Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.202000253

Diffusion of Labile Chemical Species in HTPB and HTPB-XT Solid Propellants and Its Effect over Solid Rocket Motor Properties on Aging – A Study

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Abstract: Hydroxyl terminated polybutadiene resin (HTPB) based solid propellants are being currently used in solid rocket motors of launch vehicles. HTPB-XT (HTPB blended with the hydrocarbon oil, Extol-21) was developed to enhance the pot life of the propellant slurry and to overcome the problems in the propellant processing due to the shorter pot life of present HTPB propellants. The diffusion study of labile chemical species in HTPB and HTPB-XT propellants (with low and high viscosity hydrocarbon oils) was carried out. Analog cartons simulating the propellant of the main motor were cast with 120 kg mix level propellant and subjected to an aging study at room temperature and an accelerated condition at different intervals over a period of 100 days. Samples from the cartons were subjected to Soxhlet extraction and analyzed for concentration of chemical species in insulation rubber as well as in propellant. The change in concentration of species from the insulation to interior propellant was also studied and compared with HTPB propellant. The diffusion of the other chemicals along with plasticizer was also observed in these studies. Nonax-D, a solid ingredient also migrated due to its solubility in the propellant matrix but not due to the movement of solid particles. Due to the migration of propellant chemicals into insulation, there was a significant reduction in their initial concentrations in the propellant regions adjacent to the insulation surface. The rate of diffusion of the chemically unbound species was affected by temperature and time. The results of viscosity build-up, mechanical, interfacial, ballistic properties for HTPB and HTPB-XT propellants are presented and discussed.

Keywords: HTPB propellant · HTPB-XT propellant · Migration study · Extol-21 · Pot life

1 Introduction

In present-day solid rocket motors, composite solid propellants based on Hydroxyl-terminated polybutadiene (HTPB) have become the workhorse propellants. The propellant compositions for these solid motors have resulted in higher end-of-mix viscosity, viscosity build up [1], and lower pot life [2,3]. Since the viscosity of propellant has bearing on the quality of casting and production of defect-free grain, every effort has to be made to complete the casting of propellant before the slurry viscosity rises to about 16,000 poise. Several operations were involved for each batch of propellant slurry (having a weight of ~2500 kg) from the end of mixing to the beginning of casting of these solid motors. These operations usually take considerable time (~1 hour) and leave very limited time of the available pot life (two and half hours) for effective casting. At present, extraordinary care has to be taken to achieve various requirements like safety, quality of the grain while minimizing the slurry wastage due to the shorter pot life of the slurry. This limitation leaves no room for any unforeseen delays while processing large rocket boosters. Hence, HTPB-XT (HTPB blended with the hydrocarbon oil namely Extol-21) was proposed in place of HTPB to overcome this ongoing problem of lower pot life. Extol-21 is a hydrocarbon oil and basically employed as an extender.

The development of HTPB-XT [4] is an improvement of the existing operational propellant. During such a development, retention of all the good qualities of the present formulation has been given top priority while incorporating a small change to effect pot life enhancement. Typical propellant formulations used for the diffusion study are presented in Table 1. The extended utility of HTPB polymer is achieved by the physical blending of paraffin liquid with the base HTPB resin and obtained several fold (more than 3 times) increase of pot life over present HTPB formulation with comparable ballistic properties and acceptable mechanical and aging properties.

A layer of insulation material is always needed to provide thermal protection from combustion gases over the in-

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Table 1. Typical propellant formulations used for diffusion studies.

Ingredients	HTPB (%)	HTPB-XT (%)
HTPB Resin	10±2	–
HTPB-XT Resin	–	10±2 Balance – Extol
DOA	3.0	3.0
Nonax-D	0.1	0.1
Ammonium perchlorate	67±5	67±5
Aluminium powder	17.0±5	17.0±5
Additives and Curator	Max. 2	Max. 2

ternal surface of the motor case [5–8]. This layer is typically vulcanized rubber consisting of filling material. It does not bond effectively to the propellant with sufficient strength to withstand environmental and operational stresses during the lifetime of a rocket motor. A thin layer of adhesive, known as "liner" is necessary for effective bonding of the insulation and the solid propellant [9,10]. The liner is applied to the insulation surface and pre-cured before propellant casting. After casting, a complete cure of liner also occurs along with propellant curing, and chemical bonding is accomplished since formulations are set to it. Thus, there are three types of interface that must be dealt with: propellant-to-liner, liner-to-insulation, and insulation-to-motor case [11]. The insulation rubber used was prepared from silica, nitrile butadience rubber, dioctyl phthalate, and capolyte resin. The liner used was carbon-black filled HTPB containing 12% solids with no plasticizer [12].

