CHAPTER - IV

SUMMARY
Solid propellants are preferred for the propulsion of missiles and space vehicles, in view of their reliability, longer life and ready to use system availability. Continuous efforts are being made to fulfill demand of solid propellants with improved performance in terms of density, energy, thermal and mechanical properties, reduced signature profile etc. R&D efforts indicate that the use of energetic binder systems along with high energy ingredients is a potential means of increasing the energy output of solid rocket propellants. The trend in the development and formulation of advanced energetic binder based propellants include use of nitrate ester plasticized prepolymer, oxidizers and nitramines along with metallic fuels. Advances in nitrate ester plasticized energetic binder based solid rocket propellant technology is largely attributed to the advances in hydroxyl-terminated elastomers. This includes polyether/polyester prepolymer such as polyethylene glycol (PEG), polypropylene glycol (PPG), propylene oxide-ethylene oxide (PO-EO) based co-polymers, polytetrahydrofuran (poly-THF), polyglycoladipate and polycaprolactones.

R&D work on the usage of hydroxyl-terminated polycaprolactone prepolymer as binder was started by a few research groups. A synthetical route has been reported in literature for the preparation of pentaerythritol-polycaprolactone prepolymer (PE-PCP), which on plasticization with nitrate ester (NG) can be used as an energetic binder. This prepolymer has high density and excellent miscibility with energetic nitrate ester plasticizers viz., NG, BTTN, TMETN etc. as compared to HTPB. In spite of higher density and excellent mechanical properties to the propellant. Being polyester polyol prepolymer, PE-PCP has higher mass percentage of the oxygen (~35%). Therefore, it is not necessary to use high levels of oxidizer in the propellant formulation to achieve the higher specific impulse, as in the case of HTPB. Because of the high ratio of oxygen in the prepolymer due to ester functional groups, this prepolymer shows decrease in the enthalpy of formation. Its glass transition temperature ($T_g$) is on higher side (-54°C) and it can take comparatively lower percentage of solid loading as that of HTPB. However, when highly plasticized with energetic nitrate ester (NG), energetic binder has $T_g$ of the order of -62°C. Further, the
combustion potential / energy levels of nitrate ester plasticized PE-PCP based propellants could be raised by inclusion of high percentage of well-known high explosive oxidizers like RDX/HMX. However, highly filled RDX or HMX based propellants exhibit demerits of low burning rates and high pressure exponents (n). Although formulation and overall properties of high molecular weight PE-PCP (M_n 10,000 - 20,000) based propellants have been reported, information on various technical aspects such as processibility of propellant slurry mix w.r.t. solid loading and particle size distribution, propellant slurry viscosity and its pot life for processing of case bonded rocket motors and nitrate ester compatible insulator system; mechanical properties w.r.t. plasticizer to prepolymer ratio and curative system; burn rate behaviour, catalysis and particularly suppression of pressure exponent; sensitivity, thermal behaviour and ballistic properties etc. are not available in open literature.

Therefore, present thesis reports synthesis and characterization of medium molecular weight ($M_n 5700$) hydroxyl-terminated pentaerythritol-polycaprolactone prepolymer (PE-PCP). This has been followed by formulations of NG-PE-PCP energetic binder and processing of NG-PE-PCP-AP-Al-HMX based high energy propellant compositions. In this study, effectiveness of NG plasticized PE-PCP as an energetic binder for making high-energy propellants for case bonded applications along with the catalysis and thermal decomposition of PE-PCP, NG-PE-PCP cured binder and NG plasticized PE-PCP based propellants have been studied in detail and the results are presented.

Theoretical prediction of ballistic parameters of few selected formulations was also carried out. A few selected NG-PE-PCP based propellants were statically evaluated and their ballistic properties have been discussed based on the pressure-time (P-t) and Thrust-time profiles. The study also concentrates on the effect of NG on insulator system and its bonding properties with propellant for selection of compatible insulator system for the processing of case bonded motors using advanced propellants containing high percentage of nitrate ester plasticizer.
Propellants were prepared by slurry casting technique by casting in aluminium trays for generating data on physical, mechanical, thermal properties; sensitivity etc. Burn rates were determined in the pressure range of 3.5-11 MPa by ‘Acoustic Emission Technique’. Impact and friction sensitivities of propellant compositions were determined by Fall Hammer method on Julius Peter’s apparatus. Mechanical properties were determined on Hounsfield, UK- Universal Testing Machine, while thermal analysis was carried out on Mettler Toledo Star system DTA/TG apparatus. Subsequently, a few selected propellant compositions were scaled-up to 5 kg level and propellant slurry was cast and cured in aluminium moulds to obtain cartridge type tubular shaped grains and also in case bonded motors having EPDM based insulator. Inhibited propellant grains and case bonded motors were evaluated in static mode for generating information on ballistic properties like burn rates, pressure exponent (n) value, Isp, characteristics velocity etc. at ambient (+27 °C), hot (+55 °C), and cold (-40 °C) conditions.

