

STUDY ON COMBUSTIBLE CARTRIDGE CASES AND POLYMERIC RESIN BINDERS IN ITS COMPOSITION

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in

POLYMER TECHNOLOGY

Submitted by

Jitendra Singh

2K19/PTE/04

Under the supervision of

Dr Raminder Kaur



DEPARTMENT OF APPLIED CHEMISTRY
DELHI TECHNOLOGICAL UNIVERSITY
Shahbad Daultapur, Main Bawana Road
Delhi-110042

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Bawana Road, Delhi-110042

CANDIDATE'S DECLARATION

I, Jitendra Singh, 2K19/PTE/04 student of M.Tech hereby declare that the project Dissertation titled "**Study on combustible cartridge cases and polymeric resin binders in its composition**", which is submitted by me to the **Department of Applied Chemistry**, Delhi Technological University, Delhi in the partial fulfilment of the requirement for the award of the degree of Master of Technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma, Associateship, Fellowship or other similar title or recognition.

Place: Delhi

Date: 30 July 2021



Jitendra Singh

2K19/PTE/04

Department of Applied Chemistry
DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Bawana Road, Delhi-110042

CERTIFICATE

I hereby certify that the Project Dissertation titled “**Study on combustible Cartridge cases and polymeric resin binders in its composition**” which is submitted by **Jitendra Singh**, 2K19/PTE/04, Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the Master of Technology, is a record of the project work carried out by the student under my supervision. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi

Date: 31/07/2021

Raminder Kaur
31/7/2021

Dr Raminder Kaur

(SUPERVISOR)

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ABSTRACT

An understanding of the compatibility of different binder resins is essential for the upgradation of the properties of cartridge cases used in the propulsion systems of various ammunitions. This is essential in designing a new composition with a binder resin having higher glass transition temperature, in order to increase the serviceability of these cartridge cases in the areas with high atmospheric temperatures. The present studies have been done to investigate the suitability of thermoplastic resins having higher glass transition temperature in order to replace the existing polyvinyl acetate resin in the composition of cartridge cases. Experiments were performed with the comparative study of three different resins viz. Polyvinylacetate, Polyvinyl butyral and Polyvinyl chloride by making their blend with Nitrocellulose and cellulose in a proportion of 70:15:15 by weight. The processibility of resins in the composition of CCC is ensured by study of viscosity variation with respect to stress gradient and constant stress system. The prediction of their performances in the composition is carried out by the virtue of mechanical testing, modelling and simulation of thermal properties and ballistic performance followed by mechanical strength evaluation for each composition.

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CHAPTER-1

INTRODUCTION

1.1. Gun Ammunition

In conventional warfare the target destruction was carried out by transferring the energy contained by a projectile to the target. It is executed by the virtue of colliding a projectile on to the target. The projectiles are of many types viz. kinetic energy projectile to penetrate the target, Shells (containing explosive) etc. These projectiles need to reach the target with certain pre-calculated velocity so as to eliminate the target. These pre-calculated velocities are imparted into the projectiles by two main components i.e. 1. Gun and 2. Propulsion system. The propulsion system and Projectile together forms a system called Ammunition. Although the projectile may be attached with propulsion system or can be separate, together they are called as ammunition. Gun is a system of machines which provides logistics to the ammunition to act in such a way that propulsion system ably throws the projectile up to the target with required range or velocity.



Fig.1.1. Conventional Gun ammunition

1.2. Gun Ammunition Components

Gun ammunition usually consist of following four components as shown in Fig. 1.2

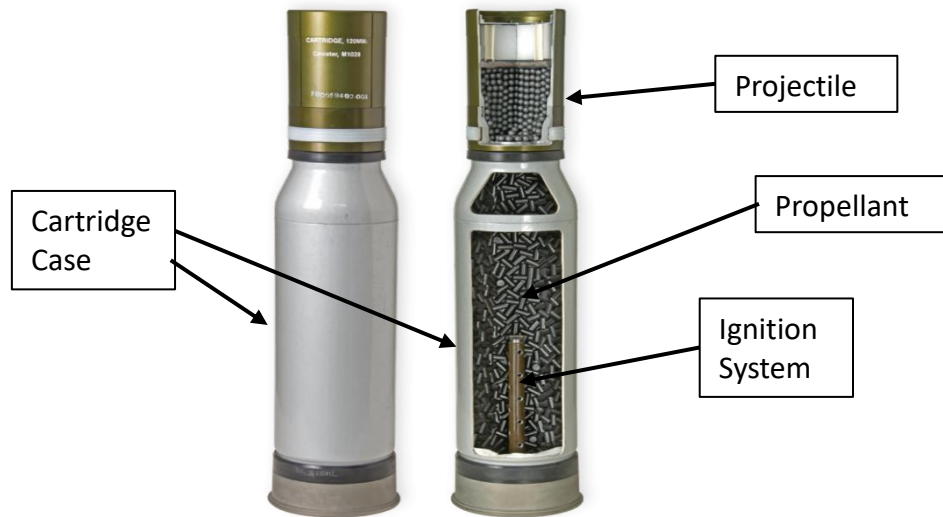


Fig. 1.2 Components of Ammunition of large calibre guns

A short description of these components is given below;

- i. **Propellant:** It is a substance which helps the projectile move forward to attain the required velocity to hit the target. Propellant is a composition of chemical compounds formulated and designed in a manner to create an efficient system; which when ignited properly produce gases. These gases try to expand inside the gun chamber and thus pushes the projectile towards open end of the gun barrel (muzzle end).
- ii. **Ignition System:** This is a composition of chemical compounds which creates spark to ignite and initiate the burning of the propellant.
- iii. **Cartridge Case:** It provides housing for propellant and ignition system. It holds the propellant inside and thus saves it from spillage. It also provides a definite shape to the propulsion system in order to make it loadable in to gun chamber
- iv. **Projectile:** Also called as Shell or warhead responsible for diffusing the target.

Propellant, Ignition system and cartridge case together may be called as propulsion system.

1.3. Description of Cartridge Cases

In earlier times, following two types of systems were used to provide housing to the propellant charge;

1. Metal cartridge cases- Made of Brass or steel.
2. Textile bags- Made of combustible textile.



Fig. 1.3.1 Conventional Cartridges of Large Caliber Guns

Fig.1.3 shows conventionally used metal cartridges cases and bag charge cartridges for large calibre guns. These were having various functional and logistic disadvantages. Disadvantages of metal cartridges are listed in the Table 1.3;

Table-1.3 Advantages and disadvantages of metal cartridge cases

Metal cartridge cases	
Advantages	Disadvantages
Robust design, very strong	Made of Brass, hence very expensive
Long service life	High weight
	Sticking problem due to thermal expansion of metal
	Disposal problem of spent cartridges
	Toxic cupric oxide gases gets generated while firing

On the other hand textile bags are free of the problems shown by metal cartridges, but these are difficult to load in the gun chamber due to irregular shape, hence reduces the rate of firing.

Above reported problems attributed by metal cartridge cases and textile bags were overcome with the invention of combustible cases. Now combustible cartridge cases (CCC) are used in both tank as well as field gun ammunitions.



Fig. 1.3.2 Combustible Cartridges for Large Caliber Guns

As CCC gets consumed during the application, it eliminates the need to eject the metal case after firing. It also adds to the energy of the propulsion system (due to use of high energy materials in the composition) and lowers wear and erosion of the tube (barrel). But the same time it has compromised the strength and robustness of cartridge cases in comparison with the metal counterparts.

1.4. Scope of Study in CCCs

Researchers are working to increase the strength of the cartridge cases with different possible routes. Abhijit DEY et al. [1] have reported the geometrical deformation of resin based combustible cartridges at high temperature. The root cause of this deformation is outlined as low glass transition temperature of the thermoplastic resin used in the composition. The problem of deformation is claimed to be solved with incorporation of nano clay in the same resin binder.

It may be advantageous if a resin binder with higher value of Tg is incorporated into the composition of the combustible cases. Such resin binder may be used to replace the existing PVAc resin fully or partially in the composition. Hence experiments performed with the comparative study of three different binder resins viz. Polyvinylacetate, Polyvinylbutyral and Polyvinylchloride by making their blend with Nitrocellulose and cellulose in a proportion of 70:15:15, followed by mechanical strength and ballistic evaluation through simulation and modelling using computer program.

Chapter 2

LITERATURE REVIEW

The CCC have now become necessary as a part of propulsion system as metal cartridges have many logistic disadvantages. Various researches have worked on design and development of combustible cartridge cases and studies related to them. In a chain of evaluation of different types of CCCs, it has utilized many ingredients and undergone many kind of processes.

2.1 Types of Combustible Cartridge Cases

CCCs may be classified in following types;

i. Multilayered CCC:

As the name suggests multilayered CCC consist many layers of nitrated fabric or NC paper. These are bind together by pasting one layer over other layer with the application of pressure.

ii. Gelatinized CCC:

CCC first formed using raw materials like NC, cellulose, etc. is gelatinized using a solvent like acetone.

iii. Resin Based CCC:

A thermoplastic resin is incorporated into the composition which increases binding between the fibers, hence called as resin based CCC.

2.2 Main Ingredients of CCC

CCC formulations have some energetic materials in its composition to provide energy for complete combustion during firing whereas mechanical strength is provided by adding a binder. Nitrocellulose, a widely used ingredient of gun propellants turned to be main energetic ingredient in development of CCCs. Nitrocellulose also alters mechanical properties of CCC as it depends on the percentage of nitrogen content present in NC used. A higher nitrogen content in NC shows lower mechanical properties whereas lower nitrogen content in NC used attributes to higher mechanical strength. However, NC having low nitrogen content has lower calorimetric value. Using nitrocellulose of low nitrogen content results in low rate of burning and low energy

content in CCC. In order to maintain good calorific value, high burn rate and adequate mechanical strength, range of nitrogen content in NC is optimized at 12.0 to 12.6 percent. It is well known that fibres which do not have hydroxyl groups and lack other mutually attracting groups cannot be made into a satisfactory/cohesive sheet. Since NC has less hydroxyl groups, to make a sheet of pure NC is impractical. Secondly, during pulping the molecular weight and thereby the fibre length is also reduced.

