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Fatigue of HNBR blends and the effects of thermal ageing

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Abstract

HNBR (Hydrogenated Nitrile Butadiene Rubber) is a synthetic rubber with good resistance to heat and oil products; due its properties, HNBR is utilized in high-demanding applications in oil exploration, aerospace, automotive, and other industries. However, compared to other industrial rubbers, there are only few published studies on the fatigue behavior of HNBR. Moreover, it is important to understand how fatigue resistance is affected by the formulation of HNBR, specifically by the content of acrylonitrile (ACN) monomers and percentage of hydrogenation (number of saturated bonds). First, fatigue experiments are carried out for unaged samples at 120°C, which is the median operating temperature for these HNBR blends. Five HNBR blends are tested with various contents of acrylonitrile and various percentages of hydrogenation. Afterwards, testing is carried out one of the blend, i.e. HNBR with 36% ACN and 96% hydrogenation at 150°C for simultaneous ageing and fatigue conditions. For fatigue life experiments, the Wöhler curve is built according to a novel experimental approach of true stress control for four loading levels and R=0 loading ratio. Preliminary results with thermal ageing are subsequently presented.

Keywords: HNBR; fatigue life; thermal ageing.

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1. Introduction

Various rubbers have been in use for well over a century. The versatility of rubber materials is attributed to their ability to withstand large strain in mostly elastic manner. Rubber is used for a wide variety of parts (such as tires, hoses, seals, etc.) and in many industries (automotive, aerospace, civil, energy, etc.). HNBR (Hydrogenated Nitrile Butadiene Rubber) is a synthetic rubber with good resistance to heat and oil products. Due to its properties, HNBR is utilized in high-demanding applications in oil exploration, aerospace, automotive, and other industries [1]. Additionally, HNBR has relatively good mechanical properties. Improvement of the characteristics of NBR blends in terms of heat, chemical and environmental resistance, and abrasion is achieved by high saturation level of the HNBR, where the double carbon-carbon bonds in the polymer chain are removed by a selective hydrogenation reaction [2]. In simple terms, HNBR is made out of saturated and unsaturated butadiene and acrylonitrile (ACN) monomers [3]. In general, increasing ACN content leads to a better chemical resistance (fuels, solvents, etc.) and increasing the percentage of hydrogenation (amount of saturated C-C bonds) to a better heat resistance [2], [4], [5].

One of the principal modes of failure of industrial rubber products is fatigue, i.e. the material is weakened when it is subjected to cyclic loading. This failure process is characterized by nucleation of cracks and their subsequent growth [6]. Indeed, fatigue properties of rubbers can be investigated by two complementary approaches: fatigue crack nucleation and fatigue crack propagation [7]. In the present work, the former approach is considered.

The aim of the present work is to first study the fatigue life of unaged HNBR. Compared to other industrial rubbers, there are only few published studies on the fatigue resistance of HNBR [8]–[11], from which it is difficult to draw relevant conclusions. Moreover, it is important to understand how fatigue resistance is affected by the formulation of HNBR, specifically, the content of acrylonitrile monomers and percent hydrogenation. The second objective is the study of the effects of thermal ageing; simultaneous fatigue and ageing experiments are carried out at an elevated temperature of 150^{o}C.

2. Experimental method and materials

For fatigue experiments, five HNBR blends are tested with various contents of acrylonitrile (24%, 36%, and 44%) at a constant percentage of hydrogenation (96%), and with various percentages of hydrogenation (91%, 96%, and 99%) at a constant rate of acrylonitrile content (36%); HNBR with ACN content of 36% and 96% percent hydrogenation is taken as the reference material. All blends are filled with carbon black and cross-linked with peroxide. Additionally, the blends contain antioxidants and plasticizers. The reference material was used in simultaneous fatigue and ageing experiments. The naming convention is given in Table 1.

Table 1. Naming convention of HNBR blends.

	A44H96	**A36H96**	**A24H96**	**A36H99**	**A36H91**
% hydrogenation	96	96	96	>99	91
% ACN	44	36	24	36	36
Zetpol 1010	X				
Zetpol 2010		X			
Zetpol 3310			X		
Zetpol 2000				X	
Zetpol 2020					X

Figure 1 shows the specimen utilized in uniaxial tensile and fatigue experiments. The gauge length is 10 mm and the stress state is one of simple uniaxial tension. Specimens are cut using a die from compression molded sheets of the material.