In general, PE-PCP in combination with various other high-energy ingredients decreased their sensitivity to impact and friction. However, incorporation of high percentage of fine particles of AP (5-6.5 μm) and HMX increased both impact and friction sensitivities. In addition, PE-PCP acts as an effective desensitizer for highly sensitive nitrate ester plasticizer NG. This further helps in processing the propellants without the use of non-energetic plasticizer, viz. NG.

PE-PCP when plasticized with NG, produces low viscosity (12 Poises at 27°C) energetic binder, and has impressive wetting properties towards solid ingredients. NG-PE-PCP energetic binder is also capable of taking up higher levels of solid loadings (78%) with excellent processibility and long pot life (> 5 hours). For present study, solid loading was restricted up to 75% for processing of the propellant formulations. Use of higher percentage of AP and Al in the NG-PE-PCP based formulation contributes towards higher burn rates and increased cal-val (partial heat of combustion) of the propellants (~1880 cal/g) due to better oxygen balance of the
propellant composition. However, Isp value drops down with higher percentage of AP, as mean molecular weight of the combustion products increases due to formation of more amount of HCl. The energy levels (Isp) of NG plasticized PE-PCP based propellant is further enhanced by inclusion of HMX in the composition. Thus, NG-PE-PCP energetic binder, when filled with solid fillers like HMX-AP-Al can offer propellants with higher density, enhanced energy and superior low temperature strain capability. In view of the fact that HMX at higher levels (> 25%) acts as one of the major energetic ingredient to improve Isp and is capable of influencing the combustion and pressure exponents, burn rate behaviour of PE-PCP based propellants was also studied.

During this study with NG-PE-PCP binder system having 75% solid loading, it was observed that by changing HMX content in the propellant from 5 to 25% burn rate decreases. However, with 30% HMX in the composition, burn rate was found to increase. Replacement of AP by 25% of HMX decreased burn rates by about 32% at 5 MPa and 26% and 24% at 7 and 9 MPa pressures respectively. As expected, pressure exponent registered an increase as the percentage of HMX was increased in the propellant formulations as compared to that of AP-Al based system. For a propellant composition containing 25% HMX, incorporation of 6-8% fine particle size AP out of total 32% AP, helped in controlling the pressure exponent to 0.5 level. However, by increasing HMX percentage to 30%, there was a marked increase in pressure exponents.

It was observed that advanced energetic propellants studied under this programme aiming for case bonded application, are having lower tensile strength properties as compared to conventional composite propellants. This may be because of PE-PCP based propellant formulations containing lower percentage of prepolymer (7.5%) and high plasticizer (Pl) to polymer (Po) ratio. Furthermore, for same percentage of solid fillers (HMX-AP-Al), propellant compositions showed reduction in tensile strength as compared to AP-Al based system. There was marginal increase in
the percentage elongation, as AP was replaced by HMX. For processing of advanced PE-PCP based propellant compositions suitable for case bonded applications, various chain extenders / adducts were also evaluated. Use of these materials helps in achieving required mechanical properties.

Surprisingly, both the tensile strength and percentage elongation was found to be increased at cold condition (−40°C) as compared to ambient and hot conditions. This appears to be one of the unique features of PE-PCP based binders, which will be extremely useful for case bonding high caliber propellant charges for numerous applications. Similar observation was made by Kolonko et.al during their work on high molecular weight PE-PCP. It is felt that this type of behaviour may be because of coiling type structure of cured binder at lower temperatures in highly plasticized matrix, which gets unwound slowly during stretching of samples, leading to higher elongation, as shown by the following illustration (Fig 4.1).

