UDK 678.4:675.92.028.2
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
Mater. Tehnol.

STUDY ON VULCANIZATION CHARACTERASTICS AND COMPOSIT PROPERTIES OF AEM/ACM WITHIN HMDC VULCANIZATION SYSTEM

ŠTUDIJ VULKANIZACIJE IN LASTNOSTI KOMPOZITA VRSTE AEM/ACM V VULKANIZACIJSKEM SISTEMU HMDC

Xingbing Yang[1,2,3]*, Qian Wu[1,3], Wei Li[3], Xue Fu[3], Tingting Zhang[3], Qin Zhang[3]

[1]Special Polymer Materials for Automobile Key Laboratory of Sichuan Province, Sichuan Institute of Arts and Science, Dazhou 635000, China
[2]Key Laboratory of Low-Cost Rural Environmental Treatment Technology, Sichuan Institute of Arts and Science, Dazhou 635000, China
[3]College of Chemical and Chemical Engineering, Sichuan Institute of Science and Engineering, Dazhou 635000, China

Prejem rokopisa – received: 2024-09-07; sprejem za objavo – accepted for publication: 2025-01-29

doi:10.17222/mit.2024.1297

In the application field of rubber materials, ethylene acrylate rubber (AEM) provides advantages such as notable tensile strength, elongation and low-temperature resistance. However, AEM is expensive and susceptible to permanent compression deformation. In contrast, acrylate rubber (ACM) exhibits excellent high-temperature and oil resistance properties. This study aimed to solve the cost and compression deformation problems of AEM, and a rubber material combination scheme with both performance and cost advantages was developed by mixing AEM and ACM. The research innovation is the determination of the optimal increase in the use of inexpensive ACM while satisfying specific performance requirements, such as the elongation at break (250 %), tensile strength (12 MPa), and high-temperature aging performance (200 % beyond 190 °C, with a tensile strength of 9 MPa and a minimum brittleness temperature of 40 °C). First, the appropriate AEM/ACM ratio was determined according to the mechanical properties, and then, the influences of different dosages of vulcanizing agents on the sulfurization characteristics of the composite were examined in depth. The vulcanization characteristics, mechanical properties and activation energy of the composite were comprehensively studied to bridge relevant research gaps and provide comprehensive data support for the composite application. The results indicated that increasing the AEM dosage could significantly increase the ACM processing safety, physical performance and hot-air aging performance, and reduce the brittleness temperature. At an AEM/ACM ratio of 7:3, the comprehensive performance satisfied the design requirements. The use of the HMDC vulcanizer promoted the rapid vulcanization of the rubber mixture, with an activation energy of approximately 76.30 kJ/mol. With increasing HMDC dosage, the maximum torque (MH) first increased and then decreased, reaching a maximum value at 1.2 parts. Moreover, the positive vulcanization time, the hardness and tensile strength gradually increased, and the elongation at break gradually decreased. With increasing DOTG dosage, both the t10 and MH values decreased, the positive vulcanization time also decreased, the hardness and tensile strength slightly increased, and the elongation at break decreased. This study provides a new direction for the modification and application of rubber materials, which is important for promoting the research and development of high-performance and low-cost materials in the rubber industry. This approach helps expand the application range of rubber materials under high-temperature, high-pressure and high-requirement conditions and increases the overall quality and economic benefits of rubber products.

Keywords: carboxylate acrylic rubber, vulcanization characteristics, activation energy, vulcanizing agent, ethylene acrylate rubber

Med gumijasti materiali ima etilen-akrilatna guma (AEM; angl.: ethylene acrylate rubber) mnoge prednosti; kot so naprimer odlična natezna trdnost in raztezek ter dobra odpornost proti nizkim temperaturam. Vendar pa je AEM draga in ima slabo odpornost proti trajnim tlačnim deformacijam, medtem ko ima cenejša akrilatna guma (ACM; angl.: acrylate rubber) visoko temperaturno odpornost in dobro odpornost proti oljem. V tem članku avtorji predstavljajo študijo v kateri so poizkušali rešiti probleme vezane na visoko ceno in slabo odpornost proti tlačnim deformacijam tega materiala. Zato so raziskovali lastnosti gumijastih materialov, ki so bili izdelani iz mešanic AEM in ACM v različnih deležih. Cilj inovacije je bil čim bolj povečati delež cenejšega ACM in pri tem izpolniti specifične zahteve glede mehanskih lastnosti; kot so raztezek do zloma gumijastega materiala (250 %), natezna trdnost (12 MPa), odpornost proti staranju pri visoki temperaturi (200 % pri 190 °C), natezna trdnost 9 MPa, najmanjša temperatura krhkosti –40 °C. Najprej so avtorji določil ustrezno razmerje med AEM in ACM glede na doseganje optimalnih mehanskih lastnosti. Nato so temeljito raziskali vpliv različnih odmerkov vulkanizacijskega sredstva na žveplanje kompozitnega sistema. Za celovito poznavanje kompozitnega sistema so avtorji torej analizirali vulkanizacijo, mehanske lastnosti in aktivacijsko energijo kompozitnega sistema. Rezultati raziskave so pokazali, da lahko povečan odmerek AEM bistveno izboljša procesno varnost ACM, izboljša fizikalne lastnosti in odpornost proti staranju na vročem zraku ter zniža temperaturo pri kateri material postane krhek. Avtorji ugotavljajo, da so pri razmerju AEM/ACM je 7:3 izpolnjene zgoraj navedene zahteve. Uporaba heksametilendiamin-karbamatnega (HMDC) vulkanizatorja pospešuje hitrost vulkanizacije mešanice in njena aktivacijska energija je približno 76,30 KJ/mol. S povečanjem dodatka HMDC se maksimalni vrtilni moment (MH; angl:: maximum torque) najprej dvigne in nato pade ter doseže največjo vrednost pri deležu 1,2. Podaljšal se je tudi pozitivni čas vulkanizacije, trdota in natezna trdnost sta postopoma naraščali in raztezek pri porušitvi se je postopoma zniževal. Po mnenju avtorjev so s to študijo odprli novo smer modifikacije in uporabe gume, kar je zelo pomembno za spodbujanje raziskovalnega procesa in razvoja novih visoko zmogljivih in nizkocenovnih materialov za gumarsko industrijo. Razširja pa se tudi obseg uporabe gumijastih materialov pri visokih temperaturah in tlakih, kar v celoti izboljša splošno kakovost in gospodarske koristi uporabe zelo zahtevnih vrst gumijastih izdelkov.

