Studies on Curing of an Aluminized Ammonium Perchlorate Composite Propellant Based on Nitrile Butadiene Rubber Using a Quinol Ether of 1,4-Benzoquinone Dioxime

Sudhir Singh1*), Sidharth Raveendran1), Dhirendra R. Kshirsagar1), Manoj Gupta1), Chetan J. Bhongale2)

1) High Energy Material Research Laboratory, Sutarwadi, Pune 411021, India
2) Defence Institute of Advanced Technology, Deemed University, Pune 411025, India
*E-mail: sudhirss007@gmail.com

ORCID information
Sudhir S.: https://orcid.org/0000-0002-3901-2733

Abstract: The isocyanate-based curing agents used for polyurethane are toxic and hygroscopic in nature. In the present work, an alternate approach was adopted, a reaction between the unsaturated rubber having an \(\alpha\)-methylene hydrogen atom and a dinitrosobenzene (DNB) – generating system (quinol ether of 1,4-benzoquinone dioxime, QE) without a catalyst, thus generating a cured system. QE is a novel curing agent for propellant applications which imparts the necessary curing. The curing reaction between nitrile butadiene rubber (NBR) and quinol ether (QE) was studied by FTIR and the results revealed the formation of anil groups (Ar–C=\(\equiv\)N). The anil group results from the reaction between NBR and DNB, generated on decomposition of QE. Propellant formulations were prepared with variation of the curing agent from 0.2 to 0.5%. The composition and rheological, mechanical, ballistic and thermal properties of the resulting
cured systems were investigated. The viscosity and spreadability were suitable for casting. The tensile strength, modulus, and hardness show an increasing trend and the elongation decreases on varying QE from 0.2 to 0.5% in the propellant. However, all of the compositions showed nearly the same burning rate and pressure exponent. The QE based curing system is non-hygroscopic and has extremely low toxicity. The experimental results revealed that the proposed curing agent may find application in explosives and propellants.

**Keywords:** dinitrosobenzene, nitrile butadiene rubber, quinol ether, unsaturated rubber

**Abreviations:**
- AP – Ammonium perchlorate
- DBP – Dibutyl phthalate
- DNB – Dinitrosobenzene
- MAC – Maximum allowed contamination [mg/m^3]
- NBR – Nitrile butadiene rubber
- QE – Quinol ether of 1,4-benzoquinone dioxime
- SC – Spreadability coefficient
- TS – Tensile strength
- VA – Vulcanizing additive

1 **Introduction**

Composite solid propellants are a class of special particle reinforced composites, which are commonly used for the energy source of rockets and missiles. Presently, sophisticated weapon systems place greater demands on the comprehensive performance of the propellant charge in the solid rockets or missiles; furthermore, the performance of the propellant under extreme operating conditions depends mainly on the binder matrix [1].

HTPB/AP/Al formulations, *i.e.* composite propellants based on hydroxyl terminated polybutadiene (HTPB), ammonium perchlorate (AP) and aluminum (Al), with 86% solids and cured with isophorone di-isocyanate (IPDI) or toluene di-isocyanate (TDI) are used in most rockets and missiles [2-6]. Isocyanates are extremely toxic, carcinogenic in nature and moisture sensitive. Isocyanates react with water to release CO\(_2\) and form bubbles in the cured propellant, leading to poor mechanical properties. There is a need for strict control of moisture and humidity during processing. The reaction rate of the hydroxyl group of HTPB with a di-isocyanate is rapid since it has
a primary functional group and consequently the pot life of the propellant slurry is comparatively short [7]. The order of reactivity in uncatalyzed isocyanate (polymerization) reactions typically decreases in the order: primary aliphatic amines > secondary aliphatic amines > aromatic amines > primary alcohols > water > secondary alcohols > carboxylic acids > ureas > urethanes.

The composite propellant formulations processed with an HTPB binder have a limited pot life of 6–8 h [8]. Additionally, isocyanates are incompatible with new energetic oxidizers, such as ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF), etc. Hence there is a need to explore alternative curing systems for replacement of the polyurethane based curing system.

