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High Performance Binder for EMCDB Propellants

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ABSTRACT

A novel block polymer has been synthesised from caprolactone using hydroxy terminated polybutadiene as ring opening initiator. Usefulness of this polymer as propellant binder has been studied by generating data on physico-chemical properties of the polymer. The polymer exhibited high miscibility with nitrate ester and high solid loading capability. Preliminary data generated on typical propellant formulation indicated higher performance as compared to composite propellant.

1. INTRODUCTION

Elastomer modified composite double-base (EMCDB) propellant has emerged as a separate class in recent times meeting the low temperature strain requirement in air-to-air missile propulsion applications[1]. Diverse approaches are being adopted in developing this class of propellant. The attempt is either to modify the conventional double-base (DB) matrix by incorporating various elastomers or to alter the binder characteristics in composite propellant (CP) so as to facilitate use of energetic plasticisers. However, both the routes converge in their search for novel binder systems from the vast polymer field. Evans, *et al*[2] have reported an excellent summary of their work with various polymeric binders for EMCDB propellants.

Hydroxy terminated polybutadiene (HTPB) is a well established polymer binder in composite propellants because of its high intrinsic energy and high solid loading capability. However, it has limited miscibility with nitrate ester plasticiser. On the other hand, polyethylene glycol (PEG) or polycaprolactone (PCP) binder commonly used in EMCDB propellant, though has high miscibility with nitrate ester plasticiser, produces low intrinsic energy and limited solid loading capability. Nitrate ester miscibility is a property sought after, especially when ammonium perchlorate (AP) is avoided as an oxidiser in the smokeless propellant formulations. Significant effort in modifying HTPB and PCP binder has been patented[3,4] claiming improvement in wide range of propellant parameters.

The present paper reports the synthesis and characteristics of a hydroxy terminated block copolymer (HTBCP) and the parameters of propellant made using this copolymer as a binder in a formulation containing AP and aluminium powder (*Al*).

2. EXPERIMENTAL DETAILS

2.1 Copolymer Synthesis

Synthesis of copolyester diols from E-caprolactone (CL) and polymerisation chemistry is reported in literature[5-8]. Ring opening polymerisation of CL can be initiated by water, alcohols and several other hydroxy compounds. In the present paper HTPB has been used as an initiator. Reaction was carried out in a three-necked glass vessel fitted with stirrer, thermowell and under nitrogen atmosphere using standard laboratory practice. The HTPB having molecular weight 2800-3000 and functionality ? and CL having density 1.075 g/cc at 20 °C and purity more than 98 per cent obtained from trade were used as starting materials. Both ingredients were heated/distilled under vacuum to eliminate moisture before use. Stannous octoate in

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0.1 weight per cent was used as a catalyst. The reaction was carried out at 110-115 °C for 24 hr to get HTBCP of PCP and polybutadiene. The reaction product was transferred and on cooling to ambient temperature solidified to form a waxy material.

2.2 Binder Preparation

Binder sheets were cured by crosslinking the block polymer using an isocyanate terminated prepolymer prepared from castor oil (CO) and toluene di-isocyanate (TDI). Minor amounts of diethylphthalate (DEP) was used as plasticiser. In energetic binder formulation nitroglycerine (NG) was used as explosive plasticiser either alone or in desensitised form (DNG) by partially replacing NG with DEP. Plasticiser-to-polymer ratio can be maintained as high as 2-2.5, without exudation.

2.3 Propellant Processing

Ammonium perchlorate and *Al* were incorporated in the polymer-plasticiser solution by following the normal propellant slurry cast method[9]. However, curing of propellant formulations using CO/TDI prepolymer was found not satisfactory, especially with high plasticiser-to-polymer (Pl/Po) ratio and with high solid loadings. In these cases a reaction product of mixed polyols and TDI having average functionality around 3.5 was used as a curing agent. A combination of triphenylbismuth (TPB) and ferric acetyl acetonate was used as a curing catalyst.