Ključne besede: karboksilatna akrilna guma, značilnosti vulkanizacije, aktivacijska energija, vulkanizacijsko sredstvo, etilen-akrilatna guma.

---

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

© 2025 The Author(s). Except when otherwise noted, articles in this journal are published under the terms and conditions of the Creative Commons Attribution 4.0 International License (CC BY 4.0).

1 INTRODUCTION

Acrylate rubber (ACM) exhibits excellent high-temperature and oil resistance characteristics, making it widely applicable in high-temperature and oil environments.[1] Compared with ACM, ethylene acrylate rubber (AEM) provides superior tensile strength, elongation, and low-temperature resistance;[2,3] therefore, AEM is typically applied in environments that require high oil resistance and notable high-temperature resistance. However, AEM is expensive and constitutes a relatively single-product model. So far, AEM has only been produced by DuPont. Hence, its application range in industrial production is limited.

The modification of acrylic rubber has been studied extensively, including the addition of functional monomers[4] during synthesis, the addition of special materials[5–7] during mixing, and the use of multiple rubbers.[8–13] By comparison, the combination of multiple raw materials not only simplifies and controls the production process but also significantly reduces the cost of acquiring raw materials. Therefore, this method is widely employed in the rubber production industry. There are many studies on blending modification of ACM, including the blending of ethylene-propylene-diene monomers (EPDMs) and ACM, the blending of vinylidene fluoride hexafluoropropylene rubber (FPM) and ACM, the blending of dimethyl siloxane (SIR) and ACM, and the blending of acrylonitrile butadiene rubber (NBR) and ACM.[14–17] Jia Hongbing investigated the blending of ACM and AEM. His research focused mainly on the blending of PA-522HF and AEM, and he reported the effects of the blending ratio, vulcanizing agent, promoter, environmentally friendly vulcanizing promoter, and environmentally friendly plasticizer on the properties of AEM and ACM mixed rubber.[18–21]

Our research team has been involved in the research and development of acrylic rubber for a long time[3–4]. This study meets the following performance requirements for transformer sealing rings: the elongation at break should be ≥250 %, and the tensile strength should be ≥12 MPa. After high-temperature aging at 190 °C, the elongation at break is ≥200 %, the tensile strength is ≥9 MPa, and the minimum brittleness temperature is ≤ –40 °C. If these properties cannot be achieved through the use of carboxyl-based acrylic rubber alone, the cost of using AEM alone increases, as does the permanent compression deformation. Therefore, at the design stage, AEM can be selected as the main body, which can be combined with ACM to reduce costs and increase the permanent compression performance of the product. The mechanical properties of sulfide products affect the reliability and durability of rubber products in practice. A composite study of AEM and ACM, through an investigation of the mechanical properties of sulfide, can be conducted to better understand the influence of different factors on the performance of the final product. To optimize the design, the mechanical properties of sulfide can be significantly modulated. However, there are few reports on the vulcanization characteristics of composite systems. In this study, inexpensive ACM was employed as much as possible while satisfying the performance requirements. First, the appropriate AEM/ACM ratio was determined on the basis of the mechanical properties, and then, the influence of different amounts of vulcanization agent on the vulcanization characteristics of the composite system was studied. Herein, not only the vulcanization characteristics but also the mechanical properties and activation energy within the composite system were studied, providing the basic data and application data support for applying the composite system, and yielding certain innovations.

2 EXPERIMENTAL PART

2.1 Raw materials

The following raw materials were used: carboxylic acid acrylic rubber, brand AX-613, Shanghai Daofu Industry Co., Ltd.; AEM, brand Vamac IP, DuPont, USA; carbon black, N550, N330, N774, Cabot Corporation; stearic acid processing aid, 18-amine anticoking agent, 445 antiaging agent, hexamethylene diamine carbamate (#1 vulcanizing agent, HMDC), DOTG-75 covulcanizing agent (containing 75 % DOTG-75 masterbatch rubber), RS-735 plasticizer, WB-212 internal release agent, and FG-200 dispersant, Qingdao Nanchuan International Co., Ltd.

2.2 Instruments and equipment

The following instruments were employed: TH-200 Shore hardness tester, produced by Beijing Times Peak Technology Co., Ltd; KL-6 open mill, produced by Shanghai Qingpu Baihong Co., Ltd; ML-1.5L internal mixer, produced by Shanghai Qingpu Baihong Co., Ltd; MN-2000 Mooney instrument, produced by Shanghai Dejie Instrument Equipment Co., Ltd; MDR-S3L rotorless vulcanizer, produced by Shanghai Nojia Instrument Co., Ltd; GT-7061-ND1 low-temperature brittleness tester, GT-7040-L oil-resistant tank, GT-7017-ELU aging chamber, and HI-7000M tensile testing machine, all produced by Taiwan High-Speed Rail Testing Instrument Co., Ltd.