There is continuous worldwide research for the development of new binders and curing agents for propellant application. One of the alternative approaches for curing a propellant is dinitrosobenzene (DNB) and DNB generating compounds [9]. These are widely used for curing rubber based systems. The curing of composite systems based on unsaturated rubbers was carried out using dinitrosobenzene-generating systems. These include compounds such as 1,4-benzoquinone dioxime and 1,4-naphthoquinone dioxime and their derivatives combined with an oxidant, derivatives of 1,4-dinitrosoarenes, 1,4-dinitrosonaphthalene and 1,3-dinitrosobenzene. Curing of butyl rubber and natural rubber has been reported with p-quinone dioxime dibenzoate [10]. Recently, it has been found that butyl rubber rapidly forms a three dimensional network in the presence of oxidizing agents, using quinone dioxime and its esters.

In regard to curing reactions, very little research has been published on the reactions of nitroso groups with olefinic double bonds. Pure DNB polymerizes on storage, hence a masked derivative of DNB is preferred. Masked derivatives ensure the controlled and slow release of the curing moiety, so the curing rate can be controlled. In the present work a new DNB generating compound, a quinol ether of 1,4-benzoquinone dioxime (QE), is explored for curing a nitrile butadiene rubber (NBR)/AP/Al propellant. QE is a masked ether of benzoquinone dioxime. The curing reaction of QE can be tuned by changing the chemical structure of the masking agent and substituents on DNB [9].

QE belongs to class of low hazard compounds. QE does not ignite when heated up to 300 °C. It is not irritating to mucous membranes and skin, and is not resorbed through the skin. The maximum allowed contamination (MAC) of this chemical in the air of a working zone is 4 mg/m³. Whereas TDI (MAC = 1.01 mg/m³) causes skin and eye irritation, and may cause allergy or asthma symptoms or breathing difficulties if inhaled. It may also cause an allergic skin reaction, and is suspected of causing cancer [11].
However, as NBR has good mechanical properties and can be plasticized with polar and a non-polar plasticizers, it has been selected as a candidate material for NBR based binders used for propellant applications [12, 13]. NBR is an unsaturated copolymer of acrylonitrile and butadiene. The general structure of NBR is shown in Figure 1.

![General structure of NBR](image)

**Figure 1.** General structure of NBR ($m$ and $n$ are the acrylonitrile and butadiene contents, respectively)

An exhaustive literature search revealed that little information is available on propellant formulations based on NBR, AP and Al (NBR/AP/Al). Considering the advantages of QE as a curing agent, a systematic study has been carried out on NBR/AP/Al based composite propellant formulations using QE as the curing agent.

## 2 Experimental

### 2.1 Materials

AP of 300 μm was procured from M/s Pandian Chemicals Ltd., Cuddalore (India), and was used as such as in the propellant formulation. Fine AP of 50 μm was prepared by size reduction methods using an air classifying mill. Al powder was supplied by M/s Metal Powder Company, Madurai (India). Quinol ether (QE), dibutyl phthalate (DBP) and NBR was procured from Indian Adhesives and Glues, Pune (India), and used as such in the propellant formulation.

### 2.2 Method

The propellant composition was designed based on the NBR/DBP binder, AP/Al as fillers and QE as the green curing agent. Propellant batches with variable amounts of QE were prepared. The processed propellant compositions were designated as VAC1, VAC2, VAC3 and VAC4, having concentrations of curing agent of 0.2, 0.3, 0.4 and 0.5 wt.%, as presented in Table 1.
Table 1. Propellant compositions of varying curing agent concentrations (wt.%)  

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>VAC1</th>
<th>VAC2</th>
<th>VAC3</th>
<th>VAC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passive binder</td>
<td>15.8</td>
<td>15.7</td>
<td>15.6</td>
<td>15.5</td>
</tr>
<tr>
<td>VA</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>AP Coarse (300 µm) and AP fine (50 µm)</td>
<td>66.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al (6 µm)</td>
<td></td>
<td></td>
<td></td>
<td>18.0</td>
</tr>
</tbody>
</table>

