

Study on the high-temperature resistance of nitrile rubber ANBR3305 and NBR3305E

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Abstract: This article conducts a comparative study on the microstructure and physical and mechanical properties of Lanzhou ANBR3305 and NBR3305E, including tests on micro-condensed structure such as glass transition temperature, acrylonitrile content, and content of various sequence structures, as well as tests on the processing properties, vulcanization characteristics, physical and mechanical properties, and heat-resistant oxygen aging resistance of vulcanized rubber. The results indicate that ANBR3305 exhibits superior heat-resistant oxygen aging resistance compared to NBR3305E when no antioxidant is added, and when antioxidants 4010NA, RD and BLE are added; antioxidant NAPM can significantly improve the heat-resistant oxygen aging resistance of NBR3305E; 4010NA and RD are beneficial to improving the heat-resistant oxygen aging resistance of ANBR3305; BLE is detrimental to its heat-resistant oxygen aging resistance.

Key words: nitrile rubber; micro-properties; physical and mechanical properties; thermal-oxidative aging resistance

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Nitrile rubber (NBR) is a widely used synthetic rubber. The polar acrylonitrile groups contained in its molecular chain make NBR excellent in resistance to non-polar media, and it is widely used in oil-resistant hoses, tapes, O-rings, oil seals, and other fields. However, the traditional antioxidant system in rubber formulations tends to fail due to extraction by oil, solvents, and heat during use. To address this issue, besides using nitrile rubber with high acrylonitrile content, the use of hydrogenated nitrile rubber can also improve the heat resistance, oxidation resistance, and oil resistance of products, but its high price often limits its application in ordinary rubber products. Therefore, reactive antioxidants are often polymerized onto the rubber molecular chain through copolymerization and grafting. Polymerized stable nitrile rubber is obtained by polymerizing the reactive antioxidant NAPM onto the molecular chain during the polymerization

stage, resulting in a functional rubber that is stable under use conditions. The antioxidant will not be lost from the product due to oil, solvents, and heat, extending the service life of nitrile rubber.

This study primarily compares the raw rubber microstructure, physical and mechanical properties of rubber compound, heat resistance to air aging, and heat resistance to oil aging of Lanzhou ANBR3305 and NBR3305E. Additionally, it investigates the influence of anti-aging systems on the heat resistance of ANBR3305 and NBR3305E, providing a reference for the application of nitrile rubber in high-temperature conditions.

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1 Experimental part

1.1 Main raw materials

ANBR3305, NBR3305E, products of PetroChina Lanzhou Petrochemical Company; Carbon black N330, zinc oxide, stearic acid, vulcanizing agent, and antioxidant are all commonly used auxiliary materials in the rubber industry and are commercially available.

1.2 Main instruments and equipment

X(S)K-160 open mill, a product of Shanghai Shuangyi Rubber & Plastics Machinery Co., Ltd.; Rheomix 3000 torque rheometer, a product of Germany's HAAKE company; Av500 1H-NMR nuclear magnetic resonance spectrometer, a product of Bruker Technology Co., Ltd.; DSC 1/700 differential scanning calorimeter (DSC) instrument, a product of Switzerland's Mettler-Toledo company; RPA2000 rubber processing analysis (RPA) instrument, a product of the American company TA; XLB-D flat vulcanizing press, a product of Zhejiang Huzhou Dongfang Machinery Co., Ltd.; GT-7017-URP hot air aging oven, GT-7080S2 Mooney viscometer, GT-TCS-2000 tensile testing machine, products of High-Speed Rail Testing Instrument Co., Ltd.

1.3 Experimental formula

Standard test formula (parts by mass):

NBR,100; ZnO,3; S,1.5; SA,1; N330,40; TBBS,0.7.

Anti-aging system formula (parts by weight):

NBR,100; ZnO,3; S,1.5; SA,1; N330,40; TBBS,1.

A-1[#] is blank; A-2[#] is NAPM 1.75; A-3[#] is RD 2,4010NA 1; A-4[#] is BLE 3.

B-1[#] Blank; B-2[#] RD 2, 4010NA 1; B-3[#] BLE 3 (A represents ANBR3305, B represents NBR3305E).

1.4 Sample preparation

Preparation of rubber compound: Plasticize NBR raw rubber on the open mill, add small materials such as zinc oxide and stearic acid to the accumulated rubber on the covering roll. After the powder is fully incorporated, add carbon black, antioxidant, and accelerator in sequence, and finally sulfur; cut and turn the rubber evenly with left and right cutting blades, mix evenly, adjust the roll gap to 1~2 mm, maintain a certain amount of rubber between the rolls, thin-pass 4~5 times, and make triangular bales 5 times; adjust the roll gap to about 2 mm to obtain a smooth-surfaced, bubble-free rubber compound.