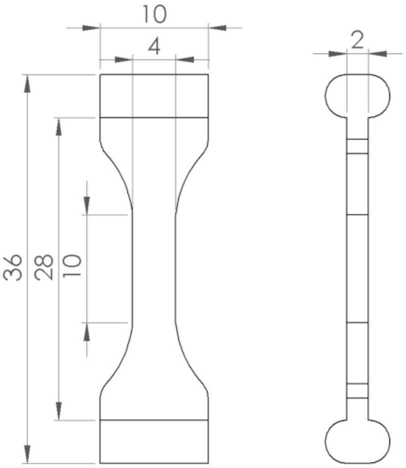

Figure 1. Specimen geometry and dimensions.

For fatigue life experiments, the S-N curve is built controlling the true stress throughout experiments. Testing is performed on an electrically driven machine, *Instron E10000,* with a thermal chamber set to a temperature so that the surface temperature of the specimen under loading, measured by a pyrometer, is 120°C. Additionally, a high speed camera is utilized for digital image correlation (DIC) measurements. In order to carry out fatigue tests under prescribed maximum and minimum true stress values, a novel procedure has been developed [12]. This procedure allows testing of individual specimens, and is extended for testing several specimens in parallel since fatigue life experiments require a large number of specimens for statistical relevance; in this way, an original setup has been designed and manufactured to test up to eight specimens simultaneously, as shown in Figure 2.

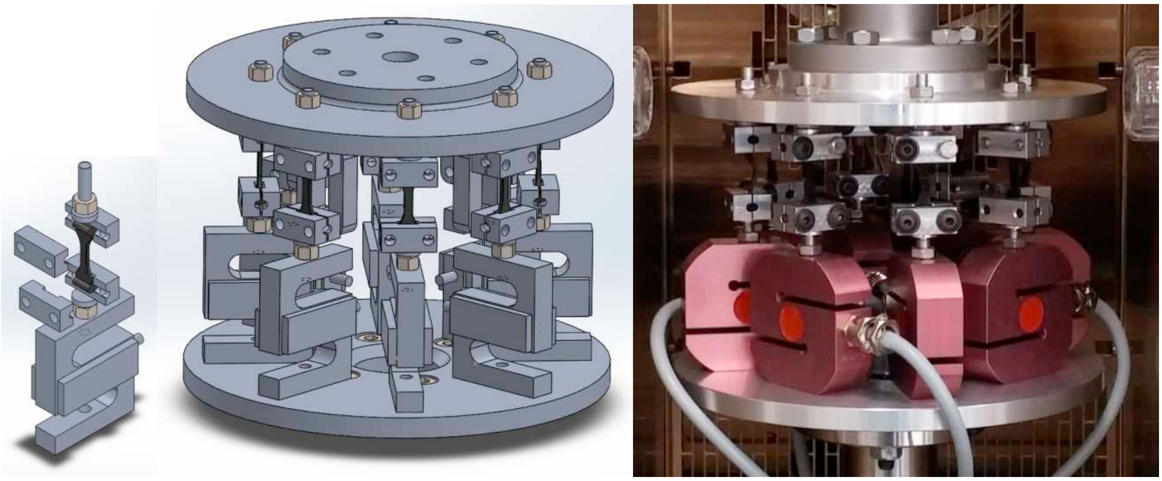

Figure 2. Experimental setup for true stress fatigue life experiments with eight specimens in parallel.

For simultaneous fatigue and ageing experiments, the testing temperature is increased to 150°C. Preliminary ageing experiments (interrupted and continuous stress relaxation) have been carried out *a priori* to determine the appropriate time required for ageing phenomena to take effect.

All specimens are tested at an R-ratio equal to 0 with four loading levels of true stress amplitude: 4, 6, 8, and 10 MPa. Fatigue limit is considered equal to 2 million cycles. A constant average stress rate of 20 MPa/s is considered; it should be noted that prescribing a constant frequency is not ideal because the stress rate is not constant for different loading levels. Fatigue life is defined as the number of cycles until complete failure of the specimens.

