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Research paper

Simulation of Stress Relaxation Behaviour of Composite Propellants with Varying Solid Loading Using the Generalized Maxwell Model

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Abstract: Hydroxyl-terminated polybutadiene (HTPB) based composite propellants possess viscoelastic behaviour and hence time and temperature dependent mechanical properties. The mathematical analysis of viscoelastic behaviour of composite propellants becomes complex due to the non-linearity involved under various loading conditions. In the present study, a linear viscoelasticity assumption was considered to simulate stresses related to storage conditions. In this paper, a study of stress relaxation behaviour of composite propellants was carried out using the Generalized Maxwell model to obtain the material viscoelastic characteristics. The relaxation behaviour of composite propellants having solid loading varying from 85% to 89% were studied at different temperatures, from –27 to +32 °C, using a Dynamic Mechanical Analyser (DMA). The generated relaxation curves were curve fitted using MATLAB (R2022a) with the Generalized Maxwell model. The simulation demonstrated that a maximum of four elemental parameters of the Generalized Maxwell model are sufficient and can represent a best fit of the relaxation behaviour of the studied composite propellants. The equilibrium modulus was also evaluated at different temperatures, along with other material constants that are essential parameters for performing the structure integrity analysis of a solid propellant rocket motor. It was observed that the equilibrium modulus decreases with an increase in temperature, but increases with an increase in solid loading in the propellant composition formulations.

Keywords: composite propellant, viscoelastic, stress relaxation, DMA, temperature, equilibrium modulus

1 Introduction

A structural integrity analysis of case bonded solid propellant rocket motors is quite challenging due to the complex behaviour of HTPB-based composite propellants. The mechanical response of a composite propellant is time and temperature dependent and hence possesses viscoelastic behaviour [1-3]. The mathematical analysis of the mechanical behaviour of composite propellants becomes non-linear as it mostly depends on various loading conditions. But for some loading conditions, like storage condition where the strain induced is low, a linear viscoelasticity assumption is admissible. When the strains involved are of very small (infinitesimal) magnitude, the propellant behaviour can be idealised to linear elastic. When the strains involved are of slightly larger magnitude, the materials are considered as linear viscoelastic and an appropriate model can be applied. In the case of storage of solid propellant rocket motors, the strain induced is slightly larger and hence the assumption of linear viscoelasticity is valid. The linear viscoelastic model is simpler and can be considered for viscoelastic characterization of composite propellants. The structural integrity analysis of solid propellant rocket motors has been carried out mostly by considering the elastic properties of the propellant. It has also been observed that the structural integrity analysis of solid propellant rocket motors with elastic properties is very conservative. Hence it is essential to obtain the viscoelastic properties of the composite propellant that will be the input for the structural integrity analysis of solid rocket motors in order to obtain more realistic results.

In this paper a comprehensive study of the stress relaxation behaviour of HTPB based composite propellants having solid loading varying from 85% to 89% were performed at different temperatures, from −27 to +32 °C, using a Dynamic Mechanical Analyzer (DMA). The above range of temperatures was selected based on the storage temperature envelope required for the studied composite propellants.

2 Experimental

2.1 Materials

Five types of HTPB/ammonium perchlorate (AP)/aluminum (Al) based composite propellants were formulated having solid loading varying from 85% to 89%. AP with an average particle size of 300 ±10 µm was received directly from the supplier. An average particle size of 50 µm was obtained by grinding 300 µm AP. A ratio of weight percentage of course AP to that of fine AP was maintained at 4:1 in all compositions. Al powder, with an average particle size of 15 ±3 µm was procured directly from the supplier. HTPB, along with other ingredients like curing agent, plasticizer, anti-oxidant and bonding agent were also procured and used as received from the supplier. The composition details are listed in Table 1.

Table 1. Propellant formulations with varying solid loading

Propellant	Binder [wt.%]	AP [wt.%]	Al [wt.%]	Solid loading [%]	Density [kg/m^3]
C1	15	67	18	85	1747
C2	14	68		86	1765
C3	13	69		87	1773
C4	12	70		88	1782
C5	11	71		89	1791

Each propellant composition was manufactured at 5 kg batch level. Solid loading in the propellant formulation was increased up to 87% solid loading composition by reducing the plasticizer, and further to 89% solid loading composition by reducing HTPB. For all formulations, the ratio of isocyanate group (–NCO) to hydroxyl group (–OH) was maintained at 0.8. All five types of propellant slurry were mixed using a vertical planetary mixer. After mixing, the slurry was cast in a mould under vacuum and cured at 50 °C for 5 days. Afterwards, propellant samples were prepared from each type of propellant.

