Journal of Physics:
Conference Series

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Mechanical properties assessment of composite solid propellant based on different aziridine bonding agents

To cite this article: Mohamed F. Eissa *et al* 2024 *J. Phys.: Conf. Ser.* **2830** 012027

Mechanical properties assessment of composite solid propellant based on different aziridine bonding agents

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Abstract: The employment of the dynamic mechanical analyzer (DMA) represents a modern methodology for the monitoring of the thermo-mechanical characteristics and also the thermomechanical loads of polyurethane-based composite solid rocket propellants during combustion. A meticulous preparation of composite propellant samples based on different bonding agents was carried out to examine the influence of various bonding agents on mechanical properties. To simulate the effects of natural aging, an accelerated aging program was implemented and subjected to the propellant samples for 5-day exposure at 90°C, equivalent to 5 years of natural aging. The dynamic mechanical modern analysis technique was used to assess the viscoelastic behavior and degree of viscoelasticity of both fresh and aged propellant samples. It is concluded that M4 based on MT-X bonding agent is the most valuable formulation of CSRP with tan δ of 0.183591, also with mechanical results; implying that M4 formulation based on MT-X bonding agent has the highest degree of viscoelasticity.

Keywords: MAPO, MT-X, Aging, Bonding agent, and Dynamic Mechanical Analysis.

1. Introduction

The Dynamic mechanical analyzer (DMA) is a contemporary approach employed for the monitoring of the thermo-mechanical attributes of polyurethane-based composite solid rocket propellants. This technique is utilized to investigate and classify materials [1]. The composite solid rocket propellant comprises a viscoelastic substance consisting of a portion of a viscous polymeric matrix and another portion of an elastic solid that reinforces the matrix. The study of the viscoelastic behavior of polymers finds its greatest utility in this technique. By applying sinusoidal stress and measuring the resulting strain in the material, one can ascertain the modulus [2]. The modulus can be influenced by either the temperature of the sample or the frequency of the stress, leading to variations in its values; This method can be employed to determine the distinctive fingerprint of the material's relaxation processes, and its glass transition temperature [3]. The dynamic mechanical analyzer is commonly utilized to determine the dynamic modulus, loss modulus, and mechanical damping or internal friction of polymeric materials [4]. Due to the application of sinusoidal stress, the modulus can be expressed as follows: The complex modulus (G^*) = Stress*/Strain, serves as a measure of the material's overall resistance to deformation, while the storage modulus (G') = $G^*\cos\delta$, quantifies the elastic response of the CSRP sample (measuring the stored energy), and the loss modulus (G") = G*sin δ, determines the viscous response of the CSRP sample (measuring the energy dissipated as heat) [5]. Tan δ, plays a significant role in describing the viscoelastic properties and indicates the degree of viscoelasticity exhibited by composite material. Tan δ represents the proportion of loss to storage and is commonly referred to as damping. This metric quantifies the dissipation of energy within a substance, providing insight into its capacity to absorb energy. Essentially, tan delta serves as an indicator of the composite propellant material's modulus; Tan δ = G"/G' [6]. The angle delta ranges from 0° to 90°, with decreasing δ values indicating purely elastic behavior, and increasing δ values indicating primarily viscous characteristics [7]. A smaller value of tan δ or δ corresponds to a higher degree of viscoelasticity, resembling a more solid-like behavior [8]. The value of tan δ indicates the composite propellant material's potential for energy dissipation, while a decrease indicates a more elastic behavior, storing the applied load. [9]. The phase angle δ represents the angular difference between the stress and strain [10]. A polymer is considered viscoelastic as it displays both elastic and viscous properties. Plotting the elastic modulus as a function of temperature yields a characteristic profile for a polymer system.

