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PREPARATION AND CHARACTERIZATION OF NOVEL BINDER FOR COMPOSITE SOLID ROCKET PROPELLANT

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Abstract

Azido hydroxy terminated polybutadiene (AHTPB) is a candidate energetic binder for composite propellants having the same properties of hydroxy terminated polybutadiene (HTPB) but has an advantage over HTPB concerning its energetic property due to presence of azide group. Thermochemical calculations were done with different AHTPB percentages and the reference HTPB to examine the effect of binder change on the specific impulse and the flame temperature which are from the important parameters for the propellant performance and gun barrel age. AHTPB prepolymer was prepared by two steps method in which hydroxy terminated polybutadiene (HTPB) is firstly saturated with bromine (Br_2) at room temperature giving bromo hydroxy terminated polybutadiene (BHTPB). Secondly, the formed BHTPB undergo substitution reaction using sodium azide (NaN_3) at 70°C for 30 hours on batches giving AHTPB with density of 0.967 g/cm^3 and viscosity of about 5000 cP. The prepolymer was successfully prepared with conversion of (15%) and characterized by using some techniques such as infrared spectroscopy, elemental analysis, water content measurements and milligram equivalent (OH).

Key Words

Azido hydroxy terminated polybutadiene, Binder Systems, thermochemical calculations, preparation of AHTPB, Characterization of Prepolymer, Composite solid rocket propellants.

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Introduction

Design of future weapon systems requires using modern types of explosives and propellant formulations having enhanced performance and reduced vulnerability during storage and transportation. Several important design considerations for such formulations include improved mechanical properties, decreased plum signature, extended service life and reduced environment impact during manufacture, utilization and disposal [1].

Composite propellants are made of a polymeric matrix, loaded with a solid powder oxidizer, and possibly a metal powder that plays the role of a secondary fuel component. The first composite propellants used thermoplastic binders such as asphalt, polyvinyl chloride, and polyisobutylene which require softening or melting a temperature increase. Around 1950, the first liquid binders allowing crosslinking appeared. From 1950 until 1965, composite propellants were made with polysulfide (thiokols) and polyurethane polymers. From 1965 on, new binders emerged, with a functional polybutadiene basis: acrylonitrile-acrylic acid-butadiene, acrylic acid butadiene copolymer, and homopolymers with functional ends called telechelics. These polymers led to increasingly better performing elastomeric binders, since they offered higher solids loadings and a wider operating temperature range, especially at low temperatures and good processing but, they are inert binders having low ballistic performance. So, the use of new energetic binders has emerged. Azido hydroxy terminated polybutadiene (AHTPB) is useful as an energetic prepolymer in plastic bonded explosives and in rocket propellants to enhance the propellant performance, stability and keeping high solids loading, wider operating temperature range especially at low temperatures and good processing [2].

AHTPB prepolymer was prepared by two steps method in which hydroxy terminated polybutadiene (HTPB) dissolved in normal hexane is firstly saturated with bromine (Br_2) also dissolved in normal hexane at room temperature giving bromo hydroxy terminated polybutadiene (BHTPB). Secondly, the formed BHTPB undergo substitution reaction using sodium azide (NaN_3) at which the ($-\text{N}_3$) group substitute ($-\text{Br}$) group at 70 °C for 30 hours on batches. The introduction of the azide group to the HTPB increase its energy and so increases the performance of the propellant formed by the new AHTPB keeping the physical and chemical properties of HTPB which is suitable to be used in composite propellant. A full series of characterizations was being done to examine the product through physical, chemical and instrumental analysis. Thermochemical calculations were performed on some formulations to measure the effect of azide group introduction on the propellant characteristics [3, 4].

Thermochemical Calculations

Thermochemical calculations have been used with considerable success as a fast and effective tool to investigate the characteristics of different types of propellant formulations. Thermochemical calculation is an essential step for choosing propellant formulations that are candidate for a given practical application and to minimize many costly experiments which are used to evaluate the performance and properties of new propellant formulations [5, 6].

