Comparative study on the performance of ANBR3305 and NBR40H

Zhang Baogang[1*], Gao Zhixing[2], Liu Xiao[3], Zhang Luchen[1], Feng Xiaomeng[3]

(1. Engineering Research Center for High-Performance Polymers and Molding Technology, Ministry of Education, Qingdao University of Science and Technology, Qingdao 266042, Shandong, China;
2. PetroChina Company Limited Lanzhou Petrochemical Branch, Lanzhou 730060, Gansu, China;
3. Qingdao Haishengtai Materials Co. LTD., Qingdao 266000, Shandong, China)

Abstract: This article primarily compares the microstructure, physical and mechanical properties, and processing performance of ANBR3305, a cold-process soft polybutadiene rubber with medium acrylonitrile content from Lanzhou Petrochemical Company, and NBR40H, a hot-process hard polybutadiene rubber with high acrylonitrile and gel content. The results indicate that ANBR3305 exhibits superior oil resistance, low-temperature performance, and good heat resistance, while maintaining a balance between cold resistance and oil resistance. Its heat resistance can be further studied for applications in general sealing and hose products. NBR40H demonstrates good mechanical properties at room temperature, possibly due to its high gel content, which benefits its mechanical properties at room temperature. It also exhibits good oil resistance, but poor cold resistance and elasticity. Its comprehensive performance can be further studied for applications in harsh environments such as oil.

Key words: nitrile rubber; acrylonitrile; cold soft polymerization; hot hard polymerization; heat-resistant oxygen aging resistance

Classification number: TQ330.46 **Article number:** 1009-797X(2026)10-0023-04

Document code: B **DOI:** 10.13520/j.cnki.rpte.2026.10.010

Nitrile rubber (NBR) is a kind of widely used synthetic rubber. The polar acrylonitrile groups contained in its molecular chain make NBR exhibit excellent resistance to non-polar media, and it is widely used in oil-resistant hoses, rubber belts, O-rings, oil seals, automotive seals, and other fields.

The new heat-resistant nitrile rubber ANBR3305 is a functional rubber obtained by introducing the reactive antioxidant NAPM during the cold polymerization stage. The antioxidant will not be lost from the product due to the effects of oil, solvents, and heat, thereby extending the service life of nitrile rubber. The new heat-processed nitrile rubber NBR40H is obtained through heat polymerization and utilizes an environmentally friendly emulsification system. That is, the development of environmentally friendly auxiliaries has led to the creation of a new type of heat-processed polymerized nitrile rubber with high acrylonitrile content.

This study primarily compares nitrile rubber ANBR3305 and NBR40H in terms of raw rubber microstructure, physical and mechanical properties of rubber compound, heat-resistant oxygen aging performance, and oil resistance, providing a reference for the practical application of nitrile rubber under working conditions.

1 Experimental part

1.1 Main raw materials

ANBR3305, NBR40H, products of PetroChina Lanzhou Petrochemical Company; carbon black N330, N550, zinc

Biography: Zhang Baogang (1988-), male, PhD candidate, senior engineer, primarily focuses on the engineering and performance-based research of polymer materials.

Project Fund: Supported by the Open Research Fund of the Key Laboratory of Advanced Rubber Materials, Ministry of Education (Project No.: XJCL2025007)

oxide, stearic acid, vulcanizing agent, antioxidant, and plasticizer are all commonly used auxiliary materials in the rubber industry and are commercially available.

1.2 Test formula

(1) Standard test formula (parts by mass):

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

(2) Vulcanization system formula (parts by mass):

NBR, 100; ZnO, 3; SA, 1; N330, 20; N550, 30; RD, 2; 4010NA, 1.5; DOA, 15.

Sulfur vulcanization system: S, 0.6, TMTD, 1; CZ, 1.5; Peroxide vulcanization system: DCP, 1.5; TAIC, 1.5; M11: ANBR3305 + sulfur vulcanization system; M12: ANBR3305 + peroxide vulcanization system; M21: NBR40H + sulfur vulcanization system; M22: NBR40H + peroxide vulcanization system.

1.3 Main instruments and equipment

Torque rheometer, Rheomix 3000 model, product of HAAKE company in Germany; Rubber Processing Analysis (RPA) instrument, RPA2000, product of TA company in the United States; Open mill, X(S)K-160 model, product of Shanghai Shuangyi Rubber & Plastics Machinery Co., Ltd.; Flat vulcanizing press, XLB-D, product of Zhejiang Huzhou Dongfang Machinery Co., Ltd.; GT-7040-1 constant temperature oil bath, GT-7017-URP hot air aging oven, GT-7080S2 Mooney viscometer, and GT-TCS-2000 tensile testing machine, product of High-Speed Rail Testing Instrument Co., Ltd.