Fig 4.1: Illustration showing coiling of polymer chain at subzero temperature

CMDB propellants containing double base matrix loaded with AP-Al and composite propellants based on HTPB loaded with AP-Al are known to produce higher energy and higher burn rates. Hence, effect of both AP and HMX on NG plasticized PE-PCP matrix was studied. The results obtained indicate that energy levels and burn rates are dependent on percentage of ingredients used. However presence of HMX makes the system more sensitive. Propellant compositions without nitramines containing 52-57% AP gave higher burn rates and the highest burn rates were obtained by incorporation of higher percentage of fine AP. NG-PE-PCP-AP-Al
propellant without nitramines had the lower pressure exponent value of 0.43 in the pressure range of 5.0-9.0 MPa. By and large, pressure exponent values were higher for HMX based formulations. Inclusion of 25% HMX in NG plasticized PE-PCP based high energy propellants reduced burn rates at all pressures. However, burn rates of the order 12 mm/sec. at 7.0 MPa pressure were obtained by varying AP particles size and also by using trimodal particle size distribution of AP for the propellant compositions containing 5-30% HMX. Thus, overall pressure exponent values were reduced as the percentage of fine AP was increased, although propellants sensitivity also increased on increasing the fine particle AP.

In order to take care of the problem of higher pressure exponent values due to the presence of HMX in advanced propellant compositions, HMX concentration was kept at 20-25% level, but fine particle size AP (6.5 μm) was incorporated in propellant compositions. For a propellant composition having 25% HMX and 32% of trimodal AP (9.6 % fine), there was increase in burn rates at 7.0 MPa pressure by almost 9% as compared to propellant composition having 3 % fine AP. Similarly, on inclusion of 13% fine particle size oxidizer (AP), the burn rate at 7.0 MPa pressure was increased by 14% as compared to a composition containing 3.2% fine AP.

A few NG-PE-PCP-HMX-AP-Al propellant compositions were processed with 25% HMX, after incorporation of one part per 100 parts of selected ballistic modifiers (e.g. inorganic oxides and Pb-salts etc.). Incorporation of inorganic oxides (Fe$_2$O$_3$, CuO, Cr$_2$O$_3$, PbO and Cu$_2$O) increased burn rates marginally for HMX-AP-Al filled propellants. All the ballistic modifiers studied for HMX filled propellants exhibited marginal effect on burn rates changes and pressure exponent changes. No plateau effect was observed in any pressure range studied. It was observed that PbO:Cu$_2$O:CB and BLS:CB combination brought down the pressure exponent values in the higher-pressure region (7.0-11.0 MPa). A combination of basic lead salicylate (BLS) and carbon black in 1:0.3 ratio marginally brought down the pressure exponent values. Comparatively lower catalytic effect of inorganic and lead salts on PE-PCP based high
energy propellants as compared to CMDB class of propellants may be due to non-uniform distribution of ballistic modifiers in propellant matrix, as propellants were made by slurry cast technique.

For the thermal decomposition studies, samples were subjected to controlled heating rate for the determination of kinetic parameters. Since most of the reactions of decompositions are exothermic, samples are subjected to temperature changes during the decomposition. The prepolymer showed good thermal stability, when evaluated by using TGA by heating the sample from 50 °C to 500 °C at a heating rate of 10 °C/ min. The maximum weight loss of 97.5% was observed at 460 °C, although 5% weight loss was observed at 320 °C. Further, thermal characterization of prepolymer was carried out on Differential Scanning Calorimeter (DSC) instrument in the temperature range from -170 °C to 100 °C at a heating rate of 20 °C/min in helium atmosphere to determine the glass transition (T_g) temperature of the prepolymer. The thermogram obtained showed T_g of PE-PCP as -55 °C and heat capacity Delta Cp=0.31 J/g°C. The melting was observed at 64 °C, with Delta H of 109.3 J/g.

PE-PCP can be easily cured with diisocyanates like TDI, IPDI etc. The samples of cured prepolymer were also studied in the same manner as the prepolymer. The thermal properties of the cured PE-PCP were evaluated with TGA by heating the sample from 50 °C to 500 °C at the heating rate of 10 °C/ min. The polymer shows good thermal stability in TGA experiment also. In this case, the maximum weight loss of 97.5% was observed at 442 °C. T_g of the cured prepolymer was - 48 °C. To understand the decomposition pattern of cured PE-PCP, DSC was carried out from 50 °C to 500 °C at a heating rate of 10 °C/min in nitrogen atmosphere. The small endothermic peak was observed at 53 °C which may be due to softening of the cured polymer. No other exothermic or endothermic transitions were observed up to 500 °C.

Plasticized prepolymer (NG-PE-PCP energetic binder) was cured with different curing agents like TDI and IPDI at 50 °C. The tack free sheet samples were obtained after curing the energetic binder at NCO/OH ratio of 0.9. T_g of the energetic binder
samples cured with TDI, IPDI and H_{12}MDI were -60.0 °C, -62.4 °C and -61.5 °C respectively. No other transitions were observed in the samples. From T_g results, IPDI was chosen as the curative for the binder in all the formulations, as it offers lowest T_g as compared to TDI and H_{12}MDI. TGA results showed two-stage decomposition, first where 59% weight loss in the temperature range of 150-200 °C may be due to decomposition of NG and second of 33% weight loss in the temperature range of 400 – 450 °C may be due to polymeric binder.

