Thermal Aging Behavior of H-NBR/NBR Blend

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H−NBR/NBR 블렌드의 열노화거동

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ABSTRACT : In the present investigation, thermal aging behavior of H-NBR/NBR blend with various H-NBR content was investigated. Mixture of dicumyl peroxide and sulfur were used as a curing agent. The influence of the thermal aging of the H-NBR/NBR blends on the solid state properties such as tensile strength, elongation at break, hardness and abrasion resistance was investigated. Tensile strength was increased with increasing H-NBR content, while abrasion resistance was decreased. Both elongation at break and hardness were not affected by the addition of H-NBR. The properties such as hardness, tensile strength and elongation at break of the aged samples were lower than unaged samples. However, the rate of deterioration of those properties was decreased by increasing the H-NBR content, which indicated that improved thermal aging behavior was obtained by the addition of H-NBR. Abrasion loss was increased with increasing aging time, but it became less by the addition of H-NBR addition.

요 약 : 본 연구는 H−NBR 함량 변화에 따른 H−NBR/NBR 블렌드의 열노화 거동에 대하여 살펴보았다. 이 때 가교제로는 dicumyl peroxide와 황 혼합물을 사용하였으며, 열노화에 따른 H−NBR/NBR 블렌드의 인장강도, 파괴신율, 경도 그리고 내마모성의 변화를 살펴보았다. H−NBR을 첨가함에 따라 인장강도는 증가하였으나 내마모성은 감소하는 현상을 나타내었다. 파괴신율과 경도는 H−NBR의 영향을 받지 않았다. 노화가 진행된 모든 시편은 초기 시편보다 낮은 인장강도, 파괴신율, 경도를 나타내었다. 그러나 H−NBR의 함량이 증가함에 따라 이러한 물성저하 속도가 감소함을 알 수 있었다. 즉 H−NBR 첨가에의해 열노화 특성이 향상됨을 알 수 있었다. 모든 NBR/H−NBR 블렌드는 노화시간이 증가함에 따라 내마모성이 감소하였으며, H−NBR을 첨가한 경우 내마모성의 저하가 상대적으로 낮음을 알 수 있었다.

Keywords : NBR, H-NBR, blend, thermal aging; mechanical property

Ⅰ. Introduction

Nitrile butadiene rubbers (NBRs) belong to the class of specialty elastomers that offer a broad range of thermal and oil resistance properties. These elastomers are extensively used in automobile and oil-drilling applications. However, the presence of unsaturation sites in the NBR backbone chain limits its application at higher temperatures. These double bonds from the nitrile rubber backbone could be removed by catalytic hydrogenation that results in the significant improvement in the ozone and UV resistant properties. Generally, the hydro-genation reaction of the nitrile rubber is carried out through homogenous catalytic reactions, which in turn faces problem in removing the catalyst from the polymer mixture, and it is in fact the main reason for the high cost of the H-NBR.[1]

Blending of polymers offers a means of producing new materials with tailored properties and has been extensively used in plastics, rubbers, composites, films, fibers, coatings, and adhesives.[2] The objective of polymer blending is to achieve commercially viable products having desired properties and low cost. Performance of the blends depends on the extent of miscibility of the components. The blends with apparent miscibility but with good adhesion between phases show good performance. During the last two decades, significant research

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has been done by various research groups on polymer blends based on butadiene rubbers and other polymers.[3-7] Thomas et al., have studied the blends of NBR with polypropylene and poly(ethyl-co-vinyl acetate).[8-9] They could correlate the blend morphology with the variation on the dielectric properties and blend composition. Bromitz and Kosfield have reported NBR/ phenolic resin blends which are used in abrasion resistant gaskets and cables.[10] Sirishinha et al., reported the influence of the blending conditions on the oil resistance properties of natural rubber (NR)/ nitrile rubber (NBR) blends.[11] The influence of structural parameters such as acrylonitrile content and Mooney viscosity on the blend morphology and properties of the nitrile rubber (NBR)/ styrene-co-acrylonitrile (SAN) blends is studied by Ahn et al.,[12] Severe and White,[13] observed the miscibility behavior of the hydrogenated nitrile rubber (H-NBR) with polar polymers such as chlorinated polymers and reported that the strong interactions between the functional groups are responsible for the interfacial miscibility between these polymers.