The propellants with the formulations stated in Table 1 were cast into the motor case (120 kg level) and bonded to the rubber by a thin layer of adhesive liner. The thin layer of the adhesive liner prevents the separation of the bond system which can also act as a barrier to control the diffusion of mobile species in solid rocket motors [13]. The plasticizers such as DOA are being used in these propellants as a lubricant and to increase the flexibility of the polymeric chains and softness and workability of the propellants. As a result, the rheological properties were improved during processing and the viscosity of the system was also reduced. Such addition of DOA as a plasticizer to the propellant composition provides properties suitable for storage, application, and transportation [14,15]. In addition to migration of DOA [4,14–19], other chemical species which are not bounded to the matrix, such as burn agent catalysts, antioxidant and cure agent can also migrate [13,20–25].

The mechanical properties of the propellants may undergo degradation due to the diffusion of DOA and other chemical species such as DOP (from rubber insulation), Extol-21 (in HTPB-XT propellants), and antioxidants due to their low molecular weights. This degradation process occurs mainly at the interfaces of the propellant, liner, and rubber insulation and can cause separation between the insulation and the propellant which affects the performance of solid motors [13,18,20].

Aging of these composite solid propellants as it determines the service life of solid rocket motors is an important issue in rocket motor applications. Hence, aging is defined as the deterioration of the solid propellants which alters the performance characteristics of the solid motors. Owing to chemical energy potential and large surface area, the composite propellants are subjected to deterioration during handling and storage stages leading to changes in both the ballistic and mechanical properties such as modulus, hardness, elongation, and stress [13,17,26–28]. Loss of plasticizers (DOA from the propellant side and DOP from the insulation side) by diffusion and oxidation of the polymeric matrix are the factors which are attributed to the aging process [26]. These processes usually occur at room temperature which can be accelerated by increasing the temperature during the aging period. As a prior study [12] was already carried out at RT, 60 °C and 80 °C for 60 days, aging studies were performed at RT and 50 °C for 100 days as reported in this manuscript.

It is necessary to determine the ultimate mechanical/interfacial properties of the propellant for the structural analysis of the propellant grain. These properties are needed for failure analysis and a comparison with the values of real stresses or strains, which may be significantly variable, depending on the environmental influence or the variable pressure or the thrust of the rocket motor. According to Byrd and Guy [13], the diffusion of various chemical species can interfere with the curing of the propellants which results in a weak bond between the interfaces. Hence, comprehensive information on physical, mechanical, interfacial, ballistic, and aging properties of propellant were studied similar to that of HTPB propellant in addition to earlier trials of our group [29] to accept HTPB-XT for regular production of boosters.

This study presents the aspects of the migration of chemical species within the structure of the propellant grain over a period of time in HTPB-XT propellant as compared to HTPB propellant. Figure 1 shows the structural constitution of the propellant with metallic hardware, liner, and insulation.

As a result of diffusion, the concentration of chemicals is expected to vary with respect to time. Critical attention is needed at the interface of the propellant and insulation layer. Evolution of the effects of migration viz., degradation of mechanical and bonding properties between insulation and propellant were studied and are presented in this manuscript. This study is focused to answer the aspects such as migrating species, nature of the concentration profile and whether it develops with respect to time and temperature or not, effects of bond degradation, and overall effect as a result of the migration of chemical species on the propellant properties.

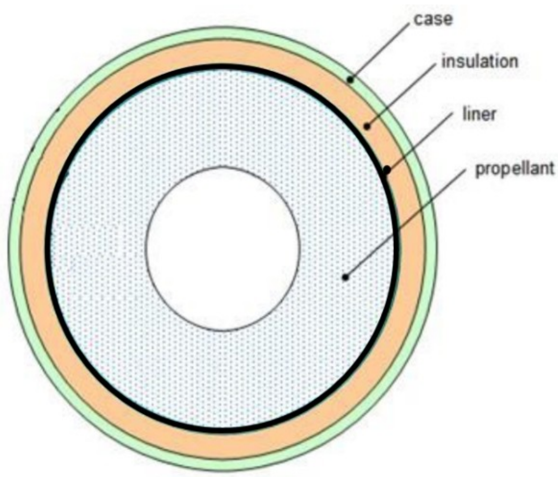

Figure 1. Structural constitution of the propellant with metallic hardware, liner, insulation, and case.