2.4 Equipment

Polymerisation reaction was carried out in 5 litre glass vessel and propellant processing was done in 5 litre capacity planetory mixer. An IR spectrum was obtained for polymer using Perkin-Elmer IR-spectrometer. Mechanical properties were determined for binder sheet and propellant samples in Universal testing machine, using test pieces conforming to ASTM D 412. Cal-val was determined in Karl-Fischer adiabatic bomb calorimeter with 0.016 g/cc loading. Burning rate was obtained by burning 6 mm propellant strands in an indigenously designed burner fitted with instrumentation to sense the acoustic emission during burning of strands. Thermal decomposition was determined in an indigenously fabricated differential thermal analyser (DTA) equipment at 10 °C/min heating rate. Ignition temperature, impact and friction sensitivity data were generated using Julius-Peter apparatus. Thermochemical data were calculated using NASA-SP-273 programme[10].

3. RESULTS AND DISCUSSION

3.1 Block Copolymer

The lactone polymerisation reaction is initiated in the present study using HTPB as initiator. The initiator is consumed in the initial step and propagation continues till the whole of monomer is consumed. The block polymer thus formed has a central HTPB block flanked by two side blocks of CL with terminal hydroxyl groups. A simple representation of the reaction scheme and the characteristics of HTBCP are presented in Table 1 and the IR spectrum of the compound in Fig. 1. It is evident from the reaction scheme that molecular weight of the copolymer formed increases to around 8000, resulting in a waxy material at room temperature. The copolymer gave density and hydoxyl value of 0.9 g/cc and 15 mg *KOH*/g, respectively. Solidification and structural integrity of the filled and unfilled polymers is obtained by the reaction of terminal hydroxy groups with isocyanates, forming urethane linkages. In the present case, as the molecular weight of the polymer is high with only two terminal hydroxy groups, curing could not be obtained when the reaction was carried out using

Table 1. Hydroxy terminated block copolymer of polycaprolactone and polybutadiene

Reaction	
$O\text{-}(CH_2)_5\text{–}CO + HO\text{–}(C_4H_6)_n\text{-}OH + OC\text{–}(CH_2)_5\text{–}O \rightarrow$ $HO\text{–}[(CH_2)_5\text{–}COO]_x\text{-}[C_4H_6]_n\text{–}[OOC\text{–}(CH_2)_5]_y\text{–}OH$ where x and y = 20 and n=50	
Polymer Characteristics	
Chemical formula	$C_{0.061}H_{0.096}O_{0.011}$
Molecular weight	6000-8000
Appearance	Waxy solid
Softening point	40-50 °C
Density	0.9 g/cc
Hydroxyl value	15 mg/*KOH*
Functionality	2 %
Heat of formation	–213 cal/g
Oxygen balance	–250
Cal-val	–1500 cal/g
Decomposition temperature	
Inception	438 °C
Peak	487 °C

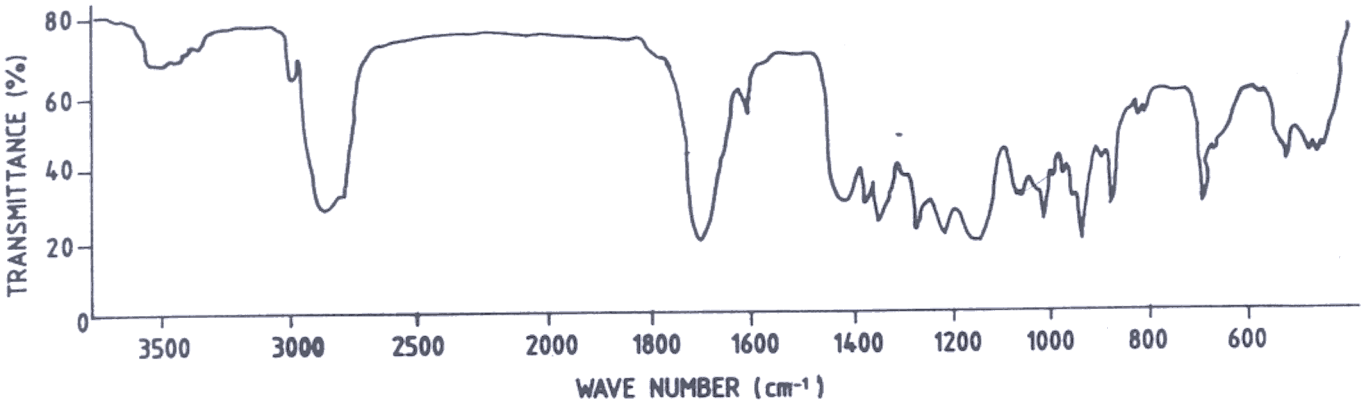

Figure 1. IR spectrum of HTBCP.

di-isocyanates. However, with polyisocyanates having functionality more than 3, satisfactory curing could be obtained with the availability of more reaction sites. Other data relevant to the propellant chemists have also been included in Table 1. Calculated values of heat of formation, oxygen balance and cal-val are of the same order as that of other polymer binders used in the propellant field. Thermal decomposition carried out in air showed an exotherm at 487 °C.