2.3 Basic formulas

The basic formula for the ACM experiment is as follows: AX-613 raw rubber, 600 parts (mass, the same as below); N550, 300 parts; N330, 120 parts; HMDC, 3.6 parts; DOTG, 12 parts; 18-amine, 3 parts; 445 antiaging agent, 12 parts; RS735 plasticizer, 18 parts; FG200 dispersant, 6 parts; WB212 internal release agent, 12 parts; and stearic acid processing aid, 6 parts.

The basic formula for the AEM experiment is as follows: AEM Vamac IP raw rubber, 600 parts (mass, the same as below); N550, 300 parts; N774, 180 parts; HMDC, 3.6 parts; DOTG, 12 parts; 18-amine, 3 parts; 445 antiaging agent, 12 parts; RS735 plasticizer, 18 parts; FG200 dispersant, 6 parts; WB212 internal release agent, 12 parts; and stearic acid processing aid, 6 parts.

2.4 Preparation of mixed rubber

According to the formula of ACM and AEM mixed rubber provided in Section 2.3, the raw materials were accurately weighed and then mixed in an internal mixer. First, the raw rubber materials and additives were placed into the internal mixer and mixed for 2 min. Then, carbon black and the antiaging agent were added; the mixture was evenly dispersed and introduced into the vulcanization system. After mixing for 10 min, the mixture was discharged to produce ACM and AEM mixed rubber.

The mixed rubber (ACM/AEM) was weighed based on the mass percentage of the raw rubber and mixed evenly in an open mill for 10 min. After 5 passes, the film was removed. After obtaining the mixed film, it was vulcanized in a vulcanization machine. Then, secondary vulcanization was performed, and the relevant performance properties were analyzed.

2.5 Performance testing

To determine the content of the original gel, acetone was used as the solvent, and the raw rubber material (0.05 g) was cut and placed into a 100-mL volumetric flask. The sample was dissolved in darkness for 17 h. Then, the samples were filtered (70 μm), dried in an oven at 105–110 °C for 1 h and weighed. The filter was soaked in glue and placed in an oven. The mixture was dried at 105–110 °C for 2 h. After removal, the mixture was placed in a dryer and cooled to room temperature. The gel content in the sol solution was determined via the weight increase method as follows:

$$\text{gel} = \frac{m_1 - m_0}{m} \cdot 100\% \tag{1}$$

where m_1 is the total mass (g) of the filter grid and gel, m_0 is the quality of the filter grid (g), and m is the mass of the solvent (g).

Tensile tests, air and oven aging tests, and low-temperature brittleness tests were conducted according to ASTM D5668, ASTM D4574, ASTM D1646, ASTM D5289-2017, ASTM D2240, ASTM D412-16, ASTM D412, and ASTM D746.

3 RESULTS AND DISCUSSION

3.1 Raw rubber testing

In this study, ACM and AEM were subjected to testing and analysis, and the test results are listed in **Table 1**. The Mooney viscosity of AEM is relatively low, only 25.8, whereas AX-613 exhibits a much higher Mooney viscosity than AEM. Moreover, ACM exhibits slightly lower ash and volatile contents than AEM, mainly because ACM was washed and dried more thoroughly in the experimental process.

Table 1: Analytical data for acrylate rubber

	$ML_{1+4}100$	Volatile/%	Ash/C%	Gel/C%
ACM	32.5	0.18	0.08	1.87
AEM	25.8	0.23	0.12	3.02

Note: The mass percentage is given in this table

3.2 Effect of the blending ratio on the vulcanization characteristics

In this study, actual products were combined. Notably, AEM and ACM are typically blended for sealing components such as oil seals in automotive engines. This type of product requires high strength and low compression, with a design hardness value of 75 ± 5. Therefore, we chose 774 carbon black, which not only provides a relatively large filling amount but also ensures small compression deformation. The vulcanization curves and vulcanization characteristic parameters of AEM/ACM blends with different blending ratios are shown in **Figure 1** and **Table 2**, respectively. The t_{10} and t_{90} values of AEM are greater than those of ACM, and the difference between the maximum torque (MH) and the minimum torque (ML) is large. Thus, AEM exhibits better processability. Moreover, **Figure 1** shows that the vulcanization curve of AEM is relatively smooth at the early stage, and indicates continuous vulcanization at the later stage, which is beneficial for increasing the crosslinking degree and density of the blend.[18] With increasing amount of ACM, the value of $ML_{1+4}100$ first increases and then decreases, but the torque difference (MH–ML) does not vary greatly when ACM and AEM are vulcanized separately. When the amount of ACM is increased, the effect on the resulting MH–ML is not significant. The maximum value of $ML_{1+4}100$ is reached at AEM/ACM = 7:3, which differs from the findings of other researchers.[20,21]

