UDK 691.173:675.92.028.2
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
Mater. Tehnol.

PREPARATION AND VULCANIZATION CHARACTERISTICS OF EXTREMELY COLD-RESISTANT CARBOXYL-BASED ACRYLIC RUBBER WITH BUTYL FUMARATE AS A VULCANIZING MONOMER

PRIPRAVA IN ZNAČILNOSTI VULKANIZACIJE V HLADNEM IZJEMNO ODPORNEGA AKRILNEGA KAVČUKA IZDELANEGA NA OSNOVI KARBOKSILA Z BUTILFUMARATOM KOT VULKANIZACIJSKIM MONOMEROM

Xingbing Yang[1,2,3]*, Wenyu Yan[1], Hanyi Liu[1,4], Changbing Qiao[1], Xinyue Xu[1], Yanxue Li[1], Yi Xie[1], Gang Chen[1], Wenting Zhao[1]

[1]College of Chemical and Chemical Engineering, Sichuan University of Arts and Science, Dazhou 635000, China
[2]Key Laboratory of Low-Cost Rural Environmental Treatment Technology, Sichuan University of Arts and Science, Dazhou 635000, China
[3]Special Polymer Materials for Automobile Key Laboratory of Sichuan Province, Sichuan University of Arts and Science, Dazhou 635000, China
[4]Key Laboratory of Exploitation and Study of Distinctive Plants in Education Department of Sichuan Province, Sichuan University of Arts and Science, Sichuan Dazhou 635000, China

Prejem rokopisa – received: 2025-09-27; sprejem za objavo – accepted for publication: 2026-02-19

doi:10.17222/mit.2025.1573

In this article, ethyl acrylate, butyl acrylate, and 2-methoxyethyl acrylate are used as reaction monomers; butyl fumarate (BFM) is used as a vulcanization crosslinking point monomer; ammonium persulfate and sodium bisulfite are used as initiators; and sodium dodecyl sulfonate is used as an emulsifier to prepare extremely cold-resistant acrylic rubber (ACM). The synthesized raw rubber is mixed and vulcanized, and the vulcanization characteristics are tested to characterize and analyze the structure of the raw rubber. Moreover, the influence of the BFM amount on the mechanical properties, air-aging resistance, and oil resistance is studied. The structure and design of the acrylic rubber are consistent with expectations, with a glass transition temperature of –34.62 °C. As the BFM amount increases, the vulcanization rate and the tensile strength increase, while the elongation at break decreases. Furthermore, the ACM with BFM as a vulcanizing monomer exhibits excellent hot-air aging performance and good oil resistance. Therefore, this product can be widely used in oil and high-temperature environments and is particularly recommended for automotive oil seals and pipes.

Keywords: acrylate rubber, sulfurization, air aging resistance, lotion polymerization, oil resistance

V članku avtorji opisujejo pripravo in vulkanizacijske značilnosti v hladnem izjemno odpornega akrilnega kavčuka. Kot reakcijske monomere so za njegovo pripravo uporabili etil akrilat, butil akrilat in 2-metoksietil akrilat. Butil fumarat (BFM) so uporabili kot monomer za zamreženje pri vulkanizaciji, amonijev persulfat in natrijev bisulfit pa so uporabili za iniciacijo. Natrijev dodecil sulfonat so uporabili kot emulgator za pripravo v hladnem izjemno odpornega akrilnega kavčuka (ACM; angl.: extremely cold-resistant acrylic rubber). Sintetiziran surov kavčuk so zmešali in vulkanizirali. Vulkanizacijske lastnosti so okarakterizirali z analizo strukture surovega kavčuka. Poleg tega so preučili vpliv količine BFM na mehanske lastnosti, odpornost proti staranju na zraku in odpornost proti olju. Struktura in zasnova akrilnega kavčuka sta bili v skladu s pričakovanji in s temperaturo steklastega prehoda -34,62°C. Z naraščanjem količine BFM sta se povečevali hitrost vulkanizacije in natezna trdnost ter zmanjševal se je raztezek pri pretrgu. Poleg tega je imel ACM z BFM odlične lastnosti po staranju na vročem zraku in dobro odpornost proti olju. Avtorji tako ugotavljajo, da se ta material lahko široko uporablja v oljnih in visokotemperaturnih okoljih, še posebej pa je priporočljiv za uporabo avtomobilskih tesnil in cevi, ki so v stiku z motornim oljem.

Ključne besede: akrilatni kavčuk, žveplanje, odpornost proti staranju na zraku, polimerizacija z losjonom, odpornost na olje

1 INTRODUCTION

Acrylate monomers are used for lotion polymerization, followed by demulsification, washing, drying and other processes, to prepare acrylate rubber.[1] Acrylate rubber is characterized by oil resistance and high-temperature resistance[2–3] and is widely used in the preparation of components such as transformers, automotive sealing rings, as well as oil seals and pipes in the mechanical field.[4–5] According to the different vulcanization monomers (crosslinking points), acrylic rubber can be divided into active chlorine-type acrylic rubber, carboxyl-type acrylic rubber, epoxy-type acrylic rubber, and double-crosslinked acrylic rubber. Lotion polymerization is widely used in the production of coatings,[3] adhesives,[6] and rubber[7] because of its ability to easily control reactions and the large molecular weight of the products. As a product with a certain stress structure, rubber needs a relatively high molecular weight. Therefore, some rubbers, such as styrene butadiene rubber (SBR),[8,9] nitrile butadiene rubber (NBR) ,[10] chloroprene rubber (CR)[11] and acrylate rubber (ACM), are produced by lotion polymerization.[12,13]