1.4 Sample preparation

Preparation of rubber compound: Start the open mill, add NBR raw rubber, and after wrapping the rollers, add basic formula ingredients such as zinc oxide and stearic acid to the accumulated rubber. After the powder absorption is complete, add carbon black, plasticizer, antioxidant, and accelerator in order, and finally add the vulcanization system; cut with left and right knives, mix evenly, adjust the roller gap to 2~3 mm, and perform thin-pass and triangle packing 6 times in succession; roll and cut to obtain the rubber compound.

Let the rubber compound stand at room temperature for more than 16 hours, then place the prepared rubber compound on a flat vulcanizer for vulcanization at a temperature of 170℃, a pressure of 10 MPa, and a duration of t90+2 minutes.

1.5 Performance testing

(1) Tensile strength of vulcanized rubber: Tested in accordance with GB/T 528-2009 "Rubber, Vulcanized or Thermoplastic - Determination of Tensile Stress-Strain Properties";

(2) Heat and oxygen resistance: Conducted in accordance with GB/T 3512-2014 "Rubber, Vulcanized or Thermoplastic - Accelerated Aging and Heat Resistance Tests - Air Oven Method", with test conditions of 100 ℃ for 24 hours and 125 ℃ for 24 hours;

(3) Oil resistance: The test is conducted in accordance with GB/T 1690-2006 "Rubber, Vulcanized or Thermoplastic - Resistance to Liquids - Test Method". The test conditions are 15# hydraulic oil at 120 ℃ for 24 hours;

(4) Compression set performance: The test shall be conducted in accordance with GB/T 7759.1-2015 "Rubber, Vulcanized or Thermoplastic - Determination of Compression Set - Part 1: Under Normal and Elevated Temperature Conditions". The test conditions are 100 ℃ for 24 hours and 125 ℃ for 24 hours.

2 Results and discussion

2.1 Microscopic properties of raw rubber

2.1.1 Sequence structure and relative content of raw rubber

Observing the data in Table 1, the molecular chains of the two raw rubbers are primarily composed of BBB, BBA, ABA, and BAB sequence structures. The acrylonitrile content varies significantly, which aligns with the grades of the rubber compounds, indicating that ANBR3305 belongs to the medium acrylonitrile content nitrile rubber category, while NBR40H belongs to the high acrylonitrile content nitrile rubber category. Furthermore, the BBB content of ANBR3305 is higher than that of NBR40H, suggesting that the molecular chain flexibility of ANBR3305 is superior.

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

Project	ANBR3305	NBR40H
BBB	34.7	22.2
BBA	11.4	10.2
ABA	32.8	38.9
BAB	21.1	25.0
Combined acrylonitrile content /%	34.9	41.4

2.1.2 Gel content, glass transition temperature

As can be seen from Table 2, the gel content of ANBR3305 is relatively low, while that of NBR40H is relatively high. This indicates that during the thermal polymerization of nitrile rubber, in the initial stage of the reaction, as the polymerization temperature increases, the probability of molecular chain crosslinking increases, the decomposition rate of the initiator accelerates, and the concentration of free radicals in the reaction system rises, leading to a gradual increase in the gel content of the raw rubber. In the later stage of the reaction (after the conversion rate exceeds 60%), high temperatures intensify the branching and crosslinking of molecular chains, forming more three-dimensional network structures, resulting in a rapid increase in gel content.

Table 2 Gel content and glass transition temperature of raw rubber

Project	ANBR3305	NBR40H
Gel content, %	4.1	83.1
Tg, ℃	-25.63	-17.78

The glass transition temperature of ANBR3305 is lower, while that of NBR40H is higher, indicating that the molecular chain flexibility of ANBR3305 is better. This is consistent with the results of raw rubber gel content and the content of sequence structure BBB.

2.2 Processing performance and vulcanization characteristics of rubber compound

The Mooney viscosity, vulcanization characteristics, and physical and mechanical properties of the two types of nitrile rubber are shown in Table 3.

Table 3 Mooney viscosity, vulcanization characteristics, and physical and mechanical properties of nitrile rubber

Project	ANBR3305	NBR40H
LM Mooney (raw rubber)	47	95
LM Mooney (Rubber Compound)	61	116
△ LM	14	21
Rlx a	-0.4463	-0.2977
Rla A	644.37	1629.5
F_L/(dN·m)	2.73	1.80
F_{max}/(dN·m)	17.63	15.88
F_{max}-FL/(dN·m)	14.90	14.08
t_{10}/min	1.59	1.93
t_{90}/min	8.51	7.16
Shore A hardness/degrees	71	64
Tensile strength / MPa	17.2	18.7
Elongation at break, %	252	360
100% modulus at fixed extension/MPa	6.0	3.1

As can be seen from Table 3, there is a significant difference in the Mooney viscosity between the two types of nitrile rubbers. ANBR3305 has lower Mooney, Rlx a, and Rlx A values, indicating better processability; NBR40H has higher Mooney viscosity and △ LM, indicating poorer processability, which is consistent with the higher gel content of NBR40H in Table 2. The tc10 values of the two standard formulations of nitrile rubber compounds are low, indicating poor process safety. The value of Fmax-FL/dNm can reflect the degree of crosslinking of the vulcanizate to some extent. As can be seen from Table 3, the degree of crosslinking between the two types of nitrile rubbers is not significantly different.

