



## Improvements in the Structural Integrity of Resin Based Combustible Cartridge Cases (CCC) at Elevated Temperatures

Abhijit DEY\*, Javaid ATHAR, Siddhartha GOGOI,  
Pradeep B. NAVLE, Arun K. SIKDER\*\*

*High Energy Materials Research Laboratory,  
DRDO, Sutarwadi, Pune, 411 021, India*

*E-mails: \*abhidey\_bkn@yahoo.com, \*\*ak\_sikder@yahoo.com*

**Abstract:** An advanced, solvent-less resin based Combustible Cartridge Case (CCC), designed to resolve the inherent problems of shrinkage and limited mechanical strength associated with the gelatinisation of nitrocellulose, has already been developed. The felt-moulded components contain thermoplastic polyvinyl acetate (PVAc) resin as the binder and the enhanced mechanical strength is achieved by carrying out hot compaction of dry felts at an elevated temperature ( $105 \pm 2$  °C). Presently, resin based technology is adopted for tank gun ammunition and also for the developed modular CCCs, *i.e.* the Modular Combustible Case (MCC) for different types of artillery gun ammunition. However, during exhaustive trials conducted with the resin based CCCs in 120 mm tank gun ammunition at three temperatures, *i.e.* -10, 27 and 55 °C, severe geometrical deformation was noticed when the rounds were conditioned at 55 °C for 24 h., adversely affecting the loading of rounds into the gun chamber. This was attributed to the combined effects of softening of the resin at that temperature and the load of the projectile/shell (14.4 kg) experienced by the CCC region during conditioning of the round in the horizontal mode. In order to resolve this problem of deformation, PVAc resin was required to be modified. The PVAc resin was modified to the form of a nanocomposite. PVAc nano composite was prepared by dispersing organically modified nano clay, *i.e.* Cloisite 30B, into the resin before making the CCCs. The nanocomposite of PVAc resin was characterized by FTIR, DMA, softening point measurement *etc.* The results showed a remarkable improvement in the glass transition temperature ( $T_g$ ) and in the softening temperature of the modified PVAc resin. This modified PVAc resin was used to prepare CCCs. Furthermore, these CCCs were coated with hexamethylene diisocyanate (HMDI) on the inner and the outer surfaces. The isocyanate coating becomes crosslinked in the matrix, thereby improving the softening point as well as the mechanical properties of the CCCs.

These modified CCCs were repeatedly tested at 55 and 60 °C for 24 h. After testing, it was found that no deformation had taken place and the assembled rounds were easily loaded into the gun chamber. The use of the PVAc nanocomposite in the preparation of resin based CCCs, followed by isocyanate coating, is an effective means of achieving the required improvement in structural integrity of the resin CCCs at elevated temperatures.

**Keywords:** CCC, deformation, PVAc, ammunition, cartridge, gun

## 1 Introduction

Conventional metallic cartridge cases and cloth bag charges, used in tank and artillery gun ammunition respectively, are being replaced globally with Combustible Cartridge Cases [1-3] (CCCs) in modern warfare because of their usefulness at higher chamber pressures and higher firing rates. CCCs are also being widely used because they impart energy to the system and no residue/ash/char is left behind after firing. CCCs house the propellant charge and the ignition system. In the case of 120 mm tank gun ammunition, the rear end of the CCC is fitted with a metallic stub, which acts as an obturator. The projectile or shell (wt. 14.4 kg) is attached to the forward end of the CCC.

According to the literature, the application of polyurethane [4], vinyl [5], acrylic [6], and styrene-butadiene [7] type resins for the manufacture of CCCs has already been reported. Different processing methods have also been highlighted [8-15], such as impregnation of the resin in the felted combustible components in order to obtain the desired mechanical properties, felt-moulding, and winding. However, the information reported in the literature is either classified or patented. Recently, an advanced, solvent-less resin based CCC has been developed by felt-moulding techniques in order to resolve the inherent problems of shrinkage and limited mechanical strength associated with CCCs made through felt-moulding and compaction at ambient temperatures of the gelatinised CCC matrix. Here, the felt-moulded components contain thermoplastic PVAc resin as a binder and enhanced mechanical strength is achieved by carrying out hot compaction of the dry felts at an elevated temperature (105 °C). Currently, resin based technology has been adopted for artillery tank gun ammunition.