The effect of the content of prepared AHTPB and the reference binder HTPB on the specific impulse and adiabatic flame temperature of the composite solid rocket propellant formulations containing the prepared prepolymer was examined by using a special computer program. Some formulations were selected with changing the binder content from 10% weight percent to 20% to determine the effect of variation of binder content on the propellant characteristics. In these formulations, the dioctyl azalate DOZ was selected as the plasticizer for the prepolymers HTPB and AHTPB. Its content was taken as 25% based on the used weight of prepolymer. Hexamethelene Diisocyanates HMDI was selected as the curing agent

in mg. equivalent NCO/g of HMDI = 11.9 and the ratio of NCO/OH was selected to be = 0.9. The calculated summary formula (S.F) and the enthalpy of formation (ΔH_f) of one kg of polyurethane binder based on HTPB and AHTPB were listed in table (1).

The content of different ingredients in composite solid rocket propellant formulations containing polyurethane binder based on HTPB prepolymer and AHTPB, and the calculated values of specific impulse I_s and adiabatic flame temperature T_f of these formulations are listed in table (2,3). The dependence of the calculated values of I_{sp} for all formulations F1 – F22 on the binder content is illustrated in figure (1) while the effect of the binder content on the calculated values of T_f for the same formulations are shown in figure (2). It was found that the I_{sp} and T_f decreases by the increase of the binder content. By discussing I_{sp} and T_f at the optimum binder percentage which was (14%), it is found that the I_{sp} was increased from 240s for HTPB to 253s for AHTPB and so the flame temperature was increased from 3405K to 3490K which the gun barrel can withstand. Results of thermochemical calculations were very important for propellant compositions that are candidate for preparation and expected to give the required performance of the needed application.

Table (1) Summary formula and (ΔH_f) of one kg PU binder based on HTPB or AHTPB and that of basic ingredients

Binder Ingredients	ΔH_f kcal/kg	Summary formula / kg			
		C	H	O	N
HTPB	65.00	74.07	111.11	-	-
AHTPB	62.500	73.26	109.89	-	10.99
DOZ	-880.30	60.58	116.32	9.693	-
HMDI	-351.60	46.92	70.381	11.73	11.73
PU Based on HTPB	-135.43	70.20	110.54	2.425	0.582
PU Based on AHTPB	-136.00	69.60	109.25	2.382	8.925

Table (2) Specific impulse and flame temperature of HTPB-CSRPF formulations

Formulation (%)	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇	F ₈	F ₉	F ₁₀	F ₁₁
HTPB	10.00	11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
APC	73.06	72.25	71.44	70.62	69.80	69.00	68.19	67.38	66.56	65.75	64.90
Al powder	16.94	16.75	16.56	16.38	16.20	16.00	15.81	15.62	15.44	15.25	15.10
I_s (s)	269.3	267.3	265.6	254.6	240.4	234.3	228.1	221.8	216.6	213.3	212.0
T_f (K)	3677	3631	3571	3494	3404	3344	3275	3178	3070	2971	2900

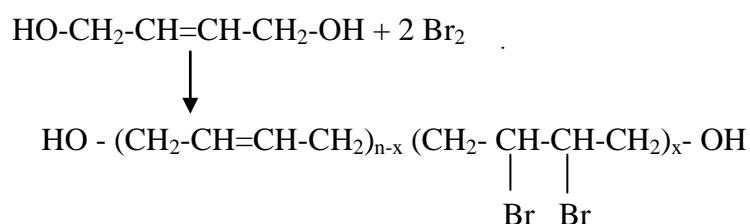
Table (3) Specific impulse and flame temperature of AHTPB-CSRPF formulations

Formulation (%)	F ₁₂	F ₁₃	F ₁₄	F ₁₅	F ₁₆	F ₁₇	F ₁₈	F ₁₉	F ₂₀	F ₂₁	F ₂₂
AHTPB	10.00	11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
APC	73.06	72.25	71.44	70.62	69.80	69.00	68.19	67.38	66.56	65.75	64.90
Al powder	16.94	16.75	16.56	16.38	16.20	16.00	15.81	15.62	15.44	15.25	15.10
I_s (s)	268.1	268.5	269.3	263.3	253.0	239.7	233.8	228.2	222.6	217.5	212.7
T_f (K)	37067	3664	3621	3562	3490	3405	3349	3289	3200	3102	2995