The experimental mixing of the composite propellants was carried out at 8 kg batch level in a vertical planetary mixer. First, the binder was prepared by adding NBR (15.5%) to DBP (84.5%), mixing was carried out in an anchor blade mixer. The NBR/DBP binder was charged to the vertical planetary mixer (capacity 15 L) and mixed well for 30 min, followed by mixing under vacuum for a further 30 min to remove entrapped air. 18% of Al powder was added and mixed carefully for 30 min. After this, 66% of AP was added and mixed homogenously. The temperature of the overall mixing was maintained at 50 ±2 °C. After complete addition of the solid ingredients, the composition was further mixed under vacuum for 1 h. Finally, 0.2 to 0.5% of the curing agent QE – regarded as vulcanizing additive (VA) – was added and mixed for another 1 h. The speed of rotation of the stirrers in the mixer was 21 rpm for the agitator and 5 rpm for the planetary. The composition was cast in molds by the vacuum gravity method and cured at 60 °C for 20 days [3].

3 Characterization Methods

Mechanical properties such as tensile strength (TS), E-modulus (E-mod) and % elongation (% E) were determined using a Hounsfield universal testing machine (UTM) conforming to ASTM-D-638 type IV, at a cross head speed of 50 mm/min at ambient temperature. The width and thickness of the specimens were measured and placed in the appropriate grips of the testing machine and aligned properly. The specimen was stretched at the rate of 50 mm/min and the load/extension measurement/curves were recorded to determine the TS, % E and E-mod values.

The Shore A hardness indentation method was used to measure the hardness of the propellant samples.

A Thermo Scientific (Pycnometric EVO) helium gas pycnometer was used to determine the density of the propellant samples. A sample was cut into pieces of 25×25×25 mm (±0.1 mm) and filled to 60-70% volume in the sample vessel.
The sample vessel was placed in the sample chamber of the instrument and the
density of the sample was measured.

A Brookfield dial type viscometer (model HBT) with a T-C spindle at
a rotating speed of 2.5 rpm at a programmed temperature was used to measure the
viscosity of the propellant slurries. The slump test or spreadability was measured
by using a specially designed instrument, and was used to determine the yield
stress of the propellant samples [14].

The burning rate of the cured composite solid propellant samples was
determined by the acoustic emission technique under an inert nitrogen atmosphere
at different pressures in a 750 cm³ stainless steel bomb. The bomb was fitted
with a lid with a panel for holding the propellant strand and a piezoelectric
transducer [15, 16]. The propellant samples of dimensions 150×6×6 mm
were made in the form of strands and ignited from one end with the help
of a nichrome wire. The acoustic signals produced due to the rapid release of
energy on combustion of the propellant were recorded. An accuracy of ±0.2 mm/s
is expected in the measured burning rate due to manual measurement errors.

DSC-TGA analysis for thermal decomposition of the propellant samples
was carried out using a Q-600 instrument (TA, USA) with nitrogen flow rate
100 mL/min and heating rate 10 °C/min.

4 Results and Discussion

4.1 Characterization of QE
The chemical structure of QE is shown in Scheme 1 (Section 4.2). The QE was
characterized by DSC. The DSC curve (Figure 2) showed an endothermic peak
at 160.43 °C, followed by an exothermic peak at around 185.44 °C. The first
(endothermic) peak is due to the melting of QE and the second (exothermic)
peak is for decomposition of QE. QE completely decomposes in a single step
at 185.44 °C. QE is a pale yellow solid powder (Figure 3).
4.2 Curing of the propellants
Curing of the propellants was carried out at 60 °C for up to 20 days with the QE of 1,4-benzoquinone dioxime. Tensile strength (TS) was taken as the indicator of curing with time. As curing proceeds, the TS value increases and attains a nearly constant value after completion of curing. Thus the TS values have been taken as the qualifying criteria for curing. Each specimen was tested in triplicate at room temperature. The mean value of the three readings was recorded. The TS value was recorded at 5, 10, 15 and 20 days for studying the curing progress. The data in Figure 4 shows that the TS value for the propellant compositions increases with time and becomes almost constant at the 15th day. After 15 days there is no appreciable change in TS. Accordingly, curing of the compositions has been performed for 20 days.
Figure 4. Variation of TS values with time

