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Preparation and Characterization of Modified Butyl Rubber with Maleic Anhydride or Itaconic Acid

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ABSTRACT
This study presents a systematic comparative analysis of the structure–property relationships of butyl rubber (IIR) modified with maleic anhydride (MAH) and itaconic acid (IA). Both carboxyl functionalizers were successfully grafted onto the IIR backbone via NaH-mediated melt grafting. MAH modification introduced additional unsaturated sites, resulting in a 45–54% increase in crosslink density and an enhancement in tensile strength up to 146 kgf/cm²—properties advantageous for structurally demanding applications. In contrast, IA modification enhanced peel adhesion to CFRP prepreg by up to 153% (114 N/mm) without increasing crosslink density, owing to the introduction of highly polar carboxyl groups. These findings demonstrate that MAH and IA deliver complementary performance improvements through distinct mechanisms: MAH provides mechanical reinforcement via increased crosslinking, whereas IA enhances interfacial adhesion through polarity-driven interactions. Accordingly, selecting the appropriate modifier enables the development of optimized rubber compounds for diverse applications such as automotive damping systems, aerospace sealing materials, and high-performance composite structures.
***Keywords* -** Butyl rubber, Carboxylic functionalization, Sodium hydride, Maleic anhydride, Itaconic acid

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I. INTRODUCTION

The engineering of rubber-composite interfaces represents a critical challenge in the development of high-performance materials for aerospace, automotive, and structural applications [1,2]. Among various elastomeric materials, butyl rubber (IIR) occupies a unique position due to its exceptional gas barrier properties, superior damping characteristics, and excellent thermal stability [3,4]. However, the predominantly saturated hydrocarbon structure of IIR, containing only 0.5-2.5 mol% unsaturation from incorporated isoprene units, inherently limits its chemical reactivity and interfacial compatibility with polar substrates and reinforcing materials [5].

The introduction of functional groups onto polymer backbones has emerged as a powerful strategy for enhancing specific material properties while preserving the inherent advantages of the base polymer [6,7]. For IIR, carboxylic acid functionalization is particularly attractive as it introduces polarity for improved adhesion, provides reactive sites for further chemistry, and can influence vulcanization kinetics through interactions with curing agents [8]. The strategic placement of these functional groups at the limited reactive sites in IIR requires careful consideration of both the modifier structure and the reaction pathway.

Among potential carboxylic modifiers, maleic anhydride (MAH) and itaconic acid (IA) present interesting comparative cases. MAH, with its cyclic anhydride structure and inherent α,β-unsaturation, offers dual functionality—introducing both polar groups and additional crosslinking sites [9,10]. In contrast, IA, despite also being an α,β-unsaturated dicarboxylic acid, behaves differently upon grafting, providing purely polar functionality without contributing additional unsaturation to the polymer backbone [11]. This fundamental difference in post-grafting structure suggests that these modifiers could enable orthogonal control over mechanical and interfacial properties.

Recent advances in reactive processing have enabled direct functionalization of polymers in melt state, eliminating many of the environmental and economic drawbacks associated with solution-based modifications [12,13]. The use of strong bases such as sodium hydride (NaH) as activating agents has proven particularly effective for generating reactive sites on polymer chains, enabling subsequent grafting reactions under relatively mild thermal conditions [14,15].

This study presents a systematic comparison of MAH and IA as functionalizing agents for IIR, examining how their structural differences translate into divergent material properties. By employing identical processing conditions and comprehensive characterization techniques, we elucidate the structure-property relationships governing vulcanization behavior, mechanical performance, viscoelastic response, and interfacial adhesion. The ultimate goal is to establish design principles for creating application-specific rubber compounds through targeted functionalization strategies.

II. EXPERIMENTAL

2.1. Materials

Commercial grade butyl rubber (IIR 368S, unsaturation: 2.30mol%) was obtained from Exxon-Mobil and used as received. Sodium hydride, Maleic anhydride and itaconic acid was obtained from Sigma-Aldrich and used as grafting agents. All rubber compounding ingredients were industrial grade: zinc oxide, stearic acid, silica, sulfur and accelerators (TMTD and DM) were used without further purification.

