Thermax® N990 Thermal Carbon Black in Nitrile Rubber Compounds

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Outline

1. ABSTRACT

Thermax® medium thermal carbon black N990 is manufactured by the thermal decomposition of natural gas. This process produces a very unique carbon black characterized by a large particle size and low structure. This paper will provide a general description of medium thermal carbon black and the effects of this carbon's unique properties on nitrile elastomer compounds. Advantages of using Thermax® medium thermal carbon black, including high loadability, low compression set, low compound viscosity and the potential for compound cost savings, will be discussed. A study conducted on behalf of Cancarb Limited by the Indian Rubber Manufacturers Research Association, Thane, India will be presented.

2. INTRODUCTION

Carbon black is a crucially important component of most rubber compounds and is usually the largest volume ingredient after the polymer itself. Carbon black will affect many properties of a rubber compound as well as many aspects of the mixing cycle. Due to the importance of carbon black to a rubber compound and the potential for high filler loading, recognizing the total quality cost of using a particular grade of carbon black in the compound is essential.[1] To assess the total quality cost of a carbon black in any given compound, aspects such as cost per unit volume of the filler, handling time and labour, mixing time and energy consumption, factory scrap rates for both mixing and final product, processability and final product performance, must be examined.

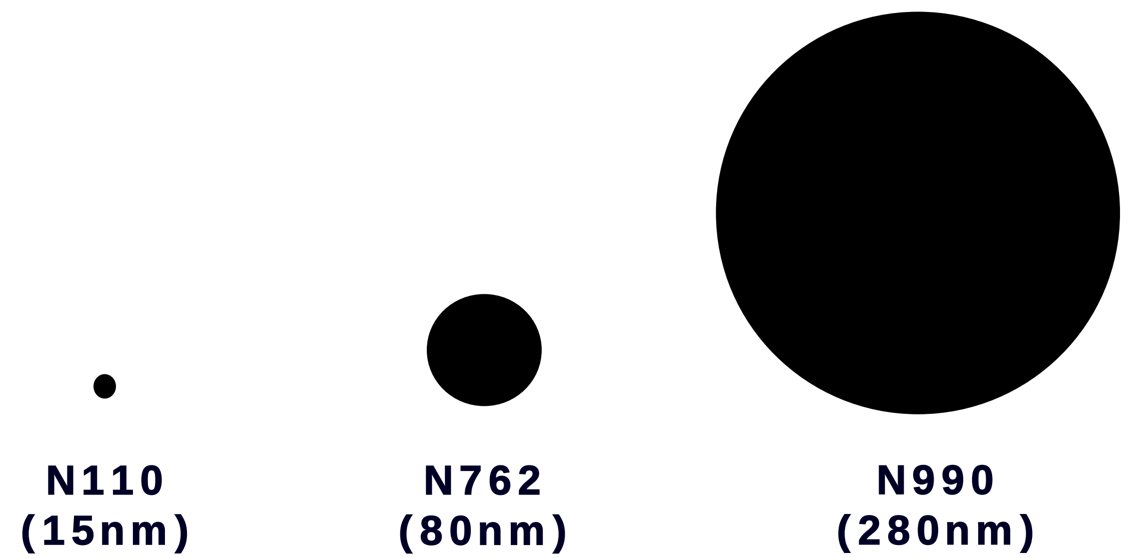
Although the term carbon black is often used in a generic sense, there are five main types; acetylene black, channel black, lamp black, furnace black and thermal black. The focus of this paper will be on medium thermal carbon black N990. The effects of using thermal black N990 in a nitrile rubber compound for both compound properties and total quality cost will be demonstrated.

3. Classification and Properties of Thermal Carbon Black N990

Although furnace carbon black comprises most of the world's carbon black consumption, thermal carbon black plays a very significant role especially in compounds utilizing high performance polymers. Carbon black can be generally defined as very fine particulate aggregates of carbon with an amorphous quasi-graphitic molecular structure. Thermal carbon black is produced using a clean natural gas feedstock in a thermal decomposition reaction to produce a high purity carbon black with large particle size and low structure.