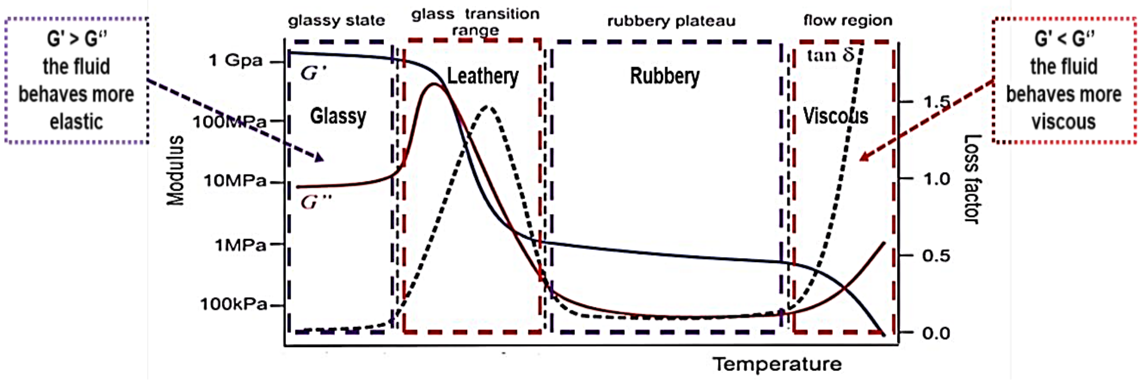

Figure 1. Typical DMA scan of viscoelastic material.

The ability of polymer chains to store or dissipate energy depends on the rate at which the chains can alter their conformation and their entanglements relative to the frequency of the load shown in Figure (1) [11]. At the transition zone, the duration of oscillation becomes insufficient for the complete rearrangement of chain conformation. The presence of ample mobility leads to significant friction between segments of the chain. In the glassy zone, configurational rearrangements do not occur within the oscillation period. The stress response to a given strain is high, resembling that of a glass-like solid, and the tan δ value is approximately 0.1 [2].

2. Experimental

2.1 Materials

Ammonium perchlorate (AP) is available in different particle sizes, namely around 400, 200, and 7-11 (μm). Aluminum (Al) can be obtained in grain sizes of 40 and 20 (μm) from the Aldrich Chemical Company in the UK. The Hydroxyl-terminated polybutadiene prepolymer (HTPB) can be sourced from Iverise Co., Brazil, and possesses properties such as a density of 0.91 g/cm^3, an OH value ranging from 0.8 to 0.9. The plasticizer, dioctyl azelate (DOZ), is available from the Aldrich Chemical Company in England. Hexamethylene diisocyanate (HMDI) is from Aldrich Company in England. Additionally, bonding agents MAPO, MT-4, MST, and MT-X are utilized.

2.2 Preparation of Composite Solid Propellant Formulations

Four CSRP compositions were created using a casting method [12]. A binder consisting of HTPB (10.53 wt. %) prepolymer with an OH equivalent of 0.85 mg/g HTPB, DOZ (2.63 wt. %), and bonding agents MAPO, MT-4, MST, and MT-X were utilized with a fixed percentage of 0.3. The prepolymer, binder, and plasticizer were mixed at 50-60°C, followed by the addition of AP (69 wt. %), and Al (17 wt.%). Mixing lasted for 30 minutes. In the final stage, the curing agent HMDI (0.54 wt. %) was added to maintain an NCO/OH ratio of 0.7. Degasification techniques were used to remove air bubbles from the slurry. The castings were degassed, neutralized, and poured into a mold to form blocks. The blocks were cut into panels and cured in an electric oven for 7-8 days at 55°C. The CSRP was then removed from the mold and placed in a package with a silica gel dryer. The oven was switched off.

2.3 Mechanical properties and hardness measurements

The stress-strain properties, Young's modulus, and hardness were measured using a ZWICK testing device. Tensile testing was performed using five samples at temperatures of 25°C. The results were analyzed based on the mechanical parameters required for the CSRP [13]. Following the standards established by the committee (JANNAF), a specific cutting machine was employed to produce the specimens.

