A SOLUTION TO THE AGE-STIFFENING PROBLEM IN NATURAL RUBBER AND POLYBUTADIENE ELASTOMERS

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Abstract

Natural rubber (NR) and polybutadiene (BR) elastomers are used in the manufacture of many vibration isolation devices in rotorcraft, including high-capacity laminate (HCL) rotor bearings and Fluidlastic™ blade dampers. Investigations show that all conventionally-formulated NR and BR elastomers stiffen over time during storage at ambient conditions and they also stiffen when aged at elevated temperatures. Studies determined that an increase in the elastic shear modulus G' of 8% to 12% in six months is not out of the ordinary for a typical NR/BR blend, and the increase in stiffening continues for years with no evidence of reaching an asymptote. A proprietary chemistry that significantly reduces the magnitude of age-stiffening has been discovered. Although the specific chemistry is not disclosed, the data demonstrates that it is possible to greatly reduce both shelf age-stiffening and stiffening due to heat ageing without sacrificing the fatigue resistance associated with conventional sulfur cure systems.

1. INTRODUCTION

Blends of natural rubber (NR) and polybutadiene (BR) have long been used in applications such as tires and engine mounts that need to resist degradation due to fatigue. For similar reasons, natural rubber and polybutadiene blends are used in the manufacture of many vibration attenuating devices in rotorcraft including high-capacity laminate (HCL) rotor bearings (Figure 1) and Fluidlastic™ blade dampers (Figure 2). Natural rubber contributes high strength and tear resistance, while polybutadiene reduces the stiffening at low temperatures and improves fatigue and abrasion resistance.
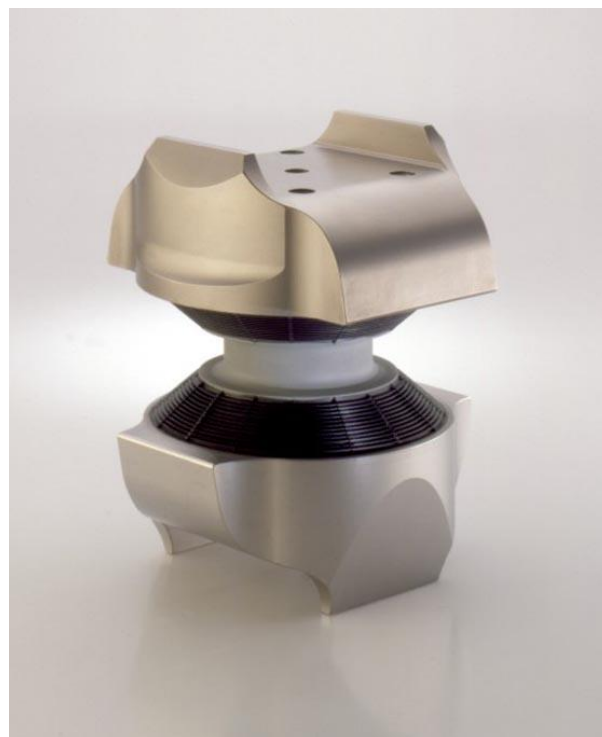

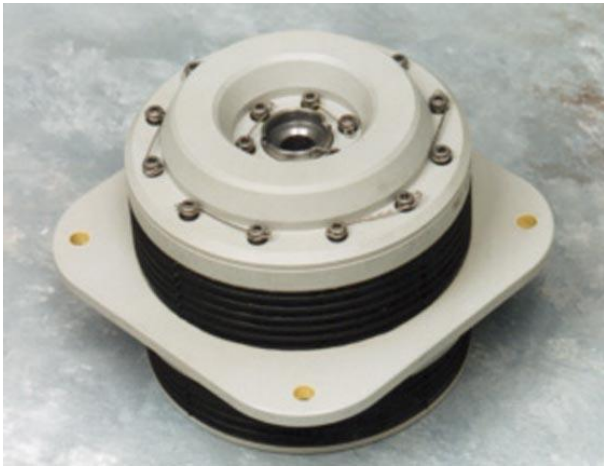**Figure 1: High Capacity Laminate (HCL) Rotor Bearing**

Figure 2: Fluidlastic™ blade damper

Investigations show that virtually all high-diene elastomers, including NR and BR, stiffen over time during storage at ambient conditions; they also stiffen when aged at elevated temperatures. Aircraft parts are somewhat unique in the rubber industry because many are considered critical parts. These critical parts are individually serialized and 100% tested after manufacture. Test records are retained, making it possible to retest a part that has been in storage for some time and compare the retest results to the original results from the time of manufacture. For decades, it has been recognized that parts made from NR and BR stiffen measurably as they sit on the shelf.