3.1 Particle Size Classification of Thermal Carbon Black N990

The majority of rubber grade thermal and furnace carbon blacks are classified using a four-character naming convention as described by the ASTM standard D1765. The first character is a letter that indicates the effect of the carbon black on the compound cure rate, in the case of N990 the (N) indicates a normal cure rate. The next character is a number based on the average surface area of the carbon black while the last two characters are assigned arbitrarily.[2]

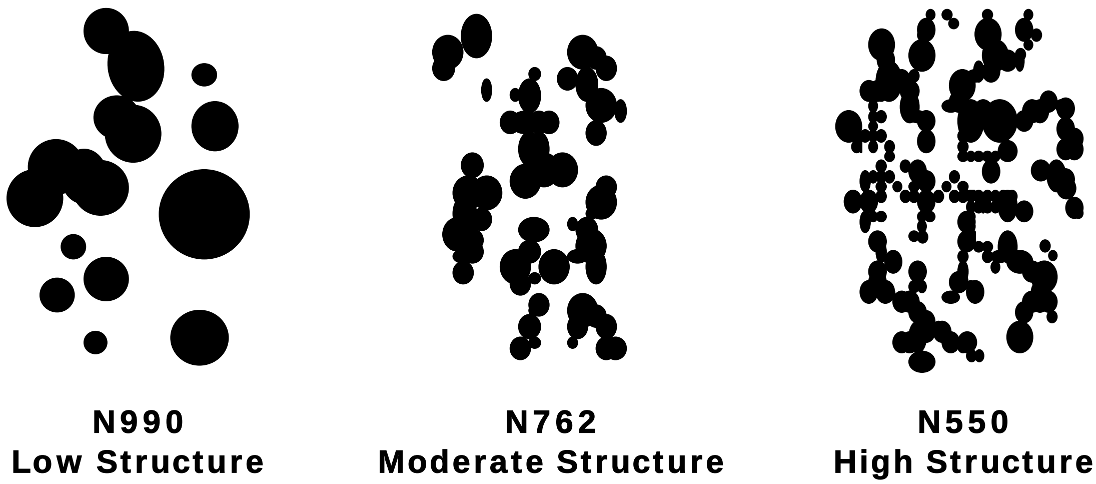


Particle Size Comparison of Furnace vs. Thermal Carbon Black

Medium thermal carbon black has the largest particle size of all the carbon blacks and therefore the lowest specific surface area at an average of 9 m^2/g. The average particle diameter of Cancarb's Thermax® N990 is 280 nm.

3.2 Structure Classification of Thermal Carbon Black N990

Structure is the degree to which primary particles of carbon black are permanently fused into aggregates. N990 medium thermal carbon black is characterized by large spherical particles with low aggregation. The oil absorption test (OAN) provides a relative measure of the degree of aggregation of carbon particles among various carbon black grades. Medium thermal carbon black has a low OAN range of approximately 32-45 ml/100g. Standard furnace carbon blacks can have an OAN range of 60-150 ml/100g. Generally, the low structure of medium thermal carbon black can contribute to lower mixing temperatures, greater scorch safety, lower compression set, and retention of the inherent resilience of the elastomer.



Structure Comparison of Thermal vs. Furnace Carbon Black

3.3 Surface Activity of Thermal Carbon Black N990

Surface activity refers to the chemical reactivity of the carbon black and its effect on the surface interaction with the polymer. Surface activity is a difficult to measure function of the chemistry and graphitic structure of the carbon and is influenced by the feedstock and production process conditions. Studies that characterize the surface energy and chemistry of carbon black suggest that the surface energy increases with increasing specific surface area and with the polyaromatic character of the carbon[3]. Carbon black produced from a high purity feedstock, such as natural gas, is characterized by low surface energy and fewer surface groups, thereby resulting in lower surface activity. It is generally recognized that carbon blacks with a high amount of surface activity provide high reinforcement to rubber. While medium thermal black is referred to as an inactive or non-reinforcing black, small particle blacks with higher levels of oxygen and sulphur surface groups tend to be very active providing high reinforcement to the rubber matrix.[4]

3.4 pH

The pH of carbon black is mostly dependent on the extent of oxidation on the surface of the particles and the characteristics of the water used during production. It will vary by both the grade and supplier. The pH of the carbon black filler must be considered for every rubber compound as variations in pH can affect the cure system resulting in processing variations. The consistent and narrow range of Cancarb's Thermax® N990 thermal carbon black, from 9 to 10, is the least acidic of all carbon blacks. Furnace carbon blacks can have a pH range of 4 to 9. Other factors that can affect the cure system of a compound include ash and sulphur levels which are also higher in furnace blacks than in thermal black.