However, during the exhaustive dynamic trials conducted with the resin based CCCs in 120 mm tank gun ammunition, marginal geometrical deformation was noticed when the rounds were conditioned at 55 °C, adversely affecting the loading of rounds into the gun chamber. This was attributed to the combined effect of softening of the resin at that temperature and the load of the projectile/

shell experienced by the CCC region during the conditioning of the round in the horizontal mode.

Nanocomposite technology is a new area in polymeric materials. While the science of the filling of thermoplastics and thermosets in order to increase their stiffness has been practiced for many years, the need to add large amounts of filler would often increase the stiffness of the thermoplastic while decreasing other desirable properties, particularly impact properties. Most products require a balance between stiffness and impact, and this need has been met using layered silicate structures at loadings of 10% or less. These nanosilicates or nanoclays enhance the mechanical, thermal, dimensional and barrier properties.

The resistance to fracture of a material is known as its fracture toughness. Fracture toughness generally depends on the temperature, the environment, the loading rate, the composition of the material and its microstructure, together with geometric effects (constraint).

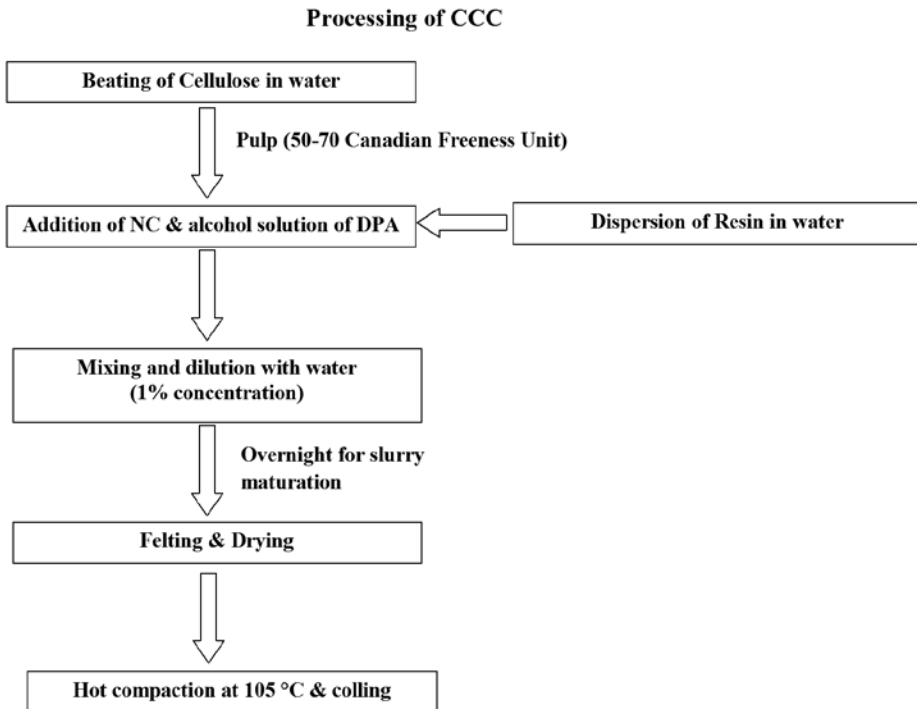
Therefore, the issues related to the geometrical deformation of a resin based CCC in 120 mm tank gun ammunition at 55 °C needed to be resolved in order to develop reliable ammunition. This article explains how the deformation problem has been overcome at elevated temperatures by modifying the existing PVAc resin with organo-clay as a reinforcing agent, followed by application of HMDI as a surface coating.

## 2 Materials and Methods

Nitrocellulose (12.6% N content) was obtained from the ordnance factory, PVAc resin was obtained from Pidilite Industries, Mumbai, cellulose and DPA of desired purity were obtained from trade sources. Table S1 to S7 (see Electronic Supporting Information) shows the analytical data for these ingredients.