Shelf age-stiffening refers to the progressive modulus increase that is observed in molded elastomeric products that have been stored at room temperature or at a slightly elevated storage temperature. Heat ageing causes a modulus increase observed when elastomeric parts are exposed to temperatures significantly above normal storage temperatures. There is no formal line of demarcation between shelf age-stiffening and stiffening due to heat ageing. Both phenomena have been observed in natural rubber and polybutadiene, and heat ageing is a well-known phenomenon in the rubber industry at large.

It was determined as early as 1861 that deteriorated natural rubber always contains combined oxygen, and this oxygen causes deterioration. By 1913, it was demonstrated that natural rubber is autoxidizable and that it oxidizes in an autocatalytic manner[1]. Over time, numerous accelerated ageing tests have been used by the rubber industry because the deterioration process at room temperature is considered too slow to be practical. Although accelerated ageing tests produce data in a shortened time frame, heat aged data does not correlate to data from room temperature ageing. Despite technological advances, little is understood about the mechanisms of room temperature age-stiffening and potential solutions have remained elusive.

Studies have determined that an increase in the elastic shear modulus G' of 8% to 12% in six months is not out of the ordinary for a typical NR/BR blend and the increase in stiffening continues for years with no evidence of reaching an asymptote (Figure 3).
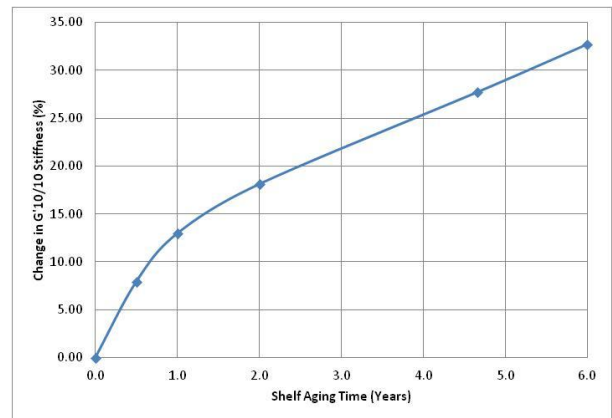

Figure 3: Shelf Age-Stiffening of a Typical NR/BR Blend at 21 °C

As bonded rubber-to-metal products become more complex and part performance requirements become more demanding, age-stiffening, during both storage and service, poses an increasing problem. It is perhaps of greatest consequence in aerospace products where tight performance specifications, high scrutiny and fatigue-intensive, flight-critical applications are the norm. With certain elastomeric compounds in sensitive applications, it may be only a matter of months in storage from the time of manufacture until a product no longer meets the specified spring rate, damping or isolation characteristics.

Investigations were undertaken to examine each component of the rubber formulation (polymer, cure system, reinforcement, and antidegradants) for clues as to how to minimize or eliminate this ageing[2].

From these studies, it was concluded that:
- Shelf age-stiffening occurs in all conventionally formulated natural rubber and polybutadiene compounds.

- The only way to study shelf ageing is to age parts at room temperature or slightly elevated temperatures.
- Using higher temperatures and shorter times appears to change the mechanism of the ageing.
- Natural rubber shelf age-stiffens less than polybutadiene even though polybutadiene is more heat resistant than natural rubber.
- There are no meaningful differences in the age-stiffening characteristics between different grades of polybutadiene or between different grades of natural rubber.
- The addition of antioxidant or antiozonant retards stiffening at elevated temperatures (heat ageing) but promotes stiffening at room temperature, which again suggests a difference in the mechanism of ageing.
- The choice of the grade of carbon black makes only a minor difference, but increasing the amount of carbon black increases the amount of stiffening.

During the investigations, a unique and non-conventional cure and stabilization system was discovered that practically eliminates shelf age-stiffening and significantly improves heat age degradation when compared to conventional cure systems.