---

*Corresponding author's e-mail:
yxb19830528@163.com (Xingbing Yang)

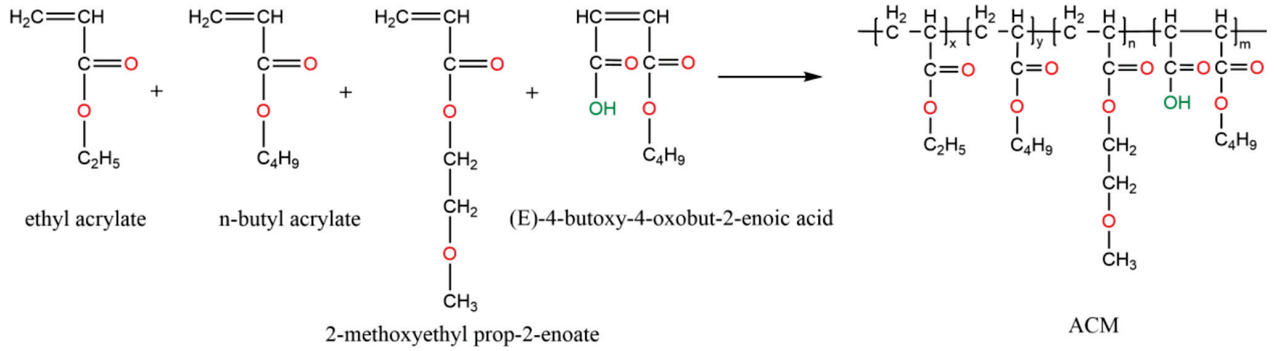

Figure 1: Reaction equation for the synthesis of the target polymer

Extremely cold-resistant active chlorine acrylate rubber[1] and general active chlorine acrylate rubber[14] have been synthesized via lotion polymerization. Weiwei Wang[12,15] investigated the product from carboxylic acrylic rubber with acrylic acid as a crosslinking agent. During the use of this material, the permanent compression deformation of the active chlorine acrylic ester is large, especially under high-temperature conditions, such as 175 °C × 72 hours, and the permanent compression deformation is greater than 30 %. If acrylic acid is used as a cross-linking monomer to prepare carboxylic acrylic rubber, it cannot be used for a long time at a high temperature of 175 °C, and the product mixing and processing times are longer.[16] Therefore, on the basis of the above research, our research team chose easily synthesized and high-temperature-resistant monobutyl fumarate as a crosslinking agent to prepare carboxyl-based acrylic rubber. The introduction of new vulcanizing monomers can improve the heat resistance and processing performance of the product.

The reaction equation for this study is shown in **Figure 1**.

2 EXPERIMENTAL WORK

2.1 Materials

The materials included analytical-grade butyl acrylate (BA), analytically pure ethyl acrylate (EA), analytically pure 2-methoxyethyl acrylate (MOEA), analytically pure monobutyl fumarate (BFM), analytically pure sodium dodecyl sulfonate (SDS), analytically pure ammonium persulfate and sodium bisulfite; all the above reagents were obtained from Chengdu Kelong Chemical Reagent Factory. Antioxidant 445 was obtained from Koju Ya (the United States). Sodium stearate and potassium stearate, both chemically pure, were produced by Kao Corporation (Japan). Carbon black (grade N 550; industrial grade; Shanghai Cabot Chemical Co., Ltd.), a rubber mold-releasing agent (product number: FG-200), microcrystalline wax, stearic acid, 1# vulcanizing agent, an assistant vulcanizing agent (1,3-di-O-tolylguanidine, DOTG), 5S calcined kaolin, calcium chloride and plasticizer (RS-735) are all commercially available products.

2.2 Instruments and equipment

Characterization was performed with a Bruker Avance 500M nuclear magnetic resonance spectrometer (Bruker, Switzerland), a Nicolet Magna-IR550 FTIR instrument (Nicolet Company, USA), a 209 F1 TG analyzer (Netzsch, Germany), a Solarix XR mass spectrometer (Bruker, Switzerland), a DL-b175BL two roll open mill (Baolun Precision Testing Instrument Co., Ltd.), a VC-150T-FTMO-3RT vacuum flat-plate vulcanizer (Jiaxin Electronic Equipment Technology Co., Ltd.), an LX-A Shore A rubber hardness tester, a CH-B rubber thickness tester, and a CP-25 tablet press, which are all products of Wuxi Liyuan Electronic and Chemical Equipment Co., Ltd. The AI-7000SUI tensile testing machine, M-3000AU rotor less vulcanization machine, MV-3000AU Mooney viscometer, GT-7061-ND1 brittleness testing machine, GT-7017-ELU aging test chamber, GT-7024-BL1 vacuum drying oven, and SC-L (LT) 9/11/SKM muffle furnace are all products of the Taiwan High-Speed Rail Testing Instrument Company.