The rubber compound is left to stand at room temperature for more than 16 hours, and then vulcanized on a flat vulcanizer at a temperature of 170 °C, a pressure of 10 MPa, and a vulcanization time of t90+2 minutes.

1.5 Performance testing

All properties of the rubber compound are tested in accordance with the corresponding national standards.

2 Results and Discussion

2.1 Microscopic properties of raw rubber

2.1.1 Sequence structure and relative content of raw rubber

Table 1 Sequence structure and relative content of raw rubber of three types of NBR

Project	ANBR3305	NBR3305E
BBB	34.7	34.3
BBA	11.4	11.4
ABA	32.8	32.8
BAB	21.1	21.6
Combined acrylonitrile content /%	34.9	35.6

Observing the data in Table 1, there is little difference in the sequence structure between Lanzhou ANBR3305 and NBR3305E, both of which are primarily composed of cis-1,4 structures. Additionally, there is little difference in the 1,2 structure between the two. The 1,2 structure in NBR3305E is slightly higher than that in ANBR3305. The acrylonitrile content in NBR3305E is not significantly different from that in ANBR3305, being slightly higher than that in ANBR3305.

2.1.2 Gel content and glass transition temperature of raw rubber

As can be seen from Table 2, the Tg of NBR3305E is -27.59 °C, while that of ANBR3305 is -25.63 °C. The lower glass transition temperature of NBR3305E is attributed to the introduction of benzene rings, amino groups, and amide groups into the molecular chain of ANBR3305, which increases intermolecular forces, hinders the movement of the molecular chain, reduces the flexibility of the molecular chain, and raises the glass transition temperature. Additionally, the gel content of ANBR3305 is lower than that of NBR3305E, possibly due to the addition of the reactive antioxidant NAPM, which inhibits the polymerization reaction and reduces the gel content.

2.2 Processing performance of standard rubber compound

Table 2 Gel content and glass transition temperature of raw gel

Project	ANBR3305	NBR3305E
Gel content, %	4.1	8.3
$T_g/^{\circ}\text{C}$	-25.63	-27.59

As can be seen from Table 3, the raw rubber Mooney viscosity of ANBR3305 is relatively low (47), while that of NBR3305E is higher (52), which is consistent with the gel content comparison results in Table 2.

Table 3 Vulcanization characteristics of rubber compound

Project	ANBR3305	NBR3305E
LM Mooney (raw rubber)	47	52
LM Mooney (rubber compound)	61	76
Δ LM	14	24
$F_L/(\text{ANBR} \cdot \text{m})$	1.61	1.54
$F_{\max}/(\text{ANBR} \cdot \text{m})$	14.79	17.63
$F_{\max}-F_L/(\text{ANBR} \cdot \text{m})$	13.18	16.09
t_{10}/min	1.84	2.19
t_{90}/min	5.97	7.63

t_{10} represents the scorch time of the rubber compound, t_{90} denotes the optimal vulcanization time for the process, FL stands for the minimum torque, and FH signifies the maximum torque. It can be observed that t_{10} of NBR3305E is slightly higher than that of ANBR3305. Additionally, NBR3305E has a larger t_{90} and a longer vulcanization time. By comparing the difference between t_{90} and t_{10} , it is evident that the vulcanization rate of NBR3305E is slower, whereas that of ANBR3305 is faster.

F_L reflects the flowability of the rubber compound, and it can be seen that there is little difference in flowability between the two. F_H 's maximum torque is related to the shear modulus, hardness, modulus at a fixed extension, and crosslinking density of the rubber compound. The maximum torque value serves as one of the indicators of the degree of crosslinking in vulcanized rubber. NBR3305E has a higher F_H , and the difference between F_H and F_L reflects the degree of vulcanization and crosslinking of the rubber compound. It can be seen that the degree of crosslinking in NBR3305E is greater than that in ANBR3305.

2.3 Comparison of the properties of vulcanizates with standard formulations

As can be seen from Table 4, the properties of the two types of rubber compounds before and after aging indicate that after aging at 120°C for 24 hours, the tensile strength of

both vulcanizates increases while the elongation decreases. After further aging for 72 hours, both the tensile strength and elongation of the vulcanizates decrease significantly. Under the condition of 120°C for 24 hours, both types of vulcanizates exhibit good aging performance; under the condition of 120°C for 72 hours, although the change in tensile strength of ANBR3305 is small, and the change in hardness of NBR3305E is also small, the change in hardness of both is close to 10, and the change in tensile elongation at break is close to 50%, indicating that the viscoelastic properties of the rubber compounds have failed.