In order to get better mechanical properties in produced CCC, cellulosic fibres were also added into the composition. Cellulosic materials improve the mechanical properties but affects the combustibility of CCC. Mechanical strength is such a parameter which cannot be compromised, as ignoring it will cause breaking of CCC while handling, which will draw the whole system to failure. Hence cellulose is also used universally with nitrocellulose in CCCs.

Incorporation of other energetic ingredients was also thought of. Picrite (nitroguanidine) which is a well-known ingredient of triple base propellant was added due to its thermochemical behaviour. Picrite (nitroguanidine) produces a high amount of combustion gases, connected with relatively low heat of explosion, hence a relatively low flame temperature. Picrite acts as a coolant so prevents the gun barrel from damage. On decomposition it produces large amount of nitrogen gas, which helps in suppressing the flash at muzzle end.

Other additives such as Dibutylphthalate (DBP) and Diphenylamine are also added as and when required. DBP work as non-explosive plasticiser and DPA is a stabilizer to NC (decreases rate of degradation of NC with time). Other additives like dyes, pigments etc. are also added as per requirement

2.3. Production Process of CCCs

The CCCs are mainly made through these main processes;

- I. Binding or Calendaring
- II. Gelatinized CCC
- III. In-situ resin based CCC
- IV. Post resin impregnation

2.3.1 Winding or Calendaring

As per VV Puri [2], Winding or calendaring technique was used in manufacture of CCC as per following steps;

1. Direct nitration of textiles, nonwoven rayon fabric such as Mira-cloth, cotton gauze etc, and - impregnation of nitrated textiles with wet strength resins.
2. The nitrated cellulosic fabric was laminated by winding around a collapsible mandrel which is rotated under pressure against a rotating internally heated, stainless steel cylinder roll.
3. The fabric sheets were moistened with solvents like di-isobutyl ketone, ethylacetate, cyclohexanone, butyl acetate, methyl ethyl ketone, nitrobenzene etc in order to increase the strength of the laminate bond.

2.3.2 Gelatinized CCC

G.R. Kurulkar, R.K. Syal and Haridwar Singh [3] have reported the manufacturing of Gelatinised CCC. The steps to produce such CCCs are as follows,

1. Ingredients nitrocellulose (NC), nitroguanidine (NiGu), cellulosic fibres, dibutylphthalate (DBP) and diphenylamine were formed in the required shape and size by using felting technique (details of felting process is given in clause 2.3.5)
2. The preformed are then dried to remove moisture attain constant weight. The dry preform is dipped in acetone for a predetermined time.
3. Preforms are dried in hot air oven till acetone percentage is reduced to 20% by weight.
4. The preforms containing impregnated acetone is then pressed by applying isostatic pressure of 30 kg/cm².
5. CCCs are further dried with hot air at temperature of 50 ± 2°C for about six hours and are coated with a thin film of air drying varnish and trimmed to required size.

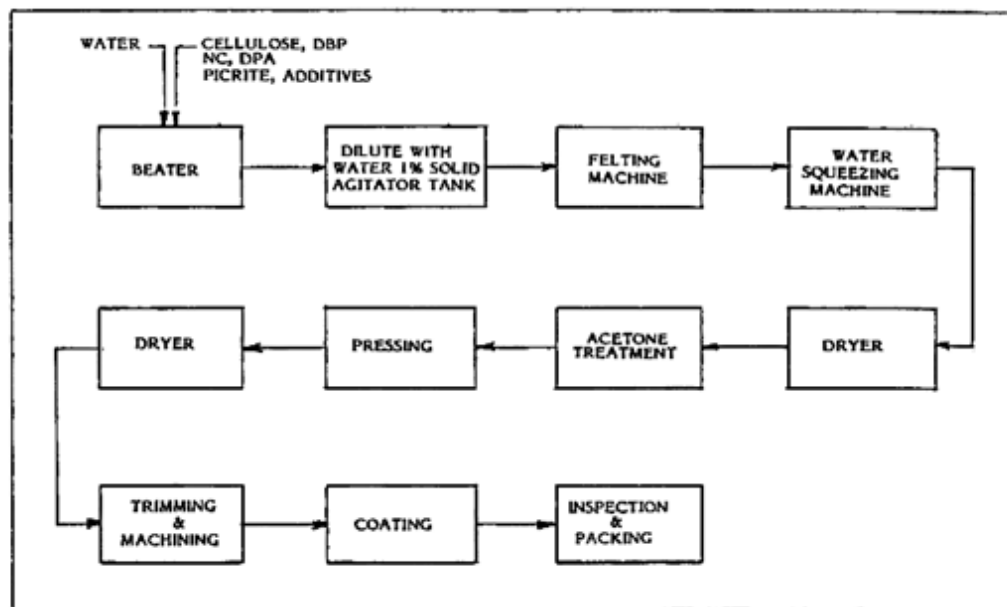


Fig.2.3.2. Processing of gelatinized CCC [3]

The process of impregnation of acetone into nitrocellulose fibers followed by pressing, results in the gelatinization of nitro cellulose. Hence it is called as gelatinized CCC.

G.R. Kurulkar, R.K. Syal and Haridwar Singh [3] also studied the formulation of gelatinized combustible cartridge case by changing the percentage of its ingredients as per following table 2.3.2;

Table 2.3.2. Gelatinized Combustible Cartridge Case Compositions

Composition No.	NC%	Picrite %	Cellulose%
1	70	15	15
2	65	20	15
3	60	25	15
4	55	30	15
5	50	35	15

These researchers through various tests such as burning characteristics, tensile strength, maximum pressure, force constant etc., characterized all the compositions and came to a conclusion, that the composition 3 is optimal for gelatinized CCC. These gelatinized CCC have become obsolete as, shrinkage was observed time due to evaporation of residual acetone present in these.

2.3.3. In-situ Resin Based CCC

M.T. Shedge, C.H. Patel, S.K. Tadkod, and G.D. Murthy [4] have studied resin based CCC with nitro cellulose, cellulose and resin binder (polyvinyl acetate) in-situ in the composition to developed resin based CCC, using felting process of manufacturing followed by hot compaction and other finishing steps. The process of in-situ resin based CCC is given below in step by step basis

- i. Dry cellulosic fibers added in aqueous medium in a beater to impart requisite freeness between fibers.
- ii. Weighed quantity of NC and alcoholic solution of DPA were added to the slurry.
- iii. Required quantity of diluted resin added under constant stirring.
- iv. Diluted with water to get 1 per cent solid content slurry
- v. Felting Operation- The slurry was then taken in a disc-making machine to form the discs under vacuum.
- vi. The thickness and the weight of the discs were controlled by feeding measured quantity of slurry.
- vii. Water from felted discs was then removed by pressing between the two perforated aluminium plates at 0.3 MPa and the discs were dried in a steam-heated oven at 60 ± 5 °C.
- viii. Hot Compaction- Strength was imparted to the dry-felted CCC disc by pressing it in preheated metal moulds for a specified duration using a hydraulic press at 6.9 MPa.

This process is also called as Beater additive process of production of resin based CCC.

2.3.4. Post Resin Impregnation Process

It is very similar to beater additive process; in beater additive processes the resin is mixed in to the composition with the other ingredients before molding, however, the post impregnation process involves dipping of the preforms in binder resin followed by hot compaction. Both manufacturing processes have nitrocellulose fibers, cellulose fibers and a resin binder as raw material, but former have resin in the slurry to produce preforms and later do not have binder resin in the slurry itself.

Joseph W. Colburn, Frederick W. Robbins [5] have explained the difference between In-situ and post impregnated resin based CCC, through comparative study of resin concentration in cross-sectional area of the produced combustible cartridge cases. Post impregnated cases have shell-like, high resin density regions near their outer surfaces and a very low resin density in the interior, while a beater additive case has a much more uniform resin density, and is much more flexible. Figure shows how resin density varies with distance from the outer case wall in cases formed using the two processes.

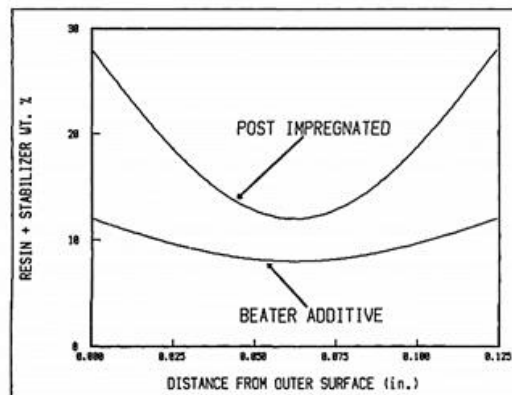


Fig 2.3.4. Concentration difference in material of CCC (In-situ Vs Post impregnation)[5]

2.3.4. it is evident that two CCC made with two different technics with similar raw materials shows different pattern of resin concentration in the material of CCC. In beater additive produced CCC the concentration of resin is almost same throughout the cross-section, whereas resin concentration in post impregnated CCC falls continuously from a very high value at outer surface to a very low value at the midpoint of the material.

2.3.5. Felting Process:

The setup of felting process is given in Fig.2.3.5.