2.3 Preparation of acrylate rubber

The basic formula for the 500 g-level experiment, which refers to the previous results of our research group,[1,14] is adjusted slightly and combined with the actual production process. Then, the effect of the amount of monobutyl fumarate on related properties was studied, and the amount of fumaric acid was adjusted only on the basis of this ratio in the experiments. H_2O (1000 mL) and SDS (15 g, 52.0 mmol) were added to the reactor, which was subsequently heated to 15 °C and stirred for 0.5 h. A premixed solution consisting of BA (135.00 g, 1.05 mol), MOEA (150.00 g, 1.15 mol), BFM (15 g, 0.087 mol) and EA (200.00 g, 2.27 mol) was added to obtain a total of 500 g. The mixture was stirred for 1 h for calibration. $(NH_4)_2S_2O_8$ (4.0642 g, 17.8 mmoL) and $NaHSO_3$ (2.0264 g, 19.5 mmoL) were added successively to initiate the reaction at 34 °C. After successful initialization of the reaction, the emulsion was held at 80 °C for 4 h and then cooled. The prepared emulsion was poured into a 70 °C 10 % $CaCl_2$ solution for demulsification treatment and continuously stirred for 20 min; after complete separation, it was filtered through a filter cloth. The filtered solid rubber was washed with water at 60 °C three times and then dried in a vacuum drying oven at 100 °C to obtain the raw acrylic rubber material.

2.4 Formula of the mixed rubber

Table 1: Compound formula

Material name	Quality/portion
Synthesized ACM	100
Stearic acid	1
Antioxidant 445	2
Microcrystalline wax	1
intblFG-200	1
1 # sulfurizing agent	0.6
Assistant vulcanizing agent DOTG	2
18 amine	0.5
Carbon black N550	60
Plasticizer RS735	3

2.5 Preparation of the mixed rubber

The raw materials were accurately weighed according to the given formula and then mixed in an open mill. First, processing aids (such as stearic acid, silicone oil, and wax) were added to the roller. After dispersion, the raw rubber was added and mixed for 2 min. Afterward, carbon black and antiaging agent were added, the mixture was dispersed evenly, and a vulcanization system was added. After 5 passes, the material was cut to obtain a mixed film. The mixed rubber was first vulcanized on a flat vulcanization machine at 180 °C for 10 min. Then, it was subjected to a second stage of vulcanization in a vacuum drying oven at 175 °C for 4 h. Finally, it was left at room temperature for 24 h before the samples were cut for testing.

2.6 Test analysis

FTIR analysis: The potassium bromide tablet method was used for testing. The acrylic ester raw gel obtained after demulsification and drying was dissolved in acetone to prepare a polymer solution with a specific concentration, which was applied onto potassium bromide tablets. After drying, the sample properties were detected at room temperature using an FTIR instrument.

Thermogravimetric (TG) gas chromatography–mass spectrometry (GC–MS) analysis: The pyrolysis products of the sample under a nitrogen atmosphere were tested using TG–gas chromatography–Fourier transform ion cyclotron resonance–mass spectrometry.

^{1}H-NMRR analysis: Characterization was performed with a Bruker Avance500M nuclear magnetic resonance spectrometer (Switzerland, Bruker Company) using deuterated chloroform as a solvent and BBO probe testing.

Testing the volatile and ash contents of the raw rubber: The volatile and ash contents of the raw rubber were determined using a GT-7024-BL1 vacuum drying oven and an SC-L (LT) 9/11/SKM muffle furnace (Taiwan High-Speed Rail Testing Instrument Company) in accordance with the ASTM D5668 and ASTM D4574 standards.

Measurement of the Mooney viscosity of the raw rubber: An MV-3000AU Mooney viscometer from Taiwan High-Speed Rail Testing Instrument Company was used to determine the Mooney viscosity of the raw rubber according to the ASTM D1646 standard.

Determination of the gel content of the raw rubber: Acetone was used as a solvent. Additionally, 0.05 g of raw rubber was weighed, cut and added to a 50 ml volumetric flask, which was placed in the dark, where the rubber was allowed to dissolve for 17 hours. The filter screen (hole diameter of 70 μm, 200 mesh components) was dried in an oven at 105–110 °C for 1 h, after which the glue solution was filtered via a filter screen. The filtered solution was placed in an oven and dried at 105–110 °C for 2 h, after which it was removed and placed in a dryer to cool to room temperature. The gel content in the gel solution was calculated with the differential weight method.

Sulfurization characteristics: The vulcanization characteristics were determined according to the ASTM D5289-2017 standard. Tests to determine the volatile content, ash content, Mooney viscosity, vulcanization characteristics and hardness, as well as tensile tests, air oven aging tests and compression sets were performed in accordance with ASTM D5668, ASTM D4574, ASTM D1646, ASTM D5289-2017, ASTM D2240, ASTM D412-16, ASTM D412 and ASTM D395 standards.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Characterization of the ACM

The FT–IR spectrum of the ACM is shown in **Figure 2**. The broad peak attributed to the stretching vibration of the O–H bond is located at 3438 cm^{-1}. The peak attributed to the antisymmetric CH_3 stretching vibration appears at 2960 cm^{-1}, and the absorption peak characteristic of -C=O is at 1732 cm^{-1}, with a sharp peak shape and high intensity. The peaks attributed to the bending