2.2 Methods

The dumbbell shaped propellant samples were prepared as per ASTM D638 type IV for tensile testing using a UTM. Specimen width and thickness were maintained at around 6 ±0.2 mm and 4 ±0.2 mm respectively. Rectangular propellant samples 35×13×3 mm (length × width × thickness) were also prepared. DMA Q800 was used to characterize the relaxation behaviour of the composite propellants. A dual cantilever clamp was used for each experiment and was calibrated for position and mass before use. The test was conducted at a constant strain of 0.1% and at different temperatures of −27, −10, +10 and +32 °C, for each type of propellant. The stress with respect to time was recorded for each of the propellants at each temperature.

Stress relaxation experiments at a constant strain of 0.1% were performed for each propellant at four different temperatures. The assumption of linear viscoelasticity is valid for 0.1% of strain for the studied composite propellants. The relaxation curves obtained were studied and curve fitting was performed using the Generalized Maxwell model to obtain the propellants' viscoelastic characteristics. Generally, a viscoelastic model in the form of a Prony series or William-Landel-Ferry (WLF) equations was used for the simulations [4-16]. The Generalized Maxwell model, which represents the relaxation behaviour, can be mathematically approximated to by a Prony series. All the parameters of the Prony series were evaluated using the relaxation experimental data and curve fitting using the Levenberg-Marquardt algorithm with MATLAB.

3 Model Formulation

The Maxwell model, which was proposed by Maxwell and Wiechert, comprises of a linear spring element and a dashpot element connected in series. For a linear spring, stress possesses a linear relationship with strain as $\sigma = E\varepsilon$, where E is the modulus, and for a dashpot, stress has a linear relationship with strain rate as $\sigma(t) = \eta\dot{\varepsilon}$, where η is viscosity. The Maxwell model can only depict the relaxation behaviour of viscoelastic materials in a very limited time range. Moreover, a real material does not relax with a single relaxation time as predicted by a spring-dashpot model; the Maxwell model. Accordingly, a series of spring-dashpot models have been assembled in parallel, which represents a physical system known as the Generalized Maxwell model (multi element model) as shown in Figure 1, in order to improve accuracy in the experimental data fitting. The combination of elastic spring elements and viscous dashpot elements in the physical system could be elucidated by variable molecular-chain-segment lengths for polymer structures under different time distributions. The Generalized Maxwell model, which can be mathematically approximated by Prony series, is given by Equation 1.

$$E_R(t) = E_\infty + \sum_{i=1}^{n} E_i e^{-t/\tau_i} \tag{1}$$

where the relaxation modulus $E_R(t)$ is a characteristic of the material's viscoelasticity as used to describe the stress relaxation of the material with time t, E_∞ is the long term modulus, also called the equilibrium modulus, and n are exponential terms each have a co-efficient E_i and τ_i. It is important to simulate accurately the stress relaxation and viscoelastic characteristics of the studied composite propellants in order to design and evaluate the materials. In order to simulate the relaxation behaviour, data obtained in the relaxation experiments at different temperatures were curve fitted using the Levenberg-Marquardt algorithm with MATLAB software.

