fig2 and fig3. A computer program [6] was used to calculate the effect of the proposed formulations on both the specific impulse and the adiabatic flame temperature of the propellant based on this energetic binder(AHTPB).

RESULTS AND DISSCUSSIONS

Composite propellants which have been specially formulated on the basis of ammonium perchlorate, aluminium, and polybutadiene binders fulfil the demands of high specific impluse, high buring rate and high mechanical strength[7].Butadiene prepolymer of a number averaged molocular weight 2500-3800, provided a viscosity level required for its use as a fuel binder from which solid propellant can possibily made by means of direct casting method. In this way, an energetic binder can be regarded as any polymer or mixture which reacts exothermically and liberates high amount of energy and gaseous products. in this paper, it was suggested that the transformation of polymer binder (HTPB) to the energetic stage via its azidation .This azidation was proposed to proceed in two steps.The first one is the bromination of the HTPB by its addition to the double bond, and the second step is the conversion of the brominated polymer to the corresponding azido one through its refluxing with sodium azide in aprotic solvent for 30 hours at 50-65^{0}c, according to the following chemical equations

$$HO\text{-}(CH_2\text{-}CH{=}CH\text{-}CH_2\text{-})_n\text{-}OH \xrightarrow[\text{n-Hexane}]{Br_2} HO\text{-}(CH_2\text{-}\underset{Br}{CH}\text{--}\underset{Br}{CH}\text{-}CH_2\text{-})_n\text{-}OH$$

$$HO\text{-}(CH_2\text{-}\underset{Br}{CH}\text{--}\underset{Br}{CH}\text{-}CH_2\text{-})_n\text{-}OH \xrightarrow[\text{Reflux (50-65 }^0\text{c)}]{2n\ NaN_3} HO\text{-}(CH_2\text{-}\underset{N3}{CH}\text{--}\underset{N3}{CH}\text{-}CH_2\text{-})_n\text{-}OH + 2n\ Na\ Br$$

The bromine soulution was added dropwise on the polymeric solution until a separation of the the brominated polymer occurs . This may be attributed to the difference in solubility parameters of both HTPB and its brominated one in n-hexane at the experimental conditions, so the resultant reaction mixture can be looked as a mixture of two prepolymers. According to the micro-elemental analysis mentioned before, this mixture was proposed to contain about 20 % of the brominated one, this mixture was then refluxed as it is with sodium azide in n-hexane without its binder can be regarded as a mixture of about 20% azido form with the rest as unchanged HTPB. By this manner its energy characteristics are enhanced partially by this azidation process as it is indicated the calculation. The IR- spectrum of HTPB(in KBr disk) is shown in fig1. The presence of an absorption peak at 600 cm^{-1} in the IR-spectrum of brominated derivative shown in fig2, indicates the formation of C-Br bond [8].This peak disappeared in fig3 representing the IR- spectrum of the azido polymer and was replaced by an absorption peak located at 2100 cm^{-1} characterstic of the azido group [9].The same results were confirmed by the quantitative elemental analysis of both Br_2 and N_2 in the prepared polymeric binders. The nitrogen content was found to be 13.1%, which is considered as an important factor in calculations.

Performance of the rocket propellant based on AHTPB.

The summary gram atomic composition was calculated based on one kilogram of propellant.The nitrogen percentage of one kilogram of AHTPB was then estimated.The invstigated formulations were based on the energetic polymeric binder (AHTPB), ammonium perchlorate as oxidizer and aluminum as fuel.The performance was deduced using a computer program in which the adiabatic flame temperature and the specific impulse were calculated depending on the percentage composition of the prepared rocket propellant .The results are shown in table1, and represented graphically in fig4. these results show that the specific impulse is 252 sec for HTPB and increases gradually with the azidation according to the nitrogen content. It reaches its maximum at a value of 272 sec for 18% nitrogen content . After that it starts to decrease also gradually with the increase in the nitrogen content.This may attributed to the high exothermicity of azide groups decomposition. This phenomena can be understood according to equation:

$$I_S \ \alpha \ \sqrt{T_K / M}$$

I_S ....Specific impulse (second).
T_K... .Adiabatic flame temperature
M...Mean molecular mass of gaseous products

This equation relates the specific impulse(Is), adiabatic flame temperature(T_K) and the mean molecular weight of the formed gaseuos products(M). From fig3 it is clear that the adiabatic flame temperature (T_K) increases with the nitrogen content compared with the formulation of HTPB without azidation.