3.5 Electrical Properties

Although similar in microstructure to graphite, the carbon layers in carbon black are less ordered. This results in carbon black being an intrinsic semi-conductive material although the amount of conductivity imparted to a rubber compound also depends on other factors. Primary particle size, structure, porosity, surface oxide groups and loading all play a role in compound conductivity.[5] It has been reported that primary particle size is the major carbon black parameter that influences conductivity.[6] The average width of the gaps between the particles within the aggregate is also considered to be a factor.[7] Table 1 reports the volume resistivity, in ohms.cm, of three grades of furnace carbon black versus N990 in an EPDM test compound.[8] ASTM D991 is the normal and standard test method for the rubber property: Volume Resistivity of Electrically Conductive and Antistatic Products. However, D991 could not be followed in this experiment because the resistivity of the N990 compound was too high. Volume resistivity was therefore evaluated according to ASTM D257: DC Resistance or Conductance of Insulating Materials. The furnace black compounds could have been measured by ASTM D991, but were also evaluated by D257 for consistency.

Table 1: Compound Resistivity – Thermal versus Furnace Black in an EPDM

Compound ID	Voltage, VDC	Resultant Current	Resistivity, ohm.cm
Thermax® N990 - 75 phr	501.10	3.27×10^{-11}	4.05×10^{15}
N762 - 50 phr	500.10	1.83×10^{-4}	7.14×10^{8}
N650 - 50 phr	500.00	2.31×10^{-3}	5.62×10^{7}
N550 - 50 phr	7.55*	1.99×10^{-3}	9.75×10^{5}

*Due to the low resistivity of the N550 the test voltage had to be lowered from 500 VDC as specified in ASTM D257

The Thermax® N990 compound had the highest volume resistivity of all the samples. The resistivity for the standard furnace grades declined correspondent to their particle size. The N550, having the lowest resistivity, also has the highest structure.

The large particle, low structure Thermax® N990 is much less conductive than the other grades, and therefore the best choice for applications requiring high volume resistivity, such as low-voltage cable insulation, capacitor end plugs, coolant hose and automotive weather sealing products.

4. Using Thermax® N990 to Improve Processing and Dynamic Properties of Nitrile Rubber

The following study, conducted on behalf of Cancarb Limited by the Indian Rubber Manufacturers Research Association, Thane, India, demonstrates the effect of replacing N550 furnace carbon black with Thermax® N990 in nitrile rubber compounds of differing shore A hardnesses.

4.1 Test Compound Formulations

Formulation (phr)	Hardness 60 SH		Hardness 70 SH		Hardness 80 SH		Hardness 70 SH (High ACN)
COMPOUND	**A1**	**A2**	**B1**	**B2**	**C1**	**C2**	**D**
*NBR (JSR230SL)	100	100	100	100	100	100	--
**NBR(JSR N 220S)	--	--	--	--	--	--	100
MC sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc Oxide	5	5	5	5	5	5	5
N 550	45	30	65	40	90	60	60
N990	--	35	--	55	--	65	--
DOP	10	10	10	10	20	20	10
TDQ	1	1	1	1	1	1	1
CBS	2	2	2	2	2	2	2
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2

*NBR (JSR 230SL) of Japan Synthetic Rubber with ACN content 35 % & ML1+4 @ 100°C-42
**NBR (JSR N220S) of Japan Synthetic Rubber with ACN content 41 % & ML1+4 @ 100°C-56

4.2 Test Compound Properties

COMPOUND	A1	A2	B1	B2	C1	C2	D
Viscosity M_L (1+4) @ 100° C	31	34	38	41	49	53	58
Mooney Scorch Time t_5 @ 125° C(min)	8.09	8.02	6.28	5.35	4.38	4.32	6.11
Rheometric properties @ 160° C							
M_L (lbf.inch)	4.4	4.88	5.31	5.61	7.14	6.08	6.08
M_H(lbf.inch)	62.96	73.7	70.39	86	78.5	81.04	79.93
t_S2(min)	2.5	2.37	2.12	1.86	1.69	1.76	1.99
t90(min)	12.2	19.93	11.4	15.62	4.74	5.86	16.76

Only a slight increase in compound viscosity is noticed, accompanied by a minor decrease in mooney scorch time, even though the total carbon black loading was increased by 20, 30 and 35 phr respectively. This can translate into a reduction in the total quality cost of the compound by using more filler while maintaining good processing properties. As polymer and other compound raw material prices continue to rise, the ability to produce the required volume of a compound while using high loadings of Thermax® N990 in place of the more expensive polymer allows for compound cost reduction without increasing processing time and difficulty.