The existing formulation contained  $71 \pm 1\%$  of NC (12.6% N content) as the main energetic ingredient,  $12 \pm 0.5\%$  cellulosic fibers as reinforcing material,  $16 \pm 0.5\%$  modified PVAc as a binder and 1% DPA as a stabilizer. To eliminate the deformation problem, a nanofiller such as organo clay (Cloisite® 30B) was used at 4% to improve the overall dimensional stability of the CCCs. Cloisite® 30B is a natural montmorillonite modified with a quaternary ammonium salt. This is reported to be an additive for plastics and rubbers in order to improve various physical properties, such as reinforcement, coefficient of thermal expansion CLTE, synergistic flame retardant and barrier. Cloisite® 30B (Quaternary ammonium salt modified neutral montmorillonite polymer additive) acts as the cation exchange resin, as clay particles has been used here as an additive to the

existing PVAc resin for improving the properties of the PVAc resin. An HMDI coating was applied on the outer and inner surfaces of the CCCs. The detailed process flow chart for CCC processing is shown below in Figure 1.



**Figure 1.** Process flow chart of Combustible Cartridge Case (CCC) preparation.

In order to eliminate softening of the PVAc resin at 55 °C and to control the structural integrity of the resin CCCs, the following approaches have been adopted.

#### *Experiment 1: Modification of the PVAc resin*

The inherent moisture (typically 2 wt%) present in organo clay was removed before mixing with the PVAc resin. The existing PVAc resin was modified by adding organo-clay (4 parts with respect to PVAc), with mechanical stirring, followed by ultrasonication at 35 kHz for 3 h at 40 °C in order to obtain an homogeneous mixture of PVAc-nano clay (PVAc-nanoclay mix).

Initially, CCC discs were prepared for evaluation of the PVAc-nanoclay mix. The Beater additive technique, followed by hot compaction, was used to

prepare the discs. A slurry was prepared by pulping cellulosic fibers to the desired freeness (50-70 Canadian Freeness Units) in an aqueous medium in a beater. A weighted quantity of NC and an alcoholic solution of DPA were mixed. The required quantity of diluted PVAc-nanoclay mix was then added with constant stirring. After thorough mixing and dilution of the slurry with water to achieve the required concentration (1%), the slurry introduced to a disc making machine to prepare the discs under vacuum. The thickness and weight of the discs were controlled by feeding an appropriate quantity of slurry. The discs were dried in a steam heated oven at  $60 \pm 5$  °C. The strength of the dry felt was further improved by pressing the each disc in preheated metal moulds for a specified duration (3 min preheating and 2 min compaction) using a hydraulic press at a specific pressure. The pressed discs were cooled to ambient temperature and evaluated for their physico-mechanical properties.

The density of the resin based CCC discs was determined by ‘Archimedes’ principle. For the determination of the mechanical properties, test samples were prepared by cutting strips of size  $100 \times 25 \times 2.5$  mm and tested for tensile strength and elongation using Universal Testing Machine (UTM). For the purposes of the deformation study, CCC liners and caps with modified resin were prepared, using the same slurry procedure, felt moulding and hot compacting as enumerated earlier. Ammunition preparation was carried out and these were subjected for a deformation study at 55 °C for 24 h in a SCADA controlled water-jacketed oven.

The glass transition temperatures ( $T_g$ ) were evaluated using a Dynamic Mechanical Analyzer (DMA). After scanning the sample under test, any of the viscoelastic parameters such as storage modulus, loss modulus and  $\tan \delta$  could be used to define the  $T_g$ . The figures given in the Supporting Information (Figures S1, S2 and S3) were obtained in three frequency ranges, *i.e.* 3.5, 11 and 35 Hz, with a ramp rate of 10 °C/min.

The  $T_g$  related to  $E'$  onset occurs at the lowest temperature and is associated with mechanical failure.  $E''$  peak occurs at the middle temperature and is more closely related to the changes in physical properties attributed to the glass transition in plastics. It reflects molecular processes and agrees with the idea of  $T_g$  being the temperature at the onset of segmental motion.  $T_g$  related to the  $\tan \delta$  peak occurs at the highest temperature and has been used historically in the literature. It is a good measure of the leather-like midpoint between the glassy and the rubbery states of a polymer. The height and shape of the  $\tan \delta$  peak change systematically with the amorphous content.

Measurements of the softening point of CCC samples were carried out using a pushrod dilatometer (Model: Unitherm 1000). The temperature at which the

thermal expansion coefficient changes from positive to negative, denotes the softening point.