3. Results and discussion

3.1. Effect of formulation on fatigue life

Overall, around 240 individual specimens have been tested; at least 8 specimens per loading level for each HNBR blend. Classic Weibull statistical analysis is performed on the results. To facilitate ease of result discussion, a three-parameter Weibull probability distribution function is used,

$$f(t) = \frac{\beta}{\eta}\left(\frac{t-\gamma}{\eta}\right)^{\beta-1} e^{-\left(\frac{t-\gamma}{\eta}\right)^{\beta}}, \tag{1}$$

where η is the scale parameter, β is the shape parameter, and γ is the location parameter. The mean of the distribution is

$$\bar{T} = \gamma + \eta\,\Gamma\left(\frac{1}{\beta} + 1\right), \tag{2}$$

where Γ(x) is the gamma function. Additionally, the 95% confidence intervals are calculated. However, before statistical analysis, specimens with obvious defects (such as failure at gripping points) are removed from the analysis. Then, fatigue life results, including mean and lower bounds of the 95% confidence intervals, are plotted for various ACN contents and various percentages of hydrogenation in Figures 3 and 4, respectively. For visual aid, dashed lines are added between the statistical data at each loading level. However, it should be noted that, as for many synthetic rubbers, there is significant scattering of fatigue life results; hence, the confidence intervals are relatively large.

Figure 3 shows that fatigue resistance of HNBR increases with increasing ACN content. Examining mean results, fatigue lives of A36H96 and A44H96 are significantly longer than that of A24H96. Similarly, the lower bounds of the 95% confidence intervals of the higher ACN content HNBR blends greater than of A24H96. Moreover, the mean fatigue life of A24H96 is in the same order of magnitude as the minimum 95% confidence intervals of A36H96 and A44H96. Referring to the uniaxial response of these blends (Appendix A), the results are as expected since both A36H96 and A44H96 have similar mechanical response in the true stress range from 4 to 10 MPa. From engineering perspective, it appears that there is relatively no difference in the choice of HNBR with ACN grades of 36 and 44 percent. The relative “brittleness” of A24H96 (lower stress and elongation at break as compared to A36H96 and A44H96) might explain the decrease in fatigue resistance. From practical perspective, HNBR with low ACN content tend to be best suited for low temperature usage [1]; thus in addition to the observed uniaxial tensile response, A24H96 is expected to have weaker resistance to fatigue at 120°C.

Figure 4 shows that the difference in fatigue lives between blends with different percentages of hydrogenation are less significant. Mean fatigue live curves present no clear trend at 8 and 10 MPa loading; for lower loading levels (6 and 4 MPa), it appears that fatigue resistance improves as the percentage of hydrogenation increases. Such result is expected since an increase in hydrogenation levels improve the heat resistance of the material [4]; similar response is observed for uniaxial tensile properties, as both stress and elongation at break increase with percentage of hydrogenation. Hence, HNBR with 99% hydrogenation outperforms the other blends for long duration experiments. However, there is a contradiction if one considers the lower bounds of the 95% confidence intervals. The ranking of the blends as fatigue resistance decreases is: 96%, 91%, and 99%; it appears that A36H99 is out of order. These findings are surprising and a conclusive explanation cannot be given at this moment. However, one possibility could be due to higher scattering of fatigue life results observed for A36H99.