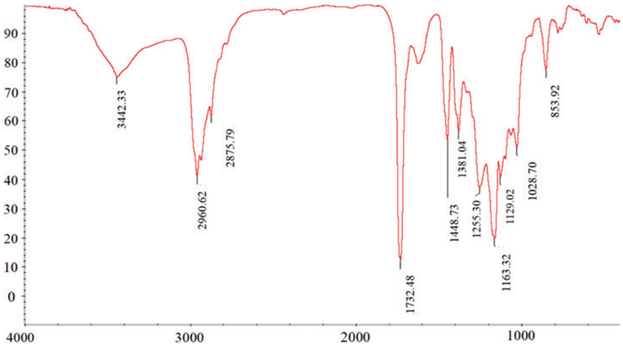

Figure 2: FT–IR spectrum of the ACM

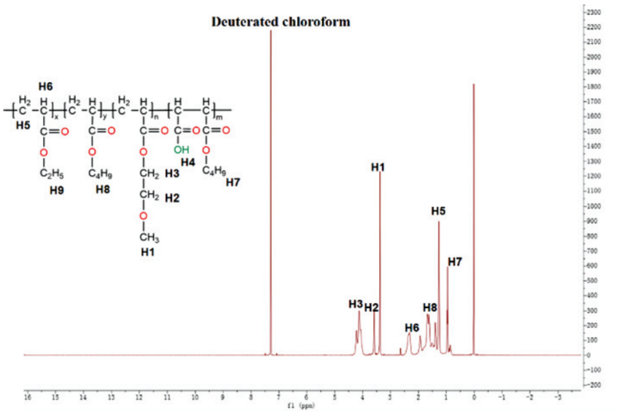

Figure 3: ^{1}H NMR spectrum of the ACM

vibration of C–H, the stretching vibration of C–OH, the asymmetric stretching vibration of ester-based C–O–C, and the stretching vibration of C–O appear at (1381, 1254, 1162 and 1028) cm^{-1}, respectively. Thus, the EA, BA, MOEA, and BFM are copolymerized.

The properties of the ACM raw rubber were further validated by ^{1}H NMR and ^{13}C nuclear magnetic resonance testing to identify the comonomers used for synthesizing the ACM, and the molar ratios of each monomer after polymerization were calculated. As shown in **Figure 3**, the residual proton signal of the solvent deuterated chloroform is at 7.2 ppm, the characteristic peak of methyl (-CH$_3$) is at 3.4 ppm, and the characteristic peak of methylene (-CH) is at approximately 2.4 ppm. The characteristic peak of methylene (-CH$_2$) is at 4.2 ppm, indicating the presence of two methylene (-CH$_2$) environments. Moreover, the ratios of the integrals corresponding to the above functional groups reveal that the three monomers – BA, EA and MOEA – and the BFM are involved in the copolymerization. The molar ratio of the raw materials (BA:EA:MOEA:BFM = 1.05:2.27:1.15:0.087) indicates that all monomers are incorporated into the polymer backbone, resulting in the formation of a copolymer. On the basis of the composition of the raw materials, the peak at approximately 85.43 ppm in the carbon spectrum (**Figure 4**) is attributed to the carbon connected to ester or ketone groups. A signal at approximately 20 ppm corresponds to a saturated alkane carbon atom (-CH$_2$-). This material is free from impurities, and the abundance of the carbon base is approximately equal to that of saturated alkanes with -CH$_2$- that are also free from impurities, which explains why each monomer polymerizes into a saturated chain structure.

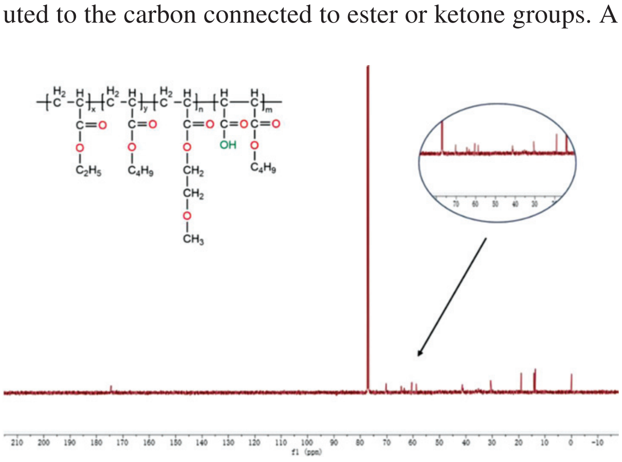

Figure 4: ^{13}C NMR spectrum of the ACM

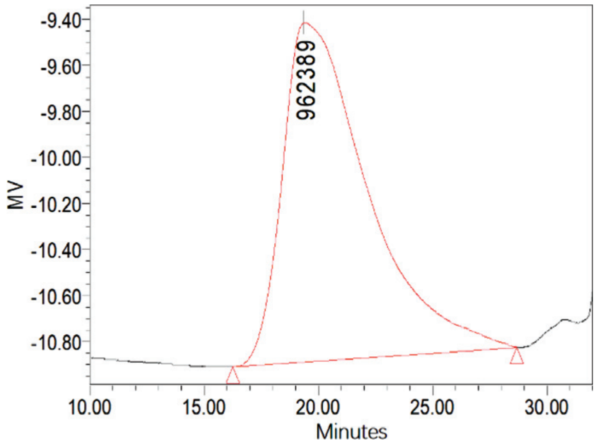

Figure 5: GPC chromatogram of the ACM

Generally, the polymers used in rubber should have high molecular weights and suitable PDIs[3]. The results of the GPC test of the acrylic rubber sample are shown in **Figure 5**. The molecular weight distribution of the ACM is uniform, with a number-average molecular weight (Mn) of 88,887, a weight-average molecular weight (Mw) of 723,714, and a polydispersity index (PDI) of 8.14, indicating that the ACM has a high molecular weight and a suitable PDI. The glass transition temperature (Tg) of the ACM was analyzed using a differential scanning calorimeter, as shown in **Figure 6**. The glass transition temperature (Tg) of the ACM is –34.62 °C, indicating that it has good low-temperature resistance performance.