The energetic propellant samples containing solid ingredients such as AP, Al, and HMX with PE-PCP binder were analyzed with DSC and TGA to study their decomposition behavior. The heating rate was maintained at 20°C/min. The AP-Al filled propellant exhibited T_g of -60 °C and Delta Cp of 0.319 J/g °C. In DSC experiment, exothermic peak was observed at 199.7 °C due to decomposition of NG. The endothermic peak at 245.7 °C may be due to phase transition of AP from orthorhombic to cubic. The peak at 293 and 379 °C may be due to further decomposition of AP.

DSC of the propellant sample with 75 % solid loading of HMX/AP/Al registered four exothermic peaks. The peak at 192°C is due to oxidative decomposition of NG. The peaks at 221 °C and 286 °C are attributed to decomposition of HMX. The exothermic peak at 372 °C is due to the complete decomposition of AP. The endothermic peak at 245 °C is due to the phase transition of AP from orthorhombic to cubic. When propellant sample was heated to 500°C for simultaneous DSC-TGA with heating rate of 20°C/min, the maximum decomposition was observed between 251 and 254°C with weight loss of 62.7 %, whereas complete decomposition was observed at 361.8°C. The T_g of the propellant sample was also confirmed by DMA and was found to be -48 °C. This further confirms that NG-PE-PCP based propellants have better low temperature strain capability (-40 °C).

The effect of nitramine loading on the decomposition pattern of the high energy advanced propellants was studied by TGA. Various formulations were processed with
5 to 30% HMX loading by replacing AP in the composition. In most of the cases, the decomposition took place in three steps. However, in case of 30% HMX loading, weight loss observed was very sharp. It showed 71.5% weight loss in a single step at 250°C, which was not seen in other formulations with lower percentage of HMX.

Theoretical performance calculations indicate an overall increase in specific impulse ($I_{sp}$) of the NG-PE-PCP-HMX-AP-Al propellant formulations by 5-6 s as compared to conventional Composite and CMDB propellants. $I_{sp}$ varied with the change in amount of HMX in the propellant composition. To assess the practical utility of PE-PCP based propellants, a few NG plasticized PE-PCP based propellants containing 7.5% PE-PCP were processed and cast under vacuum and cured at 40°C in aluminium moulds to obtain tubular shaped propellant grains and also in case bonded rocket motors having EPDM based insulator to generate data on ballistic parameters. Inhibited propellant grains were statically evaluated in Ballistic Evaluation Motors (BEM). Case bonded motors having tubular shape propellant were evaluated statically in progressive mode. In all the cases, the static firings were found to be smooth, which indicates flawless propellant and good bonding between propellant and insulator and inhibitor.

The propellant grain comprising of 70% AP-Al having physical dimensions of 190 mm length, 110 mm OD and 75 mm ID, when tested in a BEM, delivered $I_{sp}$ of 238 s, and characteristic velocity of 1530 m/s with pressure exponent value of 0.39 (5.0-9.0 MPa pressure) as against pressure exponent of 0.45 obtained by strand burning rate data. Two more propellant grains were evaluated at -40°C and +55°C temperatures also gave smooth pressure-time profiles. Temperature sensitivity of burning rate, ($\pi_p$) of this propellant was found to be 0.22%/°C, which is marginally higher than composite propellant (0.15%/°C), but lower than CMDB class of propellants (0.3%/°C). In neutral mode, static evaluation at 6.3 MPa average pressure characteristic velocity obtained was 1589 m/s and $I_{sp}$ of 242 s.
To achieve higher $I_{sp}$ levels, a few propellant compositions containing 20% and 30% HMX were evaluated. On replacement of AP by the HMX in the propellant composition, the specific impulse increased by 5-6 s. On further increasing the percentage of HMX to 30%, the specific impulse increased by another 1-2 s. It was seen that high nitramine content in the propellants results in producing higher $P_{\text{max}}$ and pressure exponent values. A 30% HMX based propellant was processed using 9% AP of 5μm particle size instead of 6.5μm particle size used earlier. When evaluated in progressive mode at ambient condition ($+27 ^\circ\text{C}$), a BEM firing showed smooth pressure-time profile, covering pressure range of 3.5-8.0 MPa without any oscillatory behaviour or tail-off. The delivered specific impulse and characteristic velocity for this composition were 247s and 1623 m/s respectively. Same propellant, when evaluated in neutral mode at ambient condition in a BEM with a throat diameter ($D_t$) of 26.5 mm with expansion ratio ($A_e/A_t$) of 6.3 produced smooth pressure-time profile with average pressure of 6.68 MPa and $P_{\text{max}}$ of 7 MPa. The delivered specific impulse and characteristic velocity for this composition were 239 s and 1642 m/s respectively.