CONCLUSION

The azido hydroxy terminated polybutadiene was successfully prepared in laboratory by treating the prepared brominated HTPB with sodium azide .The conversion was equal to 21 percent., the highest obtained value of the specific impulse is

(Is =272 sec) compared with 250 sec for HTPB, for 18 % nitrogen content and decreases with further increase in nitogen percent. It is necessary to examine the viscosity of (AHTPB) with the increase in nitogen content , to evaluate the processing characterstics in future work. The prepared energetic polymeric binder AHTPB was characterized by different analytical methods as: elemental analysis, and IR-spectroscopy.The specific impulse and the adiabatic flame temperature of the propellant formulations containing AHTPB vary with the nitrogen content. The highest value of the specific impulse (272 sec) was obtained at the value of nitrogen content equals18 %. . The adiabatic flame temperature of the prpellant formulations increases with the increase of nitrogen content. The prepared azido polymer appears to be very suitable as a component for high energy polymeric binders in explosive and proppellant systems.

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Table(1). Effect of Variation of Nitrogen Content of the prepared AHTPB On the Specific Impulse and Adiabatic Flame Temperature of Propellant Formulations Based on (AHTPB=13% / Alpowder =16% /AP =71%).

No.	Conversion percent Of AHTPB to AHTP	gram atomic composition Of 1Kg AHTPB			N2 weight%	ΔHf kcal/kg (cal.)	adiabatic flame temperature (K)	Specific Impulse Sec
		C	H	N				
1	zero	74	111.1	0	0	-138	3504	254
2	10	69.6	104.4	4.36	6.1	-94.2	3541.9	261
3	20	65.7	97.06	8.7	12.18	-51	3592	270
4	30	60.5	40.82	13.04	18.26	-8.4	3625	272
5	40	56.0	84.06	17.39	24.35	34.8	3654	271.3
6	50	51.5	77.29	21.7	30.38	78	2681	270.3
7	60	47.0	70.53	26.1	36.54	121.1	3711	270
8	70	42.51	63.77	30.44	42.64	164.4	3746	269
9	80	38	57	34.78	48.64	207.6	37771	268
10	90	33.39	50.24	39.13	54.76	250	3778	267
11	100	28.98	43.48	43.48	60.87	294	3820	265