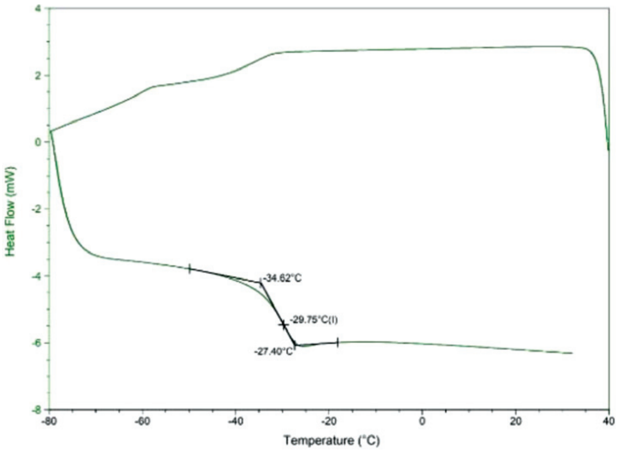

Figure 6: DSC curve of the ACM

3.2 Acrylic rubber test

The synthesized raw rubber was tested according to the relevant testing standards, and the results are shown in **Table 2**. The volatile and ash contents of the synthetic acrylic rubber are low, indicating that the product is clean and contains few impurities, thereby providing quality assurance for the later use of the rubber material. The $ML_{(1+4)}$ value of the product is 29.5, and the Mooney value of the product is slightly lower than that of the extremely cold-resistant active chlorine product.[1] This is due mainly to the changes in the monomer composition of the product. BA is a straight chain monomer with good molecular chain flexibility, and the $ML_{(1+4)}$ value decreases after polymerization.

Table 2: Test results for acrylic rubber (ACM)

Item	Standard	Test
ML (1 + 4)	30 ± 2	29.5
Volatile (%)	≤0.5	0.25
Ash (%)	≤0.6	0.16
Gel (%)	≤5	2.14
Intrinsic viscosity	≥2	2.87

3.3 Effect of monobutyl fumarate on the vulcanization characteristics of the ACM

Monobutyl fumarate is a cross-linked monomer that directly participates in the vulcanization of rubber. The vulcanization performance during the use of ACM is directly related to the mechanical properties of the product. Therefore, the effect of the amount of monobutyl fumarate on the vulcanization characteristics of the ACM was studied. In the synthesis of raw rubber, the amount of monobutyl fumarate was changed, and different amounts of ACM were prepared according to the given basic ratio. The vulcanization characteristics were tested using a vulcanization apparatus at 180 °C for 10 min. The results are shown in **Table 3**. As the amount of monobutyl fumarate increases, the torque of the ACM (ML and MH, in dN.m) gradually increases; moreover, the initial vulcanization time (T_{10}) and positive vulcanization time (T_{90}) of the product gradually decrease. This is mainly because monobutyl fumarate serves as a vulcanization crosslinking point, and as its molar amount increases, the vulcanization rate increases.[17,18]

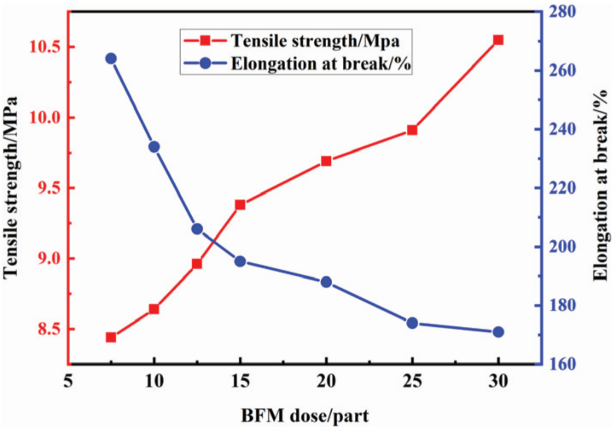

Figure 7: Effect of the amount of BFM on the tensile strength and elongation at break of the ACM
Note: The first stage of vulcanization was performed at 180 °C for 10 min, and the second stage of vulcanization was performed at 175 °C for 4 h.

3.4 Effect of monobutyl fumarate on the mechanical properties of the ACM

Carboxylic acrylic rubber with different contents of monobutyl fumarate was synthesized according to a base formulation and then mixed according to a standard rubber formulation. After the mixed rubber was sliced, it underwent the first stage of vulcanization (180 °C × 10 min), followed by the second stage of vulcanization (175 °C × 4 h). Finally, various mechanical properties of the vulcanized product were tested, and the results are shown in **Figure 7**. As the amount of monobutyl fumarate increases, the tensile strength of the ACM increases, whereas its elongation at break decreases. When 30 g of monobutyl fumarate is added, the tensile strength of the rubber reaches 10.55 MPa, but at this point, the elongation at break decreases to 171 %. The experimental results reveal that increasing the amount of monobutyl fumarate effectively increases the number of crosslinking points and the crosslink density.

