The influence of heat pretreatment time on the properties of ACM/CM blended rubber

Hao Liangci, Liu Changshun, Dai Xin, Deng Tao*

(Qingdao University of Science & Technology, Qingdao 266042, Shandong, China)

Abstract: This paper investigates the influence of different degrees of precrosslinking of CM on the properties of ACM/CM blended rubber. The results indicate that the peak torque of the vulcanization characteristics of the blended rubber increases with the increase in the precrosslinking degree of the CM phase, suggesting that precrosslinking accelerates the crosslinking rate of the CM phase after blending. The variation pattern of V_r is verified, further matching the crosslinking rate of the ACM phase. The tensile strength of the blended rubber first increases and then decreases. When the precrosslinking degree is 30%, the tensile strength reaches a maximum of 13.5 MPa, and begins to decrease after exceeding 30%. After hot air aging at 100℃ for 72 hours, the maximum elongation at break is 194% when the precrosslinking degree is 20%, and begins to decrease after exceeding 20%. After hot oil aging at 100 ℃ for 72 hours, the modulus at a fixed extension becomes larger and larger with the increase in precrosslinking degree, and the volume change rate becomes smaller and smaller, but the tensile strength continuously decreases.

Key words: ACM/CM; thermal pretreatment; crosslinking density; aging

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Acrylate rubber (ACM) is an elastomer formed through copolymerization of acrylate monomers as the main basic raw material, with chlorinated vinyl acetate, acrylonitrile, etc. Its main chain structure is a saturated molecule, and the side chains are polar ester groups. Due to its special structure, acrylate rubber (ACM) is widely used in some sealing rubber products that require resistance to hot oil and high temperatures, such as automotive oil seals. ACM not only has excellent heat resistance but also ozone resistance, heat resistance, and UV resistance. Among synthetic rubbers, ACM is cheaper than silicone rubber and fluororubber, and it is superior to nitrile rubber in terms of heat resistance, oil resistance, and resistance to thermal-oxidative aging. Acrylate rubber is a cost-effective high-temperature oil-resistant specialty rubber.

Chlorinated polyethylene rubber (CM) is prepared through a chlorination process using high-density polyethylene (hDPE), and the main chain of CM molecules is similar to that of hDPE. It exhibits excellent heat resistance, oil resistance, chemical resistance, flame retardancy, and other properties. There are no double bonds in its main molecular chain, making it a saturated rubber. The presence of polar groups disrupts the regularity of the high-density polyethylene main chain, altering the properties of the polymer. Additionally, the chlorine content of the rubber is also an important factor affecting its properties.

CM lacks double bonds in its molecular chain, which results in extremely low reactivity. Traditional sulfur vulcanization systems cannot effectively vulcanize it. Therefore, peroxide vulcanization systems and thiazole-based vulcanization systems can meet this need, thus achieving the vulcanization of CM. The characteristics of the CM rubber

Biography: Hao Liangci (2000-), a master's candidate, primarily focuses on research in rubber blending and modification.

vulcanization system are that no by-products are produced during the vulcanization process, and the performance of the vulcanized product is excellent.

Blending ACM with CM can significantly reduce costs. Moreover, the chlorine atoms in CM impart strong polarity, effectively enhancing the compatibility between the two. CM itself also has high strength, which can compensate for the lower strength of acrylate rubber. However, due to the slow vulcanization rate of CM, which significantly differs from that of ACM, there is a mismatch in the vulcanization rates of the two phases during the vulcanization process, affecting the performance of the blended rubber.

Therefore, in this paper, the chloroprene rubber (CM) in the blend was first subjected to thermal pretreatment at 165 ℃ for different durations to accelerate its vulcanization, and the effects of different thermal pretreatment times on the properties of the blended rubber after mixing were explored.

1 Experimental part

1.1 Raw materials

ACM, Jiujiang Dewei Rubber Technology Co., Ltd.; CM, Weifang Yaxing Chemical Co., Ltd.; the remaining ingredients are common industrial products.

1.2 Main experimental equipment

The instruments and equipment used in the experiment are listed in Table 1.

Table 1 Experimental instruments and equipment

Instrument Name	Model	Manufacturer
Open mill	X(S)K—160	Shanghai Shuangyi Rubber & Plastics Machinery Co., Ltd
Internal mixer	XSM—1/20—80	Shanghai Kechuang Rubber and Plastic Machinery Equipment Co., Ltd
Rotorless vulcanizer	M—3000A	Taiwan High Speed Rail Corporation
Flat vulcanizing press	LCM—3C2—G03—LM	Shenzhen Jiaxin Electronic Equipment Technology Co., Ltd
Automatic pneumatic slicer	GT—7010—AR	Taiwan High Speed Rail Corporation
Electronic tensile machine	JDL—2500N	Tianfa Experimental Machinery Co., Ltd
Aging chamber	GT—7017—M	Taiwan High Speed Rail Corporation

1.3 Experimental formula

(1) ACM101X 100, carbon black N330 50, silica 15, CaCO3 10, MgO 5, DOP 10, TCY 2.5, BZ 2.5.