*Experiment 2: Application of surface coating on existing resin based CCCs*

Epoxy coating was applied to the existing PVAc resin based CCCs on the inner surface (in one case) and on both inner and outer surfaces (in another case). CCCs thus modified were assembled with a steel cup, primer, propellant, and projectile/shell and the round was conditioned at 55 °C for 24 h.

*Experiment 3: Modification of PVAc resin and the application of a surface coating (thin) of HMDI on modified resin based CCCs*

An HMDI coating was applied on both the inner and the outer surfaces (thin coating) of modified PVAc resin based CCCs, made as described in Experiment 1. CCCs thus modified were assembled with a steel cup, primer, propellant, and projectile/shell and the round was conditioned at 55 °C for 24 h in a water-jacketed oven with a SCADA interface.

*Experiment 4: Modification of PVAc resin and application of a thick surface coating of HMDI on modified resin based CCCs*

An HMDI coating (thick) was applied on both the inner and the outer surfaces of the cap of modified PVAc resin based CCCs, made as described in Experiment 1. CCCs thus modified were assembled with a steel cup, primer, propellant, and projectile/shell and the round was conditioned at 55 °C for 24 h in a water-jacketed oven.

*Experiment 5: Comparative as well as repeatability testing of Experiment 4*

Modified PVAc resin based CCCs were made as described in Experiment 4 and assembled with a steel cup, primer, propellant, and projectile/shell to form a round. The rounds were then subjected to deformation studies at a conditioning temperature of 55 °C, as well as 60 °C, for 24 h in a water-jacketed oven.

### **3 Results and Discussion**

Table 1 shows the mechanical properties of resin CCCs, surface coated resin CCCs, and surface coated modified resin CCCs. The results show a 40% decrease in tensile strength after the application of a surface coating on resin CCCs. In sample III, a 25% increase in tensile strength was observed.

**Table 1.** Mechanical properties

Sl. No.	Mechanical properties	Resin CCC (I)	Surface coated resin CCC (II)	Surface coated modified resin CCC, (III)
1	Tensile strength, [MPa]	21.4	22.8	26.5
2	Elongation, [%]	10	4	5

Table 2 gives the glass transition temperature ( $T_g$ ) of samples I, II and III. The  $T_g$  was evaluated from the  $E''$  peak and the  $Tan \delta$  peak. For our system,  $T_g$  related to the  $Tan \delta$  peak is more relevant than that from the  $E''$  peak. The  $T_g$  is decreased in sample II by 6% compared to sample I. However in sample III, a 35% increase in the  $T_g$  value was observed compared to sample I, reflecting the improvement in structural integrity in the CCC matrix.

**Table 2.** Dynamic mechanical analysis

Sl. No.	DMA properties	Resin CCC (I) $T_g$ , [°C]	Surface coated resin CCC $T_g$ , [°C]	Surface coated modified resin CCC $T_g$ , [°C]
1	Peak $E''$	50.3	48.5	63.9
2	Peak $Tan \delta$	55.9	52.1	76.9

Remarkable increases in the softening point were observed in sample III compared to sample I. These results in Table 3 supports the DMA results.

**Table 3.** Softening point results

Sl. No.	Thermal properties	Resin CCC (I) [°C]	Surface coated resin CCC (II) [°C]	Surface coated modified resin CCC, (III) [°C]
1	Softening point	32 28	38 38	56 55

The energetic properties are expressed in terms of the force constant, *i.e.* J/g. This property was evaluated through a closed vessel firing of a strip having dimensions of 100 (l)  $\times$  25 (w)  $\times$  2.5 mm (t), and about 140 g of material was used for the firing. The force constant of regular CCCs was found to be 621 J/g. In the present compositions, the force constant of CCCs was found to be 620 J/g, showing negligible change. In a tank gun, the firing of a CCC is a millisecond phenomenon. Hence, during evaluation, the rise time is measured in place of the burn time. For regular CCCs, the rise time was found to be 1.9-2.7 ms. The





rise time in the present compositions was also in the same range, *i.e.* 2.2-2.9 ms. Table 4 gives the energetic properties and the rise time.