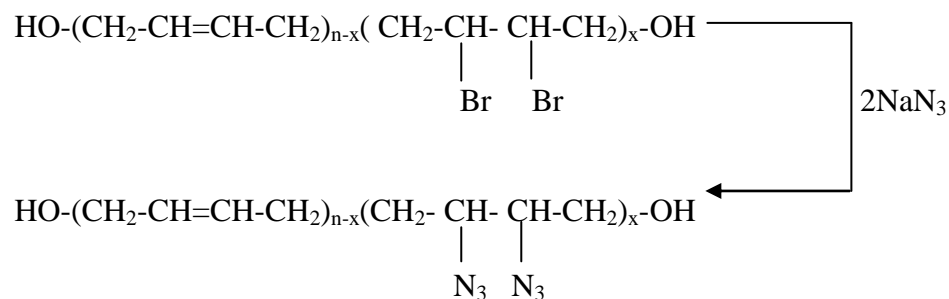
Experimental

Preparation of AHTPB

The apparatus used for preparation of AHTPB was designed to get the best control of the reaction and the highest possible conversion. It consists of water bath, 2 liter conical flask, magnetic stirrer, thermostat head, and reflux and nitrogen blanket. AHTPB was prepared on two steps reaction. Addition (bromination) step then substitution (azidation) step and they proceed as follows:



The first step was bromination at which HTPB dissolved in n-hexane at normal temperature under agitation until it was completely dissolved forming homogenous solution. Br₂ together with n-hexane were placed in a suitable conical flask, which was closed to minimize the hazards of bromine. The Br₂ solution was transferred to a dropping funnel, then start dropping the solution drop by drop at normal temperature while stirring to prevent the agglomeration of the dissolved polymer. It was found that the red color of the bromine vanishes as it reacted forming BHTPB.



The second step was the substitution step at which the azide group (-N₃) substitute the (-Br) in the HTPB molecule. The BHTPB solution together with NaN₃ was transferred to the reactor. The mixture was heated at 70°C under reflux for 30 hours on batches until the reaction was completed. While the mixture cooled down till a white precipitate of sodium bromide appears, it was filtered using an ordinary filter paper. No washing took place because all the salts were removed as AHTPB was dissolved in n-hexane, then drying took place in a rotary evaporator to get rid of water and solvent by adjusting it at 60°C and pressure 20 mbar for 2-3 hours. Then, employ severe conditions by increase of temperature to 60°C for 15 minutes and the polymer is transferred to vacuum furnace at 40°C for 24 hours. A honey like shape amber color AHTPB was produced [7, 8].

Characterization of the Prepared AHTPB

The product was characterized through physical and chemical analysis by determining the (OH) group as it is very important in the propellant curing, density which affect the volumetric loading of the propellant and so the performance, viscosity which play the main role in propellant processing, and also through instrumental analysis using FTIR principle to determine whether the azide group was introduced in the structure of HTPB, elemental analysis to determine the percentage of nitrogen content which express the energy of the propellant as nitrogen content increase the propellant become more energetic and water content is very important in the curing of propellant.

Physical and chemical characterization

Determination of (OH) mg Equivalent

The determination of the mg equivalent is very important because curing of solid rocket propellant formulations is fully dependant on it together with NCO groups (curing ratio) as the two groups forms the urethane group which is the matrix that held all the ingredients of the propellant together [8].

Value of (OH) mg equivalent of was determined according to following equation:

$$\text{mg. eqv. OH / g binder} = [(V_2 - V_1) * N] / W$$

Where:

V₁.....Volume in cm³ of NaOH solution required for titration of blank.

V₂.....Volume in cm³ of NaOH solution required for titration of sample.

N..... Normality of NaOH solution.

W.....Weight of sample in g.

