Study on the fabrication of sulfuric acid-resistant butyl rubber for military battery linings

Nguyen Ngoc Son[1*], Vu Minh Thanh[1], Pham Thi Phuong[1],
Do Quoc Manh[1], Le Gia Khiem[2], Nguyen Thi Huong[1]

[1]Institute of Materials, Biology and Environment/ Academy of Military Science and Technology, 17 Hoang Sam, Nghia Do, Hanoi, Vietnam;
[2]University of Science and Technology of Hanoi/ Vietnam Academy of Science and Technology, A21 Building, 18 Hoang Quoc Viet, Nghia Do, Hanoi, Vietnam.
[*]Corresponding author: sonorgc88@gmail.com

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ABSTRACT

This study focuses on the development of a specialized butyl rubber (IIR) material with high resistance to sulfuric acid (40% H_2SO_4 at 70 °C) for use as military battery linings. The effects of the vulcanization system, N330 carbon black loading, P150 paraffin oil content, and the TMQ/6PPD antioxidant systems on the mechanical properties and chemical resistance were systematically investigated. Experimental results indicated that the use of an efficient vulcanization system comprising of 2.0 phr DTDM and 1.5 phr TMTD established a robust mono- and di-sulfidic crosslink network, effectively minimizing acid-induced chain scission. The optimal formulation was identified as containing of 50 phr of N330 carbon black, 10 phr of P150 paraffin oil, and a synergistic antioxidant system comprising of 2.0 phr TMQ and 1.5 phr 6PPD. The resulting material exhibited a tensile strength of 14.5 MPa, an elongation at break of 510%, and retained 92.4% of its mechanical properties after 168 hours of accelerated aging. SEM analysis confirmed that the surface of the optimized sample maintained its structural integrity without micro-cracks, fully satisfying the technical requirements for military equipment applications.

Keywords: Butyl rubber; Acid resistance; Military lead-acid battery; DTDM curing system.

1. INTRODUCTION

Lead-acid batteries remain a strategic energy storage source for the military and heavy industries due to their cost-effectiveness, reliability, and high cold cranking amps [1, 2]. However, in the context of military hardware, these systems operate under extreme conditions, including temperatures ranging from -40 °C to +70 °C and continuous exposure to 30-40% sulfuric acid [3]. A primary cause of failure is the degradation of rubber linings, leading to acid leakage, corrosion, and explosion risks, which significantly compromise combat readiness [4]. Consequently, developing rubber materials with superior acid resistance is an urgent priority. Among elastomers, butyl rubber (IIR) is the optimal candidate due to its high saturation and low permeability [5, 6]. The critical challenge in hot acidic environments is the attack of H^+ ions on crosslinks [6]. Traditional vulcanization systems generate polysulfidic bonds with low bond energy (~270 kJ/mol), rendering them susceptible to thermal and oxidative cleavage [7, 8]. To mitigate this, efficient vulcanization (EV) systems utilizing sulfur donors like DTDM are preferred, as they promote the formation of stable mono- and di-sulfidic bonds (285–350 kJ/mol) [9]. However, optimizing the DTDM/accelerator ratio for IIR remains a specific technical challenge. Furthermore, material stability relies on reinforcing fillers and plasticizers. Carbon Black N330 enhances mechanical properties and creates a "tortuosity effect" that retards acid diffusion [10], provided that agglomeration is minimized. Conversely, while paraffin oil acts as a plasticizer to facilitate processing, an excessive amount is prone to extraction when exposed to the hot acidic environment. This extraction process leaves behind micro-voids within the rubber matrix, which compromise the structural integrity and accelerate acid permeation [11]. Additionally, surface aging requires control via a synergistic TMQ/6PPD antioxidant system to trap radicals and form protective films [12, 13]. Despite existing studies, a comprehensive formulation optimizing all four factors: vulcanization system, filler, plasticizer, and antioxidants, specifically for military battery linings operating in harsh acidic conditions (40% H_2SO_4 at 70 °C), is limited. This study aims to develop a specialized IIR formulation ensuring over 90% property retention and microstructural stability, providing a scientific basis for domestic defense manufacturing.