2.4 Aging Behavior Assessment

Propellant samples subjected to higher temperature ranges can expedite their chemical transformation rate under the Arrhenius formula [14]. The samples were enclosed in aluminum bags and subjected to a baking temperature of 90°C for a period of five days, after which they were cut into regular dumbbell shapes. The aging process of the synthetic propellant samples was monitored by exposing them to a temperature of 25°C during mechanical testing.

2.5 Dynamic mechanical analysis

A DMA tester uses grips and an environmental chamber to hold a sample and create various temperature conditions. The sample is positioned between two arms, set to motion by an electromagnetic driver. The DMA module measures viscoelastic properties, detects resonant frequency changes, and provides electrical energy to maintain amplitude, indicating material modulus and damping. Specimens of 60 mm in length, 13 mm in width, and 3 mm in thickness were subjected to be tested using the DMA in conjunction with the TA Instruments Universal Analysis version control software, as depicted in Figure (2). The tests were conducted using a torsion bending clamp in "DMA multi-frequency-strain" mode and "temp ramp/freq. sweep" test. The specimens were scanned over a temperature range of -100 to 200°C while maintaining a constant frequency of 1 Hz, a heating rate of 3°C/min, a soak time of 5 min, and a maximum strain of 0.007%. A preload force of 0.1 N was applied to ensure contact between the movable clamp and the specimens. The dual cantilever testing clamp was calibrated following the procedures outlined in the instrument control software [15].

Figure 2. Dynamic mechanical analyzer and tested samples

Each sample was recorded by the computer for subsequent calculations. The temperature ranges under investigation spanned from 24 to 26°C, with a heating rate of 1°C/min, and a frequency of 1 Hz, and all operations were conducted. The storage modulus and mechanical damping of the CSRP samples were measured as a function of temperature. Tan δ has limits of 0.176 to 1.000 according to a lot of practical results done for CSRP.

3. Results and discussion

3.1 Preparation of composite propellant samples

Four propellant samples based on four different bonding agents were successfully prepared. All samples were operated with the same standard production procedures without any exceptions or any required additional steps. All propellant samples are ostensibly the same.

3.2 Mechanical Properties of CSRP Samples

Determining the mechanical properties of CSRP formulations constituted a crucial initial phase in ensuring that these propellant families could withstand the expected mechanical and thermal loads during both storage and combustion. Investigations were conducted on the mechanical properties of propellant samples at a temperature of 25°C. Ascertaining the shore (hardness A_0) is a vital step in verifying that the CSRP has undergone complete curing, at which juncture it is ready to undergo mechanical testing. The mechanical tests were conducted at a temperature of 25°C. The outcomes obtained from the experiment, which are presented in Table (1) and Figure (3), indicate that M3 and M4 exhibit the highest values of maximum strain (ε), reaching 50.4% and 44.9% respectively, under a maximum stress (σ) of 8.05 and 7.39 kg_f/cm^2. The overall mechanical properties are enhanced in M3 and M4.

Table 1. The mechanical properties of fresh (unaged) CSRP formulations were measured at 25 °C.

Formulation	Max. stress σ (kg_f/cm^2)	Max. strain ε (%)	Young's Modulus E_0 (kg_f/cm^2)	Hardness A_O
M1 (MAPO)	10.20	32.30	41.90	67.00
M2 (MT-4)	9.44	39.40	37.46	60.00
M3 (MST)	8.05	50.40	27.05	58.00
M4 (MT-X)	7.39	44.9	21.42	54.00

Journal of Physics: Conference Series **2830** (2024) 012027 doi:10.1088/1742-6596/2830/1/012027

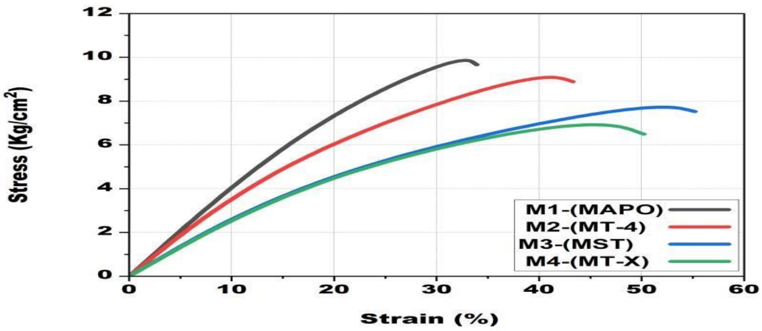

Figure 3. The mechanical properties of fresh (unaged) CSRP formulations were measured at 25℃.