QEs have been used as curing agents for unsaturated rubbers [17]. Curing of NBR with QE proceeds with reaction of the double bond of NBR with DNB [18]. Furthermore the interaction is possible by a radical mechanism as shown in Scheme 1 [18]. The reaction has been studied by FTIR.
Scheme 1. Mechanism of the curing reaction

QE is a masked ether of benzoquinone dioxime. Hence it gives various advantages, such as control of the reactive species DNB, control over of the rate of reaction, repeatability and controlled performance. The reaction rate of NBR and QE depends on the amount of the reactive DNB that is formed by thermal cleavage of QE. The curing of NBR by QE proceeds by addition of DNB to the alkene unit of NBR, possibly by a pseudo Diels-Alder addition [17]. The mechanism of curing is on the basis of reaction of the unsaturated rubber having an α-methylene hydrogen atom with a dinitroso-generating system such as QE [17]. The curing agent QE decomposes into the curing moiety p-DNB,
followed by reaction of the reactive species DNB with the unsaturated NBR resulting in a cured polymeric network [19]. As the concentration of the reactive species DNB increases, the curing with NBR is increased. The kinetically controlled reaction depends on the availability of $p$-DNB in the system [17, 20].

To check the curing reactions, FTIR spectra of NBR, QE and the cured propellant were recorded on an FTIR-1600 spectrophotometer (Perkin-Elmer) using a KBr matrix. The peak at 968 cm$^{-1}$ is attributed to the C–H stretching vibrations of the butadiene double bond, which is a characteristic moiety in NBR [19]. The data obtained from Table 3 and Figure 5 confirms the decomposition of QE into tri-tert-butyl phenol and DNB [20]. FTIR analysis showed that, the peaks at 1244 and 1662 cm$^{-1}$ are present in QE, corresponding to vibrations of the N–O group and carbonyl group, respectively, whereas these peaks are not observed in a cured propellant sample. This confirms the decomposition of QE as proposed in Scheme 1. The peak at 1641 cm$^{-1}$ in QE, corresponding to vibration of the imine group, was shifted to 1646 cm$^{-1}$ on curing, and a new C=N bond with conjugation (anil linkage) is formed due to the curing reaction of DNB with NBR (cured polymeric network) as shown in Scheme 1. Literature data assigned the 1690-1640 cm$^{-1}$ absorptions to C=N stretching [19, 20]. The appearance of the 1541, 1555 and 1578 cm$^{-1}$ peaks in the propellant sample correspond to vibrations of the aromatic ring [20]. The literature data shows that assignment of absorption bands in the region of 1300-1250 cm$^{-1}$ is most likely associated with the aromatic C–N stretching [19, 21, 22]. This aromatic C–N absorption is observed at 1269 cm$^{-1}$ in the cured propellant sample as shown in Figure 5. From the FTIR spectral analysis it is confirmed that the reaction proceeds with formation of an anil group (Ar–C=N).

<table>
<thead>
<tr>
<th>FTIR absorption [cm$^{-1}$]</th>
<th>Functional groups in QE</th>
<th>Functional groups in cured propellant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1662</td>
<td>Carbonyl group</td>
<td>–</td>
</tr>
<tr>
<td>1641</td>
<td>Imine group (C=N)</td>
<td>–</td>
</tr>
<tr>
<td>1244</td>
<td>N–O group</td>
<td>–</td>
</tr>
<tr>
<td>1646</td>
<td>–</td>
<td>C=N bond with conjugation</td>
</tr>
<tr>
<td>1269</td>
<td>–</td>
<td>Aromatic C–N absorption</td>
</tr>
<tr>
<td>1529</td>
<td>–</td>
<td>Aromatic ring</td>
</tr>
<tr>
<td>1589</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>968</td>
<td>–C–H stretching vibrations of butadiene double bond in NBR</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5. FTIR spectra of NBR, QE and the cured propellant.
4.2 Mechanical properties