(2) CM135B 20, carbon black N330 50, silica 15, CaCO3 10, MgO 5, DOP 10, TCY 2.5, BZ 2.5.

1.4 Experimental scheme

The experimental scheme for investigating the influence of CM heat pretreatment time on the mechanical behavior of ACM/CM blend is presented in Table 2.

Table 2 CM Heat Pretreatment Time

name	C_0	C_1	C_2	C_3	C_4
CM pre-crosslinking degree/%	0	10%	20%	30%	40%
CM thermal pre-treatment time (in seconds)	0	287	404	505	609

1.5 Sample preparation

ACM compound and CM compound were prepared using a mixer according to experimental formulas (1) and (2), respectively, following conventional processes. The CM compound was pre-vulcanized at 165 ℃ for different durations as specified in the experimental plan. Subsequently, the pre-vulcanized CM compound was mixed uniformly with the ACM compound on an open mill at a mass ratio of 20:80. The mixture was then sheeted, allowed to rest for 24 hours, and finally vulcanized on a flat vulcanizer under the conditions of 165 ℃/10 MPa for varying vulcanization durations.

1.6 Analysis and testing

1.6.1 Vulcanization characteristics

Tested according to GB/T 16584-1996, the vulcanization conditions are 165 ℃, 10 MPa, and 5 different test durations.

1.6.2 Mechanical properties

The tensile properties were tested using an electronic tensile testing machine in accordance with GB/T 528-2008, with a tensile speed of 500 mm/min and a test temperature of room temperature. The tear resistance was tested using an electronic tensile testing machine in accordance with GB529 standard, with a test temperature of room temperature.

1.6.3 Hardness test

The hardness is Shore A hardness, measured according to GB/T531.1-2008.

1.6.4 Thermo-oxidative aging

The aging temperature is 100℃, and the aging time is 72 hours.

1.6.5 Hot oil aging

Aging temperature is 100 ℃, aging time is 72 hours, and the medium is 42# hydraulic oil.

1.6.6 Measurement of crosslinking density by equilibrium swelling method

The solvent is methyl methacrylate, with a swelling time of 24 hours.

2 Results and discussion

2.1 Vulcanization characteristics

The effect of CM phase heat pretreatment time on the vulcanization characteristics of the blend is shown in Table 3. From the table, it can be seen that as the heat pretreatment time of the CM phase increases, the minimum torque of the blend continuously increases. This is because heat pretreatment causes initial crosslinking of CM, leading to a continuous increase in the crosslinking density of the unvulcanized blend and a decrease in fluidity. Furthermore, as the heat pretreatment time of the CM phase increases, it can be observed that t90 is continuously decreasing, indicating that heat pretreatment can promote early crosslinking of CM. This also enables it to match the crosslinking speed of the ACM phase during post-blending crosslinking, thereby accelerating the overall crosslinking speed.

Table 3 Effect of CM heat pretreatment time on the vulcanization characteristics of ACM/CM blends

Serial Number	C_0	C_1	C_2	C_3	C_4
M_H/(dN·m)	13.27	12.52	13.42	13.28	13.27
M_L/(dN·m)	1.88	1.90	1.95	2.29	2.36
M_H−M_L/(dN·m)	11.39	10.62	11.47	10.99	10.91
t_{10}/min	0.33	0.35	0.35	0.35	0.38
t_{90} /min	21.35	20.56	20.59	20.40	20.35

2.2 Physical and mechanical properties

The effect of CM heat pretreatment time on the physical and mechanical properties of ACM/CM vulcanizate is shown in Table 4. From the table, it can be observed that as the heat pretreatment time of CM increases, the hardness continuously rises, indicating macroscopically that heat pretreatment enhances the overall crosslinking density of the blend. The tensile strength and modulus at break first increase and then decrease with the increase in heat pretreatment time of CM. The maximum value is reached at a prevulcanization degree of 30%, which is 13.5 MPa. The increase is mainly due to the increase in the overall crosslinking density of the system caused by the longer heat pretreatment time of CM, making the internal crosslinking network of the system more compact. The increase in crosslinking density manifests in the overall modulus increase in macroscopic physical and mechanical properties, which also indicates that after heat pretreatment, the vulcanization rates of the two phases are similar, enabling the moduli of the two phases to match. However, the subsequent decrease is mainly due to the excessive pre-crosslinking degree of CM. Firstly, it makes it difficult for the two phases to blend evenly during the subsequent blending process. Secondly, it leads to a reduction in the number of co-crosslinking points between the two phases, and the pre-crosslinking of CM becomes a stress concentration point, causing fracture at that location, leading to a decrease in elongation at break and a reduction in the tensile strength of the blend.