Determination of Density

Density of the prepared AHTPB samples was determined by selecting an ordinary densimeter in the predicted range, inserting it in the measuring cylinder filled with sample and leaving it to reset and then take the value of density.

Determination of Viscosity

Brookfield viscometer was used for viscosity measurements of the prepared AHTPB samples. The process of selecting the spindle and the speed for an unknown fluid is normally trial and error. An appropriate selection will result in (10 – 100 cP) on the instrument scale. Two general rules will help in the trial and error process [9, 10]:

Viscosity range is inversely proportional to the size of the spindle.

Viscosity range is inversely proportional to the rotational speed.

Instrumental characterization

Infrared Spectroscopy

Shimadzu 8000 Fourier transformation infrared (FTIR) was used to detect the presence of the azide group (-N₃) in the prepared AHTPB sample, which is an indication of the azidation reaction and the appearance of AHTPB. In case of viscous liquids as AHTPB samples, a thin layer of the polymer was placed on the surface of the KBr tablet. The used wave number range was 500-4000 cm⁻¹, which is the appropriate range for most organic compounds. It is

well known that IR spectra of the organic compounds can be divided into three main regions; functional group region 4000 – 1300 cm⁻¹, finger print region 1300 – 910 cm⁻¹ and aromatic region from 910–500 cm⁻¹[11].

Elemental Analysis

PERKIN-ELMER 240 CHN elemental analyzer with AD-4 auto balance was used to detect the percentage of C, H and N in the prepared samples which facilitates the detection of nitrogen content taken as a reference to the explosophorous azide group, responsible for the excess energy of the energetic prepolymer. Obtained results make it possible to compare the theoretical and determined experimental percentage of C, H and N in the prepared samples [12].

Determination of Water Content

Water content is an important property especially if we need to use AHTPB as an ingredient in composite propellant formulations. Karl-Fisher technique was used for determination of the water content of the prepared samples. 200 cm³ of titrating solvent was added into the 500 cm³ beakers with reagent until the end-point using the diluted and standardized reagent. Then, about 2.5g of the sample were added. Repeat the titration again with diluted standardized Karel- Fisher reagent, to the end point. The water content (% by weight) was calculated as follows [13]:

$$\text{Water content \% by weight} = \frac{K.F_{\text{reagent}} * \text{titer} * 100}{\text{weight}_{\text{sample}}}$$

K.F_{reagent}..... Karel – Fisher (cm³)

Titer..... Ratio of the employed water (g) / volume of K.F_{reagent}.

W..... weight (g)

Results and Discussions

Preparation of AHTPB

AHTPB was successfully prepared by two-steps method mentioned before. Three trials were done to examine the conversion, it was noticed that the conversion was increased by increasing the amount of sodium azid, but over a certain limit agglomerations and precipitations took place and the colour was changed and no product was formed. The best conversion was found to be (15%).

Physical and Chemical Characterization

Hydroxyl number (OH)

The (OH) mg. equivalent of HTPB was (0.8541) while the (OH) mg. equivalent OH/g AHTPB was found to be (0.8516) indicating that the chemical reactions carried on HTPB to produce AHTPB did not affect the content of terminal hydroxyl group [14].

Density

Density of AHTPB was found to be about 0.967 g/cm³ and it was a promising value as it was higher than that of HTPB which was 0.903 g/cm³, giving higher volumetric loading in the rocket propellant manufacture field.

Determination of Viscosity

The viscosity of the sample was determined using Brookfield viscometer. Viscosity of AHTPB was found to be about (5039 cP) which was slightly lower than that of HTPB (5306 cP) but it was a promising value for rocket propellant processing.

Instrumental characterization

Infrared Spectroscopy

The azide as a functional group and more significantly as stretching vibration was inserted into the AHTPB structure as appears on figure (3) due to the existence of the absorption band at 2100.3 cm^{-1} which characterize the azide group. The halide peaks still appear at 499 cm^{-1} and 518 cm^{-1} as the halide group appear at the region from $600\text{--}500\text{ cm}^{-1}$ the presence of halide traces indicate that the substitution of azide group was not 100 percent and this was confirmed by the difference between the theoretical and practical percentage of nitrogen. Other absorption bands that were detected can be classified according to table (4).