NG-PE-PCP-HMX-AP-Al propellant, which was ballistically modified with one part of combination of catalyst, basic lead salicylate (BLS) and carbon black (CB) in 1:0.3 ratio, gave delivered specific impulse of 241 s and characteristic velocity of 1550 m/s. Two more propellant grains from same propellant mix were evaluated at $-40^\circ\text{C}$ and $+55^\circ\text{C}$ temperatures. They gave delivered specific impulse of 238 s and 248 s and characteristic velocity of 1630 and 1642 m/s respectively. Temperature sensitivity of burning rate, $(\pi_\tau)_p$ of this propellant was found to be 0.19 %/$^\circ\text{C}$. This means use of fine AP and basic Pb-Salicylate and CB combination of catalyst plays an important role to make the propellant formulation burn rate less sensitive to temperature.

Thus, burn rates of NG plasticized PE-PCP propellants can be tailored in the range of 10-12 mm/s and $I_{sp}$ of 245 s to 250 s can be achieved by avoiding use of non-energetic plasticizer without compromising on sensitivity. Further, the pressure
exponent of NG plasticized PE-PCP based propellants having nitramine content in the range 20-30% can be controlled by incorporating fine particle size AP, and using one part Pb-based ballistic modifier in combination with carbon black.

The basic chemical reaction mechanism in the gas phase of DBP/CMDB, which involves the reduction of NO to N\textsubscript{2} remains unchanged (because of presence of NG) by replacement of NC (ester) binder with PE-PCP (ester). As a result, the gas phase structure of PE-PCP-NG based propellant is fundamentally similar to NC-NG based propellant. However, the temperature in the flame zone is higher (3838 K) for NG-PE-PCP based propellant than that of NC-NG based CMDB propellant (3560 K). The reaction time decreases with increasing pressure for both propellants, suggesting increased reaction rate because of thermal effect, resulting in increased surface temperature. This was more pronounced with AP-Al filled propellants as compared to HMX filled propellants.

The combustion zones of PE-PCP based propellants containing crystalline energetic particles are not homogeneous due to heterogeneous nature of the propellant. AP can burn as monopropellant and its combustion products interact with the decomposition products of the NG plasticized PE-PCP based matrix. Addition of AP particles to the propellant matrix produces luminous flame streams on the burning surface. Since the decomposition gases of binder and HMX are fuel rich and that of AP are oxidizer rich, it is possible that the diffusion between the products of AP and binder and HMX shifts the equivalence ratio towards stoichiometry, which results in decreased reaction rate and flame temperature as HMX concentration goes up.

Nitramine particles sublime endothermically at the burning surface and reduce the overall heat of reaction generated at the burning surface. They are also reported to form melt layer on propellant surface. This reaction could be responsible for the reduced burn rate of NG plasticized PE-PCP-HMX-AP-Al propellants as compared to AP-Al filled conventional propellants. As the concentration of HMX increases, the luminous flame zone produced above the burning surface approaches it and the heat
feed back from the gas phase to the burning surface increases, resulting in increased burn rates.

In conclusion, results of this study have proved that advanced energetic propellants based on NG-PE-PCP binder filled with HMX-AP-Al offer high density, high energy (Isp) as compared to conventional CP and CMDB propellants. Moreover, NG plasticized PE-PCP binder based propellants also offer high strain capability at -40°C as compared to NG-NC based DBP and CMDB propellants and are therefore ideal candidate propellant for large size case bonded rocket motors required for tactical and strategic applications. The results of this study also bring out that the limitations encountered in controlling vital ballistic parameter like pressure exponent can be dealt by optimization of formulation with nitramine like HMX, and by using fine particle size AP along with ballistic modifiers like Pb-salicylate: carbon black combinations.

Since prepolymer is oxygenated, when used in combination with nitramines (oxygen lean), high-energy propellants made from this polymer may enable to use minimum quantity of AP as compared to generally used in conventional composite propellants (70%). In this way, this class of propellant can produce reduced level of chlorine free exhaust products, required for advanced green / clean or alternate propellants.