NBR elastomers exhibit an excellent oil resistant property that finds application in seals. However, it is quite sensitive to thermal aging conditions that lead to the mechanical failure and thereby limit its application aspect as high temperature oil resistant seals. Blending of the unsaturated NBR and the more flexible H-NBR elastomers could solve this problem. Though extensive research has been done on the rubber-rubber and the rubber-plastic blends based on the NBR or H-NBR elastomers, no significant research report is available on the elastomeric blends based on NBR/H-NBR elastomers. Very recently, Hussein et al. studied the miscibility and mechanical properties of the NBR/H-NBR blends.[14] They claimed that the mechanical properties such as tensile modulus and the yield stress were significantly higher in the case NBR/H-NBR elastomeric blends in comparison to the individual polymers. Though the above research report claims the application aspects of the NBR/H-NBR blends, it is necessary to understand the thermal aging properties of the blends and composites to realize its application aspects at high temperature. Unfortunately, no research report is available on the thermal aging characteristics of NBR/H-NBR blends.

In the present study, the influence of the thermal aging conditions on the properties such as tensile strength, elongation at break, hardness and abrasion resistance of the NBR/H-NBR elastomeric blends have been investigated. The role of the mixed crosslinking system, H-NBR content on the aging characteristics of the blends is also investigated.

Ⅱ. Experimental

NBR and H-NBR used in this study were commercial samples obtained from Zeon Chemicals, Japan. The NBR (NIPOL-N21) has an acrylonitrile (AN) content of 40.5%, specific gravity of 1, and a Mooney viscosity of 82.5. On the other hand, the H-NBR (ZETPOL-1020) has an AN content of 44.2, specific gravity of 0.95, a Mooney viscosity of 78. Two polymers show close AN content and Mooney viscosity (ML1_4 at 100°C). Carbon black (SRF 774) was procured from Sewon I&C Ltd., Korea, antioxidant (RD, polymerized trimethyl quinoline, TMQ), nickel dibutyl dithiocarbamate (NBC) and dicumyl peroxide (DCP) were obtained from Pyunghwa chemicals Co. Ltd. Korea and thiokol (TP-95) was purchased from Rohm and Haas Ltd. Tetramethyl thiuram disulfide (TT) and cyclohexyl benzothiazole sulfenamide (CZ) were procured from Tianjin East Richon Rubber Additives Co. Ltd. Dioctyl phthalate (DOP) was supplied by Aekyung petrochemical co. Ltd., and zinc oxide (ZnO), stearic acid and sulfur were procured from standard local suppliers.

The NBR/H-NBR compounds with different formulations (Table 1) were prepared in an open two roll mill at room temperature set at the friction ratio of 1:1.1 with the nip gap of about 1 mm. The mixing time of 15 min was kept uniformly for all the compounding formulations. Mixture of 1 phr dicumyl peroxide and 1 phr sulfur was used as curing agents.

The Mooney viscosity of the rubber blends was measured using Monsanto Mooney viscometer. The vulcanization behavior of the compounds was determined at 170 ℃ using oscillating disc rheometer (ODR, Alpha Technologies USA). Tensile sheets were prepared by curing the NBR/H-NBR rubber compounds in the hot press (Carver press) at the temperature of 170 ℃ based on the t_{90} obtained in the ODR measurements, followed by the cutting of dumbbell shape specimen using

Table 1. Basic Formulation of NBR/H-NBR Blends

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
NBR	100	95	90	85	80
H-NBR	-	5	10	15	20
SRF774	100.0	100.0	100.0	100.0	100.0
RD	1.0	1.0	1.0	1.0	1.0
ZnO	5.0	5.0	5.0	5.0	5.0
St. Acid	1.0	1.0	1.0	1.0	1.0
TP-95	10.0	10.0	10.0	10.0	10.0
DOP	30.	3.0	3.0	3.0	3.0
TT	2.0	2.0	2.0	2.0	2.0
CZ	1.5	1.5	1.5	1.5	1.5
NBC	2.5	2.5	2.5	2.5	2.5
S	1.0	1.0	1.0	1.0	1.0
DCP	1.0	1.0	1.0	1.0	1.0
Total	228.0	228.0	228.0	228.0	228.0

ASTM Die C. Similarly, the samples for measuring the abrasion resistance was prepared at the temperature of 170 ℃ for t_{90}+15 min. Thermal aging studies were carried out at various temperatures viz. 100, 110, 120, 130 and at 140 ℃ for 100 hrs. Another set of aging experiments were carried out by varying the time at a fixed temperature viz. 72, 100 and 200 h at 120 ℃. The tensile properties of the dumbbell specimens were determined following ASTM D 412 using LLOYD instrument (LF-Plus/ XLC-1000-Al model) set at the gauge length of 25 mm and test speed of 500 mm/min. The hardness of the specimens before and after aging was determined using GS-709G Type A (Techlok, Japan) hardness tester. The abrasion resistance of the heat aged samples was determined using NBS rubber abrasion tester (Daekyung Engg. Co. Ltd, DRA 150) set at the speed of 45 rpm with 300 cycles using a sand paper with the mesh size of 40.