2 Experiment

2.1 Materials

Ammonium perchlorate (APEP, India), aluminum powder (MEPCO, India), HTPB resin (NOCIL), TDI (Bayer, Germany), dioctyl adipate, and dioctyl phthalate (Indo-Nippon, India), nonax-D (ICI, India) were used as received. Drying of AP and sieving of aluminum powder were carried out in-house before propellant processing. The molecular weight (Mn) of HTPB was 2400 (end group analysis). Hydrocarbon oils (Liquid paraffin oils with trade name Extol-21) with different densities and average molecular weights (220–240 Dalton and 280–300 Dalton) were used as chain extenders. N-phenyl-2-naphthylamine is one of the commonly used antioxidants in solid propellants. It is an amine-type synthetic antioxidant and available under a variety of trade names (Nonox-D, PBNA, Antioxidant 116, Stabilizer AR, etc.). It is found to be effective at around 0.1 % level for HTPB based composite propellants and relatively less toxic. The advantage of this antioxidant is that this compound with the aromatic amino function was not found to be attached to the polymeric network by reaction with isocyanates and so considered to be free in the binder and effective for many years. Toluene (AR grade-Merck, India) was used for soxhlet extraction.

2.2 Equipments

Shore hardness A was measured by a durometer as per ASTM-D-2240. Mechanical and interfacial properties of the propellants were tested on a Universal Testing Machine (Make: Instron, Model: 4466) as per ASTM-D-638. Peel strength was measured by wheel peel at 90°. Procedures as per ASTM D412-C were followed for cutting slabs into Dumbbell shape which were kept for 24/48 h in desiccation before testing mechanical and interfacial properties respectively. Six specimens from each batch were taken each time for testing these properties. The average value of 4–5 specimens giving acceptable results was employed. Thermal aging was carried out in forced ventilation ovens (ASTM E145-94 - Reapproved in 2006) under atmospheric pressure with RH <20 %. Aging conditions were set up by following the recommendations of ASTM D3045-92 (Reapproved in 2003). Duplicate samples were subjected to soxhlet extraction and the average of the results is reported. Solid strand burn rates (SSBR) of the propellants were determined using the acoustic emission technique at 45 MPa. pressure under nitrogen atmosphere.

2.3 Preparation of Samples

2.3.1 Migration Study for HTPB-XT Propellant (Vertical Mode)

Cylindrical propellant grains with insulation (Figure 1) was cast with HTPB-XT formulation as per Table 1 and kept vertically. Propellant grains were cured at 60 °C for one day. The cured propellant grains were aged at room temperature for 100 days. Samples were collected from the fore-end and aft end side of the grain at a distance of 1 cm (PL-1), 4 cm (PL-2), and 7 cm (PL-3) from the insulation surface for migration study after aging. (Figure 1 and Figure 2)

2.3.2 Migration Depth Analysis

Propellant blocks with insulation rubber were cast with HTPB and HTPB-XT (low viscous oil) and cured at 60 °C for one day. Propellant samples were collected at different

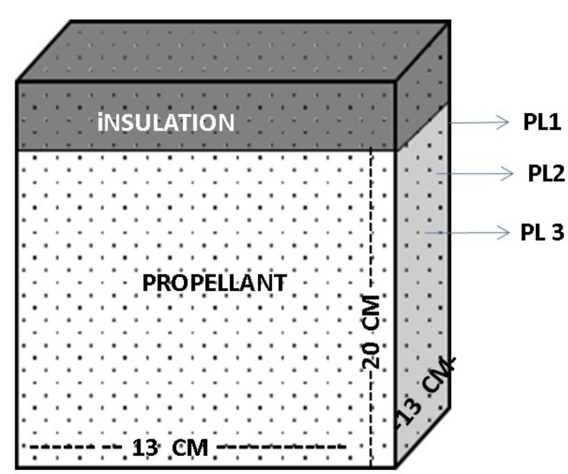

Figure 2. A typical propellant-liner-insulation assembly used for migration studies with an indication of propellant layers.

depths (PL1-1 cm, PL2- 4 cm, and PL3-7 cm) from the insulation surface after a definite aging period (1 year) and analyzed for chemical species. Insulation rubber was also analyzed for migrating chemical species (Figure 2).