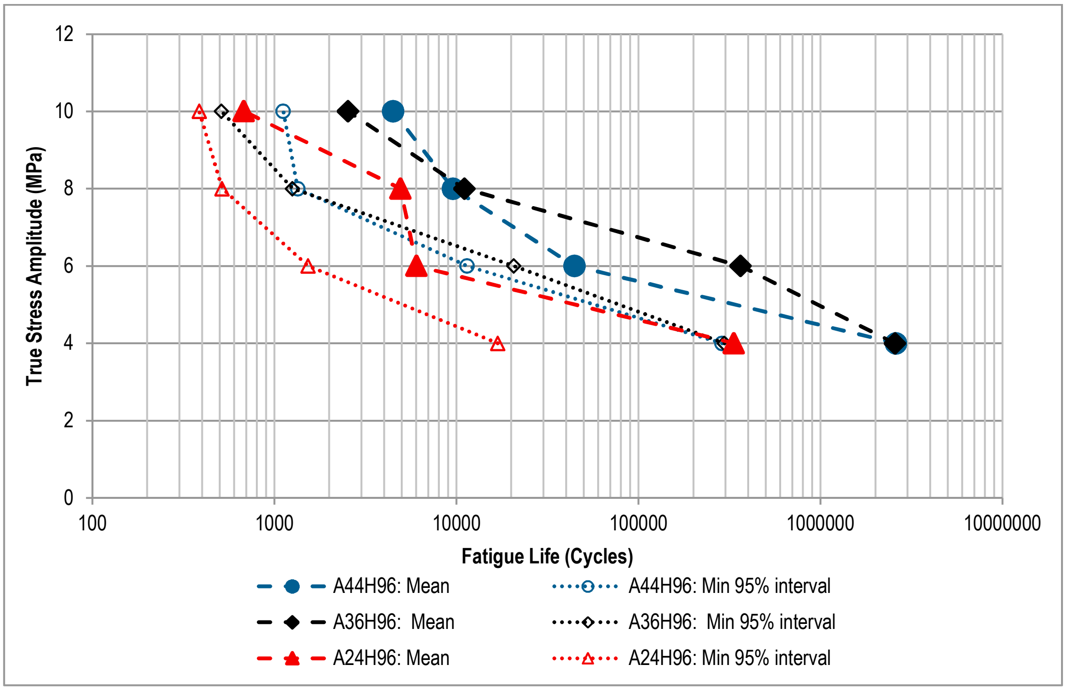

Figure 3. Effect of ACN content on fatigue life of HNBR. True stress loading conditions, *R*=0.

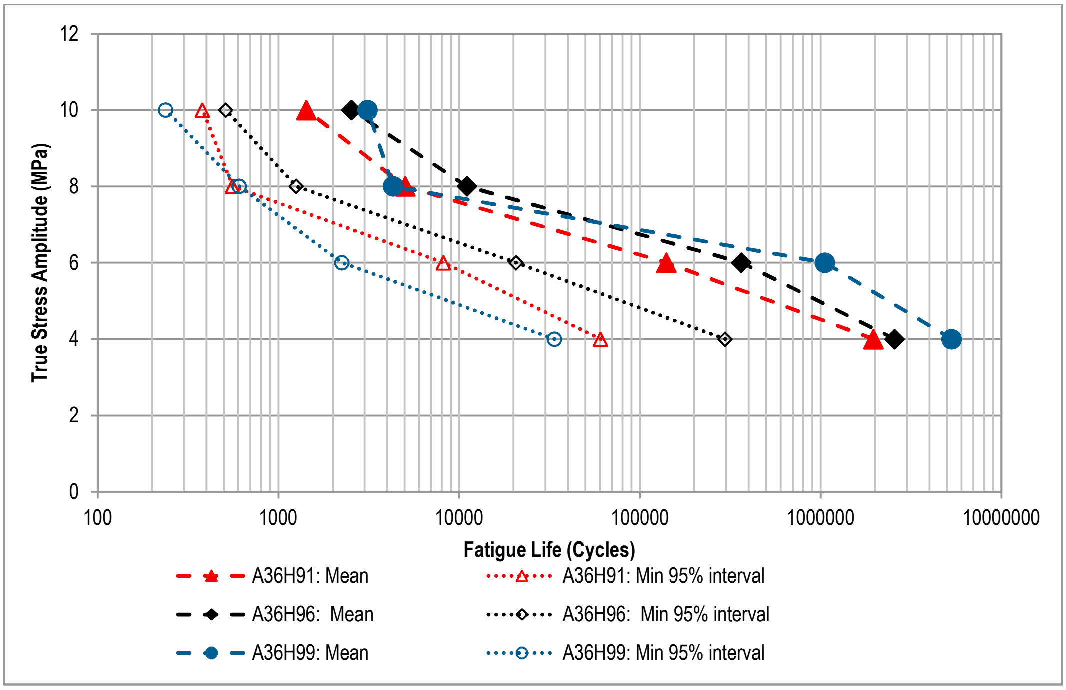

Figure 4. Effect of percentage of hydrogenation on fatigue life of HNBR. True stress loading conditions, *R*=0.