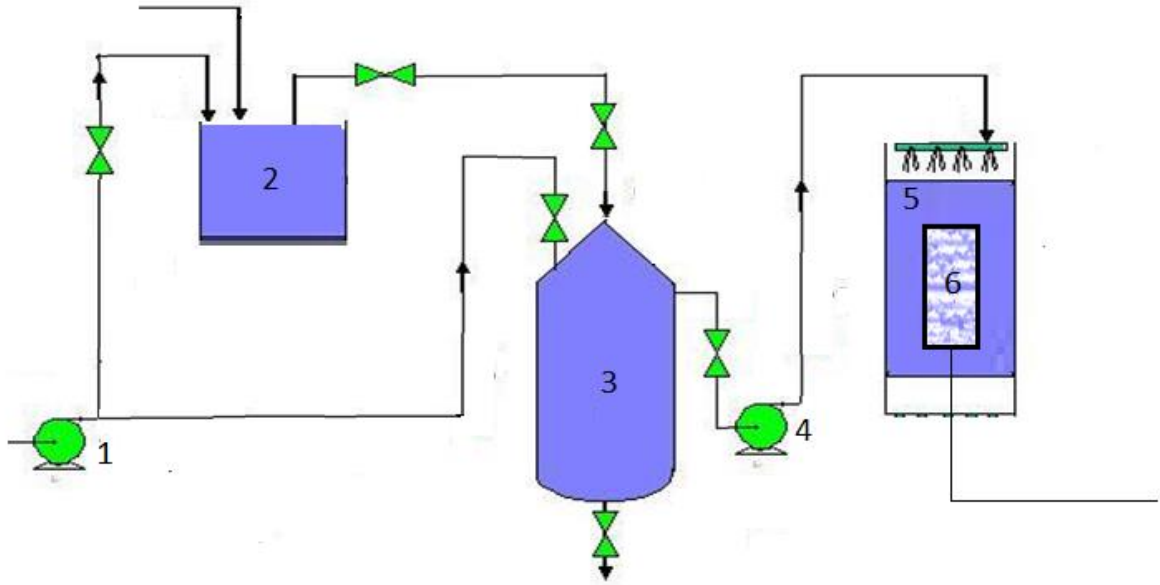


Fig.2.3.5. Felting Process for making preforms of CCC

Equipment in Fig.2.3.5 are as follows;

1. Centrifugal pump: Pumping water to Beater and Dilution tank.
2. Beater: Equipment to cut fibrous Cellulose and nitrocellulose into smaller fibre length.
3. Dilution Tank: Used for dilution of slurry as well storage of the slurry.
4. Gear Pump: Used to pump Slurry to the felting chamber.
5. Felting Chamber: Stores and provides slurry for felting.
6. Felting Mandrel: Perforated mandrel connected to Vacuum line.

Felting process is a process of producing wet preforms of CCC from its raw materials, these preforms are also called as raw felt. Cellulose fibres are fed into beater and cut to certain fiber length. All other ingredients are also added in beater and raw felts are deposited over felting mandrel under suction pressure (Similar to cake filtration process).

2.4. Evaluation of CCCs:

The performance of CCCs is evaluated through various tests for different parameters viz.

- i. Mechanical strength testing for handling and load bearing capability
- ii. Closed vessel firing for burn rate, energy content, maximum pressure, average pressure etc.,
- iii. DTA and methyl violet test for stability and
- iv. Dynamic firing for ballistic evaluation.

Apart from the above said evaluations, some other tests are also carried out to determine storage and service life etc. All the test mentioned above are physical tests and are required to be carry out in controlled environment, with suitable apparatus and equipment using CCC test samples.

Other approach to predict performance of CCC is through simulation by developing a computer program/model. The performance of compositions under study is predicted using such two programs which gives the prediction of

i. Thermochemical and Thermodynamic Parameters:

To assert the force constant and other ballistic parameters using ingredients of the composition and mass fraction of each ingredient in the composition

ii. Ballistic Predictions

To determine the usability of the CCC in actual firing condition by simulating its performance with a standard propellant using the force constant and other parameters derived from above model.

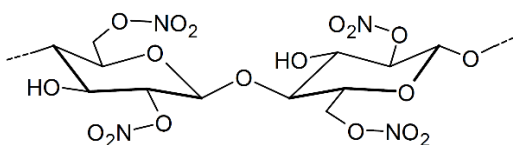
The detailed flow charts for simulation and modelling along with results are discussed in chapter-4 under section performance prediction of CCCs.

Chapter-3

MATERIALS AND METHOD

3.1. Details of Raw materials:

3.1.1. Nitrocellulose :



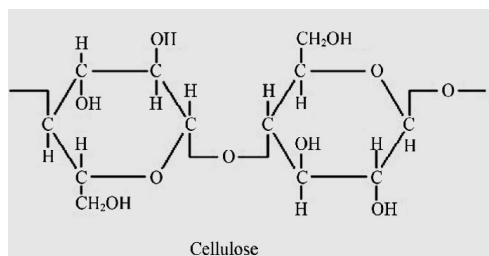
Nitro Cellulose (NC)

Industrial nitrocellulose (Ex-Nitrex) NC 10:25 was used in the study. The technical data sheet is given in Table 3.1.1:

Table 3.1.1. Specification of Nitrocellulose used in study

S.N.	Property	Value
1.	Appearance	White non-regular powder
2.	Odour	Of isopropanol
3.	Specific weight(g/cm ³) :	1.65-1.67(in water)
4.	Volatile content(wt%) :	28~32%
5.	Solids content(wt%) :	68-72%
6.	Solids content(Volumn%) :	50-60%
7.	VOC content(wt%) :	23-27%
8.	Nitrogen content(%) :	11.7-12.2%
9.	Ignition point(°C) :	≥ 180°C
10.	Pigment(wt%) :	None

3.1.2. Cellulose:

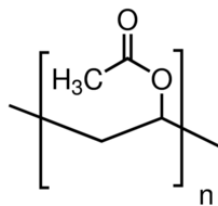


The technical data sheet is given in Table 3.1.2:

Table 3.1.2. Specification of Cellulose used in study

S.N.	Property	Value
1.	Appearance	White Powder
2.	Ash Content	Max 0.1%
3.	Bulk Density	100 to 150 gms/ltr
4.	pH	5-7
5.	Cellulose Content	Min 99.5%

3.1.3. Polyvinylacetate Resin

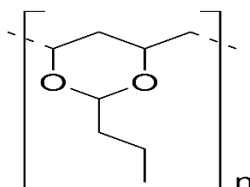


Ex. Pidilite polyvinylacetate emulsion was used. The resin technical data sheet is given in Table: 3.1.3

Table 3.1.3. Specification of polyvinylacetate used in study

S.N.	Property	Value
1.	Appearance	Milky White Emulsion
2.	Solid content	48%
3.	Viscosity @ 30 °C (poise)	500-1100
4.	pH	5-6
5.	Mol. wt. (wt. avg.) (Lakhs)	4.5±0.5
6.	Particle size (µm)	1-3
7.	Ash content (%)	≤0.5 wt%

3.1.4. Polyvinylbutyral Resin



PVB B-60 resin was selected for the study in CCC composition, as it is a thermoplastic resin with a glass transition temperature of about 68 °C. It is a polyvinyl butyral resin with a low solution viscosity. PVB B-60 is manufactured from the condensation reaction of Polyvinyl Alcohol and n-butyraldehyde. B-60 is a thermoplastic resin, which is soluble in most organic solvents with excellent film forming capability. It exhibits strong adhesion to glass, metal, plastic, leather and wood. It is a white, free flowing granule or powder and non-toxic to humans and animals. Polyvinyl butyrals are soluble in most organic solvents. The viscosity of PVB solution depends on the concentration of resin, temperature of solution and the solvents employed. PVB resin is most soluble in a mixed solvent system such as ethanol/toluene, methanol/methyl ethyl ketone, etc. Generally PVB B-60 is used in solution with alcohols

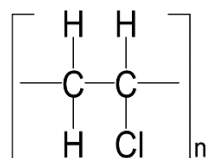
because alcohols are the best solvents for this resin. It dissolves completely in Methanol, Ethanol, N-Propanol, I-Propanol, N-Butanol etc.

Ex. Synpol PVB B-60 resin was used in the study. Technical Data sheet of the PVC resin used is given in table: 3.1.4.

Table 3.1.4. Specification of Polyvinylbutyral used in study

S.N.	Properties	Value
1	Butyral content	76 – 82 wt%
2	Hydroxyl content	18.0 – 21.0 wt%
3	Acetyl content	≤3 wt%
4	Viscosity	70 – 100 cps
5	Volatile ≤3 wt%	≤3 wt%
6	Specific gravity	1.05~1.10
7	Bulk density (for powder)	0.25 – 0.40 g/cm ³
8	Glass transition temperature	68 °C
9	Melting Point	135 – 175°C
10	Molecular weight	40,000 –50,000 g/mole
11	Degree of Polymerization	600- 700

3.1.5. Polyvinylchloride resin



PVC suspension resin was also studied in CCC composition as it is also thermoplastic polymer with glass transition temperature of 78°C. A medium molecular weight suspension type PVC resin was used as it is suitable for production of rigid extrusion products such as rigid pipes &

conduits, rigid sheets, tubular film etc. It is combination of medium molecular weight with high apparent bulk density, which makes it suitable for easy processing at high output rate, still maintaining the high mechanical properties. Its balanced heat loss property does not allow static to develop and reduces the flow time. This resin has good processing properties viz. easy bulk handling, minimum requirement of lubricant and more uniform fluxing in the extruder.

Ex. Reon PVC suspension resin was used for the study in CCC composition. Technical Data sheet of the PVC resin used is given in Table: 3.1.5.

Table 3.1.5. Specification of Polyvinylchloride used in study

S.N.	Property	Value
1	Inherent Viscosity	0.92
2	Apparent Bulk Density	0.55 g/ml
3	Flow time	25 secs
4	Max Heat Loss (ASTM D3030)	max 0.30%
5	Particle Size Distribution	
	Retention on ASTM 40 mesh	max 0.1 %
	Retention on ASTM 60 mesh	max 5.0 %
	Through ASTM 140 mesh	max 25.0 %
6	K-value (1% solution in cyclohexanone)	67
7	Glass Transition temperature T _g	78° C
8	Volatile Matter	<0.3 Wt%
9	Appearance	Clear water white free flowing powder in granular form

3.2. Details of Compositions for Study:

The reported composition of resin based combustible cartridge cases consist of the following;

Table 3.2.1 Standard composition of resin based combustible cartridge cases

S.N.	Raw material	% composition
1	Nitro Cellulose (12.2 to 12.6 % N2 content)	62-70
2	Cellulose	12-15
3	Polyvinylacetate resin	12-16
4	Other additives	1-3

Three different compositions were prepared for the comparison. The materials used in each composition is given in Tables 3.2.2 to 3.2.4 respectively, as below;

Table 3.2.2 Composition of PVAc resin based CCC (Standard)

Composition-1		
S.N.	Material	% in composition
1	Nitro Cellulose	70
2	Cellulose	15
3	Polyvinylacetate resin	15
4	Water	As diluent

Table 3.2.3 Composition of PVB resin based CCC (Standard)

Composition-2		
S.N.	Material	% in composition
1	Nitro Cellulose	70
2	Cellulose	15
3	Polyvinylbutyral resin	15
4	Isopropanol	As solvent

Table 3.2.4 Composition of PVAc resin based CCC (Standard)

Composition-3		
S.N.	Material	% in composition
1	Nitro Cellulose	70
2	Cellulose	15
3	Polyvinylchloride resin	15
4	Dimethyl formamide	As solvent

3.3. Experimental Methods:

Production of Blends: The blends of above three compositions were prepared by the following procedure:

3.3.1. Preparation of Composition-1:

Nitrocellulose	Cellulose	Polyvinyl acetate resin
Dry weight 56 g	16 g	Dry weight-16g $=16/.48=33$ ml

- i. 33 ml of PVAc resin was dissolved in 107 ml of water by stirring in magnetic stirrer for 5 min.
- ii. 16 g of cellulose added to above emulsion and agitated continuously for 5 min
- iii. 40 ml of above solution is kept aside for rheological viscosity and LOI measurement of cellulose-resin blend and named as sample-1.
- iv. 56 g of Nitrocellulose added to remaining solution and mixed thoroughly to form dough of composition-1.