The mechanical properties of the propellants with different amounts of curing agent are shown in Table 4 and Figure 6. The hardness of a sample is indicative of the degree of crosslinking and this has been studied with respect to the amount of curing agent added to the composition. Cured samples having even surfaces were used as test specimens for measuring the Shore A hardness. It is well known that the degree of crosslinking may be affected by the amount of curing agent used [23]. As the percentage of QE was increased, it resulted in increased curing, so the sample became hard and less elastic. The hardness of the cured propellant formulations was found to be in the range of 55 to 70, clearly demonstrating an appreciable change in hardness.

Table 4. Changes in hardness, density and mechanical properties on variation of the curing agent concentration

<table>
<thead>
<tr>
<th>Composition</th>
<th>Hardness [Shore A]</th>
<th>Density [kg/m³]</th>
<th>TS [kgf/cm²] ([MPa])</th>
<th>E-mod [kgf/cm²] ([MPa])</th>
<th>% E [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAC1</td>
<td>55</td>
<td>1812</td>
<td>5.46 (0.54)</td>
<td>25.3 (2.48)</td>
<td>32.2</td>
</tr>
<tr>
<td>VAC2</td>
<td>60</td>
<td>1807</td>
<td>6.19 (0.61)</td>
<td>37.0 (3.63)</td>
<td>25.9</td>
</tr>
<tr>
<td>VAC3</td>
<td>65</td>
<td>1806</td>
<td>6.90 (0.68)</td>
<td>39.3 (3.85)</td>
<td>21.5</td>
</tr>
<tr>
<td>VAC4</td>
<td>70</td>
<td>1804</td>
<td>7.80 (0.76)</td>
<td>49.8 (4.88)</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Figure 6. Mechanical properties vs. curing agent concentration

The mechanical properties were determined for the cured samples following the ASTM D-638 standard. The data from Table 4 and Figure 6 revealed that the concentration of the curing agent has a distinct effect on the mechanical properties. The % E decreased while TS and E-mod increased with an increase in the curing
agent from 0.2 to 0.5%. Increasing the amount of curing agent increases the
degree of crosslinking in the binder polymer network, which causes a concomitant
enhancement in the mechanical properties and a reduction in elongation.

4.3 Viscosity and viscosity build-up
The end of mix (EoM) viscosity and viscosity build-up of compositions
with 84% solid loading was studied using a Brookfield viscometer and the results
obtained are presented in Table 5. The data indicate that as the curing agent
concentration was increased from 0.2 to 0.5%, the EoM viscosity and viscosity
buildup in the propellant slurry increased. As the percentage of QE was increased
in the propellant, the viscosity of the composition increased.

<table>
<thead>
<tr>
<th>Period at 50 °C</th>
<th>VAC1</th>
<th>VAC2</th>
<th>VAC3</th>
<th>VAC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>EoM</td>
<td>11840</td>
<td>12160</td>
<td>13120</td>
<td>14400</td>
</tr>
<tr>
<td>After 1 h</td>
<td>15040</td>
<td>15680</td>
<td>16640</td>
<td>17600</td>
</tr>
<tr>
<td>After 2 h</td>
<td>16640</td>
<td>17280</td>
<td>18560</td>
<td>19840</td>
</tr>
<tr>
<td>After 3 h</td>
<td>18240</td>
<td>19200</td>
<td>21120</td>
<td>22400</td>
</tr>
</tbody>
</table>

4.4 Spreadability
Spreadability of the compositions was determined by the slump test. Spreadability
is an indirect method for determining the yield stress. The yield stress is a transition
stress between solid and liquid-like behaviour, where material undergoes elastic
deformation below the yield stress and flows like a viscous liquid thereafter.
A low value of the yield stress is desirable for casting flawless grains.
The yield stress measurement using the slump test or spreadability test includes
measurement of the diameter and height of the sample spread, under the influence
of gravity, at the flow stoppage. The diameter of spread and height of the
sample are related to the yield stress by neglecting the inertia effects. Two flow
regimes exist, viz. spread and slump flow, depending upon the height (H) and
radius (R) of the sample on flow stoppage [14]. The spreadability of propellant
formulations was determined by a special instrument, a schematic diagram of
which is presented in Figure 7.
The spreadability coefficient \((SC)\) is determined by the change in shape of the sample after 30 min under its own weight at 50 °C (Equation 1).

\[
SC = \frac{d_1 - d_2}{d_2}
\]

where \(d_1\) is the diameter of the propellant after 30 min (in mm) and \(d_2\) is the initial diameter (in mm).