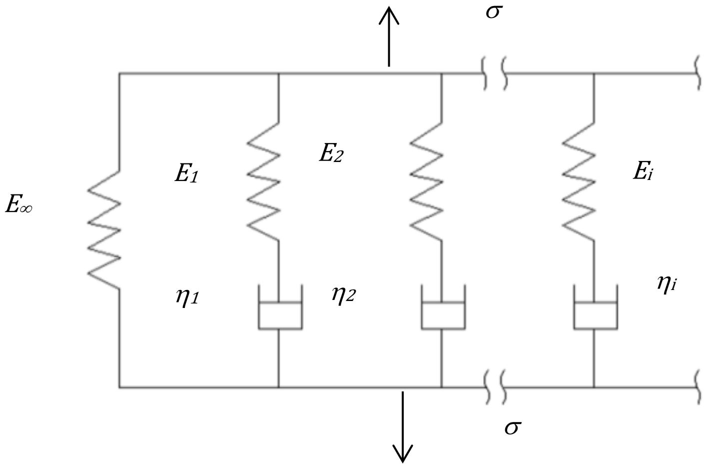


Figure 1. Generalized Maxwell Model

4 Results and Discussion

4.1 Effect of solid loading on the mechanical properties of the composite propellants

The stress-strain curves obtained for the propellant compositions C1, C2, C3, C4 and C5 respectively at 27 °C with a cross-head speed of 50 mm/min are shown in Figure 2. It can be seen from Figure 2 that by varying the solid loading in the propellant formulations, the mechanical properties are affected due to changes in the binder-filler interaction behaviour.

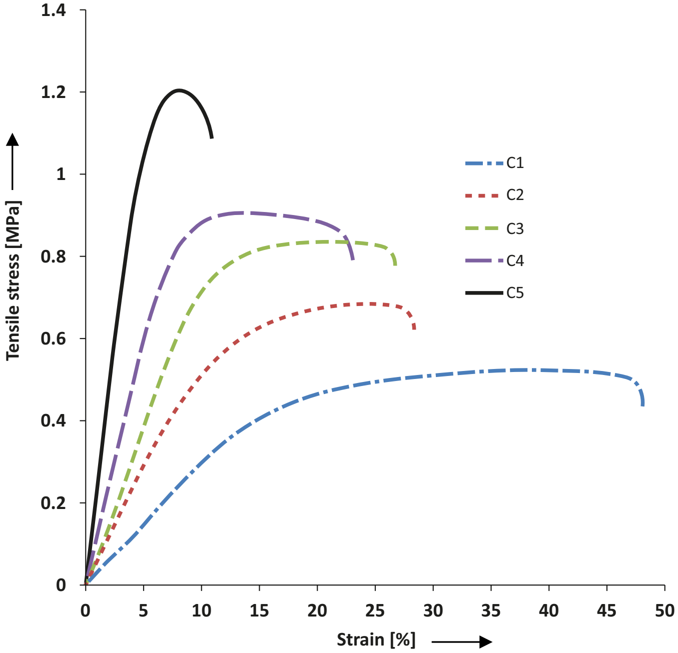
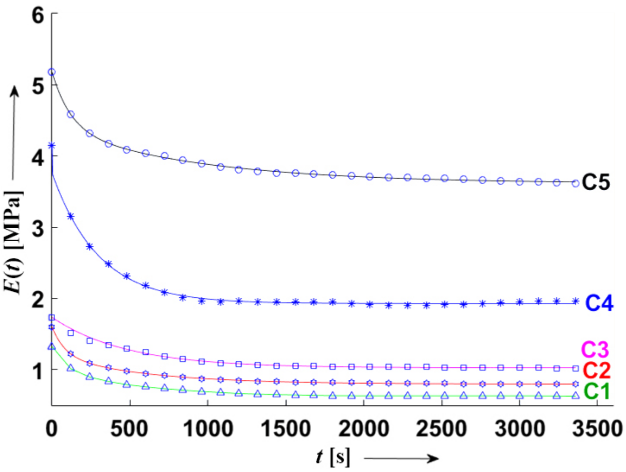


Figure 2. Stress-strain curves for different solid loading compositions

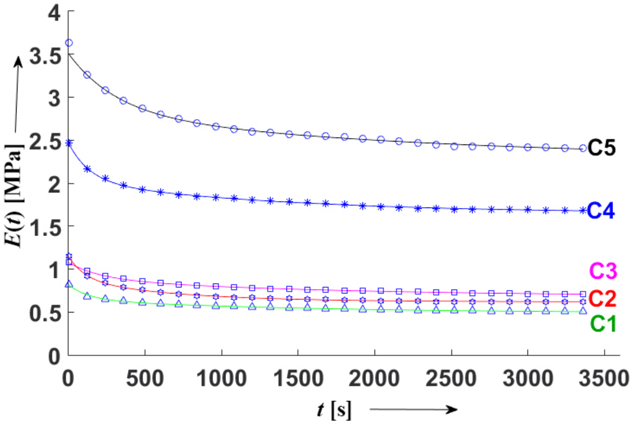
The C1 composition, which has 85% of solid loading, exhibits the highest strain capability but the lowest stress capability, whereas these characteristics are reversed in the case of C5 composition, which has 89% solid loading. The results show that as the solid loading in the compositions is increased, the strain capability of the propellant is reduced, but the stress capability is increased.