2.2. Preparation of modified butyl rubber(m-IIR)

The typical reaction procedure was as follows: IIR, NaH, and MAH/IA were sequentially introduced into an internal mixer at 100°C for 40 min. After the addition of an antioxidant, heating was discontinued and the product was discharged from the mixer. The resulting materials were designated as m-IIRs. The formulations of the m-IIRs are summarized in Table 1.

Table 1
The formulations of m-IIRs

	m-IIR-1	m-IIR-2	m-IIR-3	m-IIR-4
IIR 365S	100	100	100	100
NaH	2	2	2	2
MAH	2	4	-	-
IA	-	-	2	4

2.3. Analysis of m-IIRs

m-IIRs were purified by dissolution in cyclohexane and precipitation with ethanol.

2.3.1. Spectroscopic Analysis

Attenuated total reflectance (ATR)-Fourier transform infrared (FT-IR 6200, Jasco, Japan) spectroscopy was used to confirm the chemical components of the pristine IIR and m-IIRs. Spectra were collected from 4000 to 400 cm⁻¹ at 4 cm⁻¹ resolution, averaging 32 scans. Samples were pressed against the ATR crystal with consistent pressure using a torque-controlled clamp.

2.3.2. Grafting degree and grafting efficiency

Grafting degree (% grafting) of m-IIR was determined by the following equation:

Grafting degree = $(W_g\text{-}W_o)/W_o \times 100$
Grafting efficiency = $(W_g\text{-}W_o)/W_{IA} \times 100$

W_g: weight of the IIR-g-MAH (or IIR-g-IA)
W_o: weight of the pristine IIR
W_{IA}: weight of the MAH (or IA) used for the grafting reaction

2.4. Compound preparation and Vulcanization

IIR & m-IIR were compounded on a two-roll mixing mill at a speed ratio of 1:1.4 as the formulations given in Table 2. The compound was sheeted out from the mill at a thickness of 2mm, and then left overnight before vulcanization. The vulcanization was carried out in a heated platen press at 160°C for the optimum cure time. The optimum cure times were determined on a rubber process analyzer (RPA elite, TA Instruments, USA) at 160°C.

Table 2
The formulations of IIR/m-IIR compounds

	Control	MBR-1	MBR-2	MBR-3	MBR-4
IIR 365S	100	-	-	-	-
m-IIR-1	-	100	-	-	-
m-IIR-2	-	-	100	-	-
m-IIR-3	-	-	-	100	-
m-IIR-4	-	-	-	-	100
ZnO	5	5	5	5	5
St/A	1	1	1	1	1
Silica	40	40	40	40	40
DM	0.5	0.5	0.5	0.5	0.5
TMTD	1.0	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5	1.5

2.5. Mechanical property measurement

Tensile properties were evaluated using an universal testing machine (Instron 5567, Instron, USA) with a crosshead speed of 500mm/min. The hardness of the specimens was determined according to ASTM 2240 standards and expressed in shore A unit.

2.6. Adhesion evaluation

Interfacial adhesion was quantified using 180° peel tests following a modified ASTM D903 protocol. Carbon fiber reinforced plastic (CFRP) prepreg strips (25 mm wide) were used as the adherend. IIR/m-IIR compounds (2 mm thick) were laminated onto CFRP prepreg surfaces and co-cured at 160°C. Peel tests were conducted at 50 mm/min, and the steady-state peel force was recorded.

III. RESULT AND DISCUSSION

3.1. FT-IR analysis

FT-IR spectra of IIR and m-IIRs were shown in Fig. 1 & Fig. 2. The spectrum of m-IIRs were essentially different from that of IIR. The most marked difference between them appeared in the range of 1700~1500cm^{-1}, where two new absorption peaks showed up. In curve of m-IIRs, the peak at 1710cm^{-1} was attributed to –C=O bond in the –COO– groups of MAH/IA, and the peak detected at 1558 cm^{-1} was corresponding to –C=C– bond in the –CO–CH=CH– groups of MAH/IA. The FT-IR results indicated that –C=O and –CH=CH– groups were all successfully incorporated into the butyl rubber backbone. The results above showed up multi-functional groups can be incorporated into IIR molecular chains using NaH as activators and carbonyl compounds as modifiers in rubber processing equipment.