Ⅲ. Results and Discussion

To understand the compatibility of NBR/H-NBR blend, the Mooney viscosity of the NBR/H-NBR blends with various H-NBR contents is measured using Mooney viscometer. Generally, the Mooney viscosity of the rubber is proportional to the true shear viscosity at very low shear rates (approximately 1 to 2 s^{-1}).[15] Figure 1 shows the variation of the Mooney viscosity as a function of H-NBR content in the blend. Though the Mooney viscosity of the individual elastomer is equal, it is interesting to note that the viscosity of the blend increases linearly with increasing wt % of H-NBR following the additive rule as proposed in the following equation.

$$\log(\eta_B) = \sum_i w_i \log \eta_i$$

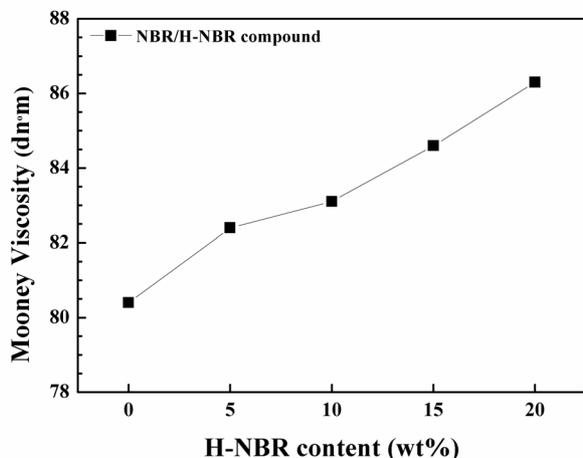where η_B and η_i represent the viscosity of the ith component

and that of the blend and w_i is the weight fraction of the ith component. Earlier reports reveal that the compatible blends lead to a positive deviation in the rheological properties such as viscosity, die swell etc and are generally termed as positive deviation blends.[16] The increase in Mooney viscosity of nitrile rubber blends with increasing H-NBR content corroborates that NBR/H-NBR are technologically compatible blends.

The influence of the H-NBR content on the thermal aging characteristics of the rubber blend composites is investigated and the results are displayed in terms of variation of the mechanical properties of the rubber blend composites before and after aging. Tensile properties represented in Figure 2 are the average of five independent measurements. The variation of the tensile strength as the function of the H-NBR content for the blend composites of the NBR/H-NBR are shown in
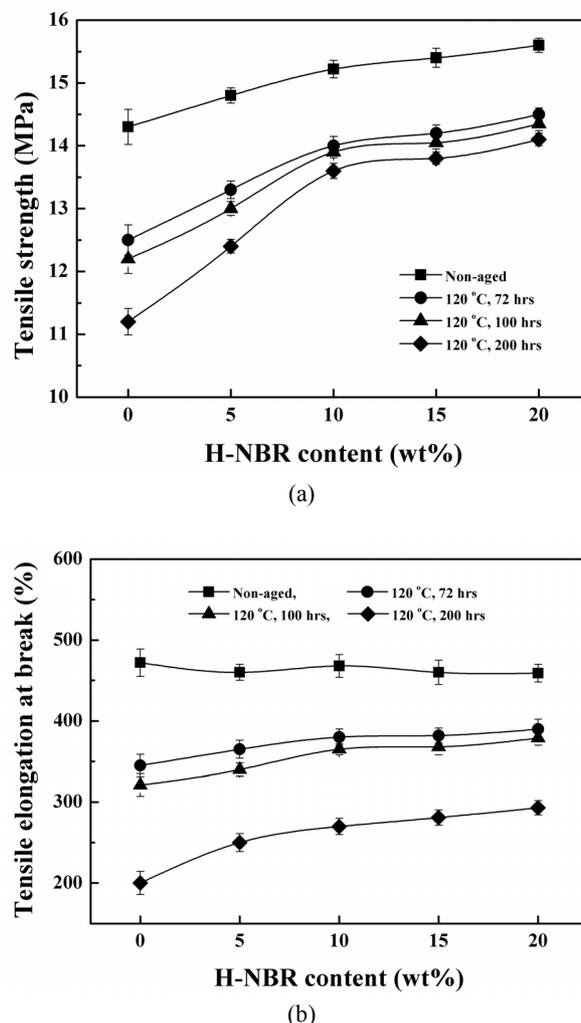
(a)