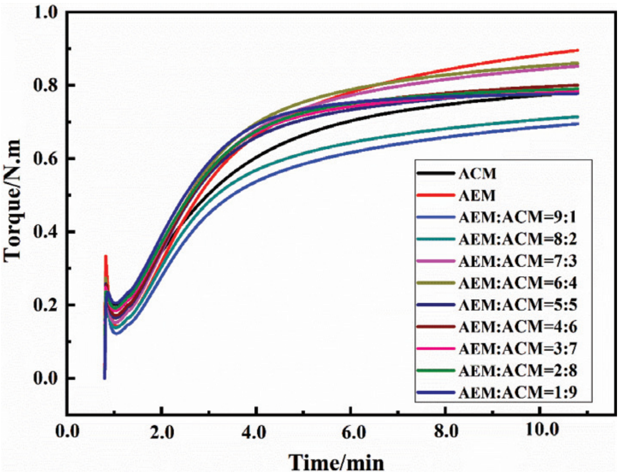

Figure 1: Curing curves of the AEM/ACM blends

Table 2: Curing characteristics of AEM/ACM

AEM/ACM	ML /(N.m)	MH /(N.m)	(MH–ML) /(N.m)	t_{10} /s	t_{90} /s	$ML_{1+4}100$
10:0	0.141	0.895	0.754	49	384	45.5
9:1	0.210	0.694	0.484	44	367	58.5
8:2	0.137	0.714	0.577	43	348	57.9
7:3	0.152	0.851	0.699	44	333	60.6
6:4	0.164	0.860	0.696	44	318	58.2
5:5	0.165	0.789	0.624	43	297	54.6
4:6	0.171	0.800	0.629	43	284	53.6
3:7	0.184	0.784	0.600	42	266	53.1
2:8	0.192	0.790	0.598	42	264	51.5
1:9	0.205	0.777	0.572	40	226	51.3
0:10	0.261	0.982	0.721	45	314	51.1

This mainly occurs because the ACM raw material used is different. Previous researchers employed PA-522HF, while ACM exhibits a lower Mooney viscosity and slower vulcanization. Moreover, differences are observed in the mixed rubber system.

3.3 Effects of the blending ratio on the physical and mechanical properties

Figure 2 shows the mechanical properties of AEM/ACM blends with different blending ratios after the first stage of vulcanization at 180 °C for 10 min and the second stage of vulcanization at 175 °C for 4 h. The strength and elongation of AEM are excellent, and it has been widely applied in high-strength and ultralow-temperature environments of industrial production. **Figure 2** shows that with increasing amount of AEM, both the strength and elongation increase.

3.4 Effects of the blending ratio on aging and low-temperature performance levels

Existing ACM and AEM aging research focuses mostly on conditions such as 100 °C × 72 h and 150 °C × 72 h.[20–22] Product manufacturing enterprises have increased the testing requirements, and both ACM and AEM exhibit excellent aging performance. Therefore, in our research, three temperature conditions, namely, 150 °C × 72 h, 175 °C × 72 h, and 190 °C × 72 h, were selected for the thermal aging analysis. To demonstrate the influences of different blending ratios on elongation and strength in high-temperature environments, three temperature conditions, namely, 150 °C × 72 h, 175 °C × 72 h, and 190 °C × 72 h, were chosen. **Figures 3**, **4**, and **5** show that with increasing amount of AEM, the strength and elongation after aging significantly increase. Under high-temperature conditions, both the elongation and strength decrease. For example, for AEM:ACM = 9:1, the strength is 13.5 MPa at 150 °C after 72 h but only 6.3 MPa at 190 °C after 72 h. Moreover, the aging pattern at a lower temperature of 150 °C for 72 h is obvious, but a decreasing trend is obvious at higher temperatures of 175 °C for 72 h and 190 °C for 72 h. In addition, there is a certain fluctuation for AEM:ACM ≥ 5:5:5, which is due mainly to the fracture of ACM vulcanization bonds or uneven mixing under high-temperature conditions.

The influences of different blending ratios on the permanent compression deformation and the minimum brittleness temperature are shown in **Figure 6**. With increasing amount of AEM, the low-temperature resistance

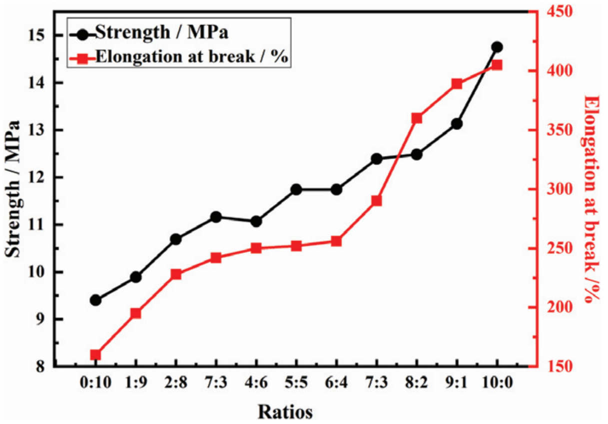

Figure 2: Tensile and elongation changes at different AEM/ACM ratios

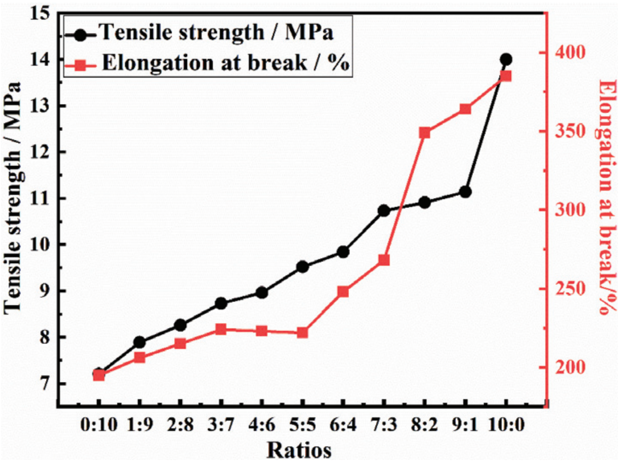

Figure 3: Effects of different AEM/ACM ratios on the strength and elongation at 150 °C after 72 h of aging

increases. When using only AEM, the minimum brittleness temperature is –58.5 °C, and when using only ACM, the minimum brittleness temperature is –25.1 °C. Notably, with increasing amount of AEM, the permanent compression deformation increases.