3.3 Mechanical Properties of Aged Propellant Samples

The addition of a small amount of bonding agent prevents the decomposition of the propellant sample and enhances the aging qualities of CSRP. The accelerated aging program conducted for 5 days at 90°C is equivalent to 5 years of natural aging [16]. The aging process of the propellant samples is reflected in the stress, strain, and Young's modulus, as presented in Table (2) and Figure (4). Among M1, M2, M3, and M4, M4 exhibits the highest maximum strain (ε) of 33.9% at maximum strength (σ) of 10.91 kg_f/cm^2.

Table 2. Mechanical properties of aged CSRP formulations at 25℃ (aged for 5 days at 90℃)

Formulation	Max. Stress σ (kg_f/cm^2)	Max. Strain ε (%)	Young's Modulus E_0 (kg_f/cm^2)	Hardness A_O
M1 (MAPO)	6.29	32.30	23.67	53.00
M2 (MT-4)	9.12	33.00	38.34	58.00
M3 (MST)	10.18	33.90	46.10	63.00
M4 (MT-X)	10.91	33.90	46.81	67.00

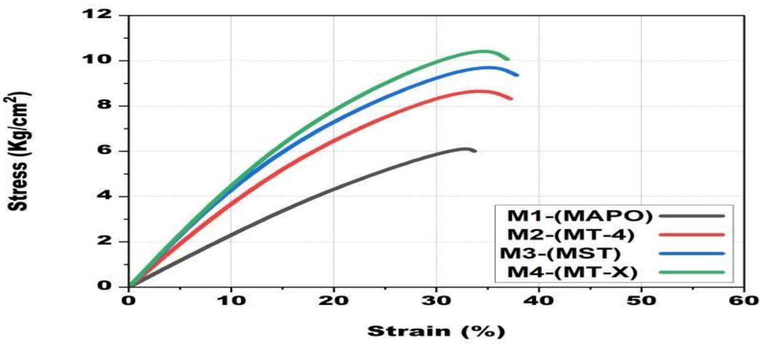

Figure 4. Mechanical properties of aged CSRP formulations measured at 25℃.

Based on the data, it is confirmed that the bonding agents utilized in this study enhance the mechanical properties of CSRP. Furthermore, the rate of failure of the bonding agent is slower in M4 compared to the other propellant formulations M1, M2, and M3.

3.4 Dynamic mechanical analysis of composite solid propellant

The results obtained from the dynamic mechanical analyzer (DMA), a typical DMA thermogram can be acquired for the fresh (unaged) formulations M1, M2, M3, and M4 measured at 24-26°C, as depicted in Table (3) and Figure (5) (a, b, c).