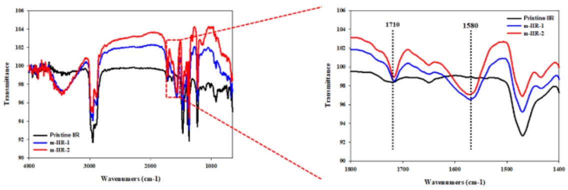

Fig. 1. FT-IR spectra of IIR and IIR-g-MAH.

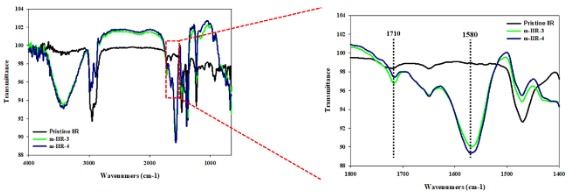

Fig. 2. FT-IR spectra of IIR and IIR-g-IA.

3.2. Grafting behavior analysis

FT-IR spectra of IIR The grafting characteristics summarized in Table 3 clearly demonstrate the concentration-dependent grafting behavior of MAH- and IA-modified IIR.

Both modifiers exhibited comparable grafting degrees at an addition level of 2 phr (m-IIR-1 and m-IIR-3), yielding grafting levels of 1.78% and 1.75%, respectively, along with high grafting efficiencies (89.0% and 87.5%). These results indicate that the reactive sites generated on IIR through NaH activation effectively participate in grafting reactions with both MAH and IA.

When the modifier concentration was increased to 4 phr (m-IIR-2 and m-IIR-4), the grafting degree increased to approximately 2.7%; however, the grafting efficiency decreased to 67.8–68.0%. This reduction is likely attributed to side reactions, steric hindrance, or saturation of the limited reactive sites at higher modifier concentrations. Considering the intrinsically low unsaturation level of IIR (2.30 mol%), the restricted number of available reactive sites is presumed to be a major factor governing the decline in grafting efficiency at elevated modifier contents.

Table 3
The grafting properties of m-IIRs

	Grafting degree (%)	Grafting efficiency (%)
m-IIR-1	1.78	89.0
m-IIR-2	2.71	67.8
m-IIR-3	1.75	87.5
m-IIR-4	2.72	68.0

3.3. Vulcanization behavior analysis

The vulcanization behavior presented in Figure 3 and Table 3 influence of carboxyl-functional modification on the vulcanization kinetics of IIR compounds. All m-IIR compounds exhibited accelerated curing, with MAH-modified compounds showing a 53–60% reduction in t_{90} and IA-modified systems an even greater 61–68% decrease relative to the control. Despite their similar effects on cure rate, MAH and IA induced distinct crosslink-density responses. MAH modification increased ΔM by 45–54%, whereas IA produced a concentration-dependent trend: m-IIR-3 retained an elevated ΔM, while m-IIR-4 decreased to a value comparable to the unmodified sample. These contrasting behaviors arise from differences in grafted structure. MAH introduces additional unsaturation into the IIR backbone, generating supplementary sulfur-curable sites, whereas IA consumes its double bond during grafting and contributes primarily polar functionalities. Consequently, MAH acts bifunctionally by enhancing both cure rate and crosslink density, while IA principally promotes vulcanization through polarity-driven interactions.

Table 3
The vulcanization properties of IIR/m-IIR compounds

	t_{90} (min)	t_{10} (min)	M_L (Nm)	M_H (Nm)	ΔM_L (Nm)
Control	11.19	1.02	1.003	1.716	0.713
MBR-1	5.21	1.11	1.115	2.149	1.034
MBR-2	4.46	1.00	1.080	2.188	1.108
MBR-3	4.34	1.08	0.935	1.931	0.996
MBR-4	3.57	1.22	0.985	1.732	0.747