From the data it was observed that the yield stress of compositions VAC1 to VAC4 increased from 57.61 to 81.34 Pa and the spreadability coefficient decreased from 1.0 to 0.93. There was no significant change in spreadability and yield stress with variation of the concentration of the curing agent from 0.2 to 0.5% (Table 6). The data indicate that the effect of the curing agent concentration on the yield stress and spreadability is less due to the slow curing reaction. Compositions were cast easily without any issues during processing.

Table 6. Spreadability coefficient and yield stress of different compositions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>VAC1</th>
<th>VAC2</th>
<th>VAC3</th>
<th>VAC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>1.0</td>
<td>0.98</td>
<td>0.97</td>
<td>0.93</td>
</tr>
<tr>
<td>Yield stress, (±3) [Pa]</td>
<td>57.61</td>
<td>62.66</td>
<td>68.25</td>
<td>81.34</td>
</tr>
</tbody>
</table>

4.5 Ballistic properties

The ballistic properties, burning rate \((r)\) and pressure exponent \((n \text{ value})\), of compositions VAC1 to VAC4, with varying percentages of QE, was studied and the results are presented in Table 7. The burning rates \(r\) were determined at pressure \((P)\) 58.83, 68.64 and 78.45 bar (5.88, 6.86 and 7.85 MPa, respectively). The solid strand burning rate (SSBR) of propellant compositions VAC1 to VAC4
at 68.64 bar (6.86 MPa) was found in the range of 5.58 to 5.72 mm/s. Variation in the QE content did not have any effect on the burning rate and the observed values were found to be within experimental error. The pressure exponent was determined by plotting a curve of ln$r$ vs. ln$P$. It was calculated from the slope of the curve by using SSBR data at 58.83, 68.64 and 78.45 bar (5.88, 6.86 and 7.85 MPa, respectively) pressures and the results obtained are presented in Table 7 and Figure 8. The pressure exponent with varying concentrations of curing agent from 0.2 to 0.5% was found to be in the range of 0.366 to 0.355. The data also revealed that the pressure exponent was nearly constant as the concentration of the curing agent was decreased from 0.5 to 0.2% [24, 25].

**Table 7.** Ballistic properties of the propellants with variation of curing agent concentration

<table>
<thead>
<tr>
<th>Composition</th>
<th>Burning rate $r$ [mm/s] at pressure $P$ [bar] ([MPa])</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>58.83 (5.88)</td>
<td>68.64 (6.86)</td>
</tr>
<tr>
<td>VAC1</td>
<td>5.24</td>
<td>5.58</td>
</tr>
<tr>
<td>VAC2</td>
<td>5.26</td>
<td>5.61</td>
</tr>
<tr>
<td>VAC3</td>
<td>5.32</td>
<td>5.66</td>
</tr>
<tr>
<td>VAC4</td>
<td>5.40</td>
<td>5.72</td>
</tr>
</tbody>
</table>

**Figure 8.** Determination of the $n$ values of the propellant compositions
4.6 Thermal properties
The DSC-TGA technique was used to study the thermal behaviour of compositions VAC1 to VAC4, and the results obtained are shown in Figures 9 and 10. The DSC curves exhibited three peaks at around 248, 298.5 and 390.5 °C. The endothermic peak around 248 °C is due to a phase change of AP from orthorhombic to cubic [26]. This is followed by a small decomposition peak at around 298.5 °C and high temperature decomposition peak at 390.5 °C, which proceeds until complete. This exothermic decomposition is attributed to AP decomposition. AP exhibits two exothermic peaks, one at low temperature and a second at high temperature. The low temperature decomposition of AP is extremely sensitive to preliminary mechanical treatment and irradiation, the presence of admixed components and the topography of the crystals. 30% decomposition occurs in the low temperature region. This data indicated that QE and its content does not significantly affect the decomposition of AP. AP being the major ingredient, more than 60%, controls the decomposition of the propellant.