4.2 Stress relaxation behaviour of the composite propellants

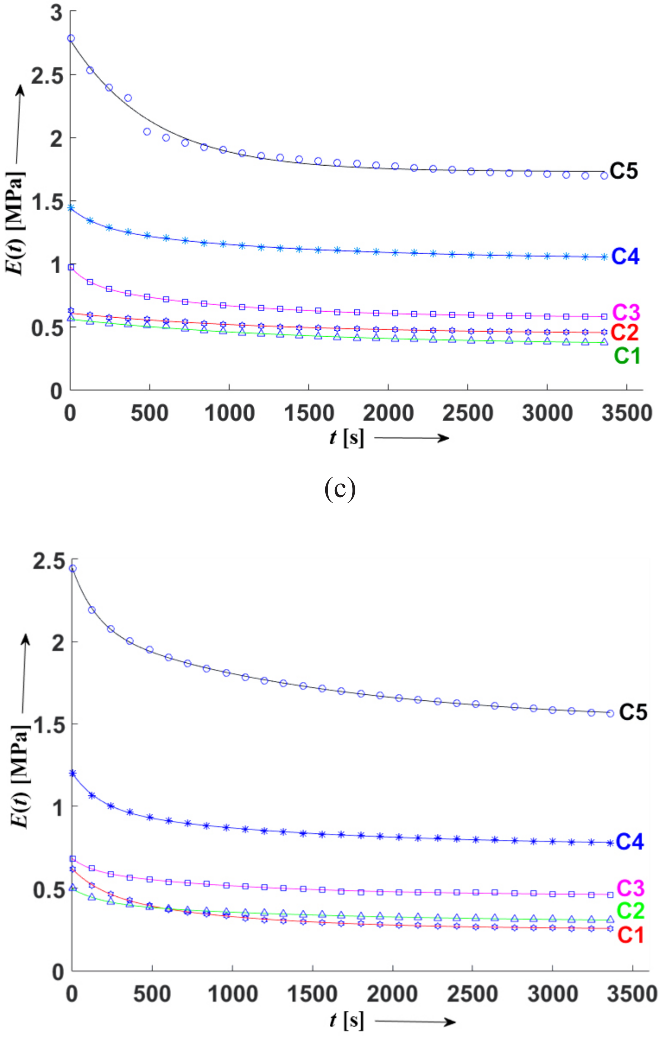
The relaxation behaviour of the composite propellants having a solid loading varying from 85 % to 89 % at temperatures from −27 to +32 °C is shown in Figure 3. Figure 3 shows that a composite propellant with a higher solid loading exhibits a higher initial modulus. The rate of decrease of the relaxation modulus of compositions C4 and C5, which have solid loading of 88% and 89% respectively, are more than those of compositions C1, C2 and C3 respectively in the initial 1000 s. The above behaviour may occur due to the higher amount of filler present in compositions C4 and C5, which affects the binder-filler interaction in the initial time range of 0 to 1000 s. After that time, there is no appreciable change in relaxation modulus observed for all of the compositions. The relaxation modulus corresponding to this stage is known as the equilibrium modulus.


6
5
4
3
2
1
E(t) [MPa]
0
500
1000
1500
2000
2500
3000
3500
t [s]
C5
C4
C3
C2
C1

(a)


4
3.5
3
2.5
2
1.5
1
0.5
0
E(t) [MPa]
0
500
1000
1500
2000
2500
3000
3500
t [s]
C5
C4
C3
C2
C1

(b)



(c)