3.5 Effect of monobutyl fumarate on the hot-air aging performance of the ACM

BFM, as a crosslinking agent, plays a significant role in the hot-air aging of rubber products. In this study, the effects of various amounts of BFM (7.5, 10, 12.5, 15, 20,

Table 3: Effect of the amount of monobutyl fumarate on the vulcanization characteristics of the ACM

Dosage (g)	ML (dN.m)	MH (dN.m)	T_{10} (s)	T_{S2} (min)	T_{90} (min)
7.5	1.72	7.00	53	2.05	7.38
10	1.86	7.05	51	2.55	7.12
12.5	1.91	7.28	46	1.83	6.97
15	1.98	7.82	45	1.50	6.75
20	2.01	8.33	34	1.07	4.95
25	2.13	9.05	32	0.93	4.90
30	2.15	9.51	28	0.90	4.05

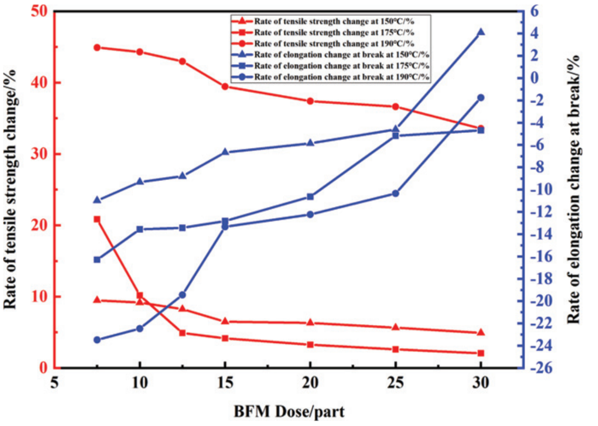

Figure 8: Effect of the BFM content on the rates of change in the tensile strength and elongation at break after aging at different temperatures

25 and 30) g on the aging resistance of acrylate rubber (ACM) were investigated. As shown in **Figure 8**, the reduction in the tensile strength and elongation at break gradually decreased after 72 h of hot-air aging at (150, 175, and 190) °C with increasing BFM content. This phenomenon can be attributed to the thermal decomposition of sulfurizing agent 1#, which generates free radicals. These free radicals preferentially attack the **á**-hydrogen of the acrylate chain to form chain radicals. BFM, as a multifunctional monomer, is grafted onto the chain radicals through double bonds.[19] However, the carboxyl group itself does not directly participate in radical cross-linking.[13] The heat resistance is actually increased by the ionic cross-linking formed by the carboxyl group of BFM and DOTG. The constructed C–C bond can withstand long-term use at temperatures of 150–180 °C,[20] thereby significantly improving its anti-aging performance.

When 30 g of monobutyl fumarate was added and the product was aged in hot air at 190 °C for 72 h, its strength reached 6.75 MPa, and the elongation reached 174 %. Since an ACM is often used in mechanical seals, the permanent compression is also an important index. The influence of the amount of BFM added on the compression of the ACM is shown in Figure 9. With increasing BFM content, the compression of the ACM gradually decreases. Under the same conditions, the permanent compression deformation of the active chlorine-type ACM is approximately 30%,[1,14] which is similar to the deformation of the carboxyl-type acrylic rubber with BFM as a crosslinking agent used in this study. However, in terms of high-temperature antiaging performance, the BFM-type ACM is superior.[1,14]

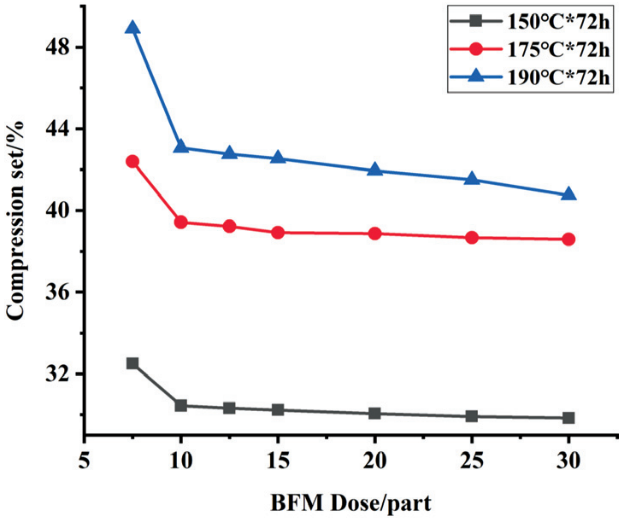

Figure 9: Effect of the amount of monobutyl fumarate on the permanent compression deformation