Figure 9. DSC of propellant compositions with varying percentages of curing agent
The thermal behaviour of the cured propellant compositions was also investigated by TGA at a heating rate of 10 °C/min under N₂ atmosphere. The TGA thermograms for compositions VAC1 to VAC4 are shown in Figure 10. All compositions exhibited a three stage mass loss in the temperature ranges of 175 to 205 °C, 285 to 325 °C and 325 to 400 °C. The first mass loss observed between 175 to 205 °C is due to evaporation of volatile plasticizer DBP. The mass losses between 285 to 325 °C and 325 to 400 °C are attributed to the partial and final decomposition of AP, respectively.

Some missiles require operating conditions down to –60 °C, so the glass transition is required to be as low as possible. The glass transition temperature ($T_g$) of the cured compositions with QE contents of 0.2, 0.3, 0.4 and 0.5% were evaluated using DSC. The low temperature characteristics of the cured propellants are shown in Figure 11. From the curves it is clear that all of the compositions have $T_g$ values less than –80 °C. Behaviour below –80 °C has not been checked due to instrumental limits. This binder system is highly plasticized (plasticizer content >80%) so $T_g$ values beyond –80 °C have not observed. As the amount of curing agent was increased, the crosslink density of the cured composition increased and resulted in a shift in the $T_g$ value to a higher temperature [23].
In order to further evaluate the effect of the curing agent content on \( T_g \), a \( T_g \) study was performed with NBR and different concentrations of QE, viz. 5, 10, 15 and 20%, without any filler and plasticizer. NBR had a \( T_g \) value of \(-18^\circ\text{C}\), which increased sequentially from \(-15.63^\circ\text{C}\) to \(-13.7^\circ\text{C}\) on addition of QE from 5 to 20% (Figure 12). This change in \( T_g \) to higher values may be attributed to the increase in crosslink density on increasing the content of QE. A higher crosslink density reduces the free volume and imparts restriction on the segmental motion of the molecules in NBR. Based on the data for \( T_g \) of NBR and QE, it may be concluded that similar results are to be anticipated for cured propellant samples.
From this analysis it can be inferred that it is convenient to use the QE curing agent, which is capable of forming a three-dimensional structure in the binder in the presence of a heterogeneous filler. These are capable of working at rather low temperatures and give chemically stable products [27].

5 Conclusions

A systematic study of NBR/Al/AP propellant with QE as the curing agent is explored. From this study the following major conclusions have emerged:

♦ The curing mechanism was interpreted by FTIR spectroscopy and the formation of the anil group linkage was established. Curing requires 15 days at 60 °C.
♦ The EoM viscosity and spreadability of the propellant compositions increased with increasing QE content. The viscosity data revealed that the viscosity of the composition increased with an increase in the reactive species DNB.
♦ When the content of the curing agent was increased from 0.2 to 0.5%, the mechanical properties of the propellant viz. TS, E-modulus and Shore hardness were all greatly improved.
♦ Based on the data for curing, and the rheological, mechanical, ballistic and thermal properties, the QE based curing system is a very promising candidate for propellant applications.
♦ The propellant has the capability for tuning of the mechanical properties by changing of the QE content. This system is less susceptible to the effects of moisture as QE is non-hygroscopic.
♦ The quinol ether of benzoquinone dioxime based curing mechanism is a nontoxic and comparatively green process. It is a very novel approach to successfully use a green curing mechanism based on QE and NBR for propellant applications.

Acknowledgement
The authors wish to thank the Director, High Energetic Materials Research Laboratory (HEMRL, Pune, India) for support and engagement during the course of this study.
References


Received: November 1, 2021
Revised: March 21, 2022
First published online: March 29, 2022