2. EXPERIMENTAL

2.1. Materials

The study utilized commercial Butyl rubber X_Butyl® RB 301 (Arlanxeo, Netherlands; unsaturation 1.85 mol %, Mooney viscosity 51 MU), reinforced by Carbon Black N330 (OCI, Korea) and plasticized with P150 paraffinic oil (Korea). The vulcanization accelerators used were 4,4'-dithiodimorpholine (DTDM) and tetramethylthiuram disulfide (TMTD). The antioxidants employed were Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD). These rubber additives were of industrial grade with a purity > 98%, supplied by Rongcheng Chemical General Factory Co., Ltd. (China). Other additives including Zinc oxide (ZnO), Stearic acid (SA), and Sulfur (S), were of analytical grade (Xilong Scientific, China). All chemicals were used as received without further purification.

2.2. Experimental methods

2.2.1. Sample preparation and vulcanization characteristics

Rubber compounds (table 1) were prepared via a two-stage mixing process on a two-roll mill. The masterbatch (rubber, fillers, activators, antioxidants) was mixed at 50–60 °C, followed by the incorporation of the vulcanization system at temperatures below 50 °C to prevent scorching. Curing characteristics were determined via MDR at 160 °C (ASTM D5289), and specimens were compression molded at 160 °C under 15 MPa for the optimum cure time (t_{c90}).

Table 1. *Formulations of the investigated rubber compounds.*

Ingredients	Sample S1 (phr)	Sample S1 (phr)
Butyl rubber IIR (X_Butyl® RB 301)	100	100
Carbon black N330	50	50
Zinc oxide (ZnO)	5.0	5.0
Stearic acid	1.0	1.0
Paraffinic oil P150	7.5	7.5
Antioxidant TMQ	1.0	1.0
Antioxidant 6PPD	1.0	1.0
Accelerator TMTD	0.5	1.5
Accelerator MBTS	1.0	-
Accelerator DTDM	-	2.0
Sulfur	1.5	0.5

2.2.2. Determination of crosslink densities

The crosslink density (ν_e) was determined using the equilibrium swelling method in toluene at 25 ºC, according to ASTM D471. Rubber specimens (initial mass m_0) were immersed in toluene for 72 hours to achieve equilibrium swelling mass (m_s). Subsequently, the samples were dried to a constant mass (m_d) to determine the polymer mass after extraction. The crosslink density (ν_e, mol/cm^3) was calculated based on the modified Flory-Rehner equation:

$$v_e = -\frac{\ln(1 - v_r) + v_r + \chi v_r^2}{V_s\left(v_r^{1/3} - \frac{v_r}{2}\right)} \tag{1}$$

Where:

- V_s = 106.3 cm^3/mol is the molar volume of toluene.
- χ is the butyl rubber-toluene interaction parameter, $\chi = 0.42 + 0.43v_r$.
- v_r is the volume fraction of rubber in the swollen gel, calculated using the equation:

$$v_r = \frac{m_d/\rho_p}{m_d/\rho_p + (m_s - m_d)/\rho_s} \tag{2}$$

Where:

- ρ_p is the density of the rubber compound.
- ρ_s is the density of toluene (0.867 g/cm^3).

Additionally, the crosslink density was also estimated from the Moving Die Rheometer (MDR) data using the following approximation:

$$v_e = \frac{(M_H - \mathrm{M}_L)}{(2\mathrm{RT}\rho_p)} \tag{3}$$

Where:

- M_H and M_L are the maximum and minimum torques (N.m), respectively.
- R = 8.314 J/(mol.K) is the universal gas constant.
- T = 433K (160 °C) is the curing temperature.

2.2.3. Mechanical test and acid resistance evaluation

Mechanical properties, including tensile strength and elongation at break, were measured according to ASTM D412, while Shore A hardness was determined according to ASTM D2240 using an Electronic universal material testing machine WDW-100 100kn Luda.

Chemical resistance was evaluated according to ASTM D543 by immersing the rubber specimens in a 40% sulfuric acid solution (H_2SO_4) at 70 °C for 168 hours. The acid resistance was quantified through the retention coefficient of mechanical properties (K_p), calculated using the following equation (4):

$$K_p(\%) = \frac{P_{aged}}{P_{initial}} \times 100 \tag{4}$$

Where:

- P_{aged} is the value of tensile strength or elongation at break after aging.
- $P_{initial}$ is the corresponding value before aging.

2.2.4. Morphological Analysis (SEM)

The surface morphology and fracture surfaces of the materials before and after acid aging were examined using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F) operating at an accelerating voltage of 5 kV. This analysis aimed to evaluate the degree of surface corrosion, the formation of micro-cracks, and the interfacial adhesion between carbon black particles and the rubber matrix.