Elemental Analysis

Elemental analysis showed a good agreement between theoretical percentage (12.5%) and the result of experimental elemental analysis (12%) as a slight change of about 4.5%.

Table (4) IR Characteristic Absorption bands

Group	Wave number (cm^{-1})
-OH	3400
C-O-H	1435
-CH ₂ -CH	2925
C-H	2875
C-Cl	740
C-O-C	1125
CH ₂ -N ₃	1281 (bending vibration)
CH ₂ -O-CH ₂	1665
CH ₂ -N ₃	2100 (stretching vibration)

Water Content

The optimum water content to be promising in composite solid rocket propellant formulations is about 0.05%. For the prepared AHTPB samples the water content was found to be 0.08%, this value was very close to applied in the field of composite solid rocket propellant[15].

Conclusions

Results of thermochemical calculations were essential for choosing propellant formulations that are candidate for a given practical application to minimize many costly experiments which are used to evaluate the performance and properties of new propellant formulations.

AHTPB was successfully prepared by two steps method with about 15% conversion. AHTPB prepolymer was characterized through a series of physical and chemical characterizations. Measurement of 0.8516 mg. equivalent OH/g AHTPB which is very close to that of HTPB (0.8541), indicating that the preparation reactions to produce AHTPB did not affect the terminal hydroxyl groups. Density was determined as 0.967 g/cm^3 which is about 10% higher than that of HTPB. Viscosity was measured as 5039 cP which is nearly within range of HTPB prepolymer 5306 cP and it was candidate to be used in the field CSRP. AHTPB prepolymer was instrumentally characterized by using infrared spectroscopy to indicate that the azide

group was inserted in the structure of HTPB and its peak appears at 2100 cm^{-1} . The experimental nitrogen content was found to be 12% which coincide with the theoretical calculated value, hence complete azidation of the repeating unit of HTPB was occurred. Water content was measured as 0.08% which is about 15% higher than that of HTPB and could be accepted from technological point of view.

The characteristics of the examined AHTPB samples gives the prepolymer the opportunity to perform good propellant processing which could be candidate to be used as a binder in solid propellant formulations

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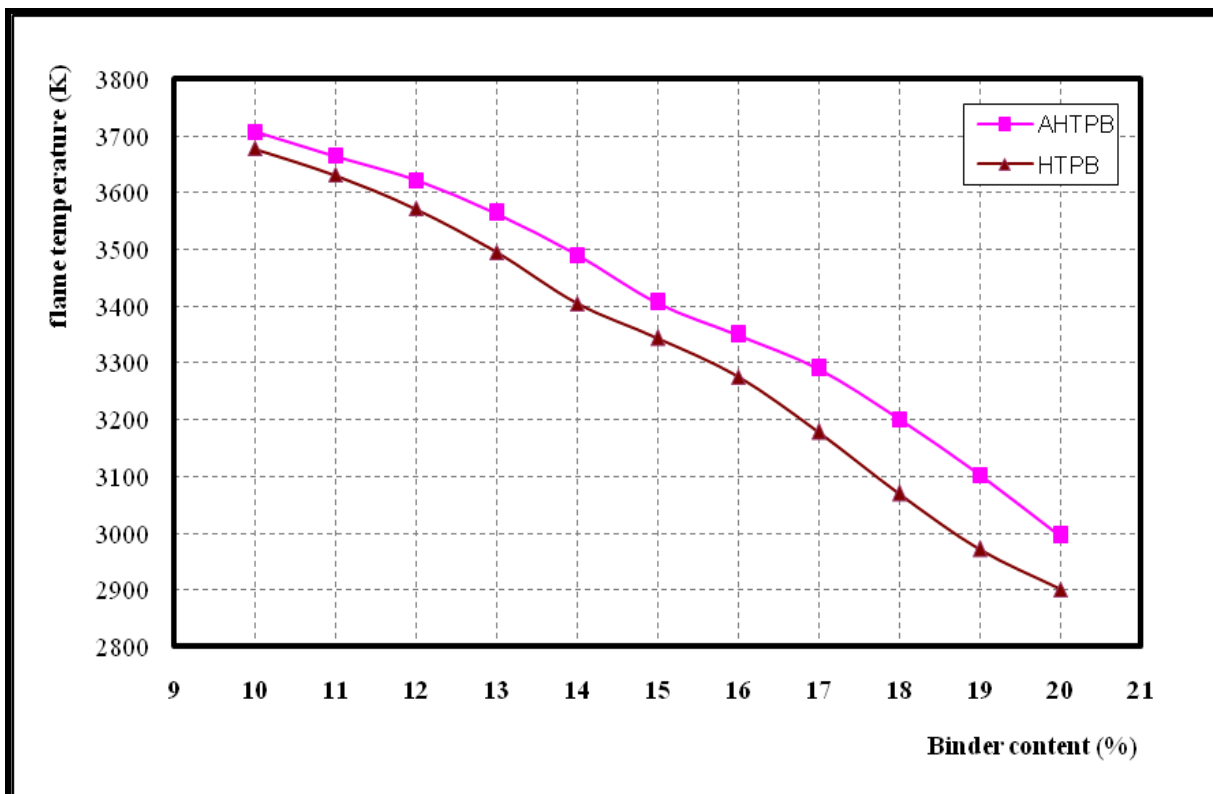