**Table 4.** Force constant and rise time

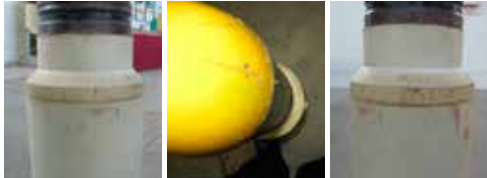



Sl. No.	Properties	Resin CCC (I) [°C]	Surface coated modified resin CCC, (III) [°C]
1	Force constant, [J/g]	621	620
2	Rise time, [ms]	1.9-2.7	2.2-2.9

For the purposes of the actual effects on their structural integrity, CCCs with the above compositions were made as described in the experimental section, and, after modification of the CCCs with and without coating, rounds were prepared with a steel cup, primer, propellant, and projectile/shell and tested at 55 °C, as well as 60 °C (for a confirmatory test), for 24 h. Several experiments were performed and the results are shown below (Table 5).

**Table 5.** Different experimental results after conditioning

Exp No.	Experiment	Test Condition	Observation
1	71% of NC (12.6% N content), 12% cellulosic fibers and 16% <b>modified polyvinyl acetate</b> as a binder and 1% DPA as a stabilizer.	55 °C for 24 h	  <p><b>Fig. 2.</b> Regular CCC. <b>Fig. 3.</b> Modified CCC.</p> <p>Comparatively less deformation (50% deformation eliminated) was observed in the Modified CCC after conditioning.</p>
2	71% of NC (12.6% N content), 12% cellulosic fibers and 16% <b>regular polyvinyl acetate</b> as a binder and 1% DPA as a stabilizer. > Inside coating (Figure 4). > Inside and outside coating (Figure 5).	55 °C for 24 h	  <p><b>Fig. 4.</b> Inside coated. <b>Fig. 5.</b> Inside and outside coated.</p> <p>In both cases deformation was observed. In the case of Fig. 5 (both side coating), much higher deformation was observed compared to inside only coating (Fig. 4).</p>



<p>3</p>	<p>71% of NC (12.6% N content), 12% cellulosic fibers and 16% <b>modified polyvinyl acetate</b> as a binder and 1% DPA as a stabilizer.                  &gt; coating of both sides of CCC with HMDI (thin coating).</p>	<p>55 °C for 24 h</p>	 <p><b>Fig. 6.</b>      <b>Fig. 7.</b>      <b>Fig. 8.</b></p> <p><b>Figs. 6, 7, 8</b> show different views of the modified CCC; slight deformation was observed (about 90% improvement). Further improvement is required to eliminate the deformation completely.</p>
<p>4</p>	<p>71% of NC (12.6% N content), 12% cellulosic fibers and 16% <b>modified polyvinyl acetate</b> as a binder and 1% DPA as a stabilizer.                  &gt; HMDI coating was applied on both inner and outer surfaces of the cap (thick coating).</p>	<p>55 °C for 24 h</p>	 <p><b>Fig. 9.</b>      <b>Fig.10.</b>      <b>Fig. 11.</b></p> <p><b>Figs. 9, 10, 11</b> show different views of a modified CCC cap. By both visual and actual measurement, no deformation was observed. The area marked was found to be unaffected by load at 55 °C.</p>
<p>5</p>	<p><b>Comparative as well as repeatability test of Experiment 4:</b></p> <p>71% of NC (12.6% N content), 12% cellulosic fibers and 16% <b>modified polyvinyl acetate</b> as a binder and 1% DPA as a stabilizer.                  &gt; HMDI coating was applied on both inner and outer surfaces of the CCCs (thick coating).</p>	<p>Conditioning pattern at +55 °C and +60 °C</p>	 <p><b>Fig. 12.</b> Conditioning pattern at 55 °C as well as 60 °C.      <b>Fig. 13.</b> Rds before conditioning.</p>  <p><b>Fig. 14.</b> After conditioning at 55 °C.      <b>Fig. 15.</b> After conditioning at 60 °C.  <b>No deformation was observed.</b></p>

## 4 Conclusions

The dispersion of organo clay (4 parts with respect to PVAc) in the PVAc resin has improved the mechanical properties, as well as the glass transition temperature ( $T_g$ ) of CCCs, and resulted in the elimination of the 80-90% deformation of resin CCCs when a modified CCC round was conditioned at 55 °C for 24 h. Furthermore, when these modified resin CCCs were coated with HMDI both inside and outside, deformation was completely eliminated when the rounds were conditioned at 55 °C, as well as 60 °C, for 24 h. Hence, the structural integrity was remarkably improved by the above mentioned process.

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