2. EXPERIMENTAL

All compounds in this study were mixed in a BR1600 lab Banbury and final dispersion was accomplished on a 15 x 30 cm. two-roll mill. Fatigue was measured using Fatigue Crack Propagation (FCP) testing. Other properties were measured using the following methods:

- Hardness: ASTM D 2240 Shore A
- Tensile, elongation, and modulus: ASTM D 412 method A
- Oven age: ASTM D573
- Dynamic properties: ASTM D5992: G' and tan delta were tested at ±10% shear strain, 10 Hz, 21 °C. Static modulus G is a 25% secant modulus, also tested at 21 °C.

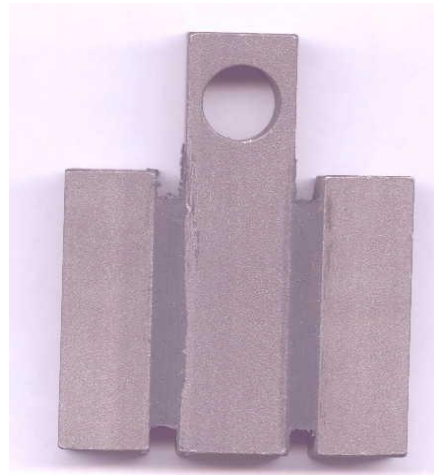Two double-lap-shear specimens (Figure 4) were tested for each compound and the results were averaged.

Figure 4: Double Lap Shear Specimen Used for Dynamic Testing

3. DISCUSSION

The most common cure systems for NR/BR blends use sulfur to crosslink the elastomer. In general, about 1.0 to 3.0 parts per hundred rubber (PHR) of sulfur is used for most rubber products[3]. These levels of sulfur have been proven over time to produce the most fatigue-resistant elastomers. Peroxide cure systems and low sulfur systems produce more heat-resistant vulcanizates, but they are invariably deficient in fatigue resistance. Previous studies have shown that peroxide cures shelf age-stiffen just as much as sulfur cure systems.

3.1 Physical and Dynamic Properties

A model compound was made based on a typical truck tire tread formulation with a conventional cure system using 2.0 phr of sulfur (Table 1). The second compound was identical except it used the proprietary cure and stabilization referred to in this paper as Non Age-Stiffening (NAS).

Table 1: Model Formulations for NR/BR Blend

Ingredient	Sulfur	NAS
CV-60 Natural Rubber	50.0	50.0
High Cis Polybutadiene	50.0	50.0
Zinc Oxide	5.0	5.0
Stearic Acid	1.0	1.0
TMQ	2.0	2.0
6PPD	2.0	2.0
Antiozonant Wax	1.0	1.0
N330 Black	65.0	60.0
Paraffinic process oil	5.0	5.0
Sulfur	2.0	-----
OBTS	1.0	-----
TMTM	0.2	-----
Proprietary Ingredients	-----	8.0

The physical properties of the resulting vulcanizates were tested and found to be similar for both cure systems (Table 2).

Table 2: Physical Properties for the Model Formulations

Physical Properties	Sulfur	NAS
Hardness (Shore A)	68	69
Tensile (MPa)	19.2	19.3
Elongation (%)	434	587
100% tensile modulus (MPa)	3.55	2.44
Tear Die C (kN/m)	48.7	53.1

The most common accelerated heat ageing conditions for NR, BR, and NR/BR blends are 22, 70, or 168 hours at 70 °C. These two compounds were heat aged for 3 months at 70 °C and they were also shelf aged for one year at 21 °C. Results show that the physical properties of the NAS system are superior to the conventional sulfur cure in both cases (Table 3).

Table 3: Aged Physical Properties for the Model Formulations

Physical Properties	Sulfur	NAS
Oven aged 3 Months at 70 °C		
Tensile (MPa)	11.6	18.4
Elongation (%)	147	398
100% modulus (MPa)	8.0	3.8
Change in tensile (%)	-39.6	-4.8
Change in elongation (%)	-66.1	-32.2
Change in modulus (%)	125.2	56.5
Shelf aged 1 Year at 21 °C		
Tensile (MPa)	17.3	17.8
Elongation (%)	398	557
100% modulus (MPa)	4.0	2.4
Change in tensile (%)	-10.2	-7.8
Change in elongation (%)	-8.2	-5.1
Change in modulus (%)	11.8	-0.6

Dynamic properties were also tested using double lap shear specimens (Table 4). The aged properties of the NAS system are clearly superior to those of a conventional sulfur cure system.