Table 4 Comparison of the properties of vulcanizates with standard formulations

project	ANBR3305	NBR3305E
Physical properties at room temperature		
Shore A hardness/degree	61	64
Tensile strength / MPa	17.3	18.5
Elongation at break, %	354	387
After hot air aging at 120 °C for 24 hours		
Hardness change/degree	+4	+3
Change rate of tensile strength, %	1.3	5.4
Rate of change of elongation at break, %	-13.6	-6.7
After hot air aging at 120 °C for 72 hours		
Hardness change/degree	+10	+8
Change rate of tensile strength, %	-15.0	-39.0
Rate of change of elongation at break, %	-44.3	-59.2

2.4 Performance of rubber compounds with different antioxidant systems

Analyzing the data in Table 5, it is observed that the hardness of each formula's vulcanizate increases, while the change rates of tensile strength and elongation at break under hot oxygen aging decrease. The comparative analysis is as follows:

(1) Compare the standard formulations of A-1# (NBR3305E) and B-1# (AN3305)

Hardness variation: B-1# < A-1#;

After 6 hours of hot air aging, the change rates of tensile strength and elongation at break of A-1# are relatively small; at 14.5 hours, 24 hours, and 48 hours, the change rates of B-1# are also relatively small;

In terms of the time to 180° brittle fracture, B-1# is greater than A-1#;

That is, the heat-resistant oxidation performance of B-1# (AN3305 standard formula) is superior to that of A-1# (NBR3305E standard formula).

(2) Compare A-2# (NBR3305E+NAPM) with B-1#

Table 5 Comparison of vulcanizate properties with different antioxidant systems

Project	A-1#	A-2#	A-3#	A-4#	B-1#	B-2#	B-3#
Shore A hardness/degree	66	66	65	67	67	66	68
Tensile strength / MPa	16.9	17.3	17.2	18.5	20.5	21.3	22.9
Elongation at break, %	404	476	529	500	428	521	491
After hot air aging at 135 °C for 6 hours							
Hardness change/degree	+5	+5	+6	+5	+3	+4	+6
Change rate of tensile strength, %	-9.8	-8.4	-13.8	-17.1	-23.1	-7.3	-2.6
Rate of change of elongation at break, %	-11	-7.7	-21.9	-30.5	-24.2	-58	-31.2
After hot air aging at 135 °C for 14 hours							
Hardness change/degree	+13	+13	+7	+9	+6	+8	+8
Change rate of tensile strength, %	-28.8	-20.8	-19.9	-30.4	-23.7	-12.1	-18.6
Rate of change of elongation at break, %	-48.9	-49.7	-54.4	-58.2	-48	-42.5	-49.4
After being aged in hot air at 135 °C for 24 hours							
Hardness change/degree	+10	+9	+9	+11	+8	+8	+10
Change rate of tensile strength, %	-46.2	-34.3	-40.3	-50.8	-41.9	-22.4	-25
Rate of change of elongation at break, %	-59.5	-52.3	-59.8	-68.8	-54.3	-49.9	-51.9

Table 6 Rubber compound hot air aging 180° folding phenomenon

Sample Name	Brittle fracture time
A1	52h, 55.5h, 70h
A2	83h, 86h
A3	86h, 94h, 96h
A4	52 hours, 70 hours
B1	77h, 94h, 102h
B3	94h, 115h
B4	86 hours, 90.5 hours, 108 hours

(AN3305 standard formula)

Hardness variation: $A-2^{\#} < B-1^{\#}$;

At 6h, 14.5h, and 24h, the change rate of $A-2^{\#}$ is relatively small; as time extends to 48h, the change rate of $B-1^{\#}$ is relatively small;

In terms of the time to 180° brittle fracture, $A-2^{\#}$ is greater than $B-1^{\#}$;

That is, the heat-resistant oxygen resistance of $A-2^{\#}$ (NBR3305E+NAPM) is superior to that of $B-1^{\#}$ (AN3305 standard formula).