The tensile strength of the two vulcanizates is not significantly different, and ANBR3305 exhibits a higher modulus at 100% extension, indicating that the nitrile rubber obtained through cold polymerization has a higher degree of structural regularity and stronger intermolecular forces.

2.3 Properties of rubber compound with different vulcanization systems

As can be seen from Table 4, M11 and M21 exhibit superior physical and mechanical properties at room temperature, indicating that the sulfur vulcanization system is more conducive to the physical and mechanical properties of the rubber compound at room temperature compared to the peroxide vulcanization system. This is consistent with the vulcanization characteristics of the rubber compound in Table 3: M11 and M21 have a higher degree of crosslinking. In terms of tensile strength and hardness, M21 is superior to M11, and M22 is superior to M12, indicating that the mechanical properties of NBR40H at room temperature are better, possibly due to its high gel content, which is beneficial to its mechanical properties at room temperature.

After 24 hours of hot air aging at 100℃, the hardness change of each rubber compound is less than 10. The aging comprehensive performance of M12 and M22 rubber compounds is relatively good, with M12 being the best. This indicates that under this aging condition, the peroxide vulcanization system rubber compound exhibits better aging performance. The ANBR3305 + peroxide vulcanization system has the best aging performance.

After 24 hours of hot air aging at 125℃, the hardness change of each rubber compound is ≥10. The change rate of

aging tensile strength of M11 and M21 rubber compounds is relatively low, indicating that under this condition, in terms of the tensile strength performance of rubber compounds after aging, the sulfur vulcanization system has a better effect than the peroxide vulcanization system;

Table 4 Comparison of Vulcanizate Properties with Different Vulcanization Systems

Project	M11	M12	M21	M22
Shore A hardness/degree	58	46	59	50
Tensile strength/MPa	14.1	7.0	16.7	10.2
Elongation at break, %	510	804	390	621
100% modulus at fixed extension/MPa	1.8	0.7	3.5	1.1
100 ℃×24 h hot air aging				
Hardness change/degree	+8	+7	+9	+5
Change rate of tensile strength, %	-24.1	4.4	-6.0	17.6
Rate of change of breaking elongation, %	-47.5	-2.6	-45.6	1.0
125 ℃×24 h hot air aging				
Hardness change/degree	+10	+11	+12	+15
Change rate of tensile strength, %	-3.5	50.0	-5.4	43.1
Rate of change of breaking elongation, %	-52.0	-17.0	-53.8	-15.0
Compression set				
100 ℃×24 h compression set/%	33	42	27	37
125 ℃×24 h compression set/%	41	49	37	40
Oil resistance (120 ℃×24 h 15# oil)				
Hardness change/degree	+10	+14	+14	+16
Change rate of tensile strength, %	-10.2	31.1	-4.3	41.0
Rate of change of breaking elongation, %	-49.3	-12.7	-47.5	-7.2
Oil resistance volume expansion rate /%	-5.4	-3.5	-8.1	-8.7
Low-temperature performance				
Compression cold resistance coefficient (-30 ℃)	38	42	2.5	6.5

In terms of compression set at 100℃×24h and 125℃×24h, M11 is superior to M12, and M21 is superior to M22. This indicates that, in terms of compression set of rubber compound, the influence of sulfur vulcanization system is superior to that of peroxide vulcanization system.

Regarding the change in hardness after oil resistance test, M11 has a value of 10, while the rest have values greater than 10. In terms of tensile strength change, M11 and M21 are superior. Regarding the change in elongation at break, M12 and M22 are superior. The oil volume expansion rate of each rubber compound is relatively small, with M11 and M12 being superior, indicating that ANBR3305 has superior oil resistance.

The compressive cold resistance coefficient of M11 and M12 is relatively high, indicating that ANBR3305 has good low-temperature performance.

3 Conclusion

(1) ANBR3305 has a higher BBB content and a lower glass transition temperature.

(2) NBR40H has a high gel content and poor processing performance.

(3) The tensile strength of the two vulcanizates is not significantly different, with ANBR3305 exhibiting a higher modulus at 100% extension, indicating that the nitrile rubber obtained through cold polymerization has a high degree of structural regularity and strong intermolecular forces.

(4) The mechanical properties of NBR40H at room temperature are relatively good, possibly due to its high gel content, which is beneficial to its mechanical properties at room temperature.

(5) For hot air aging at 100℃ for 24 hours, the peroxide vulcanization system is more conducive to the aging performance of the rubber compound; for hot air aging at 125℃ for 24 hours, the sulfur vulcanization system is more conducive to maintaining the tensile strength of the rubber compound.

(6) For compression set at 100 ℃ for 24 hours and at 125 ℃ for 24 hours, the sulfur vulcanization system has a better effect than the peroxide vulcanization system.

(7) ANBR3305 exhibits superior oil resistance and low-temperature performance.