3.3.2. Preparation of Composition-2:

Nitrocellulose	Cellulose	Polyvinylbutyral resin
Dry weight 56 g	16 g	Dry weight-16g

- i. 100 ml isopropanol was taken in a beaker and kept on heating at a temperature of 50 to 60 C.
- ii. 16 g Polyvinylbutyral resin slowly added to hot IPA and stirred continuously in magnetic stirrer to form a homogenous solution.

- iii. Added more IPA to the above solution to make it measure 140 ml.
- iv. 16 g of cellulose added to above solution and agitated continuously for 5 min.



Fig 3.2.2. Magnetic Stirrer

- v. 40 ml of above solution is kept aside for rheological viscosity and LOI measurement of cellulose resin blend and named as sample-2.
- vi. 56 g of Nitrocellulose added to remaining solution and mixed thoroughly to form dough of composition 2

3.3.3. Preparation of Composition-3:

Nitrocellulose	Cellulose	Polyvinylchloride resin
Dry weight 56 g	16 g	Dry weight-16g

- i. 100 ml Dimethyl formamide was taken in a beaker

- ii. 16 g Polyvinylchloride resin slowly added stirred continuously to form a homogenous solution.
- iii. Added more DMF to the above solution to make it measure 140 ml.
- iv. 16 g of cellulose added to above solution and agitated continuously for 5 min.
- v. 40 ml of above solution is kept aside for rheological viscosity measurement of cellulose resin blend and named as sample-2.
- vi. 56 g of Nitrocellulose added to remaining solution and mixed thoroughly to form dough of composition 3

3.4. Preparation of Sheets for Study:

Sheets of all the three compositions were processed for preparing samples to be used in mechanical properties evaluation. The sheets were processed in following steps;

3.4.1. Preparation of Preforms

- i. 3 moulds were prepared of the size 12mm x 30mm size.
- ii. Dough of all three compositions were poured in to the moulds and spread evenly by applying pressure with the help of MS plate
- iii. Kept the moulds for drying in oven at 60 C for 24 hours
- iv. Continued drying until it attains constant weight.
- v. The preforms of all three compositions carefully separated from moulds.

3.4.2. Pressing of Preforms into Sheets:

i. Equipment Used: Hydraulic Press, Ex. Santec (Fig 3.4.2)

ii. Materials Used:

Aluminum foil

Talc

Dried Preforms of composition 1, 2 and 3

iii. Procedure:

The preforms of above three compositions were pressed one by one to form sheet in following steps

- i. The pressing petals temperature was set to 100 C.
- ii. The preforms coated with talk to prevent from Sticking into aluminum foil
- iii. The preforms were put between the petals in aluminum foil and preheated for 2 mins
- iv. Preforms compacted at a pressure 5 MPa for 2 mins to form sheet of thickness 2.5 mm



Fig 3.4.2. Hydraulic Press

Chapter 4:

RESULTS AND DISCUSSION

4.1. Experimental Observations:

A set of experiments (testing) were performed in order to ensure usability of resins in the compositions. The main characteristic features which a composition requires to be fit for use in combustible cartridge cases is listed below;

The composition should burn without external oxygen to ensure splinter-less combustion during operation.

The viscosity of the composition should not exceed the processable viscosity range

Mechanical strength of CCCs produced using the composition should be good enough to withstand service conditions.

4.2. Schedule of Experiments:

Based on above said requirements, following schedule of experiments decided to evaluate resins in CCC composition:

- i. Rheological Viscosity measurement of Resin-Cellulose blends for processibility
- ii. Decomposition studies of composition through TGA.
- iii. Mechanical Strength Evaluation of Composition 1, 2 and 3
- iv. Modelling of dynamic performance of Composition 1, 2 and 3 through modeling and simulation

4.3. Rheological Viscosity Measurement of Resin-Cellulose Blends:

The measurement of viscosity was performed in order to generate a comparative data to ensure the processability of the resins in the composition as well as to identify Newtonian behaviour of the blends. The description the three samples used in the study is given above as sample-1, 2 and 3.

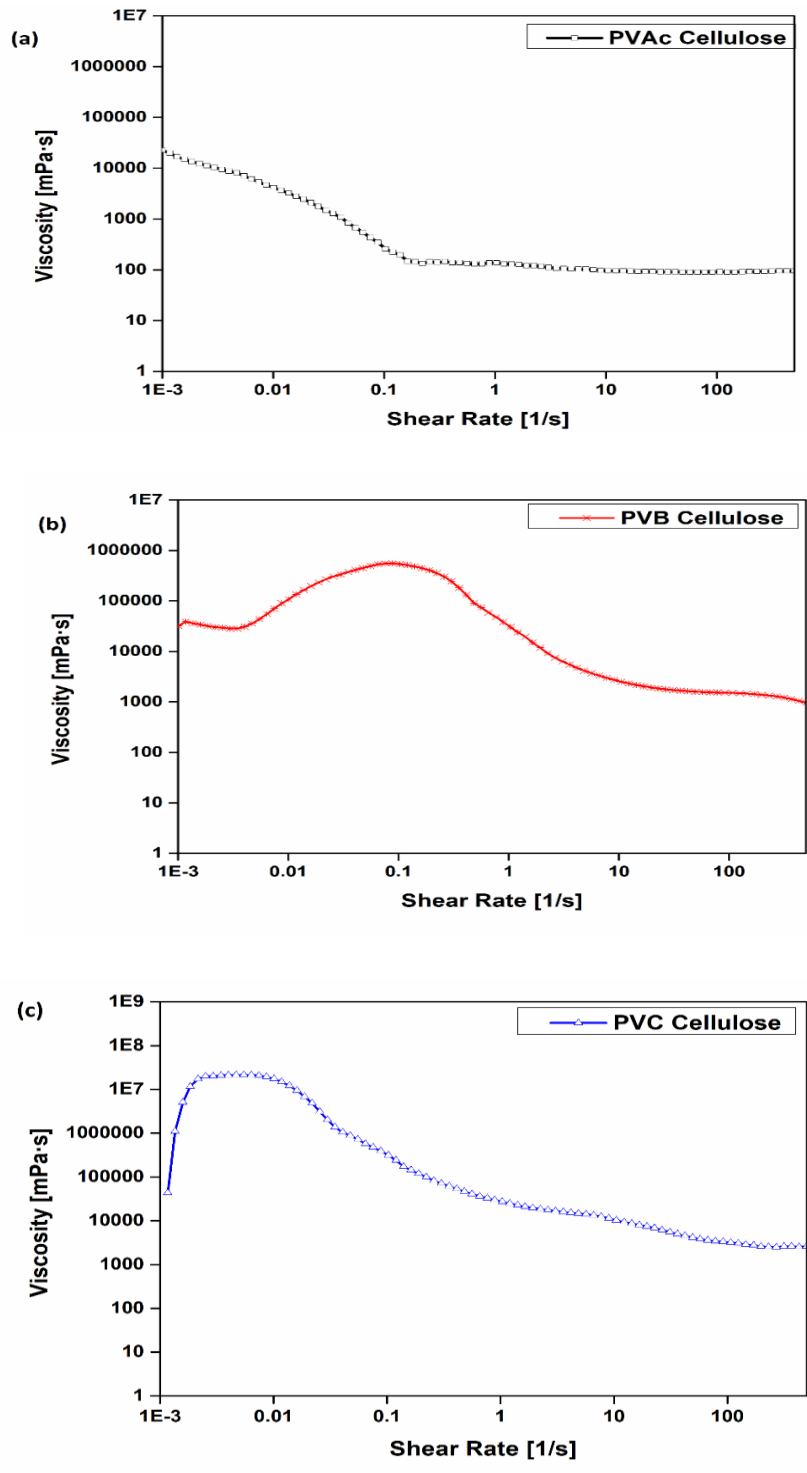
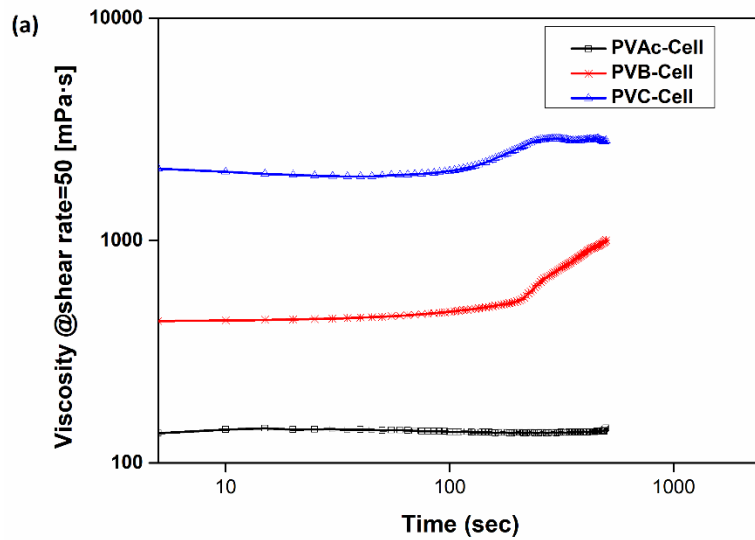


Fig. 4.3.1 Rheology of (a) PVAc-Cellulose, (b) PVB-Cellulose and (c) PVC-Cellulose at variable shear rate from 0.001 to 500 sec⁻¹

An Anton Paar rheometer (MCR 302, Anton Paar) was used to assess the rheological behaviour of various blend systems. It recorded the viscosity for varied shear rate as well as constant shear rate viscosity.