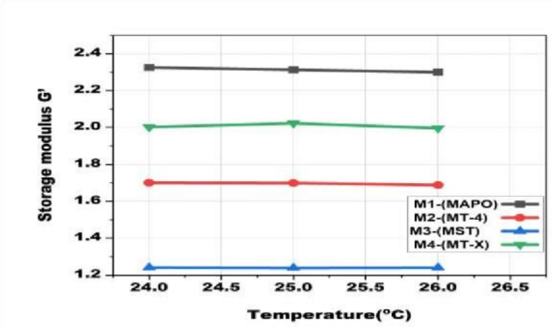

Figure 5 (a). Storage modulus of fresh (unaged) formulations M1, M2, M3, and M4

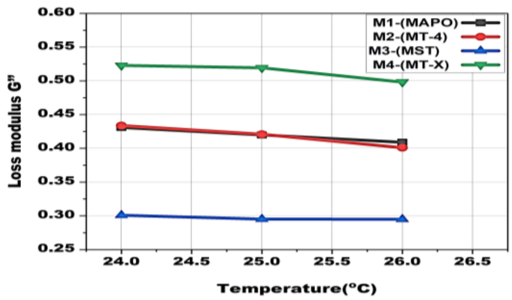

Figure 5 (b). Loss modulus of fresh (unaged) formulations M1, M2, M3, and M4

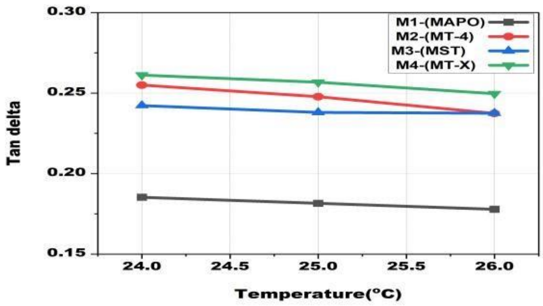

Figure 5 (c). Tan δ of fresh (unaged) formulations M1, M2, M3, and M4

Table 3. DMA results for fresh formulations M1, M2, M3, and M4 at 25 C

Formulation	M1 (MAPO)	M2 (MT-4)	M3 (MST)	M4 (MT-X)
Storage modulus (MPa)	2.31301	1.69905	1.23978	2.0227
Loss modulus (MPa)	0.41989	0.42096	0.29505	0.51928
Tan δ	0.181534	0.247762	0.237986	0.256728

To investigate the mechanical behavior of the samples, the DMA test was employed. The samples for formulations M1, M2, M3, and M4, as depicted in Figure (6) (a, b, c) were subjected to testing after being aged for a period of 5 days at 90°C [17]. The storage modulus of M1 is the highest with the result of 2.31301 MPa, the loss modulus of M4 is the highest with the result of 0.51928 MPa, and also tan δ of M4 is the highest with the result of 0.256728. The increasing value of tan δ implies that M4 possesses a greater potential for energy dissipation, thus indicating a higher level of material dissipation.

Journal of Physics: Conference Series **2830** (2024) 012027 doi:10.1088/1742-6596/2830/1/012027

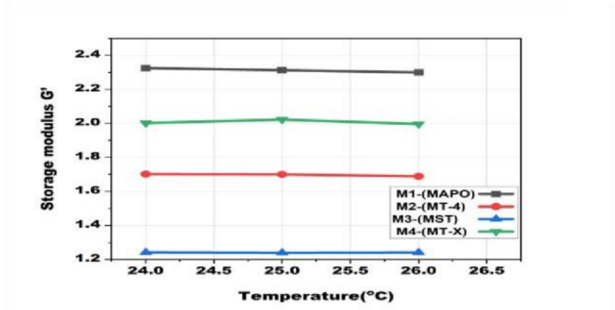

Figure 6 (a). Storage modulus of aged formulations M1, M2, M3, and M4

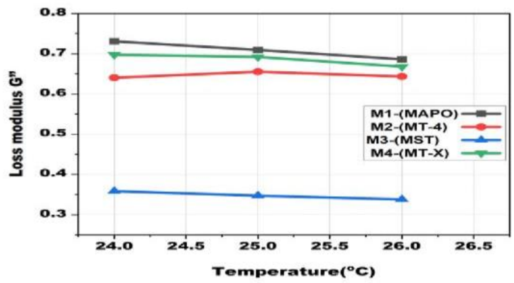

Figure 6 (b). Loss modulus of aged formulations M1, M2, M3, and M4

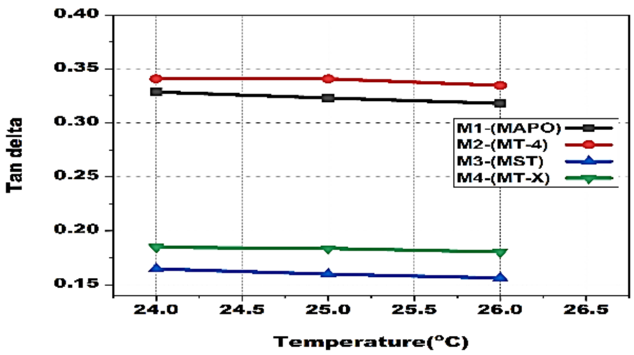

Figure 6 (c). Tan δ of aged formulations M1, M2, M3, and M4

Table 4. DMA results after accelerated aging for formulations M1, M2, M3, and M4 at 25°C