Table 4: Original and Aged Dynamic Properties for the Model Formulations

Dynamic Properties at 21 °C	Sulfur	NAS
Original		
G'10/10 (MPa)	2.50	2.40
Tan delta 10/10	0.217	0.261
25% static G (MPa)	1.91	1.85
Aged 3 Months at 70 °C		
G'10/10 (MPa)	3.61	2.77
Tan delta 10/10	0.204	0.245
25% static G (MPa)	3.09	2.10
Change in G'10/10 (%)	44.3	15.7
Change in Tan delta 10/10 (%)	-6.1	-6.2
Change in 25% static mod. (%)	62.1	13.1
Aged 1 Year @ 21 °C		
G'10/10 (MPa)	2.86	2.53
Tan delta 10/10	0.207	0.253
25% static G (MPa)	2.10	1.88
Change in G'10/10 (%)	14.3	5.5
Change in Tan delta 10/10 (%)	-5.0	-3.0
Change in 25% static mod. (%)	10.2	1.4

3.2 Fatigue Resistance

The mechanism of elastomer fatigue is not clearly understood. It is believed that initial minute flaws/cracks are always present in the elastomeric specimen regardless of the level of dispersion and

these often function as crack initiation sites. Rubber articles rarely fail in a single loading; rather, failure usually results from progressive crack growth during repeated loadings. In some instances, the main factors contributing to flex cracking and crack growth may include oxidation and attack by ozone[4]. Fracture mechanics deals with crack growth from intrinsic flaws and can be used to characterize the rate at which strain energy is released as a crack grows. This strain energy release rate is termed "tearing energy" (abbreviated as G), and it can be used to characterize the behavior of different materials intended for use in dynamic applications. Fracture mechanics as applied to fatigue began in the 1940s and it has been successfully used for a variety of materials. Fracture mechanics provides a consistent, unifying concept for a wide variety of failure phenomena in different materials including rubbers, plastics, adhesives, ceramics, and metals.

The fracture mechanics based Fatigue Crack Propagation (FCP) test which utilizes a "pure shear" test specimen, was used to determine how the crack growth behavior of rubber compounds changes with ageing[5, 6, 7]. Every compound has a characteristic crack growth rate for a given tearing energy. The crack growth rate, dC/dN, may be plotted as a function of the tearing energy G (Figure 5). At tearing energies below a value G_0, the crack growth rate is essentially zero and that which does occur is related to chemical effects. In the absence of corrosive elements, the growth rate should drop to zero and parts should have an infinite life. Above G_0, the crack growth rate increases with tearing energy and a linear relationship is commonly found. A second change occurs in the crack growth characteristics at a transition zone G_t, where the growth rate increases more rapidly than linearly. Above G_t, a power law relationship generally applies and a plot on logarithmic scale appears linear. Finally, near G_c, the crack growth rate increases very rapidly. G_c is the critical tearing energy and is basically the single-cycle tear strength of the rubber. The area of prime interest is in the power law region, which falls between G_t and G_c, as this is where most elastomeric mounts normally operate.
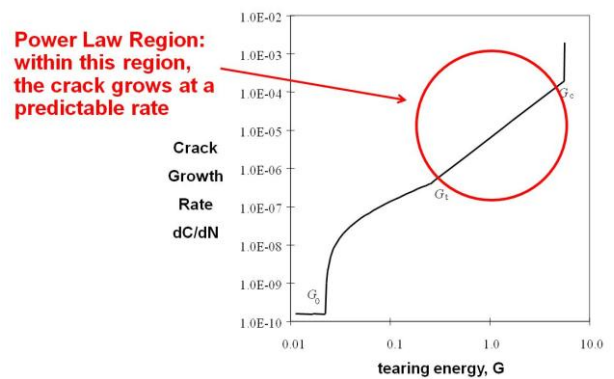

Figure 5: dC/dN as a Function of Tearing Energy (Theoretical Curve)