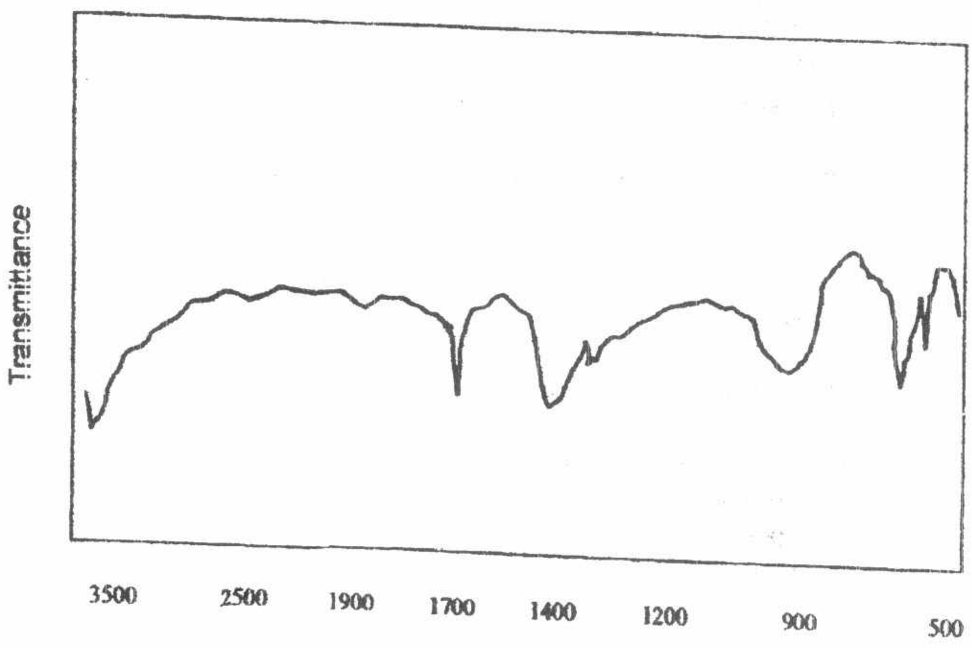

Fig1.Infrared Spectrum of HTPB

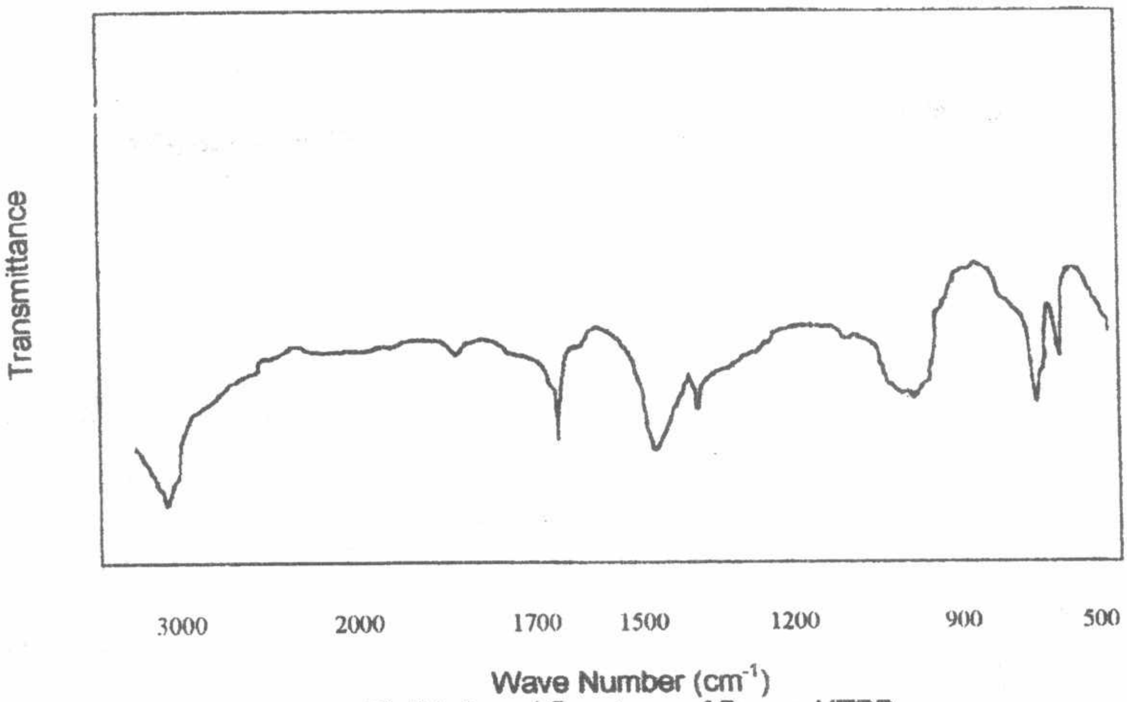

Fig2.Infrared Spectrum of Bromo HTPB

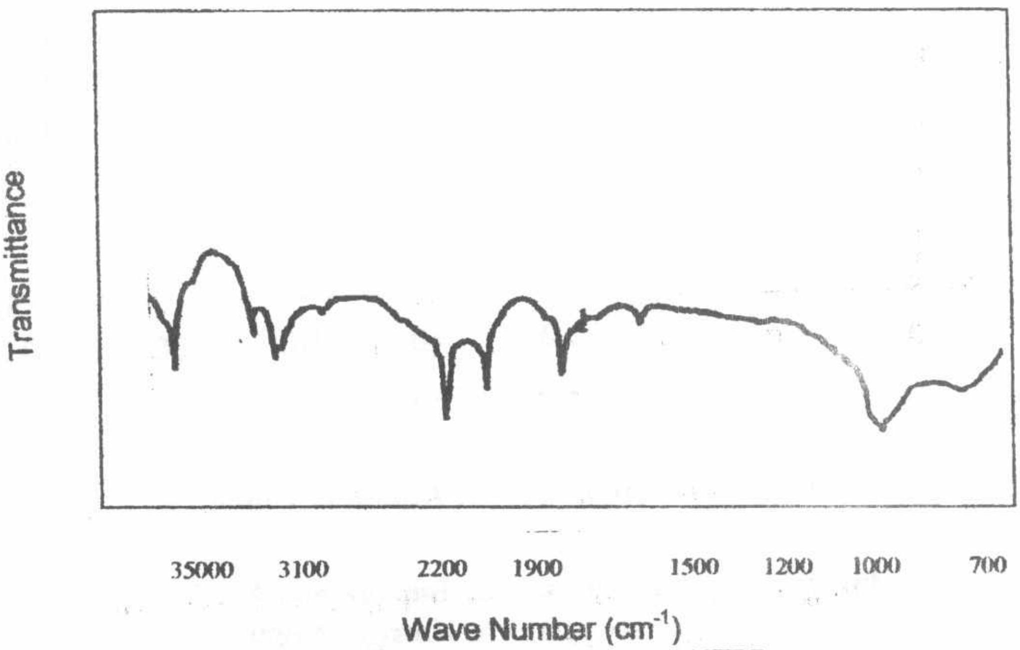