Formulation	M1 (MAPO)	M2 (MT-4)	M3 (MST)	M4 (MT-X)
Storage modulus (MPa)	2.19601	1.92202	2.17459	3.76876
Loss modulus (MPa)	0.70934	0.6551	0.34756	0.69191
Tan δ	0.323016	0.340841	0.15983	0.183591

After aging for 5 days at 90°C, the storage modulus of M4 is the highest with the result of 3.76876 MPa, the loss modulus of M1 is the highest with the result of 0.70934 MPa, and also tan δ of M3 is the lowest with the result of 0.15983, but the limits of tan δ is 0.176 to 1.000. so M4 is the most valuable one that has the highest degree of viscoelasticity because the decreasing value of tan δ suggests that the material displays a more elastic behavior, with a greater capacity to store the applied load rather than dissipating it. The mechanical properties of the propellant can be accurately assessed by comparing the results of the DMA test at 25°C with those of the tensile strength test of fresh and aged results as demonstrated in Table (5).

Table 5. DMA and tensile test results at accelerated aging for formulations M1, M2, M3, and M4

Formulation	Fresh			Aged		
	σ (kg_f/cm^2)	ε (%)	Tan δ	σ (kg_f/cm^2)	ε (%)	Tan δ
M1 (MAPO)	10.20	32.30	0.181534	6.29	32.30	0.323016
M2 (MT-4)	9.44	39.40	0.247762	9.12	33.00	0.340841
M3 (MST)	8.05	50.40	0.237986	10.18	33.90	0.15983
M4 (MT-X)	7.39	44.9	0.256728	10.91	33.90	0.183591

According to all results in Table (5), after accelerated aging, the valuable result for CSRP is that in M4 because tan δ is 0.183591 with mechanical results of maximum stress of 10.91 kg_f/cm^2 and maximum strain of 33.90%.

4. Conclusion

The mechanical tests were carried out and the results attained from the experiment explained that M3 and M4 display the highest values of maximum strain at maximum stress. Moreover, it is worth mentioning that M3 and M4 illustrate lower hardness values. Accelerated aging was applied. During the process of aging, competing processes occur, namely de-wetting recombination with cross-linking. After accelerated aging, M4 has the highest results of maximum strain at maximum stress. DMA in torsion mode was employed to elucidate the aging behavior of four CSRP formulations. The results of DMA can be interpreted by de-wetting combined with cross-linking. the increase in the loss factor indicates enhanced macromolecular mobility, which can be attributed to de-wetting between binder and filler particles. Also, the impact of accelerated aging affected the storage modulus, the loss modulus, and tan δ. The change in Tan δ is directly proportional to the change in the crosslink density and de-wetting. M4 is the most valuable formulation of CSRP with tan δ of 0.183591, and mechanical results; imply that M4 has the highest degree of viscoelasticity because a decreasing value of tan δ indicating that the viscoelastic material displays a more elastic behavior, with a greater capacity to store the applied load rather than dissipating it.