Fig (1) Binder content against flame temperature

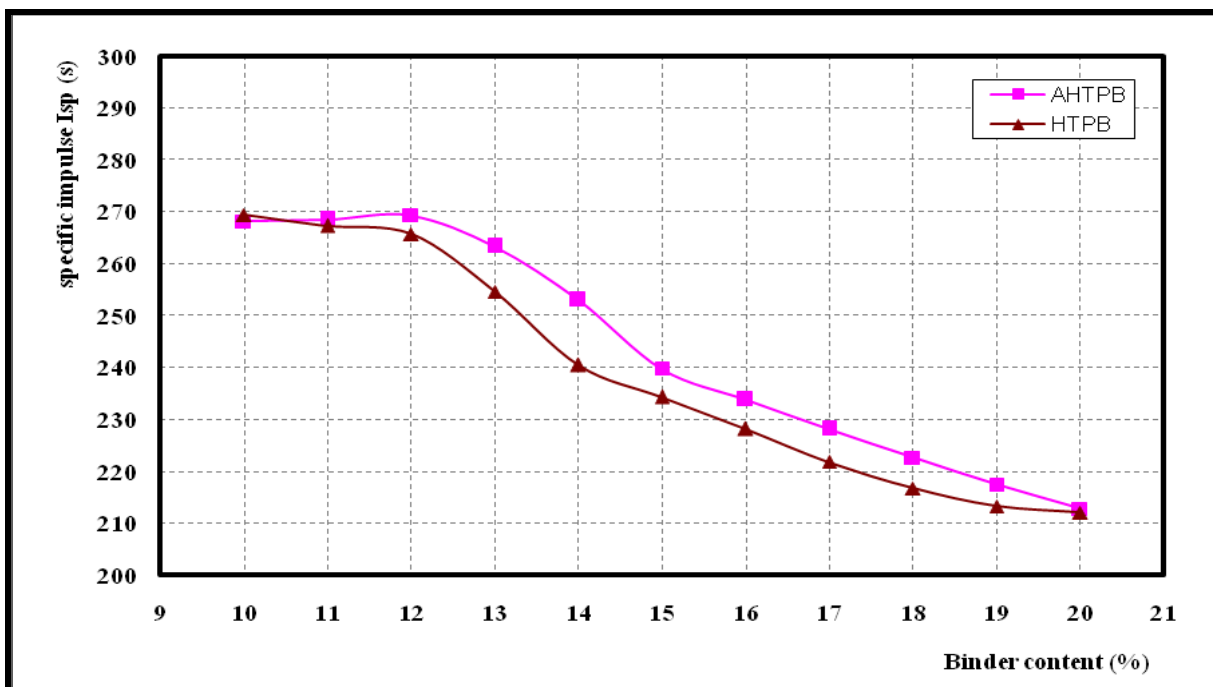