3.2 Binder Sheet

Data generated on the energetic binder sheet is given in Table 2 for a formulation with Pl/Po ratio 2.3/1, using NG as plasticiser. Cal-val of 775 cal/g more or less matches that of nitrocellulose, making it an attractive alternative binder in propellant formulations. Theoretical specific impulse of 202 s at pressure of 70 kg/cm^2 is closer to that obtained for DB f..nulations. Calculated gas composition shows preponderance of *CO* and H_2, and oxygen balance is highly negative. However, ignition temperature is comparable with that of DB propellants (160 °C). DTA thermograph showed a sharp peak at 204 °C with inception at 198 °C and completion at 219 °C as against a broader thermograph for the inert as well as for the copolymer. This is because of the incorporation of NG which decomposes at 130 to 160 °C. However, it appears that the copolymer interacts with the NG decomposition and increases its inception temperature. The energetic binder with lower Pl/Po ratio can also find application as a fuel-rich propellant formulation with or without metal additives because of its easy ignitability and high fuel value.

Table 2. Data generated on the energetic binder sheet Pl/Po=2.3/1

Oxygen balance	73 per cent
Cal-val	775 cal/g
I_{sp}	202 s
Chamber temperature	1445 °C
Gas composition (mole fraction):	
CO	0.47
CO_2	0.04
H_2	0.33
H_2O	0.05
N_2	0.09
CH_4	0.02
Tensile strength	2 kg/cm^2
Percentage elongation	200 per cent
Ignition temperature	160 °C
Decomposition temperature	
Inception	198 °C
Peak	204 °C

3.3 Propellant Formulation

The various parameters generated on one of the propellant formulations containing HTBCP 10.5 per cent are given in Table 3. The mechanical and limited burn rate data generated are comparable with the state-of-the-art composite propellants whereas the energy (cal-val) is substantially higher. Sensitivity data indicate that composition is safe to process; and also flexibility in hazard classification can be easily effected by formulation changes. Ignition and decomposition temperatures are close to the reported[11] values of NG-based propellants indicating that the initial step in the decomposition is controlled by NG.

4. CONCLUSIONS

In the present study, a hydroxy terminated copolymer of caprolactone and polybutadiene has been synthesised and characterised for its suitability as a propellant binder. The binder showed high nitrate ester absorption capability. An energetic binder formulation

Table 3. Parameters generated on the propellant formulation containing HTBCP

Composition	HTBCP, 10.5; NG, 18.0; DEP, 2.5; NC, 1.0; AP, 49.0; *Al*, 19.0; *NCO:OH*, 1.3:1 (Cured with reaction product of mixed polyols and di-isocyanate, per cent *NCO* : 20)		
Oxygen balance	30 per cent		
Cal-val	1680 cal/g		
I_{sp}	263 s		
Chamber temperature	3614 °C		
Gas composition (mole fraction):			
CO	O.27	N_2	0.09
CO_2	0.02	*HCl*	0.1
H_2	0.25	*H*	0.1
H_2O	0.12	Al_2O_3	0.04
Minor products		0.02	
Tensile strength		4 kg/cm^2	
Percentage elongation		10 per cent	
Young s modulus		57 kg/cm^2	
Burn rate at 50 kg/cm^2		8.7 mm	
Ignition temperature		150 °C (Brown fumes)	
Decomposition temperature			
Inception		160 °C	
Peak		165 °C	
Impact sensitivity (2 kg wt)		27 cm (50 per cent explosion)	
Friction sensitivity		Insensitive up to 9.6 kg/cm^2	

containing NG gave 200 per cent elongation and energetics comparable to those of DB propellant. Preliminary data generated on a propellant formulation with 68 per cent solid loading gave good mechanical properties and high calorimetric value. The data generated on the polymer have shown its potential as a promising propellant binder system for possible use in EMCDB formulations.

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