2.3.3 Accelerated Aging at Different Intervals

HTPB-XT formulations with low viscosity hydrocarbon oil ('A' Series) and high viscosity hydrocarbon oil ('C' Series) were used along with normal HTPB ('B' Series). Propellant blocks with insulated rubber were kept at 50 °C and at room temperature. Samples were drawn at different intervals and studied.

3 Extraction of Chemical Species

Propellant samples were sliced into small pieces and about 10 g of propellant was soaked overnight in 100 ml of toluene. The extraction process was carried out by using a soxhlet extraction apparatus for 4 hours [30]. The toluene extract was filtered, concentrated, and diluted to volume for quantification of migrating chemical components present in the propellant sample. Extraction was also carried out for the propellant with insulation rubber for similar studies.

4 Analysis of Chemical Species by Gas Chromatograph (GC)

Extracts were analyzed for possible chemical species by a GC method using Chrompack GC-CP 9001 equipped with FID. Maitre software (version 2.5) was used to control the instrument. It was also used to collect and process the experimental data. The experimental conditions of GC were optimized as follows: Packed Column (Make: Chrompak, Mumbai): SS (2 m × 1/8"); GC phase: 10 % SE-30; Support: Chromlite; Mesh size: 60/80; Carrier gas and flow rate: Helium, 50 ml/min.; Injector port temperature: 280 °C; Oven temperature: Initial 70 °C; Final 250 °C at 6 °C/min; Detector: Flame Ionization Detector; Detector temperature: 300 °C; Sample size: 0.2 μl.

5 Results and Discussion

HTPB and HTPB-XT (XT - low and high viscosity oils) propellants were prepared as per the compositions in Table 1. The prepared compositions were analyzed for End of Mix (EOM) viscosity. EOM viscosity of HTPB-XT propellant (for both viscous oils) was in the range of 4500–5000 Poise, whereas EOM viscosity of the normal HTPB propellant is above 6000 Poise. Viscosity after 4 hours in the case of HTPB-XT formulation is less than 10,000 Poise whereas the viscosity of standard is in the range of 14,000 Poise. A large reduction was found in the EOM viscosity of HTPB-XT propellant slurry compared to normal HTPB propellant. Under real storage conditions, propellant-liner-insulation samples of HTPB, HTPB-XT (with low and high viscosity hydrocarbon oils) were stored under controlled temperatures and periodically examined for mechanical and interfacial properties during aging of 100 days. Even though these tests indicate that a change has occurred in the sample composition, they do not define the specific cause. Hence, separation and quantification of the ingredients are essential to understand the diffusion of chemical species in HTPB and HTPB-XT propellants. The migration of chemical species from propellant to insulation surface from the time of preparation was studied by their concentration in the propellant grain at various distances from the insulation at specific intervals of aging. Studies were conducted to examine the effect of temperature and aging time on the diffusion process. Diffusion data were generated for two instances to have baseline data. When the amount of particular species reaches its equilibrium concentration value, further diffusion ceases. This diffusion depends on the nature of diffusing species and medium of diffusion. It is difficult to isolate the endpoint for diffusion and thus the estimation of equilibrium concentration becomes difficult. Hence, the concentrations of chemical species for a fixed aging time of 100 days were followed at two different temperatures.

Nitrile based rubber is being used as an insulation material between the propellant and metallic hardware of rocket motors. Control data with respect to the concentration of species in the insulation were generated. This showed the presence of 5.5 % of dioctylphthalate (DOP) as a plasticizer in the base rubber. Nonax-D, Dioctyladipate (DOA), and Extol-21 were found to be absent in nitrile rubber. Experiments were carried out to check the homogeneity of chemical species throughout HTPB and HTPB-XT propellants before aging. Measured concentrations at various locations of these propellants were matching with calculated values of individual chemical species. Top and bottom side propellant samples (from HTPB-XT propellant kept in vertical mode) were collected from the rubber side at different locations (PL1, PL2, and PL3) as described in section 2.3.1 and analyzed for chemical species after aging of 100 days. Insulation Rubber was also analyzed similarly for migrating chemicals. The study as shown in Table 2 indicated that the migration of chemical species in the propellant grain is unidirectional and is a function of radius starting from propellant and rubber interface. No vertical concentration gradient of species was observed. This pattern is also according to theoretical expectations [12].