Fig (2) Binder content against specific impulse

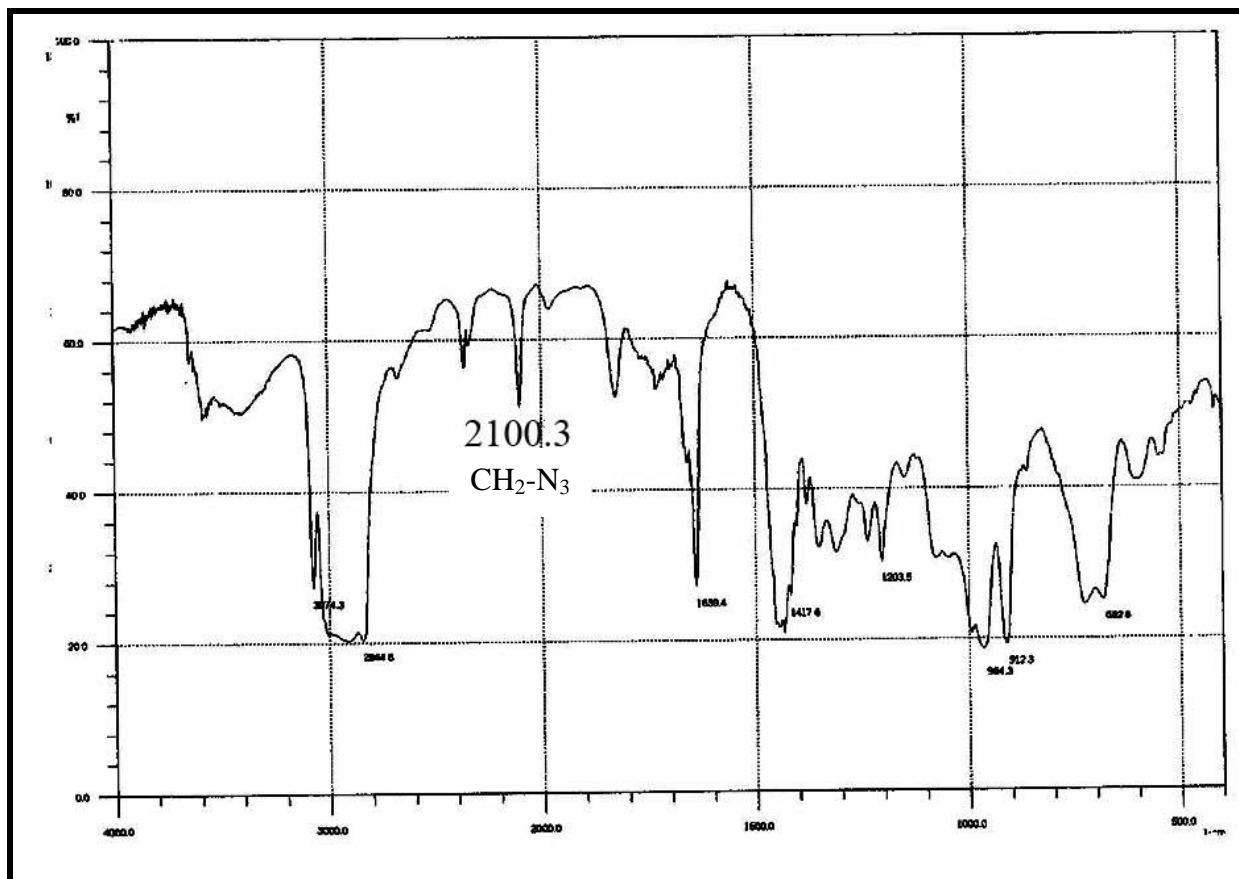


Fig (3) IR Spectrum of AHTPB