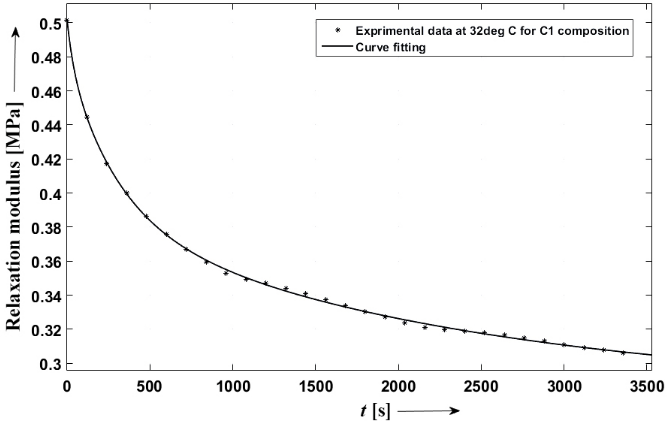
(d)

Figure 3. Relaxation Modulus vs. time with different solid loadings at temperature −27 (a), −10 (b), +10 (c) and +32 (d) °C

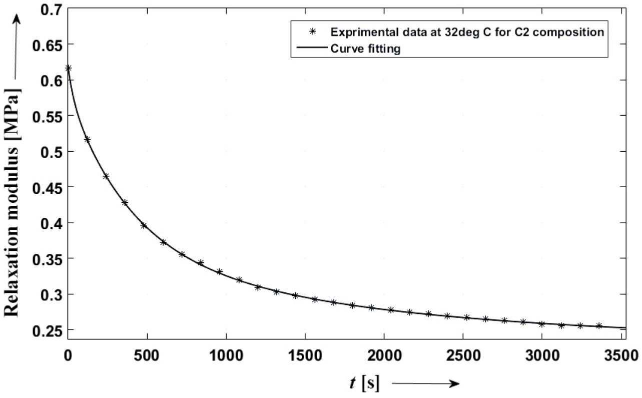
4.3 Simulation of relaxation behaviour of the studied composite propellants

The relaxation curve of each propellant obtained at different temperatures was studied and curve fitting was performed with MATLAB using the Levenberg-

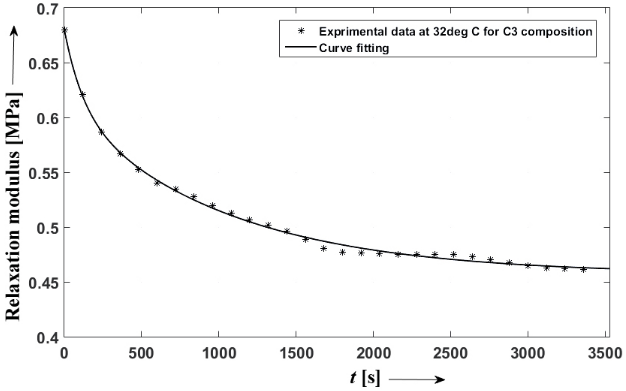
Marquardt algorithm. The curve fitting was optimized using an iteration method and it was found that the relaxation behaviour of the studied propellants can be fully depicted using a maximum of four elemental parameters of the Generalized Maxwell model. The curve fitting of the relaxation data obtained at 32 °C for all of the compositions are shown in Figure 4 with R^2 of 0.999. All of the Prony series parameters, along with the equilibrium modulus obtained using curve fitting for all of the compositions, at 32 °C are given in Table 2.



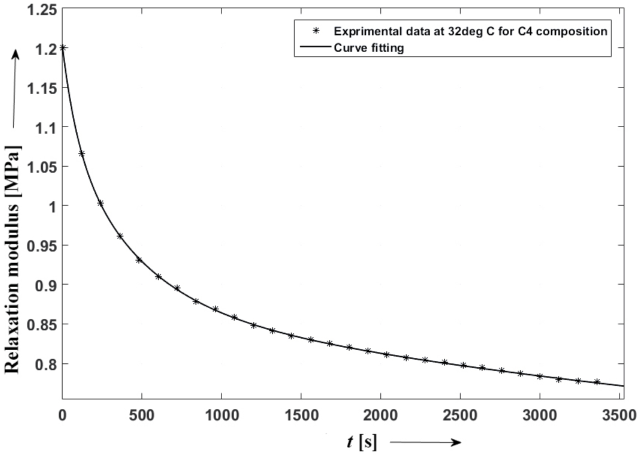
(a)