3. RESULTS AND DISCUSSION

3.1. Selection of vulcanization system

The rheological characteristics and network parameters of butyl rubber cured with two different systems are illustrated in figure 1 and table 2, while mechanical properties before and after aging are summarized in table 3. Experimental results demonstrate that transitioning from the traditional system (S1: Sulfur/MBTS/TMTD) to the efficient system (S2: Sulfur/DTDM/TMTD) significantly enhances overall performance.

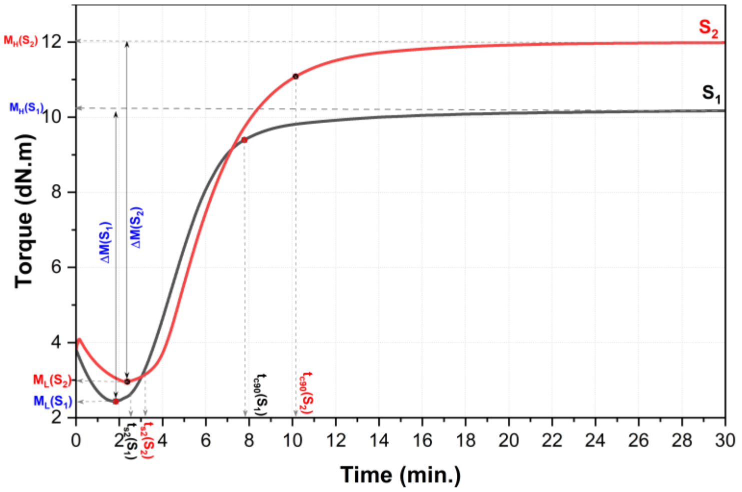

Figure 1. *Cure curves of S1 and S2 compounds.*

Table 2. *Vulcanization characteristics of the investigated systems.*

Sample	ML (dN·m)	MH (dN·m)	ΔM (dN·m)	t_{s2} (min.)	t_{90} (min.)	$\nu_e \times 10^4$ (mol/cm³)	
						Flory-Rehner	MDR
S1	2.44	10.17	7.73	2.27	7.78	1.08	1.17
S2	2.95	11.98	9.03	3.20	10.15	1.23	1.36

MDR analysis revealed that S2 exhibited a higher crosslink density compared to S1 (1.36×10^{-4} vs. 1.17×10^{-4} mol/cm^3. This tighter network structure correlated with superior initial tensile strength (14.5 MPa for S2 vs. 12.8 MPa for S1). Although the restricted chain mobility in S2 resulted in lower elongation at break (510%) compared to S1 (560%), this value remains fully sufficient for battery lining applications.

Table 3. *Mechanical properties and acid resistance of the rubber compounds.*

Properties	Unit	Compound S1	Compound S2
Before aging			
Tensile strength	MPa	12.8	14.5
Elongation at break	%	560	510
Hardness	Shore A	57	58
After aging in 40% H_2SO_4 at 70 °C for 168 giờ			
Retention of tensile strength	%	63.8	79.8
Retention of elongation at break	%	59.2	66.5
Hardness	Shore A	61	61

Crucially, the S2 system demonstrated exceptional acid resistance. After 168 hours in 40% H_2SO_4 at 70 °C, S1 suffered severe degradation, retaining only 63.8% of its tensile strength. This is attributed to the prevalence of polysulfidic linkages (-Sx-, x ≤ 3) in the sulfur-rich S1 system, which possess low bond energy (~ 270 kJ/mol) and are highly susceptible to oxidative scission6. In contrast, S2 retained 79.8% of its strength. This durability stems from the DTDM/TMTD combination facilitating the predominance of mono-sulfidic (-S-) and di-sulfidic (-S_2-) crosslinks [14, 15]. These bonds possess high dissociation energies of 285–350 kJ/mol, significantly higher than those of polysulfidic bonds (< 270 kJ/mol) [16], providing robust stability against proton attack. Consequently, S2 was selected for further investigation.

3.2. Effect of N330 carbon black loading

As illustrated in figure 2, tensile strength follows a bell-shaped trend, peaking at 14.5 MPa at 50 phr due to optimal interfacial stress dispersion. Beyond 60 phr, the tensile strength declines (dropping to 12.1 MPa at 70 phr) are caused by filler agglomeration acting as stress concentrators. Conversely, the hardness increased linearly (46 to 72 Shore A) while elongation at break plummeted (680% to 340%), reflecting restricted chain mobility within the rigid network.