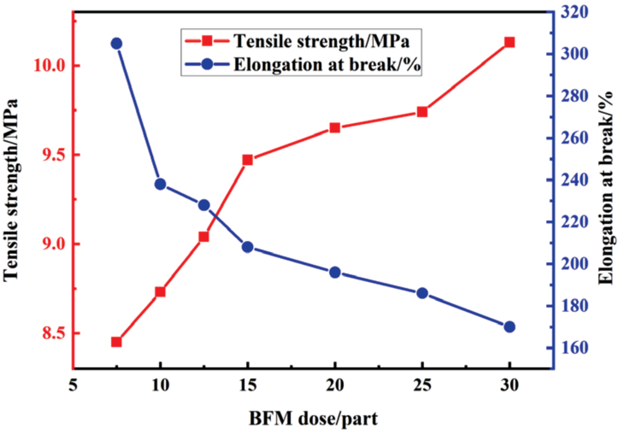

Figure 10: Effect of ASTM1 on the performance of different ACM types at 150 °C

3.6 Effect of monobutyl fumarate on the oil resistance of the ACM

Acrylate itself exhibits excellent oil resistance performance, and oil resistance is an important performance indicator of rubber. In this article, the aging of the ACM with monobutyl fumarate as a crosslinking agent in oils 1# and 3# was studied under experimental conditions of 150 °C × 72 h. The results are shown in **Figures 10** and **11**. As the monobutyl fumarate content increases, the

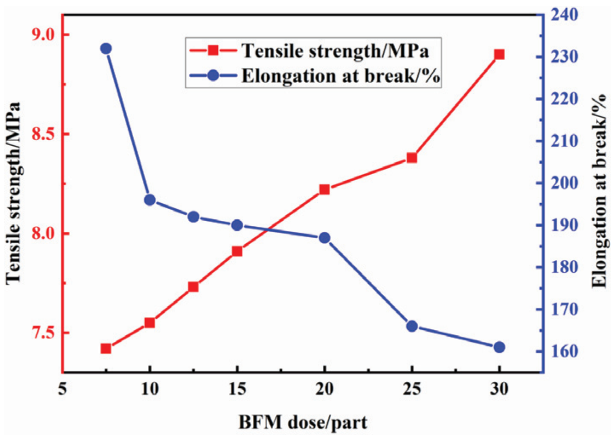

Figure 11: Effect of ASTM3 on the performance of different ACM types at 150 °C

tensile strength generally increases, whereas the elongation at break tends to decrease, indicating an increase in the number of crosslinking agents, the crosslinking strength, the iodine sulfide content, and the crosslink density in the network structure space. The mechanical strength also increases;[18,20–21] the rates of change in the volumes of oils 1# and 3# are less than 15.53 and 20.24, respectively. From the perspective of the crosslinking mechanism, the free radicals of sulfurizing agent 1# work in synergy with BFM to increase the crosslink density. The ion-type cross-linking mediated by the above materials results in the formation of a dense network, and the butyl side chain can reduce the aggregation of carboxyl groups,[12] thereby weakening the polar interaction between the oil molecules and carboxyl groups. Therefore, the ACM exhibits good oil resistance.

4 Conclusion

Monobutyl fumarate was used as a sulfurizing monomer of the ACM, and the resulting material was characterized and analyzed. The effect of changing the amount of monobutyl fumarate on the performance of the product was studied, and the following conclusions were drawn:

(1) FT–IR, TG–GC–MS, ^{1}H NMR, ^{13}C NMR and raw rubber detection analyses revealed that acrylate rubber was synthesized via lotion polymerization in a redox system.

(2) As the amount of monobutyl fumarate increases, the vulcanization time of the ACM decreases.

(3) During the mechanical performance, hot-air aging, and oil resistance experiments, as the amount of monobutyl fumarate increased, the elongation at break decreased, and the tensile strength increased.

(4) Considering the comprehensive performance and cost of the ACM, as well as the cost-effectiveness of the raw rubber materials, the addition of 30 g of monobutyl fumarate per kilogram of raw rubber is recommended. The synthesized product has excellent heat and oil resistance and can be used in extreme environments owing to its oil resistance, high-temperature resistance, and air-aging performance. Its use in automotive oil seals, such as automotive oil pipes, is particularly recommended.

Funding information

Special Polymer Materials for Automobile Key Laboratory of Sichuan Province at Sichuan University of Arts and Science (TZGC2024ZA-04, TZGC2023ZB-06)

Key Laboratory of Exploitation and Study of Distinctive Plants in Education Department of Sichuan Province (TSZW2023ZB-11).

5 REFERENCES

[1] X. Yang, T. Lei, W. Lu, X. Huang, L. Jiang, Characterization and study of the vulcanization characteristics of ultra-cold-resistant reactive chlorinated acrylic rubber prepared by emulsion polymerization, Polym. Int., 72 (**2023**), 189–194, doi:10.1002/pi.6459

[2] M. Ishihara, T. Kaeda, T. Sasaki, Silica/polymer core–shell particles prepared via soap-free emulsion polymerization, e-Polym., 20 (**2020**), 254–261, doi:10.1515/epoly-2020-0028

[3] O. M. Daraba, A. N. Cadinoiu, D. M. Rata, L. I. Atanase, G. Vochita, Antitumoral Drug-Loaded Biocompatible Polymeric Nanoparticles Obtained by Non-Aqueous Emulsion Polymerization, Polym., 12 (**2020**), 1018, doi:10.3390/polym12051018