Rheological behaviour was investigated in PVAc-Cellulose, PVB-Cellulose, and PVC-Cellulose. To make the samples comparable, their viscosities were evaluated for the same amount of non-volatile material. As seen in Fig. 4.3, the rheological behaviour has been observed with varied shear rates. PVAc-Cellulose, PVB-Cellulose, and PVC-Cellulose blends exhibit shear thinning, Newtonian, and shear thickening behaviour at low shear rates, however all blends exhibit the same Newtonian behaviour at high shear rates, as illustrated in Fig 4.3 (a), (b), and (c).

PVAc-Cellulose, PVB-Cellulose, and PVC-Cellulose rheological properties were also investigated at constant shear rates of 50 and 100 sec^{-1} , as shown in Fig. 2. All the liquid samples were tested at shear rate =50 sec^{-1} as shown in Fig. 4.3.2 (a) and at the shear rate =100 sec^{-1} shown in Fig. 4.3.2(b). At varying shear rates, all of the samples showed varied rheological behaviour.



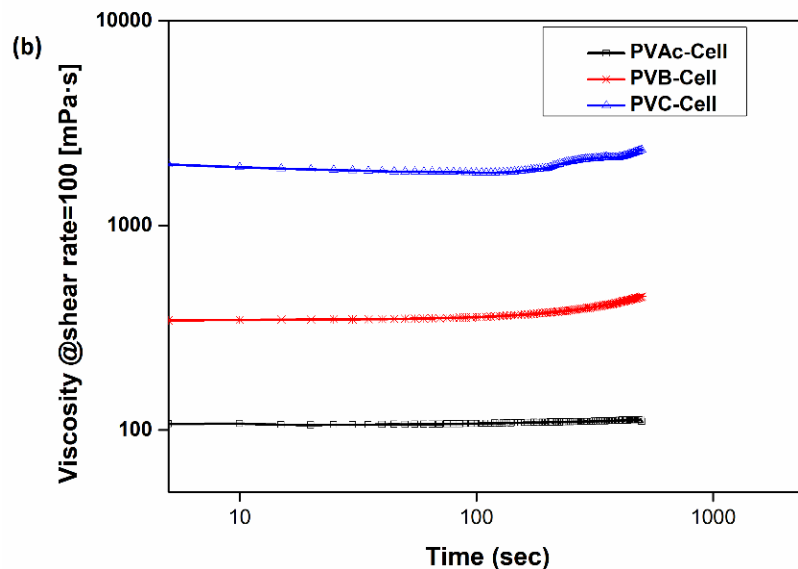


Fig. 4.3.2 Rheology of PVAc-Cellulose, PVB-Cellulose and PVC-Cellulose at constant shear rate at (a) 50 sec⁻¹ and (b) 100 sec⁻¹.

Initially, all samples exhibit Newtonian behaviour, which persists throughout the test in the case of the PVAc-Cellulose system, but later on, except for the PVAc-Cellulose system, the remaining two exhibit shear thickening at the end of the test at both shear rates of 50 and 100 sec⁻¹, as shown in Fig. 2(a) and 2(b).

4.4. Thermogravimetric Analysis (TGA)

Under nitrogen environment, thermogravimetric analysis (TGA) of several blend systems was performed on a Perkin Elmer TGA 4000 from 25 to 600°C at a heating rate of 10°C/min by taking known weights of dried samples of PVAc-NC-Cellulose, PVB-NC-Cellulose, and PVC-NC-Cellulose blends. In this study, the percentage weight loss varied as per the change in the temperature.

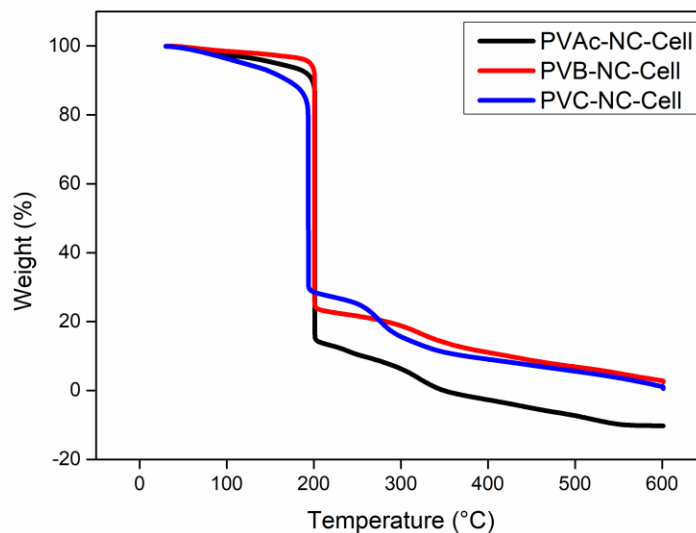


Fig. 4.4 TGA curves of PVAc-NC-Cellulose, PVB-NC-Cellulose and PVC-NC-Cellulose blend systems under inter environment

In all three blend systems, a single degradation was found. Evaporation of water or some gaseous substances can produce significant weight loss at temperatures up to 100°C. The initial degradation temperature of PVAc-NC-Cellulose, PVB-NC-Cellulose, and PVC-NC-Cellulose is approximately 192°C, 194°C, and 186°C, respectively, while the second degradation temperature of the same samples is around 201°C, 205°C, and 195°C, respectively. According to the initial and second degradation temperatures, PVB-NC-Cellulose is the most thermally stable system, PVC-NC-Cellulose is the least thermally stable system, and PVAc-NC-stability Cellulose's is in the middle.

4.5. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry under inert conditions, calorimetry was used to determine glass transition, melting, and crystallisation temperatures. The DSC was ran at a rate of 10°C per minute from 30 to roughly 170°C.

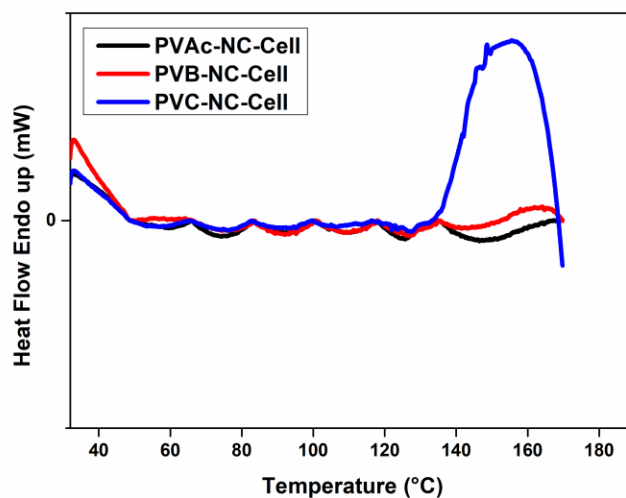


Fig. 4.5 DSC curves of PVAc-NC-Cellulose, PVB-NC-Cellulose and PVC-NC-Cellulose blend systems

The DSC curve of PVC-NC-Cellulose shows a major peak around 155°C, which is the least thermally stable system as discussed in the TGA discussion, and since it is endo first peak within test temperature, it is most likely the glass transition temperature of this blend system, which was not observed in the other two samples as shown in Fig 4.5. The peaks in the remaining two samples, PVAc-NC-Cellulose and PVB-NC-Cellulose respectively, are more likely to occur, when the temperature exceeds 170°C.

4.6. Mechanical Strength Evaluation:

Evaluation of tensile strength was carried out for composition-1, 2 and 3. The specimen were prepared from pressed sheets and tested in Universal Testing Machine (UTM).

i. Sample Preparation: The pressed sheets of composition 1, 2 and 3 were cut to form specimens of size 25 mm X 100 mm. 6 sheets of each composition were created for testing.

ii. Equipment used: Universal testing machine (UTM), Ex. Kalpak Instruments & Control

Universal testing machine (UTM) is a multipurpose machine which is used to test the mechanical properties of a given test specimen by exerting tensile, compressive or transverse stresses. The term universal is used as machine can perform a wide range of tests over different

kind of materials (metals, polymers, wood, cement etc.). Tests like tensile strength, compressive strength evaluation, peel test, flexural strength evaluation, bend test, friction test, spring test etc. can be performed using UTM.

iii. Procedure:

- i. Gauge length was set to 50mm between vertically aligned jaws.
- ii. The specimen of size 25 mm X 100 mm was fixed between vertically aligned Jaws of Universal Testing Machine (UTM).
- iii. A preload of 0.0010 kgf applied
- iv. Applied a load range of 5.20 kgf
- v. Jaws were set to move at an approach speed of 50mm/min to apply tensile stress over the specimen.
- vi. Specimen was allowed to elongate and fracture.
- vii. Results were recorded on fracture of the specimen.
- viii. Procedure was repeated on 4 specimens of each composition.

The mechanical properties of the all tree compositions is given in Table 4.6.1, 4.6.2 and 4.6.3 respectively.

Table-4.6.1. Mechanical Properties of Composition-1 (PVAc based)

No.	Thick mm	Width mm	E-mod kgf/cm ²	Tensile kgf/cm ²	Max Force kgf	Elong at Max %	Elongation %
1	2.574	25.87	5424	161.3	128.2	5.74	6.42
2	2.630	26.12	5188	154.7	122.0	5.57	6.23
3	2.588	25.64	4998	152.2	118.7	5.45	6.08
4	2.624	26.25	5409	158.4	129.1	5.83	6.48
	Mean		5254.75	156.65	124.5	5.64	6.30
	Std.Dev.		175.22	3.47	4.32	0.14	0.16

Table-4.6.2. Mechanical Properties of Composition-2 (PVB based)

No.	Thick mm	Width mm	E-mod kgf/cm ²	Tensile kgf/cm ²	Max Force kgf	Elong at Max %	Elongati on %
1	2.540	25.36	3758	107.7	80.8	8.47	8.90
2	2.500	25.31	4140	125.7	92.7	9.68	10.48
3	2.550	25.38	3969	116.5	87.7	9.15	9.56
4	2.770	25.55	3892	114.1	87.1	8.93	9.34
Mean			3940	116.0	87.1	9.06	9.57
Std.Dev.			159.65	7.45	4.89	0.50	0.67

Table-4.6.3. Mechanical Properties of Composition-3 (PVC based)

No.	Thick mm	Width mm	E-mod kgf/cm ²	Tensile kgf/cm ²	Max Force kgf	Elong at Max %	Elongati on %
1	2.639	25.57	3733	110.2	94.7	9.86	10.36
2	2.630	25.29	4078	120.3	102.1	10.20	10.52
3	2.580	26.21	4562	141.8	106.1	10.26	10.82
4	2.640	25.82	4304	124.6	96.7	9.91	10.30
Mean			4169	124.2	99.9	10.06	10.50
Std.Dev.			351.34	13.16	5.16	0.20	0.23

4.7. Performance Prediction of Combustible Cartridge Case compositions using Software:

Performance prediction is key step for development of CCC. The ballistic performance of CCC is determined by the pressure time (P-t) profile. Force constant is one of the very crucial parameter for determining the P-t profile. Along with pressure time profile, pressure space is also a key factor. Prediction of the P-t for various propellant configurations are well established and well reported. Modelling the simultaneous burning of CCC and propellant is complicated and requires special efforts.