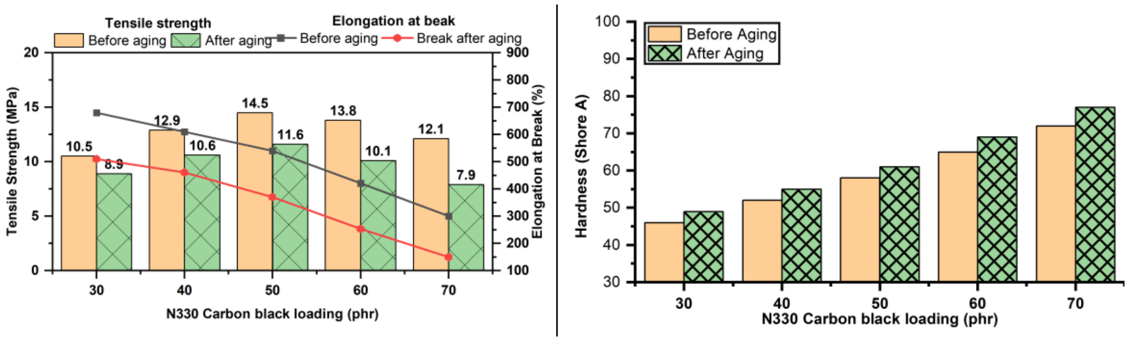

Figure 2. *Variation of mechanical properties of butyl rubber with N330 carbon black loading before and after aging (40% H_2SO_4, 70 °C, 168 hours).*

Crucially, post-aging analysis reveals significantly more severe degradation at higher loadings (60-70 phr). This is attributed to carbon black particles forming conductive pathways, facilitating deeper acid permeation into the matrix structure [17]. Consequently, 50 phr was selected as the optimal loading, offering the best balance between reinforcing efficiency (14.5 MPa) and post-aging property retention (11.6 MPa).

3.3. Effect of P150 paraffin oil content

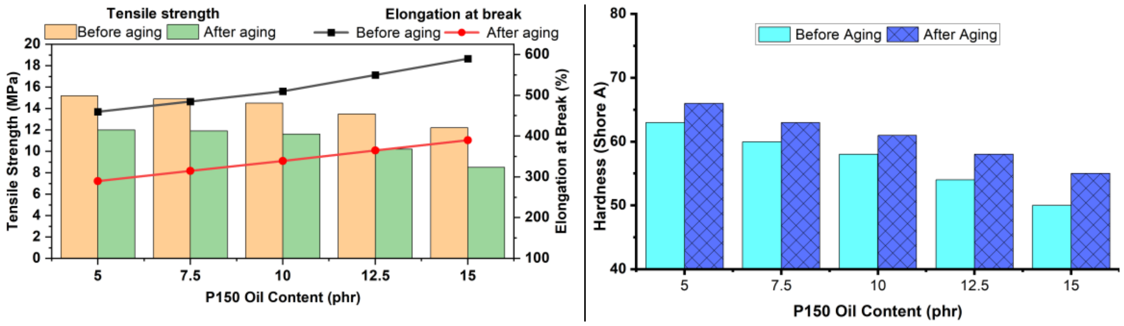

Figure 3. *Influence of P150 paraffin oil content on mechanical properties before and after aging.*

In addition to fillers, the content of plasticizer plays a crucial role in facilitating carbon black dispersion and regulating the hardness of the material. The investigation was conducted with P150 paraffin oil content varying from 5 to 15 phr. The evaluation results of mechanical properties before and after acid aging are presented in figure 3. Increasing the P150 oil content (from 5 to 15 phr) significantly improved the elongation at break (increasing from 460% to 590%) and processability, attributed to the internal lubrication effect, which reduces intermolecular friction. However, this improvement was accompanied by a gradual decrease in tensile strength and hardness due to the dilution effect on the polymer network. Notably, the acid resistance declined sharply when the oil content exceeded 10 phr. At the 15 phr level, the tensile strength after aging decreased by up to 30% compared to the initial value.

The primary degradation mechanism is attributed to the low molecular weight P150 oil being prone to extraction or migration to the surface in the hot acidic environment, leaving behind micro-voids within the matrix. Consequently, a P150 oil content of 10 phr was identified as the optimal point, ensuring high tensile strength while minimizing void formation caused by oil extraction.