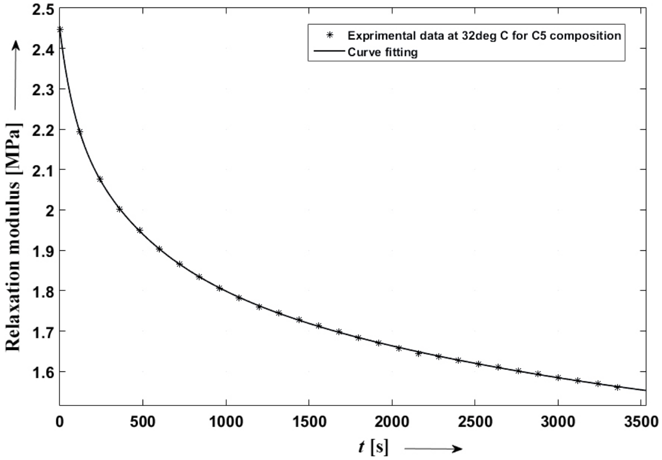
(b)


Exprimental data at 32deg C for C3 composition
Curve fitting
Relaxation modulus [MPa]
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0
500
1000
1500
2000
2500
3000
3500
t [s]

(c)


Exprimental data at 32deg C for C4 composition
Curve fitting
Relaxation modulus [MPa]
1.25
1.2
1.15
1.1
1.05
1
0.95
0.9
0.85
0.8
0
500
1000
1500
2000
2500
3000
3500
t [s]

(d)



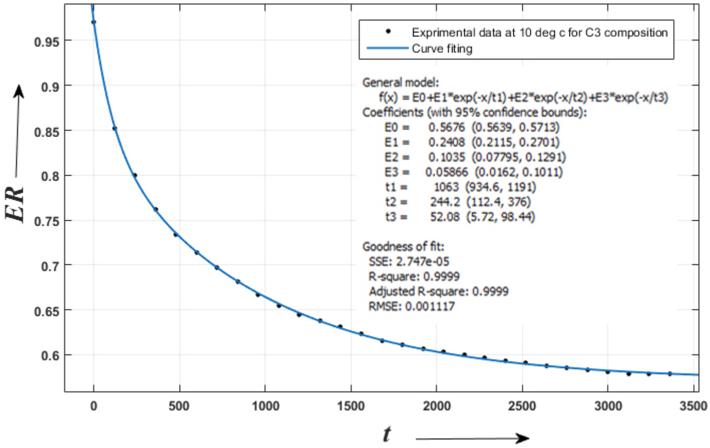
(e)

Figure 4. Curve fitting of relaxation data at +32 °C for all of the studied compositions: C1 (a), C2 (b), C3 (c), C4 (d) and C5 (e)

Table 2. Prony series parameters of compositions C1, C2, C3, C4 and C5 at 32 °C

Propellants	E_∞	$E1$	$E2$	$E3$	τ_1	τ_2	τ_3
C1	0.294	0.209	0.182	0.044	2256.83	295.79	39.04
C2	0.249	0.2152	0.345	0.058	1749.42	386.05	35.80
C3	0.4568	0.223	0.1045	0.062	1035.5	121.67	40.08
C4	0.760	0.277	0.216	0.1089	7508.0	450.8	94.13
C5	1.507	0.215	0.140	0.0817	3230.86	445.79	82.317

Curve fitting at 10 °C for the C3 composition, along with all parameters of the Prony series, is shown in Figure 5. It is clear from Figure 5 that the fit has R^2 of 0.9999. The equilibrium modulus obtained for C3 composition at 10 °C is 0.5676 MPa. Similarly for all of the compositions, curve fitting was performed and the equilibrium modulus, along with other parameters of the Prony series, was obtained at each temperature −27, −10 and +10 °C.



```
General model:
    f(x) = E0+E1*exp(-x/t1)+E2*exp(-x/t2)+E3*exp(-x/t3)
Coefficients (with 95% confidence bounds):
     E0 =      0.5676  (0.5639, 0.5713)
     E1 =      0.2408  (0.2115, 0.2701)
     E2 =      0.1035  (0.07795, 0.1291)
     E3 =     0.05866  (0.0162, 0.1011)
     t1 =        1063  (934.6, 1191)
     t2 =       244.2  (112.4, 376)
     t3 =       52.08  (5.72, 98.44)

Goodness of fit:
  SSE: 2.747e-05
  R-square: 0.9999
  Adjusted R-square: 0.9999
  RMSE: 0.001117
```