The input parameters required for prediction of performance parameters are given below;

- i. Physical parameters;
 - ii. Propellant Geometry Parameters : Web size, Form factor
 - iii. CCC Parameters : Inner diameter, Outer diameter, Length
 - iv. Gun Parameters :- Calibre, Chamber capacity, Shot mass
 - v. Interaction or practical terms: - Charge Mass Shot start pressure
-
- I. Control parameters: Time step for calculation, Shot Travel length
 - II. Propellant / CCC related parameters related to ballistic performance:

Some important Propellant / CCC related terms are: - Force constant, Co-volume, Linear burn rate coefficient, Specific heat ratio, Density

- i. Force Constant (F): It is maximum amount of work done by unit mass of propellant/CCC. It is measure of energy of the propellant/CCC and is given by:

$$F = n.R.T_o$$

Where, n= Number of moles of gases formed on combustion of propellant

R = Gas constant = 8.314 4621(75). J K⁻¹ mol⁻¹; and

T_o = Flame temperature in Kelvin

- ii. Co-volume (η): It is the volume occupied by the gaseous molecules of the product of combustion per unit mass of propellant/CCC. It is not sensitive to small changes in the composition and can only be determined experimentally by difference method.
- iii. Linear burn rate coefficient (β_1): Propellant deflagrates during burning. It burns in layers (Poibert's Law 1839). The burn rate of propellant depends on the pressure, calorimetric value, density, thermal conductivity, initial propellant temperature, particle size of crystalline ingredient, moisture content, degree of gelatinisation etc.

Veille's law (1893) :- Power law burn rate, $r = \beta \cdot P^\alpha$

Where, r = Burn rate of propellant cm/sec

P = Pressure exerted by expanding gases

β = Burn rate co-efficient; and

α = Pressure Index (exponent)

Since value of ' α ' lies between 0.8 -0.9, for practical situations value of α is taken =1.0; which gives an assumption of linear burn rate variation

$$r = \beta_1 P$$

Where, β_1 = Linear burn rate coefficient

P = Pressure exerted by expanding gases

- iv. Specific heat ratio (γ): The ratio of specific heat of gases at constant pressure and constant volume is taken at the mean condition prevailing in the gun. It is higher for cool propellants.
- v. Density (ρ): Propellant density signifies consolidation during manufacture and indicates states of porosity in the finished propellants. It is equal to mass per unit volume of propellant used.

III. Propellant Geometry Parameters

- i. Web size (D): Gun propellant charges are available in various shapes, like cord, square flakes, ribbons, slotted tubes, multi-hole tubular, rosette shaped, and aspirin shaped etc. Web is the minimum distance between the adjacent parallel burning surfaces of a propellant configuration.
- ii. Form factor (θ): Form factor relates instantaneous burning surface area or the web left with the mass of propellant consumed. It generates nature of burning pattern envisaged in course of propellant burning.

The technique of measuring the value of Web size (D) & Form factor (θ) for differently shaped propellants is not same. The determination of these parameters is carried out as per algorithm given in Table 4.7.1

Table 4.7.1 Web size (D) & Form factor (θ) of differently shaped propellants

Shape of grain	Web size D	Form factor (θ)
Long cord	Diameter	1
Long tube	wall thickness	0
Long slotted tube	wall thickness	D^2/Ω , Ω is cross-sectional area of tube
Multi tube	1.15 x distance between holes	-0.172
Ribbon	thickness	$1/\mu$ μ =width of ribbon
Square flake	thickness	$2/\mu$ μ = side of square

The major steps involved in modelling are following

4.7.1. Thermo Chemical And Thermodynamic Computation

The first step for performance parameters of CCC is computation of thermo-chemical constant. Force constant and other parameters like flame temperature, calorific value, mean molecular

heats and correction terms for co-volume in the equation of state etc. are computed using thermo-chemical and thermodynamic equations of Gun Propellant. The input parameters for these computations are the molecular formulae, heats of formation at constant volume and the percentage of the ingredients. In the first step, the program is initialized with an intelligent approximate estimate of the reaction temperature.

Normalized number of moles of formation of combustion products like CO₂, H₂O, N₂ etc. are calculated. The heat of reaction and internal energy is calculated by using Hess's law of constant heat summation, as below:

$$\Delta H_{\text{reaction}}^{\ominus} = \sum \Delta H_{\text{f (products)}}^{\ominus} - \sum \Delta H_{\text{f (reactants)}}^{\ominus}$$

If the internal energy is equal to the heat of reaction, then the estimated temperature is same as the actual reaction temperature, otherwise, the reaction temperature is iterated and the process is repeat till acceptable results are obtained. The process is explained in detail by Rao KP [6].

A computer program is developed and using the program the parameters are calculated for all three types of CCC compositions under consideration. The predicted values generated through computer program are shown in Table 4.7.2(a), (b) and (c).

NAME CODE	WT, %	C	H	N	O	MW, g/mol	OB, %	% N	HoF, cal/g
1	70.00	06.00	07.68	02.32	09.64	266.65	-37.17	12.20	-641.40
2	15.00	06.00	10.00	00.00	05.00	162.14	-118.4	00.00	-1421.00
3	15.00	04.00	06.00	00.00	02.00	86.09	-167.2	00.00	-1225.93
4									
EQV COMPOSITION									
COMP01	100.0	5.34	7.53	1.15	6.31	188.9	-68.9	8.5	-846.0

C	H	N	O	HoF, cal/g
.028263	.039854	.006087	.033397	-846.0
Loading Density, g/cc 0.2 Prop Temp, K 300				
Preliminary Estimate of Parameters				
n	.051234	Cv	.3699	T, K 1158.5
Product of Combustion: Iteration number 2				
CO2	CO	H2O	H2	N2
.00246	.02581	.00268	.01725	.00304
OH	H	NO	O2	O
.0000000	.0000000	.0000000	.0000000	.0000000
N	T, K	n	Heat, Cal/g	Int E, cal/g
.0000000	1125.1	.051234	1074.0	1075.26
T-1, K	T-2, K	T-3, K	T-4, K	Error, cal/g
1125.14	1121.95			1.27

Output Parameters after Iteration	
Loading Density, cc/g	.2000
Heat of Formation, cal/g	-846.00
Flame Temperature, K	1121.95
Force Constant, J/g	477.92
Number of Moles, n	.051234
Molecular weight	19.52
Gas Volume, cc/g	1148.35
Internal Energy, cal/g	229.26
Calorimetric Value, cal/g	254.83
Specific Heat, Cv, cal/g/K	.36976
Gamma, Cp/Cv	1.27532
H of Combustion, cal/g	3155.41
Gas Pressure, MPa	123.78
Co-Volume, cc/g	1.13913

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Table 4.7.2(a). Thermochemical prediction of composition-1 (PVAc based):

NAME CODE	WT, %	C	H	N	O	MW, g/mol	OB, %	% N	HoF, cal/g
1	70.00	06.00	07.68	02.32	09.64	266.65	-37.17	12.20	-641.40
2	15.00	06.00	10.00	00.00	05.00	162.14	-118.4	00.00	-1421.00
3	15.00	10.00	18.17	00.00	03.12	188.38	-220.4	00.00	-949.41
4									
EQV COMPOSITION									
COMP02	100.0	6.73	10.10	1.40	7.46	230.1	-76.9	8.5	-804.5

C	H	N	O	HoF, cal/g
.029252	.043900	.006085	.032425	-804.5
Loading Density, g/cc 0.2 Prop Temp, K 300				
Preliminary Estimate of Parameters				
n	.054245	Cv	.3797	T, K 996.6
Product of Combustion: Iteration number 2				
CO2	CO	H2O	H2	N2
.00243	.02682	.00074	.02121	.00304
OH	H	NO	O2	O
.0000000	.0000000	.0000000	.0000000	.0000000
N	T, K	n	Heat, Cal/g	Int E, cal/g
.0000000	950.5	.054245	987.4	987.56
T-1, K	T-2, K	T-3, K	T-4, K	Error, cal/g
950.49	949.97			.20

Output Parameters after Iteration	
Loading Density, cc/g	.2000
Heat of Formation, cal/g	-804.50
Flame Temperature, K	949.97
Force Constant, J/g	428.44
Number of Moles, n	.054245
Molecular weight	18.44
Gas Volume, cc/g	1215.84
Internal Energy, cal/g	183.06
Calorimetric Value, cal/g	190.62
Specific Heat, Cv, cal/g/K	.38107
Gamma, Cp/Cv	1.28284
H of Combustion, cal/g	3426.30
Gas Pressure, MPa	113.13
Co-Volume, cc/g	1.21290

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Table 4.7.2(b). Thermochemical prediction of composition-2 (PVB based):

NAME CODE	WT, %	C	H	N	O	MW, g/mol	OB, %	% N	HoF, cal/g
1 NC12.2	70.00	06.00	07.68	02.32	09.64	266.65	-37.17	12.20	-641.40
2 CELLULOSE	15.00	06.00	10.00	00.00	05.00	162.14	-118.4	00.00	-1421.00
3 PVC	15.00	02.00	03.00	00.00	00.00	62.50	-140.81	00.00	-316.01
4									
EQV COMPOSITION									
COMP03	100.0	4.39	6.15	1.02	5.03	168.1	-64.9	8.5	-709.5