(b)

Figure 2. (a) Variation of tensile strength with H-NBR content before and after aging at 120 ℃ for varying aging times and (b) variation of EB with H-NBR content before and after aging at 120 ℃ for varying aging times.

Figure 1. Variation of mooney viscosity with H-NBR content.

Figure 2. Tensile strength of the NBR/H-NBR blend rubber composites increases with H-NBR content, which may be attributed to the strain hardening effect of the H-NBR that results in strain induced crystallization in the blend composites and thereby the tensile strength of the blend composites.[14] As expected the tensile strength of the NBR composites decreases with increasing aging time. It decreases to about 11.3 % (72 h), 14.7 % (100 h) and 21.6 % (200 h) with increasing aging time. However, the decrease in the tensile strength with increasing aging time is drastically reduced by increasing the H-NBR content. For instance, tensile strength of rubber blend composites loaded with 20 wt % of H-NBR content decreases to about 7.5 % (72 h), 7.7 % (100 h) and 9.6 % (200 h), which is significantly lower, when compared to NBR. Similar trend is observed in elongation at break (EB). The decrease in EB values for blend composites having 20 wt % H-NBR is observed to be 14.6 % (72 h), 17.9 % (100 h) and 35.5 % (200 h), whereas the decrease in EB of NBR is observed to be 26.8 % (72 h), 32.1 % (100 h) and 57.7 % (200 h). The improvement of the tensile properties with increasing the H-NBR content is attributed to the decrease in the degradation of the NBR composites due to the loading the saturated H-NBR rubber that slightly offset the thermo-oxidative reactions during aging.

Figure 3 shows that the hardness of the NBR/H-NBR rubber blend composites is independent from H-NBR content. However the significant increment of hardness is observed with increasing aging time. Significant increase in the hardness can be attributed to the increase in the crosslinking density of the materials due to the presence of the unreacted curatives that undergo curing reactions with aging. However, it is interesting to note that the percentage improvement on the hardness with aging time is lower for NBR/H-NBR blend rubber composites in compa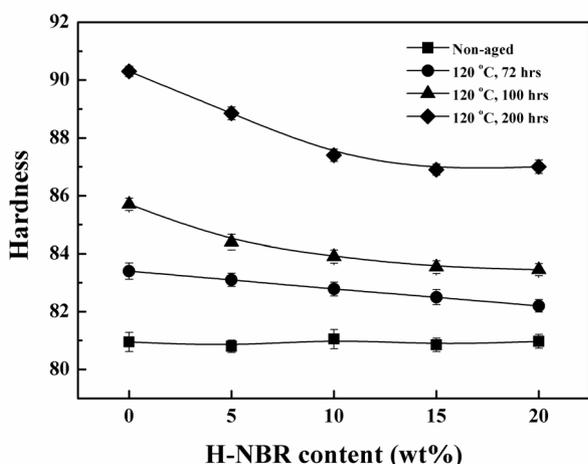rison to NBR composites. Though the amount of curatives loaded in NBR/H-NBR blend rubber composites is same as NBR composites, the number of active labile hydrogen available for curing reaction decreases on blending saturated H-NBR with unsaturated NBR rubber, which results in the decrement of the hardness of the rubber blend composites in comparison to NBR composites.

The abrasion loss with various H-NBR content is depicted in Figure 4. Aging temperature is 120 ℃ and no significant variation in the abrasion loss is observed with increasing H-NBR content. However, with increasing aging time, abrasion loss increases as depicted in Figure 4. This may be attributed to the degradation of the unsaturated NBR samples on prolonged exposure to high temperature that results in the significant loss due to abrasion. The abrasion loss decreases for the aged NBR/H-NBR rubber blend composites with increasing H-NBR content indicating the improvement in the abrasion resistance of the NBR/H-NBR blend rubber composites. The drastic reduction in abrasion loss may be attributed to the lesser degree of degradation on blending with H-NBR.