3.2. Effect of thermal ageing on HNBR (preliminary results)

The reference blend (A36H96) has been tested in simultaneous ageing and fatigue experiments. Unfortunately, only preliminary results are available in this paper. Figure 5 shows fatigue life results of single A36H96 specimens tested at 150°C. These first results show that the fatigue lives at 150°C decrease for all loading levels when compared to the results obtained at 120°C. The preliminary results at 150°C also tend to be much closer to the lower bound of the 95% confidence interval. With the present small number of specimens, it is difficult to draw more advanced conclusions. However, we propose a comment on the expected results: for high loading levels, there is primarily only the effect of high temperature on fatigue life as test duration is less than 1 day; for the lowest loading levels (6 and 4 MPa), where tests duration ranges from 1 to 7 days, it is expected to observe a decrease in fatigue life due to ageing effects as well as temperature effects.

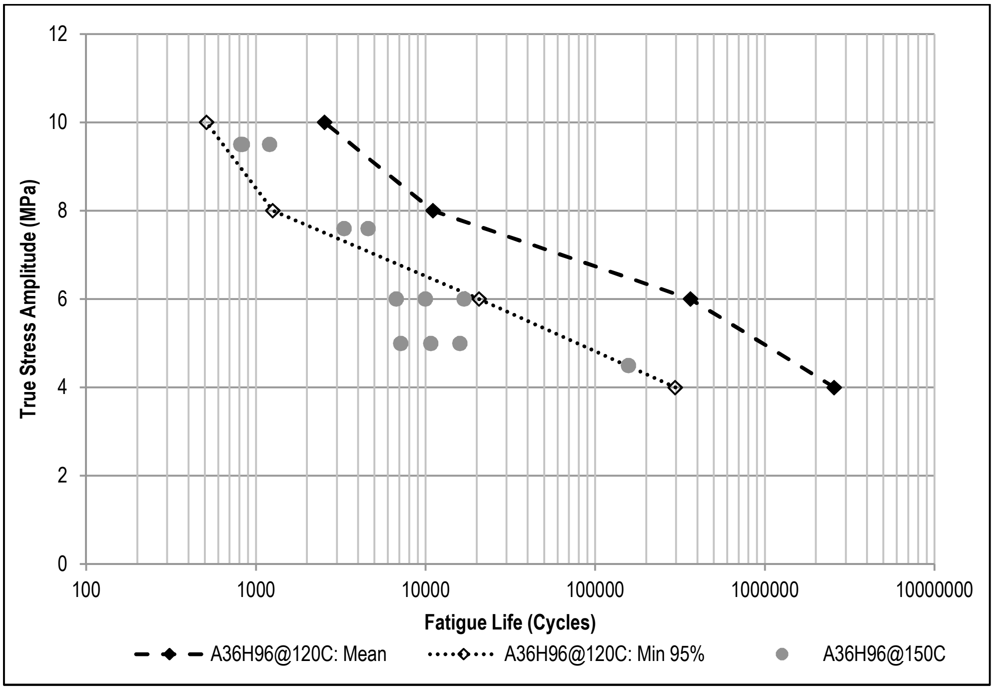

Figure 5. Preliminary results of A36H96 tested at 150ºC: influence of simultaneous ageing and fatigue.

4. Conclusions and perspectives

A complete fatigue study has been carried out on five blends of HNBR at 120°C. The experiments are carried out with an original method developed to control true stress. HNBR with 36% ACN content and 96% hydrogenation is considered as our reference material. The degree of hydrogenation varies from 91% to 99%, and ACN content varies from 24% to 44%.

In terms of ACN content, there is a small difference between HNBR blends with 36% and 44%. HNBR with 24% ACN content admits significantly worse fatigue resistance. This behavior can explained the use of low ACN grade HNBR at low temperatures. In terms of hydrogenation, it appears that fatigue resistance improves with higher percentages of hydrogenation. However, these results are not conclusive as more tests per loading level are required to reduce the 95% confidence intervals.