C	H	N	O	HoF, cal/g
.026122	.036594	.006069	.029930	-709.5
Loading Density, g/cc 0.2 Prop Temp, K 300				
Preliminary Estimate of Parameters				
n	.047454	Cv	.3378	T, K 1206.1
Product of Combustion: Iteration number 2				
CO2	CO	H2O	H2	N2
.00169	.02444	.00212	.01618	.00303
OH	H	NO	O2	O
.0000000	.0000000	.0000000	.0000000	.0000000
N	T, K	n	Heat, Cal/g	Int E, cal/g
.0000000	1174.9	.047454	933.0	935.41
T-1, K	T-2, K	T-3, K	T-4, K	Error, cal/g
1174.90	1168.83			2.42

Output Parameters after Iteration	
Loading Density, cc/g	.2000
Heat of Formation, cal/g	-709.50
Flame Temperature, K	1168.83
Force Constant, J/g	461.15
Number of Moles, n	.047454
Molecular weight	21.07
Gas Volume, cc/g	1063.62
Internal Energy, cal/g	225.91
Calorimetric Value, cal/g	244.80
Specific Heat, Cv, cal/g/K	.33740
Gamma, Cp/Cv	1.27946
H of Combustion, cal/g	2980.67
Gas Pressure, MPa	117.65
Co-Volume, cc/g	1.08029

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Table 4.7.2(c). Thermochemical prediction of composition-3 (PVC based)

4.7.2. Ballistic Predictions:

Once the properties of gun propellant & CCC are predicted, the pressure time profile of CCC and propellant is computed. The pressure time profile is computed by applying the time marching technique [7] using MATLAB-2015 software. The general steps involved in prediction of pressure time profile inside the barrel with propellant is given below.

- Initially shot remains stationary, and the propellant is initiated.
- Combustion gases start generating pressure behind the shot.
- Combustion occurs at constant volume till shot moves.
- Sufficient web is consumed before shot movement.
- Shot moves when shot start pressure is achieved.
- After shot movement, extra volume is realized.
- Rate of generation of gases surpasses rate of volume generation.
- Pressure continues to rise and shot continues to move.
- Complete propellant is consumed at around 1/3rd barrel length.
- Shot continues to move in the barrel, due to gained inertia and expanding gases.
- Calculation is continued till shot emerges out of the barrel.

Conventionally, it is assumed that the gases which are responsible for the rise in pressure in the barrel is generated only because of gun propellant. For calculating the pressure inside barrel, the mass of the propellant burned, as a function of time is calculated using lumped parameter codes.

However, when the round is made up of CCC, the gases are also generated because of CCC. The burning characteristic of CCC is completely different from the burning characteristics of the propellant. The burn rate coefficient, geometry etc of CCC is not similar to the gun propellant. Hence the gas generated because of burning of CCC, is required to be calculated separately. The different grain geometry of propellant and CCC is shown in Fig 4.7.2 (a) and (b) respectively.

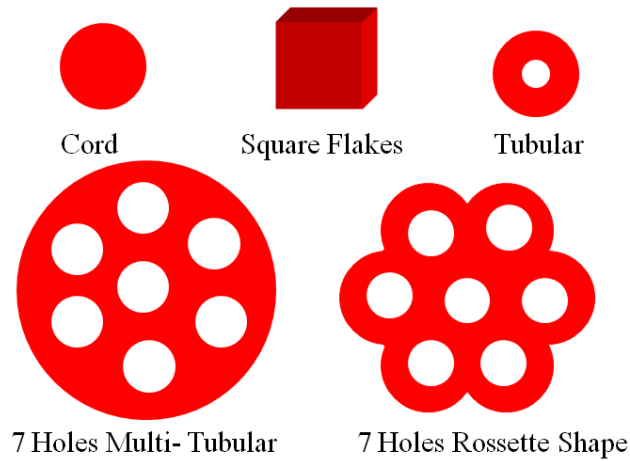


Fig 4.7.2(a). Geometrical representation of propellant grains



Fig 4.7.2(b). The grain geometries of CCC

The burning surface area is calculated for the given geometry. The burning surface area of CCC is nearly constant, as, all the dimensions are much larger than the web. The web will be equal to the thickness of the CCC. Being a porous material, the thickness of CCC is not constant. Hence for the computations, it is assumed that the static compressibility of CCC is the constant. Using the globally reported values, the thickness is assumed to be half the original value.

Propellant and CCC burns simultaneously. The burning of CCC taking place on the outside periphery of CCC material, in-depth burning (i.e., burning within the material) might also be present. The mass of gas generated because of burning of CCC is

$$\dot{m} = \rho S \frac{dx}{dt} ,$$

Where, ρ is the density of CCC, S , is the total surface area of CCC, and dx/dt the linear burning rate of the propellant. The linear burning rate is pressure dependent and increases with pressure. The relation is well known

$$r = \beta * P^\alpha$$

Where, r = Burn rate of Combustible cases cm/sec

P = Pressure exerted by expanding gases

β = Burn rate co-efficient; and

α = Pressure Index (exponent)

The mass of gas generated will increase with pressure, so, at every step of time, the rate of mass generated increases with increasing pressure.

Under these considerations, the rise in pressure because of gas generation due to combustion of CCC & propellant is calculated with following assumptions:

- Nobel-Abel equation of state is valid for gaseous product of combustion.
- Gas expands isentropically.
- Pressure is independent of spatial coordinates.
- All gaseous properties are independent of pressure and temperature.
- Trapped air is not influencing calculation.
- All the propellant charges has same geometry. They are homogenous and all the exposed surfaces ignite simultaneously.
- Propellant burns in layers and shape of propellant is not changed during burning.

Modelling & Simulation Results

Input Parameter

Table-4.7.3 Input parameters for Gun Internal Ballistics

Input parameters for Gun Internal Ballistics		
Calibre	100	Mm
Shot Travel	500	Cm
initial free volume	800	Cc
Shot Mass	5	Kg
Shot Start Pressure	5	Mpa
Charge Mass	0.1	Kg
Force Constant	1160	J/g
β_1	0.25	cm/s/Mpa
Web size	0.15	Mm
Gamma	1.25	
Time step	0.0001	Ms
Force Constant of CCC 1	477.92	J/g
Force Constant of CCC 2	461.15	J/g
Force Constant of CCC 3	428.44	J/g
Density of CCC	0.9	g/cc
Dimension of CCC	ID 100, OD 102.5 Length 20	Mm

The simulated pressure time, distance time and velocity time curve without CCC (propellant alone) is shown in Figure 4.7.3.

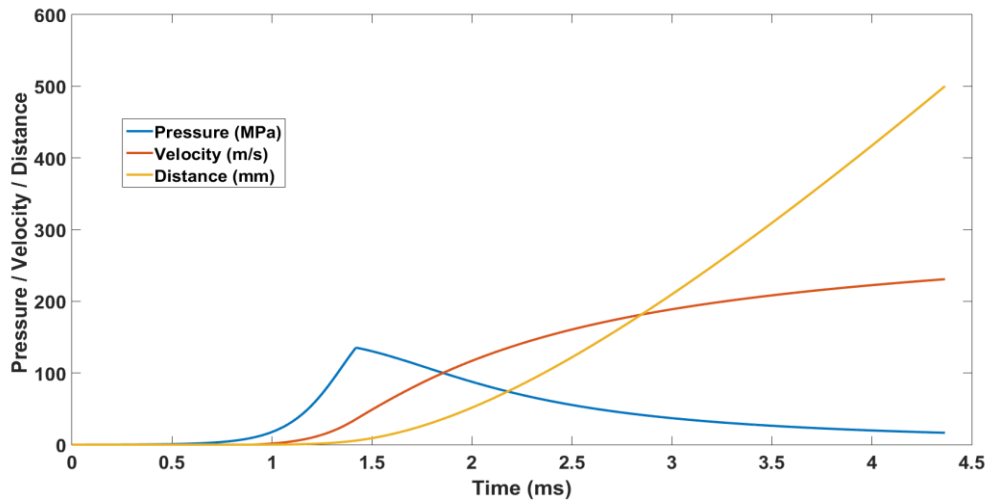


Fig 4.7.3. Pressure-time, distance-time and velocity-time curves for propellant

The pressure-time, distance-time and velocity-time curves with CCC is shown respectively in Figure 4.7.4(a), (b) and (c). Fig. 4.7.4(a) shows the curve for CCC with maximum Force (PVAc based) Constant (FC) i.e 477.92 J/g.; Fig 4.7.4(b) shows the curve for CCC with FC of 461.15 (PVC based); & Fig. 4.7.4(c) shows the curve for minimum FC i.e. 428.44 (PVB based).