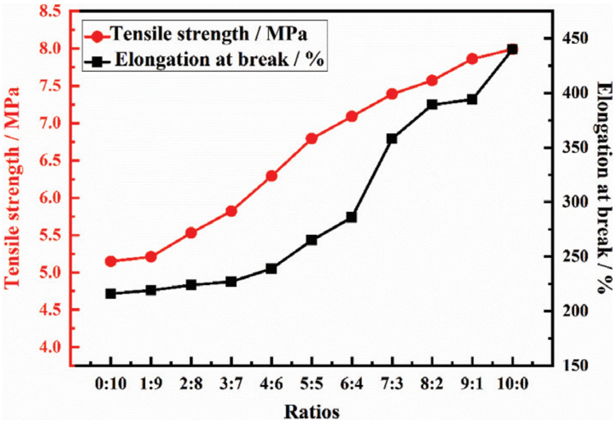

Figure 4: Effects of different AEM/ACM ratios on the strength and elongation at 175 °C after 72 h of aging

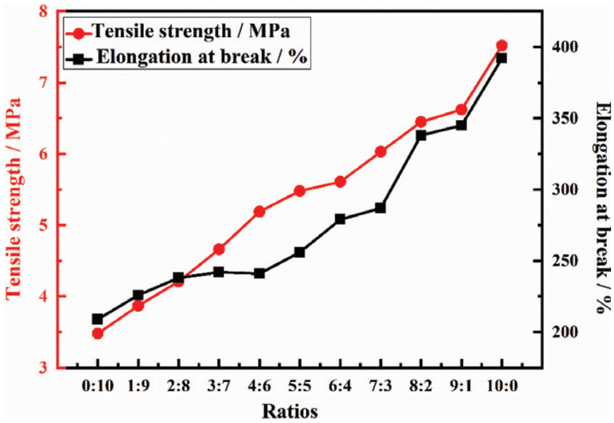

Figure 5: Effects of different AEM/ACM ratios on the strength and elongation at 190 °C after 72 h of aging

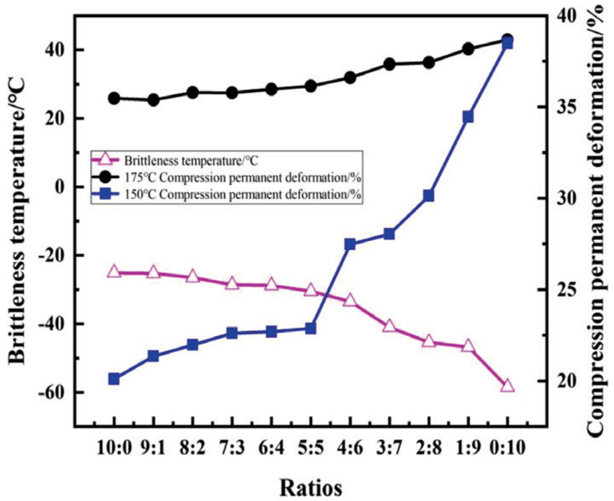

Figure 6: Changes in the permanent compression deformation and the minimum brittleness temperature

3.5 Research on the vulcanization characteristics of AEM/ACM

3.5.1 Sulfurization characteristics at different temperatures

At an AEM/ACM ratio of 7:3, the vulcanization characteristics of the prepared mixed rubber were studied using a vulcanization tester at temperatures of (130, 150, 160, 170, 180, 190, and 200) °C. **Figure 7** and **Table 3** indicate that with increasing temperature, the times to reach T10 and T90 significantly decrease, indicating that the vulcanization rate increases under high-temperature conditions. The value of MH–ML first increases and reaches its maximum at 180 °C, followed by a significant decrease at 190 °C and 200 °C. This may be due to the fracture of small-molecule acrylic rubber vulcanizing agents caused by high-temperature vulcanization. Moreover, the vulcanization curve in **Figure 7** reveals that under different temperature conditions, with increasing vulcanization time, the mechanical properties of the vulcanized rubber reach the same degrees, indicating that the vulcanization system conforms to the Arrhenius formula:

$$lg\frac{t_1}{t_2}=\frac{E_a}{2.303R}\times\frac{T_2-T_1}{T_2T_1}$$

$$lg\frac{t_1}{t_2}=E_aK \tag{2}$$

$$K=\frac{1}{2.303R}\times\frac{T_2-T_1}{T_2T_1}$$

t_1 – positive vulcanization time at vulcanization temperature T_1, min;

t_2 – positive vulcanization time at vulcanization temperature T_2, min;

R – 8.3143 J/(mol*K);

E_a – vulcanization activation energy, kJ/mol.