Figure 5 shows the effect of aging temperature on the tensile properties of NBR and its blend with H-NBR rubber composites. As expected the decrease in the tensile strength of the NBR composites with increasing aging temperature is relatively high compared to NBR/H-NBR rubber blend composites (Figure 5a). It decreases to about 4.8 % (100 ℃) ~ 28.7 % (140 ℃) with increasing aging temperature for NBR composites, while it decreases to about 1.9 % (100 ℃) ~ 16.7 % (140 ℃) for NBR/H-NBR rubber blend composites (20 wt% loading of H-NBR). At higher aging temperature, the degradation of the NBR is severe due to the presence of unsaturated groups, which results in the significant decrease in the tensile properties. However, relatively lower amount of unsaturated sites that are prone to degradation in case of NBR/H-NBR rubber blend composites results in the better tensile properties.
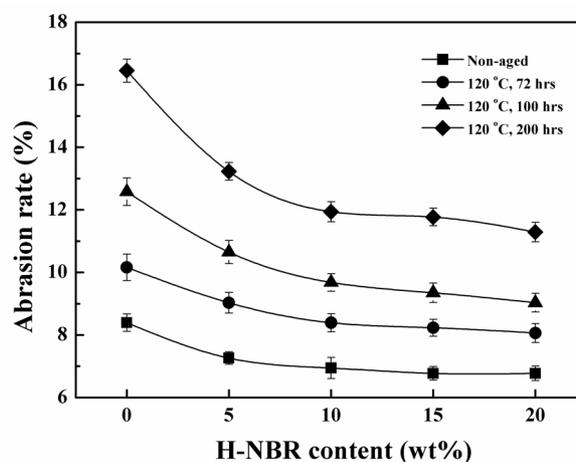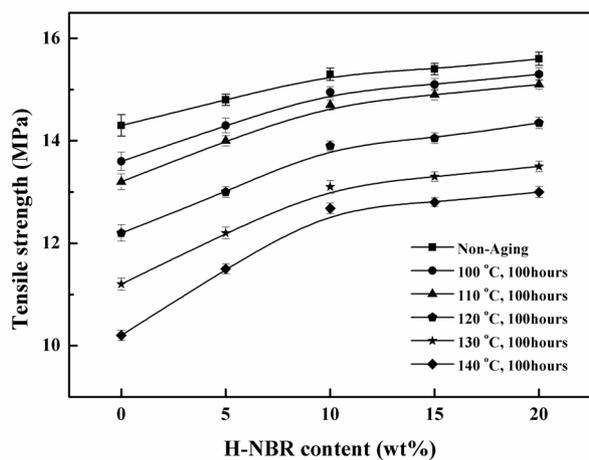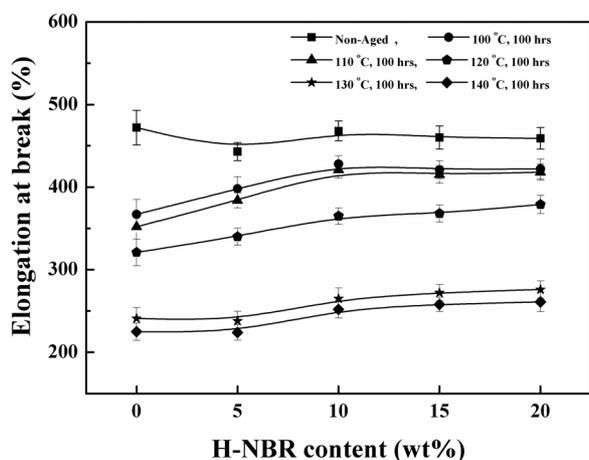

Figure 3. Variation of hardness with H-NBR content before and after aging at 120 ℃ for varying aging times.

Figure 4. Variation of abrasion loss with H-NBR content before and after aging at 120 ℃ for varying aging times.

(a)

(b)

Figure 5. (a) Variation of tensile strength with H-NBR content before and after aging at varying aging temperatures for 100 h and (b) variation of EB with H-NBR content before and after aging at varying aging temperatures for 100 h.

Figure 6. Variation of hardness with H-NBR content before and after aging at varying aging temperatures for 100 h.

Figure 7. Variation of abrasion loss with H-NBR content before and after aging at varying aging temperatures for 100 h.