4.3 Vulcanization Properties – Curing at 160˚C for t90 Minutes

COMPOUND	A1	A2	B1	B2	C1	C2	D
Hardness, Shore A	62	61	70	71	80	79	71
100% modulus(Kg/cm^2)	33	27	46	41	77	55	49
200% modulus (Kg/cm^2)	75	68	121	115	168	157	129
300% modulus (Kg/cm^2)	140	132	186	174	212	_	205
Tensile Strength (Kg/cm^2)	191	232	227	182	220	187	233
EB%	480	540	400	380	310	260	390
Tear Strength (Kg/cm)	43	43	49	45	45	45	57
Compression Set % ASTM Method B, 22 hrs/ 100° C / 25% deflection	33	24	38	27	29	32	33

Significant improvement in compression set is demonstrated for the compounds filled with Thermax® N990, the exception being the 80 shore A test compound C2 which shows a slightly higher result. This is most likely due to the high total carbon black loading causing reduced polymer to filler bonding.

The differences in tensile properties and tear strength between the control and test compounds are relatively minor given the potential benefits of the Thermax® N990 filled compounds.

With nitrile polymer being a very popular choice for sealing applications such as seals, gaskets, O-rings, and hose, improved compression set is a highly desired property. This aspect combined with the potential cost savings realized by higher loadings serves to further improve the total quality cost of the compound.

4.4 Percentage Change in Physical Properties after Ageing

After air ageing @ 100° C for 70 hours.							
COMPOUND	**A1**	**A2**	**B1**	**B2**	**C1**	**C2**	**D**
Hardness change (points)	13	15	13	13	6	7	11
100% modulus change (%)	21	22	46	49	25	76	33
200% modulus change (%)	38	37	45	46	25	_	39
300% modulus change (%)	34	34	_	_	_	_	25
Tensile Strength change (%)	8	6	8	9	4	4	5
EB change (%)	-25	-24	-30	-31	-26	-27	-25

After ageing @ 100° C for 70 hours in ASTM oil No.3							
COMPOUND	**A1**	**A2**	**B1**	**B2**	**C1**	**C2**	**D**
Volume swell 70 hrs/100°C (%)	4.37	3.34	0.91	2.93	-1	-2.54	-1.68
Hardness change (points)	-2	-2	0	0	0	0	0
100% modulus change (%)	-6	-7	-2	0	14	48	-2
200% modulus change (%)	10	11	13	14	15	_	7
300% modulus change (%)	14	15	16	14	_	_	10
Tensile Strength change (%)	-7	-6	9	14	-5	-4	-6
EB change (%)	-21	-22	-15	-16	-23	-19	-20
After ageing @ 40° C for 70 hours in Fuel B							
Volume swell 70 hrs/40°C (%)	22.9	23.37	19.1	19.55	13.95	11.1	14.96
Hardness change (points)	-8	-10	-14	-14	-12	-11	-15
100% modulus change (%)	-21	-20	-15	-14	-21	-16	-24
200% modulus change (%)	-5	-1	-5	-4	-4	-6	-18
300% modulus change (%)	-12	-13	_	_	_	_	-14
Tensile Strength change (%)	-38	-38	-23	-18	-14	-13	-24
EB change (%)	-31	-33	-30	-31	-19	-15	-25

There are no significant differences presented between the Thermax® N990 test compounds and the controls for ageing in air, ASTM oil No.3, and Fuel B.

Also of note is the comparison of the high acrylonitrile NBR test compound D, to that of test compound B2 which is a medium acrylonitrile NBR of the same shore A hardness using Thermax® N990. Both compounds exhibit similar oil and fuel ageing properties except for volume swell which was only marginally higher in the B2 compound. Cost savings can be realized by using a medium acrylonitrile NBR and Thermax® N990 in place of a more expensive high acrylonitrile NBR.

5. Conclusions

Thermax® N990 medium thermal carbon black is a unique carbon characterized by the largest particle size and lowest structure available. The choice of filler for an elastomeric compound is a critical decision for any compounder as cost, performance, processability, scrap rate and handling all must be considered when assessing the total quality cost of a compound. Thermax® N990 is an excellent choice for modern technologically advanced polymers. The advantage of Thermax® N990 in nitrile rubber compounds has been demonstrated. Thermax® N990 can reduce the total quality cost of nitrile compounds while improving or maintaining key properties.

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8. Acknowledgements

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