By calculating the activation energy at different temperatures using the above equation, the reaction activation energy of vulcanizing agent HMDC for AEM/ACM vulcanization is approximately 76.30 kJ/mol. This is approximately the activation energy reported by Richard J. Pazur[23] (75–93 kJ/mol). Moreover, linear fitting of K was performed using lg t_1/t_2. Linear correlation coefficient R^2 is 0.997, verifying that the fitting curve can accurately describe the vulcanization process.[11]

Table 3: Vulcanization characteristics at different temperatures

HMDC /°C	ML /N.m	MH /N.m	MH–ML /N.m	T_{10} /s	T_{90} /s
130	0.23	0.67	0.44	504	3118
150	0.21	0.91	0.70	182	1570
160	0.20	0.93	0.73	111	940
170	0.19	0.89	0.70	79	592
180	0.19	0.89	0.80	50	369
190	0.19	0.91	0.72	34	236
200	0.19	0.89	0.70	22	155

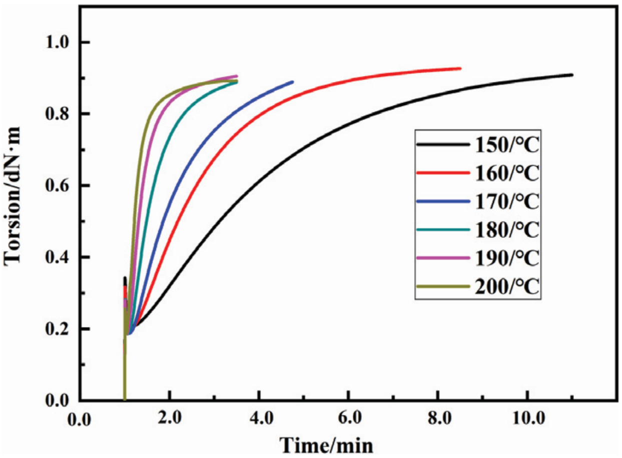

Figure 7: Vulcanization curves of the carboxyl-based AEM/ACM blends at different temperatures

3.5.2 Effect of the amount of HMDC on the vulcanization characteristics

The effect of the amount of vulcanizing agent HMDC on the vulcanization characteristics of the composite material with the AEM/ACM ratio of 7:3 was studied. The vulcanization characteristics are provided in **Table 4** and **Figure 8**. The graph shows that the MH and MH–ML values first increase and then decrease, reaching their maximum values at 1.2 parts. The positive vulcanization time continuously increases with increasing amount of vulcanizing agent, mainly because the amount of vulcanizing agent is very large, resulting in new vulcanization free radicals that are constantly generated. Thus, the positive vulcanization time increases.[12]

Table 4: Vulcanization characteristics under different HMDC dosages

HMDC /parts	ML /N.m	MH /N.m	MH–ML /N.m	T_{10} /s	T_{90} /s
0.6	0.18	0.77	0.59	43	268
0.8	0.21	0.92	0.71	48	336
1.0	0.19	0.90	0.71	49	402
1.2	0.19	0.93	0.74	49	382
1.4	0.21	0.89	0.68	51	400
1.6	0.18	0.76	0.58	51	415
1.8	0.17	0.71	0.54	49	411
2.0	0.16	0.67	0.51	50	420

3.5.3 Effect of the DOTG-75 dosage on the vulcanization characteristics

The effect of the DOTG-75 dosage on the vulcanization characteristics of the corresponding material with the AEM/ACM ratio of 7:3 was studied. The vulcanization characteristics are provided in **Table 5** and **Figure 9**. The graph shows that the values of t10, MH, and MH–ML are relatively consistent. The positive vulcanization time gradually decreases, mainly due to the addition of DOTG-75 as the vulcanization agent, which accelerates vulcanization and decreases the positive vulcanization time.

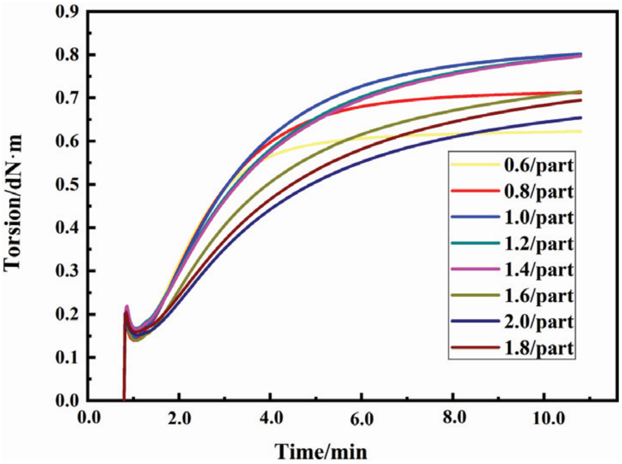

Figure 8: Vulcanization curves for different HMDC dosages

Table 5: Vulcanization characteristics of different DOTG-75 dosages

DOTG /parts	ML /N.m	MH /N.m	MH–ML /N.m	T_{10} /s	T_{90} /s
2.0	0.18	0.77	0.59	43	268
2.5	0.22	0.90	0.62	43	226
3.0	0.19	0.74	0.55	40	188
3.5	0.22	0.84	0.62	40	180
4.0	0.23	0.89	0.66	43	193
4.5	0.24	0.89	0.65	43	184
5.0	0.20	0.75	0.55	40	172

3.5.4 Effect of vulcanization on the properties of rubber materials

The effect of the DOTG-75 dosage on the mechanical properties of carboxylic acrylic rubber with the AEM/ACM ratio of 7:3 was studied, as detailed in **Table 6**. The data in the table indicate that with increasing DOTG-75 dosage, the hardness and strength slightly increased, with a difference of 4 between the maximum and minimum hardness values and a difference smaller than 1 MPa between the maximum and minimum strength values. The elongation at break generally decreased. This mainly occurred because increasing the

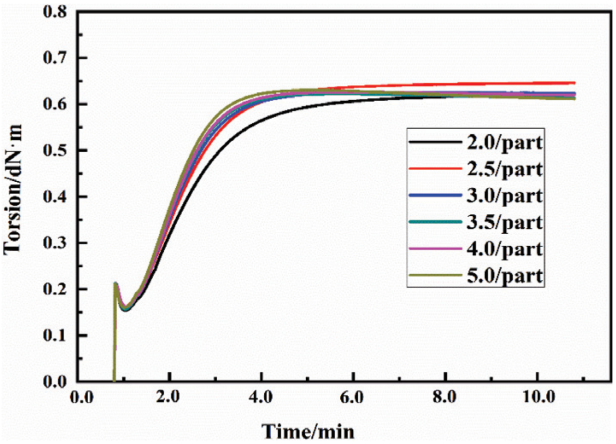

Figure 9: Vulcanization curves for different of DOTG-75 dosages

amount of vulcanizing agent is beneficial for increasing the elasticity of vulcanized rubber.[21] However, owing to the limited amount of vulcanizing agent, the mechanical properties did not differ greatly.