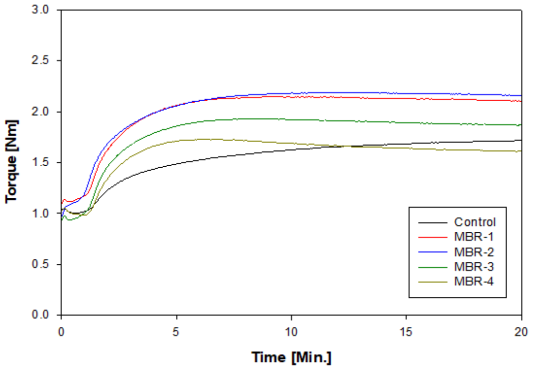

Fig. 3. Vulcanization behavior of IIR/m-IIR compounds

3.4. Mechanical properties

The mechanical data in Table 4 illustrate the distinct influence of carboxyl-functional modification on IIR performance. MAH-modified compounds exhibited a 34–45% increase in tensile strength, consistent with their higher crosslink density, while showing the expected reduction in elongation (800% → 430–450%) and a slight increase in hardness, indicative of a stiffer, more tightly crosslinked network. In contrast, IA modification produced a concentration-dependent response. At 2 phr, IA enhanced tensile strength (122 kgf/cm²) while maintaining high extensibility (650%), yielding a balanced property profile. Increasing IA to 4 phr, however, reduced tensile strength to near-control levels and partially restored elongation, reflecting diminished network reinforcement at higher modifier loading.

Table 4
The mechanical properties of IIR/m-IIR compounds

	Hardness (Shore A)	Tensile (kgf/cm^2)	Elongation (%)
Control	63	101	800
MBR-1	64	135	430
MBR-2	65	146	450
MBR-3	62	122	650
MBR-4	62	98	740

3.5. Adhesion properties to CFRP prepreg

The adhesion data in Table 5 highlight the pronounced effect of carboxyl functionalization on bonding performance with CFRP prepreg. All modified samples exhibited substantial improvements over the control (45 N/mm), with IA-modified compounds outperforming their MAH counterparts. MAH-modified samples (MBR-1, MBR-2) increased peel strength to 78–103 N/mm, attributable to the introduction of polar anhydride/carboxyl groups capable of interacting with the epoxy matrix, though the enhancement showed limited sensitivity to MAH concentration. IA-modified samples demonstrated superior adhesion, reaching 105–114 N/mm (133–153% improvement). Notably, MBR-4 achieved the highest adhesion despite its lower tensile strength, suggesting that IA's two free carboxyl groups, enhanced interfacial orientation, and reduced crosslink density promote more effective interfacial interactions and stress relaxation. These findings underscore the importance of modifier selection: MAH is advantageous for applications requiring higher mechanical strength, whereas IA is preferable when maximizing composite interfacial adhesion is critical.

Table 5
The adhesion properties to CFRP prepreg of IIR/m-IIR compounds

	Peel stregth (N/mm)
Control	45
MBR-1	78
MBR-2	103
MBR-3	105
MBR-4	114

IV. CONCLUSION

This study demonstrates that maleic anhydride (MAH) and itaconic acid (IA) provide complementary performance enhancements in the carboxyl functionalization of butyl rubber (IIR), arising from their distinct structure–property relationships. Both modifiers were effectively introduced onto the IIR backbone via NaH-mediated grafting. MAH functionalization increased crosslink density by 45–54% through the introduction of additional unsaturated sites, resulting in tensile strengths of up to 146 kgf/cm². Such characteristics render MAH-modified IIR suitable for applications requiring high mechanical robustness and durability—such as automotive engine mounts, vibration-isolation components, and high-pressure sealing systems. However, the reduced elongation at break (430–450%) may limit its use in applications where dynamic fatigue resistance is critical. In contrast, IA modification significantly enhanced adhesion to CFRP—up to 153%—without increasing crosslink density, owing to the introduction of highly polar functional groups. Notably, the 2 phr IA formulation achieved balanced mechanical properties (tensile strength of 122 kgf/cm² and elongation of 650%) while maintaining excellent adhesion (105 N/mm), highlighting its relevance for rubber–composite hybrid structural systems. Future work should address potential synergistic effects in MAH/IA hybrid modification systems, long-term durability assessments, and performance evaluation in actual composite structures. Detailed investigations into the dynamic mechanical behavior and fatigue resistance of the modified IIR will also be essential for practical implementation.

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