There is a significant reduction in the initial concentration of migrating chemicals in the propellant regions adjacent to insulation (Layer-1). The new phenomenon observed in this study was that the rubber insulation was enriched with Nonax-D (solid ingredient of the propellant) and DOP (plasticizer of rubber) was migrated into the propellant. Data from Table 2 indicate that the diffusion of DOP

Table 2. Diffusion study in HTPB-XT propellant (vertical mode).

Chemical Species (%)	Nozzle End (Top Side) Insulation Rubber	Propellant Layers (after 100 days of aging)			Head End (Bottom Side) Insulation Rubber	Propellant Layers (after 100 days of aging)		
		*PL1	PL2	PL3		PL1	PL2	PL3
DOA	5.15	1.87	2.60	2.25	4.21	2.75	3.12	2.93
DOP	0.41	0.10	0.10	0.10	0.35	0.10	0.10	0.10
Extol-21	0.86	0.58	0.91	0.64	0.74	0.58	0.84	0.71
Nonax-D	0.51	Trace	Trace	Trace	0.40	Trace	Trace	Trace

* PL-Propellant Layer

into the HTPB-XT propellant (top side) is changed to a small but significant amount. This may be due to the ability of Extol-21 to reduce the retarding effect of HTPB on DOA in drawing DOP into the propellant. Initially, Extol-21 (Hydrocarbon extender) diffusion into the insulation rubber is not much favored. Since HTPB and Extol-21 are non-polar, the diffusion of Extol-21 from propellant is relatively restricted. Once the curing is completed, HTPB is not available, and in consequence, hydrocarbons diffuse out faster. As a result of this migration, no major degradation in the propellant properties was observed (Figure 3). A similar trend was observed for the bottom side of HTPB-XT propellant also. Diffusion depth analysis was performed with HTPB and HTPB-XT propellants and compared after aging these propellants for one year to observe the migration of chemicals over this period. Results are presented in Table 3 and are comparable with that of HTPB. The pattern of diffusion of Extol-21 remains comparable to that of DOA. DOP was absent in PL1 of HTPB-XT propellant as Extol-21 reduces the retarding ef-

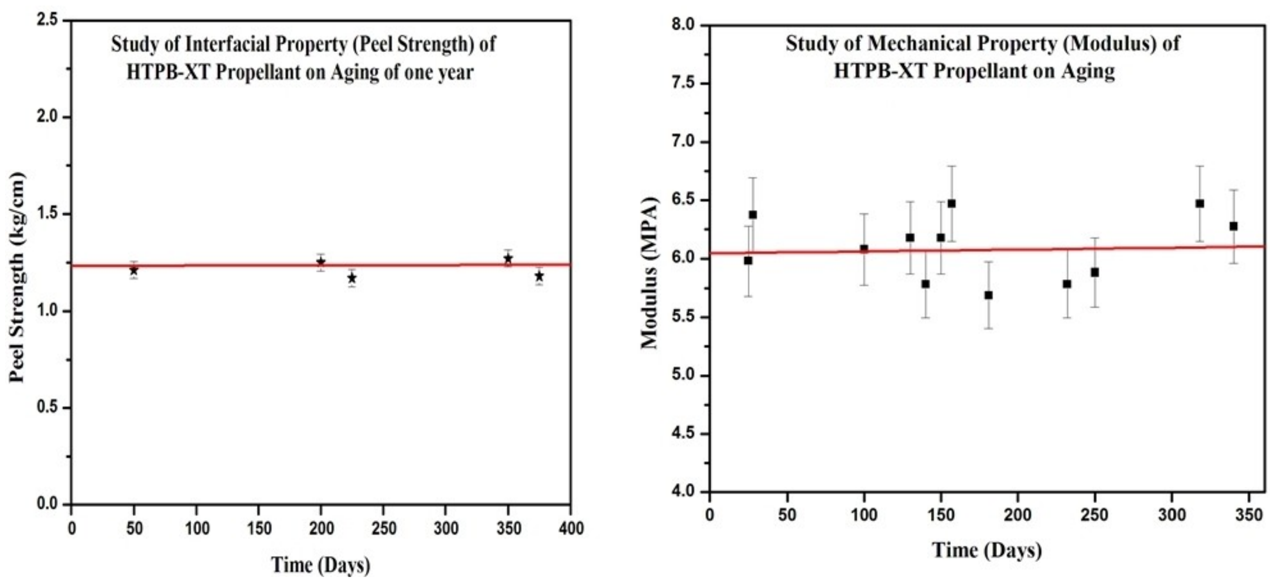

Figure 3. Interface and mechanical properties of HTPB-XT (low viscous oil) propellant after aging of one year.