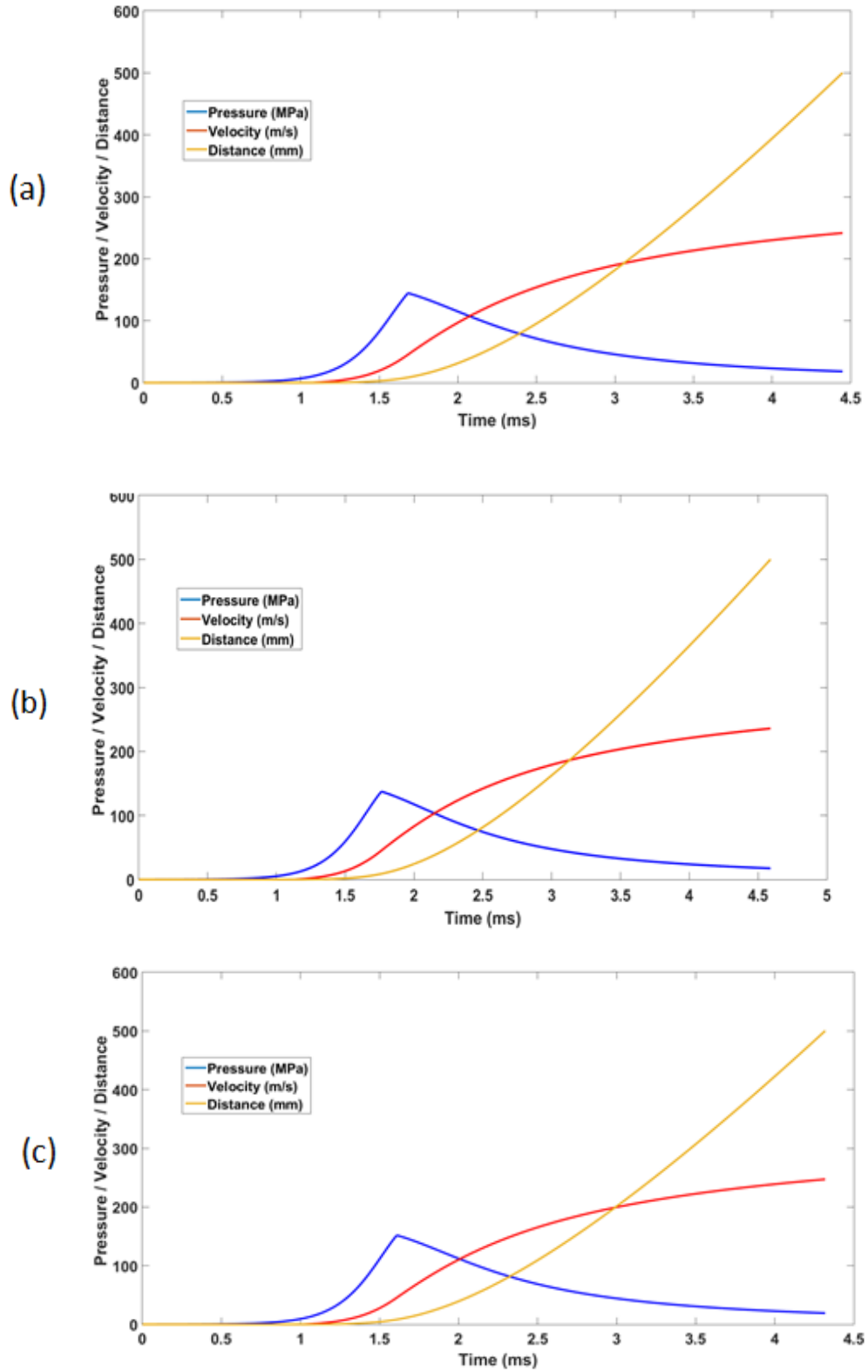


Fig 4.7.3. Pressure-time, distance-time and velocity-time curves for: (a) PVAc based CCC, (b) PVB based CCC, (c) PVC based CCC

4.8. Discussion of Results:

The outcome of each investigation is discussed in following paras;

4.8.1. Processibility:

The processibility of the resins was studied by the virtue of viscosity measurement, evaluated for the same amount of non-volatile material. The rheological behaviour has been observed with varied shear rates. PVAc-Cellulose, PVB-Cellulose, and PVC-Cellulose blends exhibit shear thinning, Newtonian, and shear thickening behaviour at low shear rates, however all blends exhibit the same Newtonian behaviour at high shear rates, as illustrated in Fig 4.3.1 (a), (b), and (c). PVAc-Cellulose, PVB-Cellulose, and PVC-Cellulose rheological properties were also investigated at constant shear rates of 50 and 100 sec⁻¹, as shown in Fig. 2. All the liquid samples were tested at shear rate =50 sec⁻¹ as shown in Fig. 4.3.2(a) and at the shear rate =100 sec⁻¹ shown in Fig. 4.3.2(b). At varying shear rates, all of the samples showed varied rheological behaviour. However, the viscosities for the three blends showed considerable variation with respect to each other. The blends with PVAc, PVB and PVC have the viscosity values in the order of 1Poise, 10Poise and 100 Poise respectively. So based on the results of viscosity measurement it can be concluded that the PVB resin may be processed in slurry, but the PVC resins is advisable to be processed with extrusion process.

4.8.2. Thermal Stability:

Thermal stability was investigated through thermo gravimetric analyser instrument. In all three blend systems, a single degradation was found. The initial degradation temperature of PVAc-NC-Cellulose, PVB-NC-Cellulose, and PVC-NC-Cellulose is approximately 192°C, 194°C, and 186°C, respectively, while the second degradation temperature of the same samples is around 201°C, 205°C, and 195°C, respectively. According to the initial and second degradation temperatures, PVB-NC-Cellulose is the most thermally stable system, PVC-NC-Cellulose is the least thermally stable system, and PVAc-NC-stability Cellulose's is in the middle. However, the stability of all three compositions fulfils the basic requirement of the blend system to be used in the CCC as the degradation temperature of each blend is more than 180°C.

4.8.3. Miscibility of Ingredients:

The glass transition temperature of PVAc, PVB and PVC are 28.7, 68 and 78°C respectively. For a polymer blend of two or more polymers, Differential scanning Calorimetry (DSC) analysis is one of the methods that can be used for determining the miscibility of the final solution/blend. If we get a single glass transition temperature, then we can conclude that they are miscible at that specific fraction which is used.

The DSC was run at a temperature range of 25°C to 170°C. DSC curve of PVC-NC-Cellulose blend shows a major peak around 155°C but no peak was observed near Tg of the PVC alone, i.e. at 78°C, hence it is most likely the glass transition temperature of this blend system, which ensure the miscibility of polymers in the blend of three polymer system, In other two samples, no peak was observed till 170°C temperature, hence, the glass transition temperature of other two blends i.e. PVAc-NC-Cellulose and PVB-NC-Cellulose is more likely to occur, when the temperature exceeds 170°C.

Hence, it may be concluded that the polymeric binders under study exhibit good miscibility in the blend with cellulose and nitrocellulose.

4.8.4. Mechanical Properties:

The compositions were investigated through Universal testing machine (UTM). The comparison of mechanical properties is given in Table-4.8.4

Table- 4.8.4. Comparative data of mechanical properties

Binder Resin Used	Average Tensile Strength (kgf/cm²)	Average Elongation (%)
PVAc	156.65	4.5
PVB	116	9.57
PVC	124.2	10.5

The composition with PVAc as binder resin exhibit better mechanical properties, than those with PVB and PVC, but the far better value of glass transition temperature (T_g) PVB=68°C and PVC=78°C against PVAc=28°C makes these resins advisable to be used in CCC composition, fully or partly as binder resin. Hence further studies are advisable on this subject.

4.8.5. Ballistic Performance:

The ballistic performance of the compositions was evaluated in two steps. The results of first step (Thermochemical and thermodynamic calculations) is shown in Table 4.8.5, below

Table- 4.8.5. Comparative data of Thermochemical properties

Binder Resin Used	Flame Temperature (K)	Force Constant (J/g)	Gas Volume (cc/g)	Co-volume (cc/g)
PVAc	1121.95	477.92	1148.35	1.13913
PVB	949.97	428.44	1215.84	1.21290
PVC	1168.83	461.15	1063.62	1.08029

From the table, it is evident that the composition with PVB binder resin is having least flame temperature. Less flame temperature means, less risk for the erosion of gun barrel, due to the burning of CCC; at the same time, it generates maximum amount of gases per gram of CCC burnt during firing, and maximum value of Co-volume. More volume of gases generated and higher Co-volume indicates more contribution towards the propulsion of projectile. Hence CCC with PVB as binder resin has proved to be highest contributor during the usage of ammunition.

In second step of simulation pressure time, the distance time and the velocity time curve for bare propellant and full ammunition (CCC along with propellant) against a projectile of known dimension and weight is simulated. The graphs were plotted for prediction of ballistic properties in case of all three compositions.

The comparison of all the four cases i.e. case 1 : Bare propellant, case II : propellant with CCC having FC of 461.15 J/g, case III : propellant with maximum FC i.e. 477.92 J/g and case IV : propellant with minimum FC 428.44 J/g is shown in Figure 4.8.

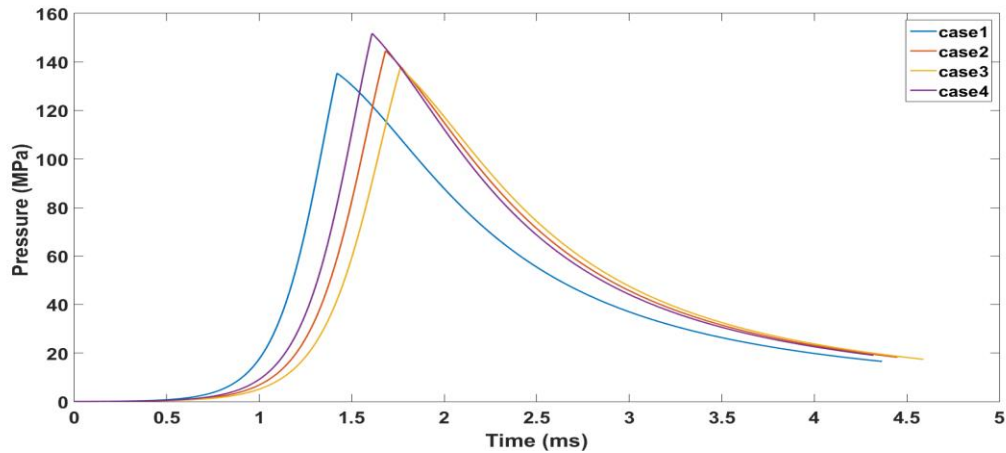


Fig 4.8. Comparative plots of Pressure- Time profile of CCCs

The graphs show very slight variation in ballistic properties in case of all three compositions; however, pressure values for all the composition falls to same point after similar time interval. It ensures the full combustion of the compositions derived with PVB and PVC at par with existing PVAc based composition.

Chapter 5

CONCLUSIONS

In this study, the scope of using different polymeric resins in the composition of CCC was investigated. The composition having polyvinylacetate, NC and Cellulose is presently used in production of CCC. Polyvinylacetate was replaced with polyvinylbutyral and polyvinyl chloride respectively for the study. From the study there are conclusive evidences, that the resin PVAc in CCC composition gives the best mechanical properties, but has a problem of deformation at elevated environmental temperatures. Whereas, the polymeric resin PVB attributes cooler CCC and better propulsion, but lesser mechanical strength. As, PVB has a Tg of 68°C as against 28°C of PVAc, which makes it prominent for the use in CCC as raw material. Hence, further studies on PVB as binder resin in CCC composition may be carried out to introduce and induct this resin in CCC as raw material.

Chapter 6

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