Figure 5. Curve fitting of relaxation data of C3 composition at 10 °C using MATLAB along with parameters of the Prony series

4.4 Effect of temperature and solid loading on the equilibrium modulus

The equilibrium moduli of composite propellant compositions C1, C2, C3, C4 and C5 were obtained at each temperature using the Generalized Maxwell model simulation. The variation of the equilibrium modulus with respect to temperature for each composition is shown in Figure 6. The mathematical correlation for variation of equilibrium modulus with temperature was developed using the least square method and it was found that it follows a third order polynomial fit with R^2 a minimum 0.988 for all compositions.

Figure 6 clearly shows that the equilibrium modulus decreases with increases in temperature for all of the compositions. It also shows that at a constant temperature, the equilibrium modulus increases with an increase in solid loading in the composite propellant formulations. The relative increase in the equilibrium modulus at lower temperatures is greater than that at higher temperatures when the solid loading is increased from 85% to 89%.

These results demonstrate that when a solid propellant rocket motor is stored at a given temperature, a structural integrity analysis should be carried out, considering the equilibrium modulus at that temperature as an input to obtain a realistic result, as it changes not only with temperature but also with the propellant composition.

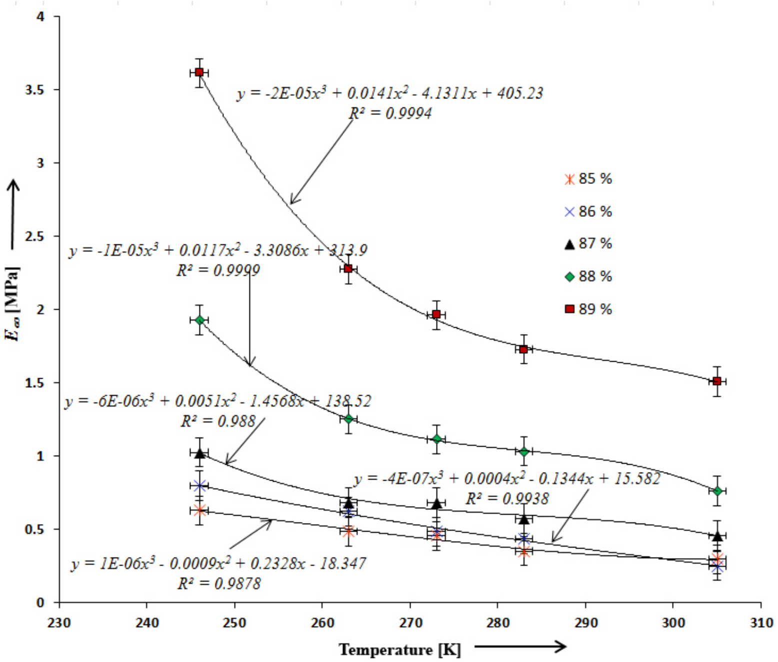


Figure 6. Variation of equilibrium modulus with temperature and solid loading

5 Conclusions

- The relaxation behaviour of HTPB/AP/Al based composite propellants having different solid loadings varying from 85% to 89% was studied using DMA at different temperatures. The relaxation behaviour was then simulated using the Generalized Maxwell model. This study suggests that the relaxation behaviour of the studied propellant compositions can be fully depicted by four elemental parameters of the Maxwell model.
- The equilibrium modulus, along with other parameters to characterize the relaxation behaviour, was determined using curve fitting by MATLAB for each propellant at different temperatures. The equilibrium modulus of the studied propellant having a 85% solid loading was found to be 0.29 MPa at 32 °C, 0.35 MPa at 10 °C, 0.48 MPa at −10 °C and 0.62 MPa at −27 °C respectively. The present study demonstrates that the equilibrium modulus is a function of both temperature and propellant composition. It decreases with increases in temperature but increases with increases in solid loading in the propellant composition formulations.

- The study also suggests that one should determine the equilibrium modulus for a given composition and given storage conditions, which should then be used as input for a structural integrity analysis of the solid propellant rocket motor, in order to obtain realistic results.

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