[4] S. Ji, H. Gui, G. Guan, M. Zhou, Q. Guo, M. Y. J. Tan, A multi-functional coating based on acrylic copolymer modified with PDMS through copolymerization, Prog. Org. Coat., 156 (**2021**), 106254, doi:10.1016/j.porgcoat.2021.106254

[5] Y. Sun, C. Fan, Y. Zhao, L. Jia, Peroxide-Cured Isobutylene-Isoprene Rubber Composite: Methacrylate Coagent and Enhanced Mechanical Properties by In Situ Formed Methacrylate Domains, Ind. Eng. Chem. Res., 60 (**2021**), 2728–2735, doi:10.1021/acs.iecr.0c05987

[6] Z. Dastjerdi, E. D. Cranston, R. Berry, C. Fraschini, M. A. Dubé, Polymer Nanocomposites for Emulsion–Based Coatings and Adhesives, Macromol. React. Eng., 13 (**2018**), 1800050, doi:10.1002/mren.201800050

[7] T. Zhang, R. A. Sanguramath, S. Israel, M. S. Silverstein, Emulsion Templating: Porous Polymers and Beyond, Macromolecules, 52 (**2019**), 5445–5479, doi:10.1021/acs.macromol.8b02576

[8] A. M. S. Medeiros, E. Bourgeat-Lami, T. F. L. McKenna, Styrene-Butadiene Rubber by Miniemulsion Polymerization Using In Situ Generated Surfactant, Polym., 12 (**2020**), 1476, doi:10.3390/polym12071476

[9] A. Zhang, Y. Zhang, Y. Zhang, Characterization of kaolinite/emulsion-polymerization styrene butadienerubber (ESBR) nanocomposite prepared by latex blending method: Dynamic mechanic properties and mechanism, Polym. Test., 89 (**2020**), 106600, doi:10.1016/j.polymertesting.2020.106600

[10] G. He, T. Luo, Y. Dang, L. Zhou, Y. Dai, X. Ji, Combined mechanistic and genetic programming approach to modeling pilot NBR production: influence of feed compositions on rubber Mooney viscosity, RSC Adv., 11 (**2021**), 817–829, doi:10.1039/d0ra07257e

[11] Y. Ishigaki, H. Mori, RAFT-mediated emulsion polymerization of chloroprene and impact of chain-end structure on chloroprene rubbers, J. Appl. Polym. Sci., 135 (**2018**), 46008, doi:10.1002/app.46008

[12] W. Wang, Z. Chang, M. Wang, Z. Zhang, Effect of carboxyl on vulcanization and mechanical properties of carboxylated acrylic rubber prepared by 60Co-γ-ray-induced polymerization, J. Appl. Polym. Sci., 102 (**2006**), 5587–5594, doi:10.1002/app.24897

[13] A. Abdel-Hakim, S. A. El-Mogy, M. M. EL-Zayat, Radiation crosslinking of acrylic rubber/styrene butadiene rubber blends containing polyfunctional monomers, Radiat. Phys. Chem., 157 (**2019**), 91–96, doi:10.1016/j.radphyschem.2019.01.004

[14] X. Yang, X. Wang, S. Huang, X. Liu, X. Huang, T. Lei, Preparation and Characterization of Universal Cold-Resistant Reactive Chlorinated Acrylic Rubber and Study of its Vulcanization Characteristics, Polymer Science, Ser. B, 65 (**2023**), 624–632, doi:10.1134/s1560090423600158

[15] H. Geng, M. Wang, X. Ge, W. Wang, Preparation and properties of the self-crosslinked acrylic rubber via gamma ray initiated emulsion polymerization, Polym. Eng. Sci., 46 (**2006**), 1748–1753, doi:10.1002/pen.20641

[16] A. Abdel Hakim, S. A. El Mogy, A. I. Abou Kandil, Novel modification of styrene butadiene rubber/acrylic rubber blends to improve mechanical, dynamic mechanical, and swelling behavior for oil sealing applications, Polym. Polym. Compos., 29 (**2021**), S959–S968, doi:10.1177/09673911211031351

[17] K. Jantanasakulwong, Y. Kobayashi, K. Kuboyama, T. Ougizawa, Thermoplastic Vulcanizate Based on Poly(lactic acid) and Acrylic Rubber Blended with Ethylene Ionomer, J. Macromol. Sci., Part B-Phys., 55 (**2016**), 1068–1085, doi:10.1080/48.2016.1238434

[18] T. Zhang, R. A. Sanguramath, S. Israel, M. S. Silverstein, Emulsion Templating: Porous Polymers and Beyond, Macromolecules, 52 (**2019**) 15, 5445–5479, doi:10.1021/acs.macromol.8b02576

[19] J. Kruzelak, R. Sýkora, I. Hudec, Peroxide vulcanization of natural rubber. Part II: Effect of peroxides and co-agents, J. Polym. Eng., 35 (**2015**), 21–29, doi:10.1515/polyeng-2014-0035

[20] P. A. Lovell, F. J. Schork, Fundamentals of Emulsion Polymerization, Biomacromolecules, 21 (**2020**), 4396–4441, doi:10.1021/acs.biomac.0c00769

[21] M. Ishihara, T. Kaeda, T. Sasaki, Silica/polymer core–shell particles prepared via soap-free emulsion polymerization, e-Polym., 20 (**2020**) 1, 254–261, doi:10.1515/epoly-2020-0028