Table 6: Effect of the DOTG-75 dosage on the performance of carboxyl-based ACM

Item DOTG/parts	Shore A hardness	Elongation at break /%	Strength /MPa
2.0	65	210	9.98
2.5	67	206	9.91
3.0	68	191	9.09
3.5	66	198	9.96
4.0	69	185	9.32
4.5	68	184	10.09
5.0	69	177	10.59

Note: The conditions in the first stage of vulcanization are 180 °C for 5 min, and those in the second stage of vulcanization are 175 °C for 4 h

The effects of the amount of vulcanizing agent HMDC on the mechanical properties of carboxylic acrylic rubber are shown in Figure 10. Notably, with increasing amount of vulcanizing agent, the tensile strength gradually increases. However, the elongation at break gradually decreases. This mainly occurs because with increasing amount of vulcanizing agent, the crosslinking density of rubber molecular chains increases, leading to an increase in the hardness and tensile strength of the vulcanized rubber, and a decrease in the elongation at break. Under the influence of external forces, the higher the crosslinking density of the vulcanized rubber network, the greater the likelihood of stress concentration, resulting in a decrease in the tear strength of the vulcanized rubber.[21]

4 CONCLUSION

This study focused on the mechanical and aging properties of AEM and ACM blended at different ratios. At a mass ratio of AEM/ACM of 7:3, the overall performance was favorable. On the basis of this composite ratio, vulcanization characteristics were analyzed, and the conclusions are as follows:

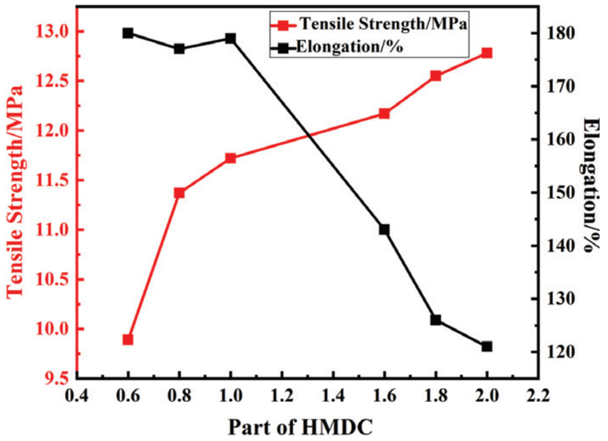

Figure 10: Effects of the vulcanizing agent on the performance of carboxyl-based ACM

a) The optimal method for AEM/ACM blending was determined; notably, according to the target performance requirements, the optimal blending ratio of AEM/ACM of 7:3 was selected via a mechanical performance test, which provided a practical matching design for the composite modification of rubber materials. In the study of vulcanization characteristics, the control variable method was adopted to examine the influences of varying HMDC and DOTG dosages on vulcanization and rubber properties, and to establish a systematic vulcanization research method that can accurately guide the optimization of rubber vulcanization.

b) With increasing ACM dosage, the value of $ML_{1+4}100$ first increased but then decreased and reached its maximum with AEM/ACM = 7:3, which differs from the findings of previous studies. This result can be attributed mainly to the characteristics of ACM, thus providing a new perspective for the study of the mechanism of ACM in the blending system. In the study of vulcanization at different temperatures, the MH–ML value first increased but then decreased with increasing temperature, indicating that high-temperature vulcanization caused the fracture of small-molecule acrylic rubber vulcanization agents, which affected the crosslinked structure. These findings enhance the understanding of the effect of temperature on the vulcanization of composite rubber.

c) The experimental data allowed the verification of the use of HMDC as a vulcanizing agent. The vulcanization reaction of this vulcanizing agent for AEM/ACM conformed to the Arrhenius formula, and the calculated reaction activation energy was approximately 76.30 kJ/mol, thereby improving the vulcanization kinetics theory for the composite system and laying a foundation for further analysis of the relationship between the vulcanization reaction rate and temperature. On the basis of the study of the relationship between the dosage of vulcanizing agent and the rubber performance, the changes in rubber hardness, tensile strength, elongation at break and other properties under the influence of HMDC and DOTG dosage variations were summarized. These modifications contribute to the theory of performance regulation in rubber materials, and allow accurate prediction and control of the final performance of rubber products.

Funding information

The Special Polymer Materials for Automobile Key Laboratory of Sichuan Province of the Sichuan Institute of Arts and Science funded this research (TZGC2024ZA-04, TZGC2023ZB-06).

