Chapter 8

Summary and Conclusions

This study is a comprehensive effort to synthesise, scale up and characterise GAP to evaluate the suitability of the system as an advanced solid propellant binder capable of improving the performance of composite solid propellants. Though information is available in literature on different physico-chemical aspects of GAP, detailed and systematic investigation looking into the suitability of GAP for propellant applications are scarce. Hence, a detailed study covering all such aspects of GAP was found to be relevant. Also studies of GAP-HTPB based blends were found to be relevant as this could indicate the merits of using GAP in conventional propellant formulations based on HTPB.

As a prelude to the study, a detailed literature survey was done and is presented in chapter 1. This chapter covers the evolution of polymeric binders and composite solid propellant systems, energetic binders, oxidisers and propellant compositions. A brief study of conventional binder systems, including synthesis and merits are also discussed. The data presented showed advantages of GAP based propellant system. The second part of introductory chapter describes the various synthetic routes of GAP and other azido polymers.

Chapter 2 describes an account of various experimental methods and equipments used in this investigation.

Studies on the synthesis and characterisation of PECH and GAP are covered in chapter 3. The detailed aspects like mechanism, initiation, propagation and termination steps in the cationic ring opening polymerisation of PECH are discussed in this chapter. The differences between activated chain end mechanism and
activated monomer mechanism are identified. Polymerisation of ECH at high temperature, using stannic chloride as initiator and the reaction mechanism are discussed.

Experimental studies carried out for the synthesis of PECH with different molecular weight ranges are presented. The effects of variation of concentrations of monomer and other reactants on the polymer properties are also studied in detail. The polymer synthesised is found to meet all physical and chemical properties required for PECH suitable for conversion to GAP. The spectroscopic analysis also showed that the polymer have all the characteristic structural groups of PECH as reported in the literature. The experimental studies done for the conversion of PECH to GAP are described in the last section of this chapter. The GAP resin synthesised by azidation reaction was analysed physically, chemically and spectroscopically and found to meet all the basic requirements in terms of molecular weight, functionality, and viscosity.

Chapter 4 covered the scale up studies carried out for PECH and GAP. The scale up methodology adopted and the criteria for selection of reactor for polymerisation of ECH are discussed. Based on the experimental results the polymerisation process for PECH was scaled up to 20 kg level. The rate controlling mechanism of the azidation reaction was identified by kinetic study. Based on the study results, a pilot plant process for GAP was carried out at 10 kg level. The GAP resin processed in the pilot plant was found to match all the requirements in terms of physical, chemical and spectroscopic properties.

Chapter 5 details the gumstock property evaluation of GAP and blends of GAP-HTPB. Effects of various experimental parameters including concentration, curing conditions and types of curatives on the gumstock properties of GAP are studied. Cured GAP-HTPB blends are prepared without phase separation and
subjected to detailed gumstock properties evaluation. Interpenetrating network formation by GAP and HTPB is suggested as the reason for the superior gumstock properties observed for the blends at specific concentration levels. Studies of the morphology of crosslinked GAP-HTPB blends by optical micrography and scanning electron micrography show typical indications of IPN formation. Compatible plasticiser systems are identified for GAP and impact of plasticiser content on gumstock properties is determined.

The structure-property relationship for crosslinked GAP network is explored by swelling experiments. The average molecular weight between crosslinks (Mc) is determined for the GAP network from swelling and initial modulus data. Using the experimental results, correlations are derived between gumstock properties and Mc values.

Thermo-analytical studies of GAP resin, cured GAP, GAP-HTPB blends and GAP based energetic compositions are presented in chapter 6. The thermo gravimetric analysis is carried out on GAP resin, crosslinked GAP and GAP-HTPB blends. The decomposition characteristics of GAP are found to closely match with reported results. From the TGA data, kinetics of thermal decomposition is evaluated by single and multiple heating rate methods. The TGA data on GAP-HTPB blends show the influence of concentrations of the constituents on the decomposition pattern. TGA studies are also carried out to find the effect of energetic additives such as RDX and HMX on the thermal decomposition of crosslinked GAP. RDX and HMX are found to affect the first stage decomposition of GAP.

The glass transition temperature (Tg) of crosslinked GAP and GAP based blends and cure kinetics of GAP are evaluated by differential scanning calorimetry. The effect of aromatic and aliphatic diisocyanate curing agents and plasticiser content on the Tg of crosslinked GAP are discussed. Ester type plasticisers and azido
plasticisers are found to be effective with GAP in reducing the Tg of the cured network. The Tg of GAP-HTPB blends are also evaluated by DSC. Study on the effect of concentration of GAP on the Tg of the blend indicated that up to 30% GAP content in the blend, the Tg is marginally reduced, indicating good compatibility. Dynamic mechanical analysis (DMA) of the blend show single transition up to 30% GAP content in the blend. The observations clearly show the impact of concentration levels on the micro-heterogeneous morphology of the IPN structure formed between GAP and HTPB networks.

Chapter 7 was divided into two parts. In part I, the studies carried out on GAP based propellant formulations are described. The theoretical studies on propellant formulations show that, GAP with ammonium dinitramide (ADN), hydrazinium nitroformate (HNF) and CL-20 could provide good performance improvement. It has been estimated that GAP-ADN based propellant can give an improvement of specific impulse by 10 seconds over existing HTPB-AP based propellant system. GAP based propellant formulations were done at small scale level and evaluated for mechanical and ballistic properties. Propellant with tensile strength of 6 ksc, elongation of 30% and modulus of 27 to 40 ksc was realised. Propellant formulation could be adjusted to get a burn rate in the range of 8-29 mm/s at 40 ksc pressure. GAP based propellant formulations were tested for advanced propellant application like micro propulsion system. The ignitability of different formulations of GAP is proven using a pre-fabricated proto model of the micro thruster.

The rheological studies carried out on GAP and GAP based propellant formulations are covered in part II. The effect of different types of plasticiser systems on the viscosity of GAP was studied. A correlation between rates of viscosity build up and curing reaction of GAP was arrived at using the kinetic data generated by viscosometry and FTIR spectroscopy studies. The relative difference in the reactivities of different diisocyanates with GAP was evaluated and explained.
based on chemical nature of the diisocyanates. Effects of different factors such as temperature, shear rate and type of curing agents on the rheological behaviour of GAP and GAP-HTPB blend based propellants were studied and the propellant is found to have good processing characteristics.

**SCOPE FOR FUTURE STUDY**

Studies on GAP based propellant with advanced oxidiser systems such as ADN, HNF and CL-20 are to be carried out. Modeling of decomposition and combustion of GAP based propellant systems with different oxidiser systems can be done to select optimum formulations for propellant and related applications. Detailed study could be taken up for assessing the compatibility of GAP with various systems such as inhibitions, insulations and liners for solid propellant. Thermal analysis of GAP based propellant formulations with advanced oxidiser systems could provide insight into the reaction mechanisms of condensed and gas phase decomposition products. Sensitivity studies of GAP propellant with advanced oxidiser systems in terms of friction, impact and auto ignition could be very valuable for propellant application.