3.4. Effect of TMQ/6PPD antioxidant system

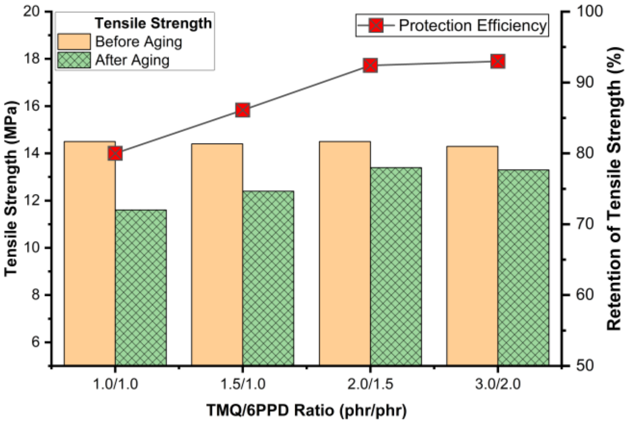

Figure 4. *Effect of TMQ/6PPD ratio on tensile strength retention after acid aging.*

Figure 5. *Surface blooming phenomenon observed at high antioxidant loading.*

To maximize service life under harsh acidic conditions, the influence of the TMQ/6PPD antioxidant ratio on the optimized S2 compound was investigated, with results summarized in figure 4. At the baseline ratio (1.0/1.0 phr), the material retained only 80% of its tensile strength (11.6 MPa) after aging (168 h, 40% H_2SO_4, 70 ºC), indicating insufficient neutralization of free radicals. However, increasing the dosage to 2.0 phr TMQ /1.5 phr 6PPD dramatically improved retention to 92.4% (13.4 MPa). This superior performance is attributed to a synergistic dual-action mechanism: TMQ acts as a heat-resistant radical scavenger within the matrix, while 6PPD migrates to the surface to form a passive protective layer against oxidant ingress. Conversely, further increasing the loading to 3.0/2.0 phr provided negligible gains (93.0% retention) and led to surface blooming (figure 5), which compromises adhesion to battery components. Consequently, the 2.0/1.5 phr ratio was identified as the optimal ratio.

3.5. Morphological analysis (SEM)

To elucidate the protective mechanisms of the vulcanization and antioxidant systems against acid attack, the surface morphology of representative samples was analyzed via SEM (figure 6).

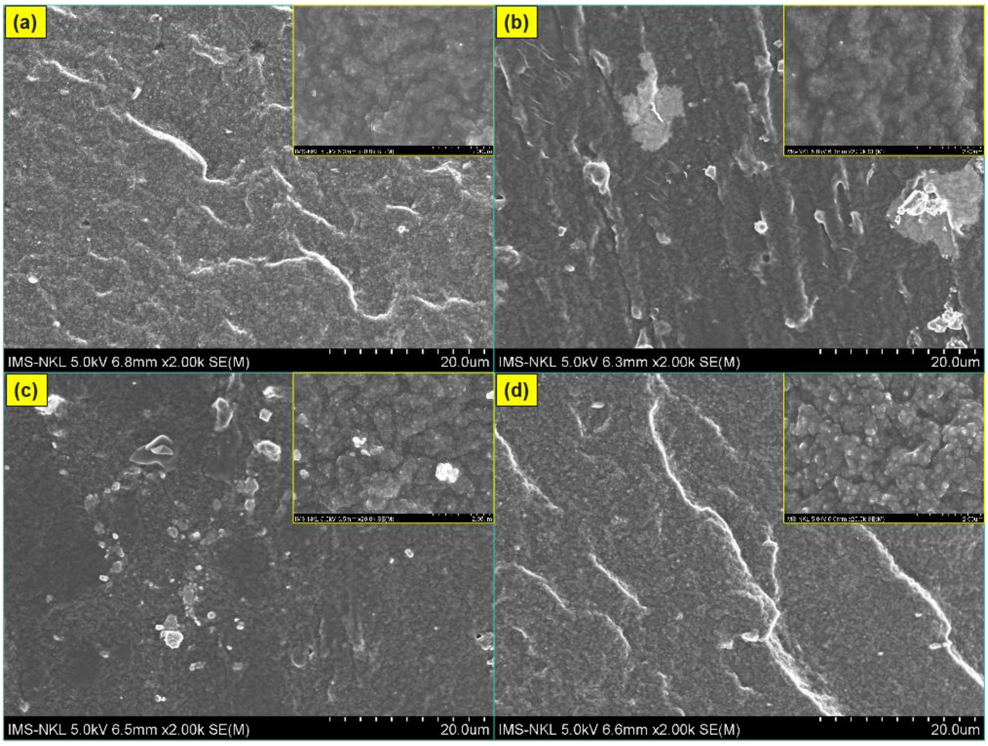

Figure 6. *SEM image of butyl rubber surfaces (magnification ×2,000):*
(a) Initial sample; (b) S1 after acid aging; (c) S2 after acid aging (basic antioxidant);
(d) S2 after acid aging (enhanced antioxidant).