Additionally, preliminary results are given for simultaneous ageing and fatigue experiments at 150°C. For higher loading levels, where the duration of experiments is relatively short (less than 1 day), there is only influence of temperature. For lower loading levels, it is expected to observe a greater contribution of ageing phenomena. In the near future, a full range of simultaneous ageing and fatigue tests is scheduled.

Appendix A. Uniaxial tension results

Uniaxial tension results at 120°C are presented in Figures 6 and 7; they are plotted in terms of stretch ratio and true stress, and represent an average of at least 3 tested specimens.

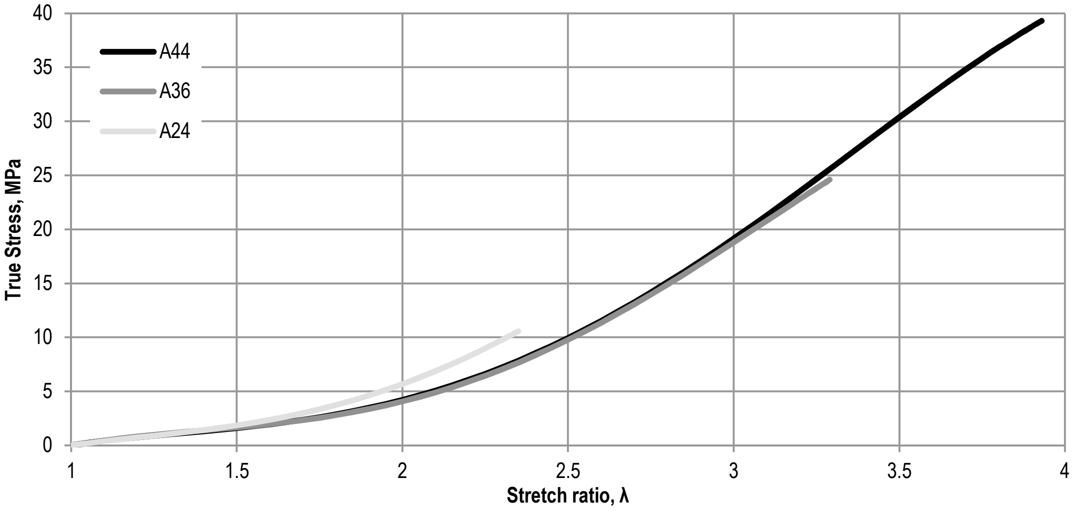

Figure 6. Uniaxial tension for HNBR blends with different ACN contents.

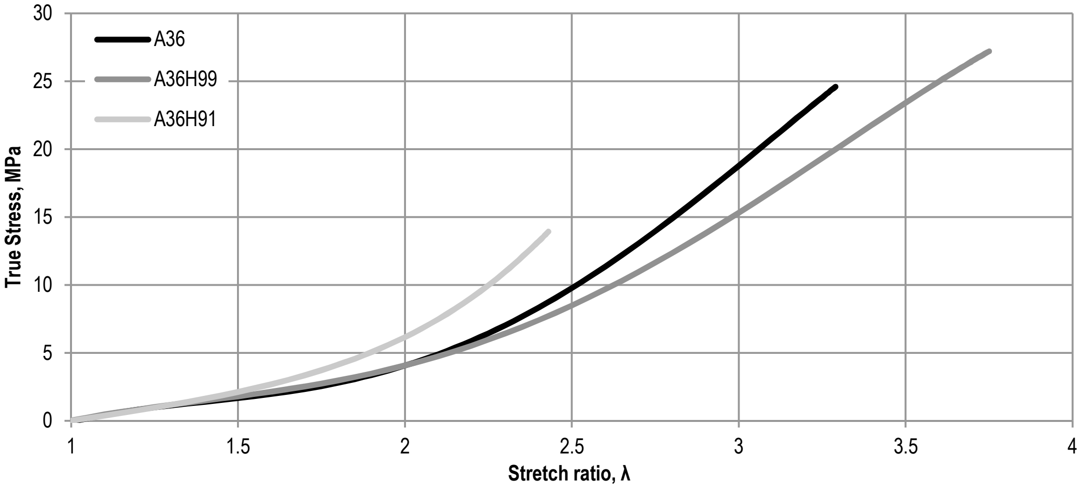

Figure 7. Uniaxial tension for HNBR blends with different percentages of hydrogenation.

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