Figure 5b depicts the effect of aging temperature on the EB. EB values of the NBR composites decreases with increasing aging temperature clearly corroborating the increase in the thermo-oxidative degradation reactions due to the presence of unsaturated groups. However, the decrement in the EB values with aging temperature is relatively low for NBR/H-NBR rubber blend composites due to the presence of saturated H-NBR that slightly offset the thermo-oxidative reactions.

Figure 6 and Figure 7 show the effect of aging temperature on the hardness and abrasion loss. As expected, the hardness of the NBR and NBR/H-NBR rubber blend composites increases significantly with increasing aging temperature. However, the increase in the hardness with aging temperature is relatively high for NBR composites compared to NBR/H-NBR rubber blend composites. This is corroborated by the 12 %
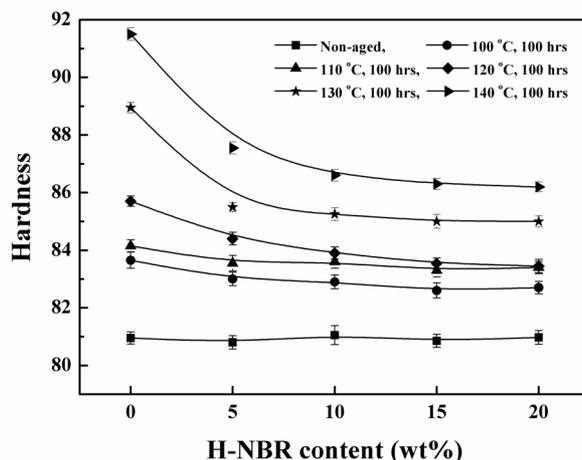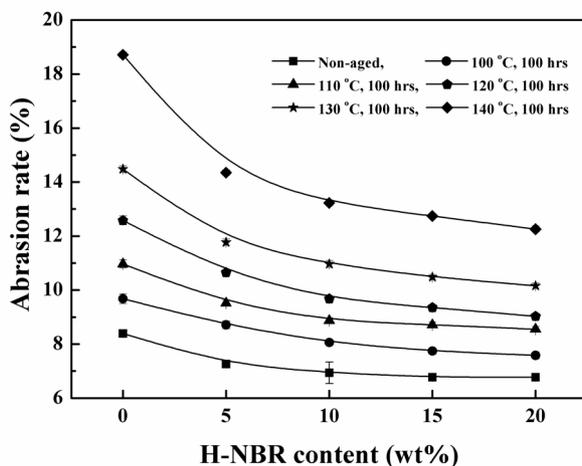
increase in hardness value, when the NBR samples are aged at 140 ℃ for 100 h, whereas the % increase in hardness value for NBR/H-NBR samples (20 wt % H-NBR content) aged at the same temperature is only 6.1 %, which can be correlated to the reduction in the post curing reactions in case of NBR/H-NBR blends. The variation of abrasion loss with aging temperature for NBR and its rubber blend composites is shown in Figure 6. Abrasion loss increases significantly with increasing aging temperature for NBR and its rubber blend composites. However, the relative increase in abrasion loss with aging temperature is low for NBR/H-NBR rubber blend composites compared to its counterpart. Relatively lower modulus and low crosslink density of the aged samples of NBR/H-NBR rubber blend composites resulted in lower abrasion loss compared to aged NBR composites.

Ⅳ. Conclusions

In this study, NBR/H-NBR blends with various H-NBR contents were prepared and subjected to thermal aging studies. The influence of H-NBR content on the properties such as tensile strength, hardness and abrasion resistance of the NBR/H-NBR blend before and after aging was investigated. With increasing aging time as well as the aging temperature, the properties such as tensile strength and abrasion resistance were reduced drastically, whereas hardness increased revealing the post curing reactions, when subjected to aging. However, with the increasing H-NBR content the relative deterioration of the abovementioned properties after aging was significantly reduced compared to the NBR.

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NBR H class. Quite the same Wikipedia. Just better. Â The North British Atlantic, later known as NBR Class H, and then as LNER Class C11 was a class of 4-4-2 steam locomotive of the North British Railway. The class was designed by William P. Reid, Locomotive Superintendent of the NBR, and entered service under his direction. They were the heaviest, longest, and most powerful (by tractive effort) locomotives ever employed on the North British Railway. The locomotives passed to the London and North Eastern Railway in 1923. They enjoyed long service, but most were withdrawn during 1936 and 1937, with none surviving into the nationalised British Rail