Figure 6(a) reveals the unaged material in an ideal state: a smooth, homogeneous surface where the rubber matrix tightly encapsulates carbon black particles without voids. Conversely, after hot acid immersion, compound S1 (figure 6b) exhibits the most severe degradation, characterized by deep cracks and extensive erosion. This confirms the vulnerability of polysulfidic linkages to acid-induced oxidative cleavage, leading to surface structure collapse. Transitioning to the efficient DTDM/TMTD system in compound S2 (figure 6c) significantly mitigated deep cracking. However, the surface remained rough with scattered micro-cracks, indicating that the mono-sulfidic network alone, paired with basic antioxidant levels (1.0/1.0 phr), could not fully prevent superficial skin aging. The critical role of the optimized antioxidant system is demonstrated in figure 6(d). By utilizing the enhanced package (2.0 phr TMQ /1.5 phr 6PPD), the surface morphology remains remarkably smooth and comparable to that of the unaged sample, with microcracks effectively eliminated. This improvement is attributed to a dual shield mechanism: migrated 6PPD sacrificially reacts with surface oxidants, while TMQ neutralizes radicals within the sub-surface layer. SEM analysis confirms that ensuring comprehensive protection in harsh acidic environments requires the synergistic combination of an efficient vulcanization system (S2) and an enhanced antioxidant dosage.

4. CONCLUSIONS

This study successfully developed a high-performance butyl rubber for military battery linings resistant to hot sulfuric acid. The efficient vulcanization system, utilizing DTDM (2.0 phr) and TMTD (1.5 phr), established a robust mono- and di-sulfidic network significantly more resistant to oxidative scission than traditional systems. The optimized formulation, incorporating 50 phr N330, 10 phr P150, and a synergistic antioxidant package (2.0 phr TMQ / 1.5 phr 6PPD), yielded a tensile strength of 14.5 MPa with exceptional property retention (92.4%) after 168 hours of acid aging. Furthermore, the butyl rubber material fabricated under optimal conditions demonstrated excellent resistance to the harsh acidic environment, maintaining high mechanical retention and superior surface integrity without micro-cracking. These findings confirm the suitability of the developed material for application as protective linings in military batteries, ensuring long-term durability and reliability.

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TÓM TẮT

Nghiên cứu chế tạo vật liệu cao su butyl chịu axit sulfuric ứng dụng làm lớp lót cho ắc quy quân sự

Nghiên cứu này tập trung phát triển vật liệu cao su butyl (IIR) chuyên dụng có khả năng kháng axit sulfuric (H_2SO_4 40% tại 70 °C) ứng dụng làm lớp lót cho ắc quy quân sự. Ảnh hưởng của hệ lưu hóa, hàm lượng than đen N330, dầu hóa dẻo parafin P150 và hệ chất phòng lão hóa TMQ/6PPD đến cơ tính và độ bền hóa chất được khảo sát hệ thống. Kết quả thực nghiệm cho thấy việc sử dụng hệ lưu hóa hiệu quả gồm 2.0 phr DTDM và 1.5 phr TMTD tạo ra mạng lưới liên kết mono/di-sulfide bền vững, hạn chế tối đa sự cắt mạch do axit. Đơn phối liệu tối ưu được xác định tại hàm lượng 50 phr than đen N330, 10 phr dầu P150 và hệ phòng lão hóa hiệp trợ 2.0 phr TMQ/1.5 phr 6PPD. Vật liệu đạt độ bền kéo 14.5 MPa, độ giãn dài 510% và duy trì được 92.4% tính chất cơ lý sau 168 giờ lão hóa cấp tốc. Phân tích SEM xác nhận bề mặt mẫu tối ưu duy trì độ toàn vẹn cấu trúc, không xuất hiện vết nứt vi mô, đáp ứng tốt yêu cầu kỹ thuật cho khí tài quân sự.

Từ khoá: Cao su butyl; Kháng axit; Ắc quy quân sự; Hệ lưu hóa DTDM.