Table 3. Diffusion depth analysis (after aging of one year).

Description	HTPB Propellant			HTPB-XT Propellant			
Distance of propellant region from the insulation (cm)	DOA (%)	DOP (%)	Nonax-D (%)	DOA (%)	DOP (%)	Nonax-D (%)	Extol-21 (%)
Insulation	4.70	0.60	0.56	4.10	0.40	0.75	0.56
PL1 - 1 cm	2.20	0.11	–	0.50	–	–	0.10
PL2 - 4 cm	2.50	0.10	0.11	3.00	0.15	0.13	0.76
PL3 - 7 cm	2.75	0.10	0.12	3.00	0.15	0.13	0.81

fect of HTPB on DOA in drawing DOP into the propellant effectively.

HTPB-XT propellant blocks with insulated rubber were prepared using low viscosity hydrocarbon oil ('A' Series) and high viscosity hydrocarbon oil ('C' Series) and kept at 50 °C and at room temperature along with normal HTPB ('B' Series). Samples were tested at different intervals. The concentration profile of chemical constituents of propellants under accelerated and normal aging conditions were studied and found to be different (Table 4). Hence, it can be inferred that the rate of diffusion of chemical species was influenced by temperature. However, the pattern of migration of Extol-21 remains comparable to that of DOA under these conditions. However, mechanical and interface bonding properties were not affected (Figure 4).

Solid Strand Burn rate (mm/s) was also tested for the specimens of these propellants and found to be in the range of 7.7 to 7.9. Interfacial and Mechanical properties of HTPB-XT (low and high viscosity oils) solid propellants on accelerated aging (at 50 °C) carried out for the duration of hundred days are provided in Figures 5 and 6.

Diffusion of DOA from HTPB-XT (A and C series) and HTPB propellants (B series) and DOP into these propellants during aging of 100 days at RT and 50 °C was very much notable. When HTPB-DOA-EXTOL-DOP systems (A and C series) are considered, the initial lowering of DOP (in the rubber insulation) is due to a reduction in the affinity of HTPB-DOA system for DOP compared to HTPB-DOA-EXTOL systems. The retarding effect of HTPB on the associations of DOA and DOP is reduced by the presence of Extol (low and high viscous oils) as Extol favors DOP. In the absence of HTPB as it is reacted out during curing/aging, diffusion of DOP is more favored. Hence, the concentration of DOP was more in these propellants after aging.

Mechanical properties of HTPB-XT propellants are comparable with that of HTPB propellant. Tensile strength of HTPB-XT propellants and normal HTPB propellants fall in the range of 0.69–0.81 MPa whereas elongation (%) is found to be in the range of 32–40. Tensile bond strength and peel strength are marginally low compared to normal HTPB. Shore A hardness was tested for all these propellants and found to be in the range of 68–72. Density was tested and found to be in the range of 1.70–1.72. Solid strand burn rate (mm/s) was also tested for the specimens of these propellants and found to be in the range of 7.7 to 7.9.

6 Conclusions

Diffusion exists in all the propellants for labile ingredients like DOA, DOP, and Extol-21. Nonax-D, a solid ingredient also migrates due to its solubility in the propellant matrix but not due to the movement of solid particles. Diffusion cannot be avoided as long as a concentration gradient ex-

Table 4. Concentration profile of chemical species in rubber and propellants during aging at RT and 50 °C for 100 days.