5 REFERENCES

[1] J. Li, Y. Meng, J. Liu, F. Yu, X. Wang, T. Wang, K. Gao, Z. Zhang, Antibacterial waterborne polyacrylate coated fabric with underwater superoleophobicity and underoil superhydrophobicity for continuous oil/water separation, Progress in Organic Coatings, (2022), doi:10.1016/j.porgcoat.2022.107149

[2] J.-L. Jiang, X. Yang, D. Zhao, Y.-K. Feng, Morphology, mechanical and thermal properties of HNBR/AEM blends, Journal of Rubber Research, (2023), doi:10.1007/s42464-023-00190-x

[3] X. B. 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, Polymer International, (2023), doi:10.1002/pi.6459

[4] X. B. Yang, T. Lei, C. Tang, X. Huang, X. Y. Wang, S. Huang, X. Liu, Preparation and characterization of universal cold-resistant reactive chlorinated acrylic rubber and study of its vulcanization characteristics, Polymer Science Series B, (2023), doi:10.1134/s1560090423600158

[5] S. Songprasob, E. Wimolmala, K. Taptim, N. Sombatsompop, Development of PP/EPDM thermoplastic elastomer by doped with 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate based neusilin® for sanitary applications, Journal of Thermoplastic Composite Materials, (2022), doi:10.1177/08927057221145540

[6] S. Norouzi, M. Mohseni, H. Yahyaei, Preparation and characterization of an acrylic acid modified polyhedral oligomeric silsesquioxane and investigating its effect in a UV curable coating, Progress in Organic Coatings, (2016), doi:10.1016/j.porgcoat.2016.04.027

[7] 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, Progress in Organic Coatings, (2022), doi:10.1016/j.porgcoat.2021.106254

[8] H. Perrin, M. Bodaghi, V. Berthé, R. Vaudemont, On the Addition of Multifunctional Methacrylate Monomers to an Acrylic-Based Infusible Resin for the Weldability of Acrylic-Based Glass Fibre Composites, Polymers, (2023), doi:10.3390/polym15051250

[9] C. M. Parada, B. Yang, C. G. Campbell, R. F. Storey, Synthesis, characterization, and photopolymerization of (meth)acrylate-functional polyisobutylene macromers produced by cleavage/alkylation of butyl rubber, Journal of Polymer Science, (2020), doi:10.1002/pol.20200524

[10] 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, Industrial & Engineering Chemistry Research, (2021), doi:10.1021/acs.iecr.0c05987

[11] K. Yimmut, K. Homchoo, N. Hinchiranan, Poly(butyl acrylate-*co*-fluorinated acrylate)-*graft*-natural rubber: Synthesis and application as compatibilizer for natural rubber/poly(butyl acrylate-*co*-fluorinated acrylate) films, Colloids and Surfaces A: Physicochemical and Engineering Aspects, (2018), doi:10.1016/j.colsurfa.2017.12.062

[12] J. Song, Z. Peng, Y. Zhang, Enhancement of thermal conductivity and mechanical properties of silicone rubber composites by using acrylate grafted siloxane copolymers, Chemical Engineering Journal, (2020), doi:10.1016/j.cej.2019.123476

[13] Y. Zeng, X. Lai, L. Hongqiang, K. Pan, Z. Liu, X. Zeng, Synthesis and application of adhesion promoter containing phenolic hydroxyl/acrylate groups for addition-cure liquid silicone rubber, International Journal of Adhesion and Adhesives, (2022), doi:10.1016/j.ijadhadh.2022.103220

[14] M. A. Kader, A. K. Bhowmick, Thermal ageing,degradation and swelling of acrylate rubber, fluororubber and their blends containing polyfunctional acrylates, Polymer Degradation and Stability, (2003), doi:10.1016/s0141-3910(02)00292-6

[15] A. Abdel-Hakim, S. A. El-Mogy, M. M. EL-Zayat, Radiation crosslinking of acrylic rubber/styrene butadiene rubber blends containing polyfunctional monomers, Radiation Physics and Chemistry, (2019), doi:10.1016/j.radphyschem.2019.01.004

[16] K. Jantanasakulwong, Y. Kobayashi, K. Kuboyama, T. Ougizawa, Thermoplastic Vulcanizate Based on Poly(lactic acid) and Acrylic Rubber Blended with Ethylene Ionomer, Journal of Macromolecular Science Part B-Physics, (2016), doi:10.1080/00222348.2016.1238434

[17] H. Yanmin, L. Lan, C. Juanjuan, L. Yuanfan, J. Demin, Mechanical and thermal properties of FPM/PHACM/ACM blends, Journal of Elastomers & Plastics, (2012), doi:10.1177/0095244312444960

[18] D. Bornstein, R. J. Pazur, The sulfur reversion process in natural rubber in terms of crosslink density and crosslink density distribution, Polymer Testing, (2020), doi:10.1016/j.polymertesting.2020.106524

[19] J. Wang, W. Wang, X. Geng, Development of high damping acrylic rubber/sliding graft copolymer composites, RSC Advances, (2018), doi:10.1039/C8RA04644A

[20] W. Wu, X. Li, Wear and thermal properties of carbon fiber reinforced silicone rubber/fluorine rubber composites, Journal of Rubber Research, (2019), doi:10.1007/s42464-019-00020-z

[21] Z. Fan, Z. Fan, Z. Yang, et al., The Effect of the Co-Blending Process on the Sensing Characteristics of Conductive Chloroprene Rubber/Natural Rubber Composites, Polymers, (2022), doi:10.3390/polym14163326

[22] S. Öztürk, E. Erbek Cömez, H. L. Hoşgün, The rheological, mechanical and aging properties of AEM/EPDM rubber blends, Journal of Rubber Research, (2022), doi:10.1007/s42464-020-00073-5

[23] R. J. Pazur, T. Mengistu, Activation energies of thermos-oxidized nitrile rubber compounds of varying acrylonitrile content, Rubber Chemistry and Technology, (2019), doi:10.5254/rct.18.82592