Table 4 Effect of CM heat pretreatment time on the physical and mechanical properties of ACM/CM vulcanizate

Number	C_0	C_1	C_2	C_3	C_4
Hardness / Shore A	82	83	83	84	84
Tensile strength / MPa	12.5	13.4	12.6	13.5	12.4
Elongation at break /%	234	240	252	206	208
50% modulus at fixed extension / MPa	2.5	2.4	2.4	3.0	3.0
100% modulus at fixed extension / MPa	5.2	5.3	5.1	6.7	6.3
200% modulus / MPa	10.5	11.7	10.4	12.4	11.9
Tear strength /kN·m^{-1}	29.9	26.2	24.0	27.8	29.9
Permanent set at break /%	10.0	10.0	10.0	5.0	10.0

2.3 Gel volume fraction of the blend

The Vr values of the blends after swelling in methyl methacrylate for 24 hours are presented in Table 5. It can be observed from the table that as the degree of pre-crosslinking of the CM phase increases, the overall Vr of the blends also increases. This indicates that the crosslinking density of the ACM/CM blends increases. This suggests that thermal pretreatment of CM can facilitate early crosslinking of CM, thereby enhancing the crosslinking speed of both phases and ultimately increasing the overall crosslinking density.

Table 5 Effect of CM heat pretreatment time on Vr of ACM/CM vulcanizate

Serial number	C_0	C_1	C_2	C_4	C_4
Vr/%	22.72	22.96	23.90	23.30	24.77

2.4 Properties of blends after aging

2.4.1 Performance before and after thermo-oxidative aging

The physical and mechanical properties of the blends after thermo-oxidative aging at 100 ℃ for 72 hours are shown in Table 2.4. From the table, it can be observed that after thermo-oxidative aging, the overall modulus increases significantly. However, from the perspective of modulus, as the degree of pre-crosslinking of CM increases, the modulus at a fixed extension rate also increases. This is mainly due to the significant difference in the crosslinking density of CM phases, which leads to more stress concentration points within the system. Therefore, after the degree of pre-crosslinking exceeds 20%, the elongation at break decreases significantly, which also results in a significant decrease in tensile strength.

Table6 Physical and mechanical properties of ACM/CM blend after thermo-oxidative aging

Number	C_0	C_1	C_2	C_3	C_4
Hardness/Shore A	86	87	87	87	87
Tensile strength/MPa	15.1	11.8	13.0	12.6	15.1
Elongation at break/%	198	160	194	156	182
Change rate of elongation at break (%)	−15.38	−33.19	−23.02	−24.27	−12.50
50% modulus at fixed extension/ MPa	3.5	3.5	3.5	4.2	4.1
100% modulus at fixed extension /MPa	7.4	7.5	7.2	8.6	9.1
Tear strength //kN·m^{-1}	32.2	33.2	31.5	33.5	30.1
Permanent set at break /%	5.0	5.0	5.0	5.0	5.0

2.4.2 Hot oil aging of blended rubber

The physical and mechanical properties of the blend after hot oil aging at 100℃ for 72 hours in 42# hydraulic oil are shown in Table 6. As the pre-crosslinking degree of CM increases, both the 50% modulus at a fixed extension and the 100% modulus at a fixed extension show a noticeable upward trend, and the volume change rate gradually decreases. This indicates that as the CM phase and the degree of crosslinking increase, the overall crosslinking density of the blend increases, making it difficult for small molecules of hydraulic oil to penetrate into the blend, thus gradually reducing its volume change rate. However, due to the increase in the crosslinking degree of the CM phase, the degree of co-crosslinking between the two phases decreases, leading to a reduction in the connecting ability between the two phases. Additionally, due to the low dosage of CM, it becomes a stress concentration point. This also results in a noticeable decrease in the elongation at break after the pre-crosslinking degree exceeds 20%, leading to a decline in the overall heat resistance of the blend to hot oil.

Table7 Physical and mechanical properties of ACM/CM vulcanizate after hot oil aging

Number	C_0	C_1	C_2	C_3	C_4
Hardness / Shore A	86	87	87	88	87
Tensile strength / MPa	13.3	13.6	11.7	12.8	12.4
Elongation at break /%	194	179	201	155	154
50% modulus at fixed extension / MPa	3.8	4.1	3.5	4.0	4.2
100% modulus / MPa	7.3	8.3	6.7	8.6	8.1
Permanent set at break /%	5	5	5	5	5
Volume change rate/%	−4.1	−4.0	−3.5	−2.8	−3.6

3 Conclusion

The study investigated the properties of ACM/CM blends by altering the degree of precuring of the CM phase in the blends. As the heat pretreatment time of the CM phase increased:

(1)The minimum torque of the blended rubber continuously increases, and Vr also continuously increases, indicating that the crosslinking density is continuously increasing.

(2) The tensile strength and modulus at break of the blend first increase and then decrease, reaching a maximum of 13.5 MPa when the degree of precuring is 30%.

(3) After thermo-oxidative aging at 100℃ for 72 hours, the modulus at a fixed extension increases. When the degree of crosslinking exceeds 20%, the elongation at break shows a noticeable decrease.

(4) After hot oil aging at 100℃ for 72 hours in 42# hydraulic oil, both the 50% modulus and the 100% modulus of the blended rubber showed a noticeable upward trend, while the volume change rate gradually decreased.