Fig3.Infrared Spectrum of AHTPB

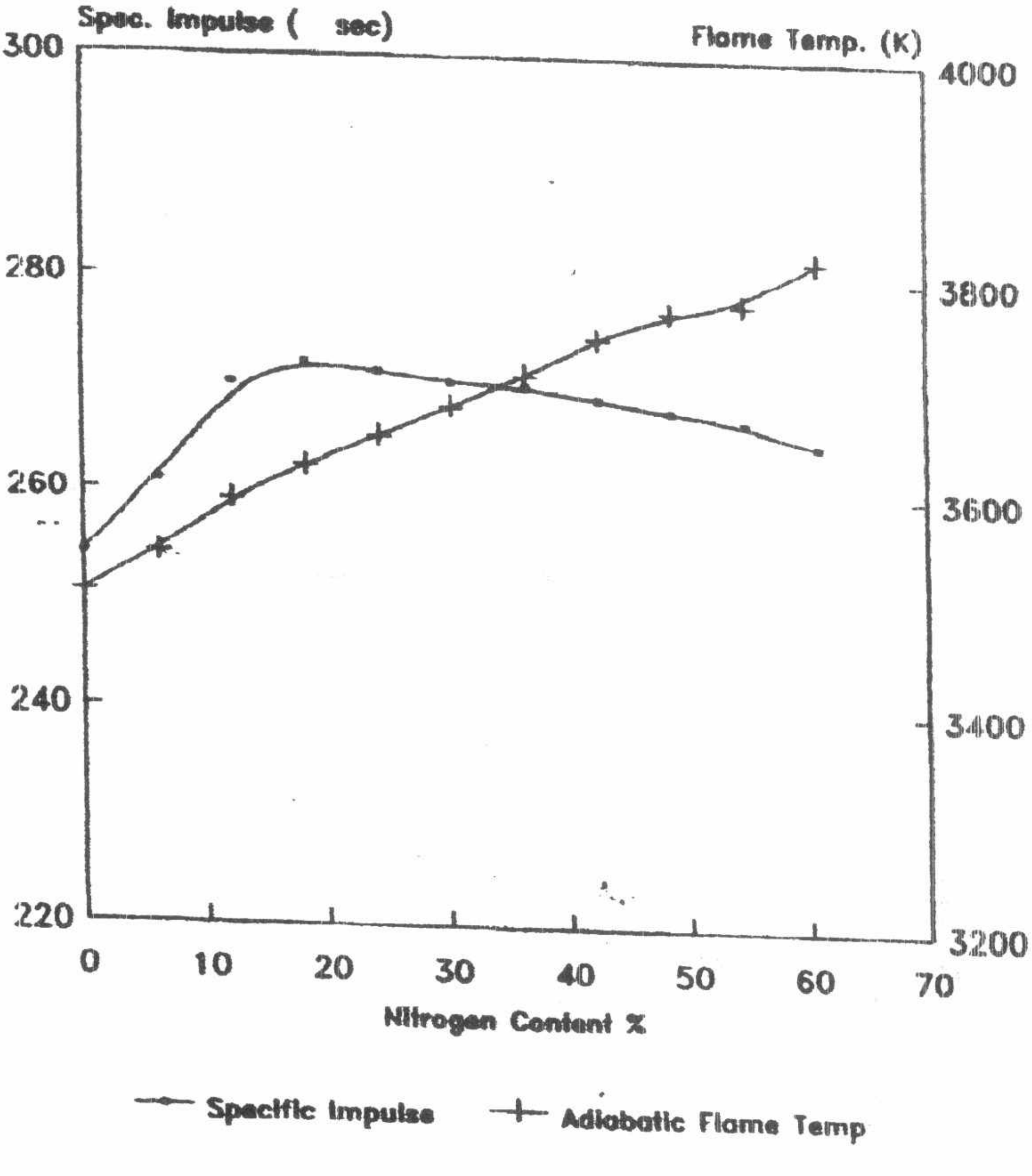

Fig.4 Dependence of Specific Impulse and Adiabatic Flame Temperature On Nitrogen Content