Aging Time (Days)	Temp (°C)	Rubber Insulation DOA (%)	DOP (%)	NonaxD (%)	Extol-21 (%)	Propellant DOA (%)	DOP (%)	NonaxD (%)	Extol-21 (%)
HTPB – XT PROPELLANT 'A' SERIES									
1	RT	1.62	3.42	0.42	0.85	2.50	0.09	Trace	1.09
1	50	2.51	3.08	0.44	1.15	2.39	0.14	Trace	1.12
14	50	3.00	2.41	0.43	1.44	2.38	0.17	Trace	0.78
28	50	3.47	1.89	0.43	0.78	2.47	0.34	Trace	0.78
65	50	4.36	1.77	0.76	0.76	2.46	0.37	Trace	0.73
100	50	4.79	1.40	0.77	0.85	2.53	0.34	Trace	0.65
100	RT	4.06	2.69	0.70	1.01	2.18	0.29	Trace	0.65
HTPB PROPELLANT 'B' SERIES									
1	RT	1.61	2.96	0.33	–	2.51	0.13	Trace	–
39	50	3.63	2.81	0.30	–	2.22	0.13	Trace	–
100	50	4.89	1.75	0.73	–	2.14	0.31	Trace	–
100	RT	3.73	3.64	0.41	–	2.28	0.38	Trace	–
HTPB-XT PROPELLANT 'C' SERIES									
1	RT	1.73	3.81	0.51	1.43	2.23	0.09	Trace	1.14
1	50	2.14	3.24	0.37	1.56	1.79	0.17	Trace	1.16
14	50	3.23	3.76	0.41	1.76	2.19	0.26	Trace	1.04
28	50	3.75	3.11	0.28	0.91	2.05	0.35	Trace	1.18
65	50	4.54	2.23	0.55	0.86	2.45	0.40	Trace	1.12
100	50	4.54	2.23	0.55	0.86	2.45	0.40	Trace	–
100	RT	3.21	2.86	0.41	–	2.36	0.36	Trace	–

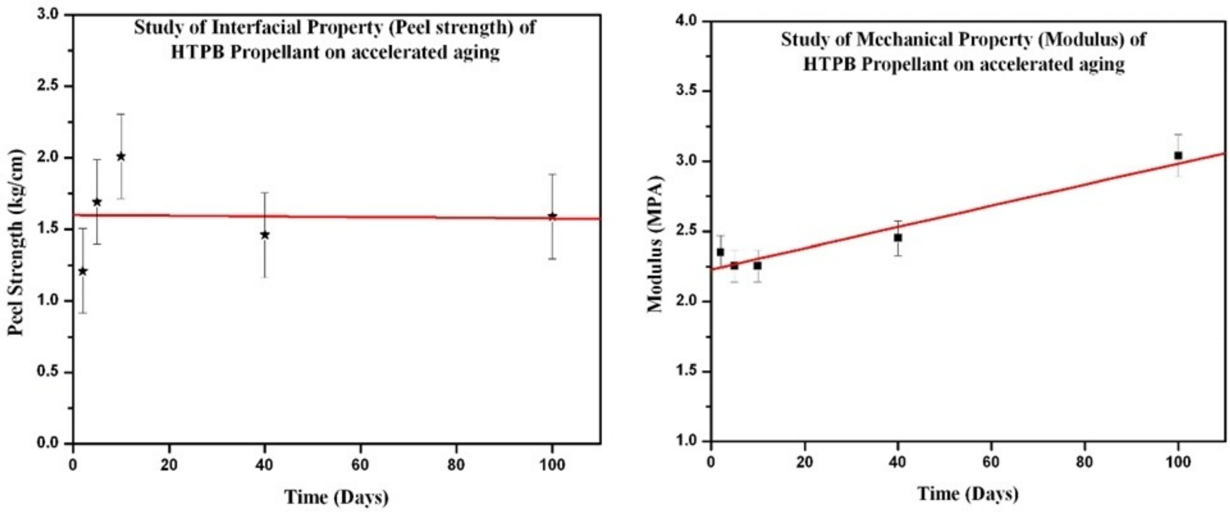

Figure 4. Interface and mechanical properties of HTPB solid propellant on accelerated aging at 50 °C.