(3) Compare $A-3^{\#}$ (NBR3305E+RD, 4010NA) with $B-3^{\#}$ (NBR3305E+RD, 4010NA)

Hardness variation: There is little difference between the two;

The change rates of tensile strength and elongation at break of $B-3^{\#}$ vulcanizate are relatively small;

In terms of the time to 180° brittle fracture, $B-3^{\#}$ is greater than $A-3^{\#}$.

That is, the thermal oxidation resistance of $B-3^{\#}$ (NBR3305E+RD, 4010NA) is superior to that of $A-3^{\#}$ (NBR3305E+RD, 4010NA).

(4) Compare $A-4^{\#}$ (NBR3305E+BLE) with

$B-4^{\#}$ (AN3305+BLE)

Hardness variation: There is little difference between the two;

The change rates of tensile strength and elongation at break for $B-4^{\#}$ are relatively small;

In terms of the time taken for 180° brittle fracture, $B-4^{\#}$ is greater than $A-4^{\#}$.

That is, the thermal oxidation resistance of $B-4^{\#}$ (AN3305+BLE) is superior to that of $A-4^{\#}$ (NBR3305E+BLE).

(3) Compare $B-1^{\#}$, $B-3^{\#}$, and $B-4^{\#}$

Hardness variation: $B-1^{\#}$, $B-3^{\#} < B-4^{\#}$;

The change rate of tensile strength for $B-3^{\#}$ and $B-4^{\#}$ is relatively small; at 6 hours, the change in elongation at break is: $B-1^{\#} < B-4^{\#} < B-3^{\#}$, and the changes in elongation at break at 14.5 hours, 24 hours, and 48 hours are not significantly different;

In terms of 180° brittle fracture time, $B-3^{\#} > B-4^{\#} > B-1^{\#}$.

That is, $B-3^{\#}$ has better thermal-oxidative resistance than $B-1^{\#}$ and $B-4^{\#}$.

The ranking of the properties of various vulcanizates is presented in Table 3.18:

Table 7 Comparison of heat and oxygen aging resistance

Label	Antioxidant	Sorting
a	Blank	$B1 > A1$
b	NAPM	$A2 > B1$
c	RD, 4010NA	$B3 > A3$
d	BLE	$B4 > A4$
e	ANBR3305	$B3 > B1 > B4$

In summary, conclusions can be drawn from groups a, c, and d: the thermo-oxidative aging properties of ANBR3305

are consistently superior to those of NBR3305E vulcanizate, whether no antioxidant is added or antioxidants 4010NA, RD, and BLE are added; conclusions can be drawn from group b: the addition of antioxidant NAPM significantly improves the thermo-oxidative aging resistance of NBR3305E, and it is superior to that of ANBR3305 with NAPM added; conclusions can be drawn from group c: 4010NA and RD are beneficial to improving the thermo-oxidative aging resistance of ANBR3305, while BLE is detrimental to the thermo-oxidative aging resistance of ANBR3305.

3 Conclusion

(1) The sequence structures of Lanzhou ANBR3305 and NBR3305E, two types of nitrile rubbers, are not significantly different, and the 1,2-structure of the two is also not significantly different. The 1,2-structure in NBR3305E is slightly higher than that in ANBR3305. The acrylonitrile content of NBR3305E is not significantly different from that of ANBR3305, but slightly higher than that of ANBR3305.

(2) The introduction of benzene rings, amino groups, and amide groups into the molecular chain of ANBR3305 reduces the flexibility of the molecular chain and increases the glass transition temperature; meanwhile, the gel content of

ANBR3305 is lower than that of NBR3305E.

(3) Under the standard formula, after being aged in hot air at 120°C for 24 hours, both the vulcanizates of Lanzhou ANBR3305 and NBR3305E exhibited good aging resistance; after being aged in hot air at 120°C for 72 hours, the comprehensive physical and mechanical properties of the rubber compound had lost their effectiveness.

(4) When no antioxidant is added, the heat-resistant oxygen aging performance of ANBR3305 is superior to that of NBR3305E, while the heat-resistant oil aging performance of NBR3305E is superior to that of ANBR3305;

(5) After the addition of antioxidants 4010NA, RD, and BLE, the thermo-oxidative aging performance of ANBR3305 consistently outperforms that of the corresponding vulcanizate formulation of NBR3305E;

(6) The addition of antioxidant NAPM significantly improved the heat-oxygen aging resistance of NBR3305E: NBR3305E+NAPM outperformed ANBR3305.

(7) When comparing various antioxidant groups, 4010NA and RD are beneficial for improving the heat-resistant oxidative aging performance of ANBR3305; BLE is detrimental to its heat-resistant oxidative aging performance.