References:

[1] L. Shi, X. Fu, Y. Li, S. Wu, S. Meng, and J. Wang, "Molecular Dynamic Simulations and Experiments Study on the Mechanical Properties of HTPE/PEG Interpenetrating Polymer Network (IPN) Binders," *Nanomaterials,* vol. 13, no. 2, p. 268, 2023.
[2] R. P. Chartoff, J. D. Menczel, and S. H. Dillman, "Dynamic mechanical analysis (DMA)," *Thermal analysis of polymers: fundamentals and applications,* pp. 387-495, 2009.
[3] A. Vassilikou-Dova and I. M. Kalogeras, "Dielectric analysis (DEA)," Thermal analysis of polymers: fundamentals and applications, pp. 497-613, 2009.
[4] J. Michels, R. Widmann, C. Czaderski, R. Allahvirdizadeh, and M. Motavalli, "Glass transition evaluation of commercially available epoxy resins used for civil engineering applications," Composites Part B: Engineering, vol. 77, pp. 484-493, 2015.
[5] E. Remišová and V. Zatkalíková, "Evaluation of bituminous binder concerning resistance to permanent deformation," Procedia Engineering, vol. 153, pp. 584-589, 2016.
[6] T. W. Teh, C. G. Tan, and M. Z. Jumaat, "Development of novel high damping rubber damper under axial compression dynamic load for energy-dissipation application," in Structures, vol. 58: Elsevier, p. 105546, 2023.

[7] T. Miri, "Viscosity and oscillatory rheology," Practical food rheology: An interpretive approach, pp. 7-28, 2011.
[8] F. Ronda, M. Villanueva, and C. Collar, "Influence of acidification on dough viscoelasticity of gluten-free rice starch-based dough matrices enriched with exogenous protein," LWT-Food Science and Technology, vol. 59, no. 1, pp. 12-20, 2014.
[9] Y. Y. Aw, C. K. Yeoh, M. A. Idris, P. L. Teh, K. A. Hamzah, and S. A. Sazali, "Effect of printing parameters on tensile, dynamic mechanical, and thermoelectric properties of FDM 3D printed CABS/ZnO composites," *Materials*, vol. 11, no. 4, p. 466, 2018.
[10] J. C. Duncan and D. M. Price, "Thermomechanical, Dynamic Mechanical and Dielectric Methods," in Principles of Thermal Analysis and Calorimetry: The Royal Society of Chemistry Cambridge, p. 164. 2016.
[11] M. Grujicic, B. Pandurangan, T. He, B. Cheeseman, C.-F. Yen, and C. Randow, "Computational investigation of impact energy absorption capability of polyurea coatings via deformation-induced glass transition," Materials Science and Engineering: A, vol. 527, no. 29-30, pp. 7741-7751, 2010.
[12] Yang, T. T., Shui, Y., Wei, C. S., Huang, L. Z., Yang, C. W., Sun, G. A., ... & Liu, D. "Effect of cyclic straining with various rates on stress softening/hysteresis and structural evolution of filled rubber: a time-resolved SANS study", Composites Part B: Engineering, 242, 110100, 2022.
[13] M. F. Eissa, M. Ahmed, M. E. Tarek, M. Abd elall Ali, and E. M. Hosam, "Aziridine type bonding agents for composite solid rocket propellant," in Journal of Physics: Conference Series, vol. 2305, no. 1: IOP Publishing, p. 012023. 2022
[14] J. P. Agrawal, High energy materials: propellants, explosives and pyrotechnics. John Wiley & Sons, 2010.
[15] S. Cerri, M. A. Bohn, K. Menke, and L. Galfetti, "Aging of HTPB/Al/AP rocket propellant formulations investigated by DMA measurements," Propellants, Explosives, Pyrotechnics, vol. 38, no. 2, pp. 190-198, 2013.
[16] M. A. Bohn and S. Cerri, "Ageing behavior of composite rocket propellant formulations investigated by DMA, SGA, and GPC," in NDIA 2010 Insensitive Munitions & Energetic Materials Technology Symposium (IMEMTS) on "International Progress in Insensitive Munitions and Energetic Materials", NDIA Event, vol. 1550, 2010.
[17] S. Cerri, M. Bohn, K. Menke, and L. Galfetti, "Ageing of HTPB/Al/AP rocket propellant formulations investigated by DMA measurements, Sol-Gel and GPC Analysis," 2010.