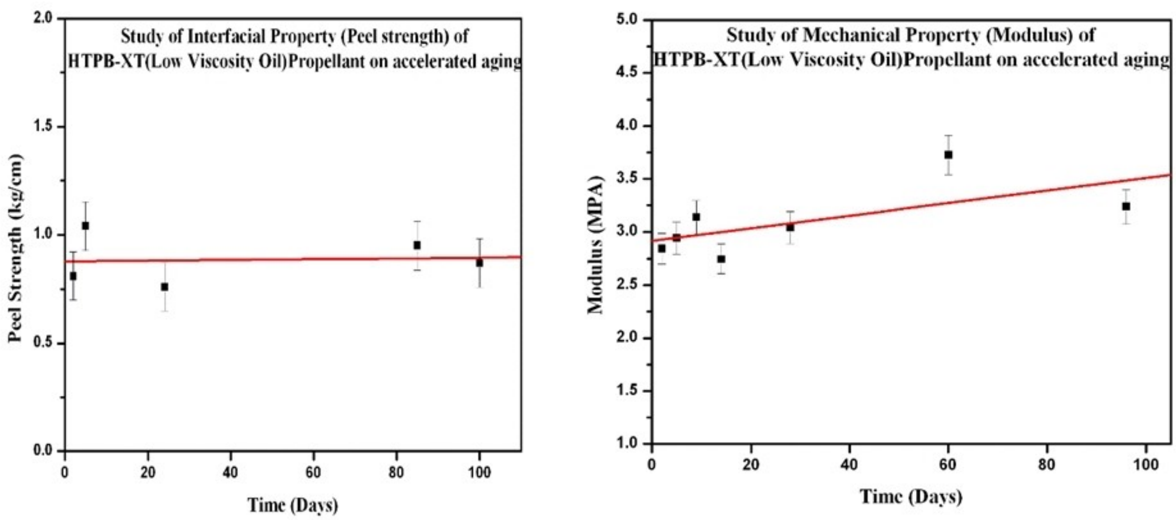

Figure 5. Interfacial and mechanical properties of HTPB-XT (low viscosity oil) solid propellant on accelerated aging at 50 °C for 100 days.

ists in the designed structural constituents. Due to the migration of propellant chemicals into insulation, there was a significant reduction in their initial concentrations in the propellant regions adjacent to insulation. Migration was a unidirectional phenomenon as expected. The rate of migration is affected by temperature and time. The decisive properties like mechanical and interface bonding which play a vital role in accepting the propellant formulation are not significantly affected due to the migration of chemical species.

Acknowledgments

Corresponding author (Dr. S. Selvakumar) acknowledges the support rendered by Dawn Raju, Colleague at CMTL and the constant encouragement by Dr.B. Muni Rathinam, General Manager, QC & CF, Dr. T. V. Ramana Reddy, General Manager (Process) and Shri. A. Syed Hamed, Deputy Director, SPROB & SPP.

Data Availability Statement

Correct version of data availability statement is available.

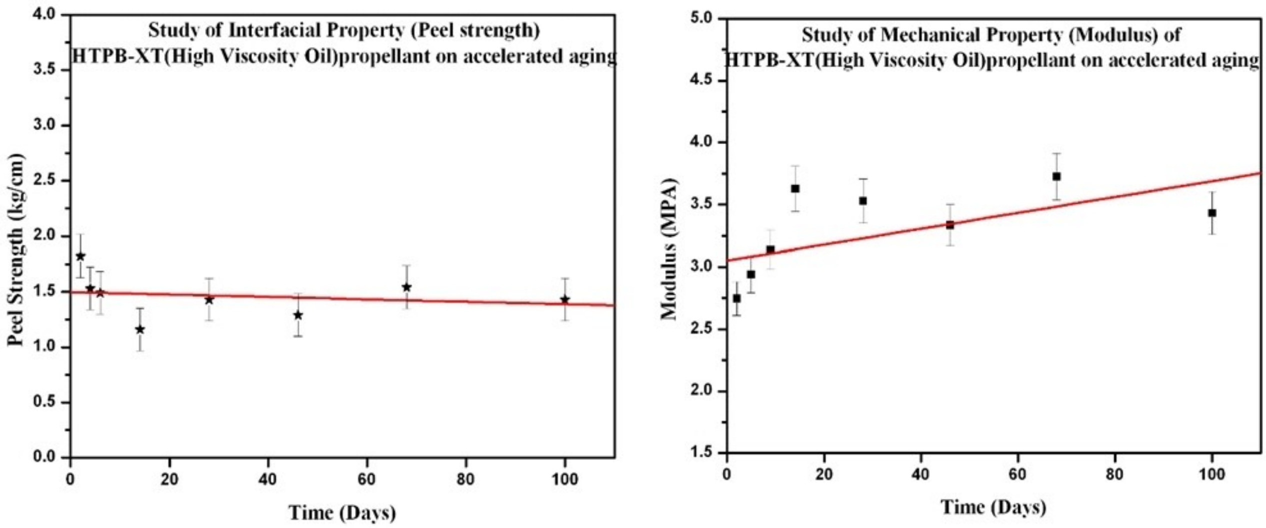

Figure 6. Interfacial and mechanical properties of HTPB-XT (high viscosity oil) solid propellant on accelerated aging at 50 °C for 100 days.

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Manuscript received: September 29, 2020
Revised manuscript received: January 5, 2021
Version of record online: March 1, 2021