An initial concern with this novel cure system was whether it can provide the fatigue resistance required for rotary wing applications. High-sulfur cure systems have been the long established choice when maximum fatigue resistance is desired. The model formulations were used to investigate both initial fatigue resistance and fatigue resistance after ageing. It was indeed surprising to find that the unaged fatigue crack growth rate for the NAS system is superior to that of the conventional sulfur system in the model compounds (Figure 6).
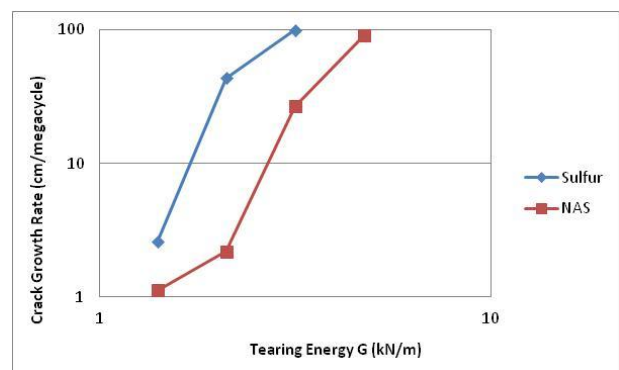

Figure 6: Fatigue Crack Propagation, Unaged

Heat ageing is usually detrimental to the properties of rubber, and 3 months at 70 °C is extreme for NR and BR formulations. Not surprisingly, the crack growth rate for the conventional sulfur cured compound increased by an order of magnitude due to the ageing (Figure 7).
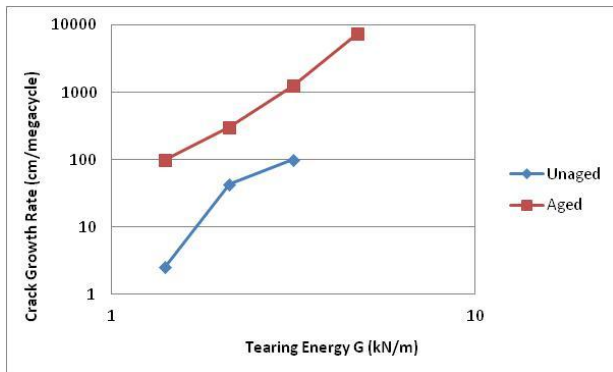
Figure 7: Sulfur Cured NR/BR Blend Before and After Heat Ageing 3 Months at 70 °C

After accounting for experimental error, there was no change in the crack growth rate observed for the NAS system after heat ageing for 3 months at 70 °C (Figure 8).
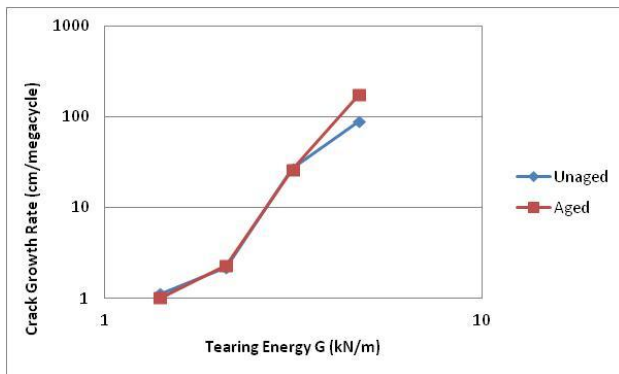

Figure 8: NAS Cured NR/BR Blend Before and After Heat Ageing 3 Months at 70 °C

Although NR and BR elastomers are known to stiffen as they sit on the shelf during storage, it has not been previously determined whether the stiffness increase has an impact on the fatigue crack growth rate. The crack growth rate for the conventional sulfur-cured compound showed a small but consistent increase after ageing for one year at 21 °C (Figure 9).
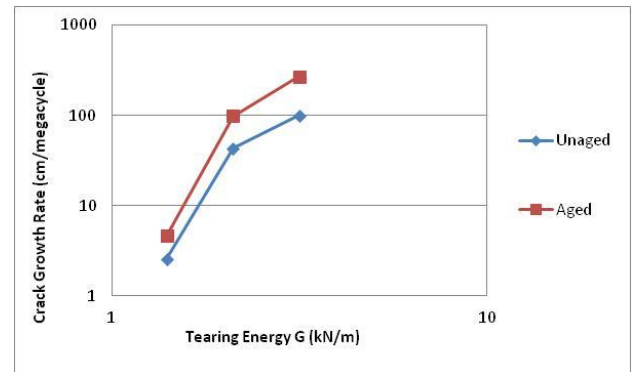
Figure 9: Sulfur Cured NR/BR Blend Before and After Shelf Ageing 1 Year at 21°C

As with the heat ageing, there was no change observed for the NAS system after shelf ageing for 1 year at 21 °C (Figure 10).
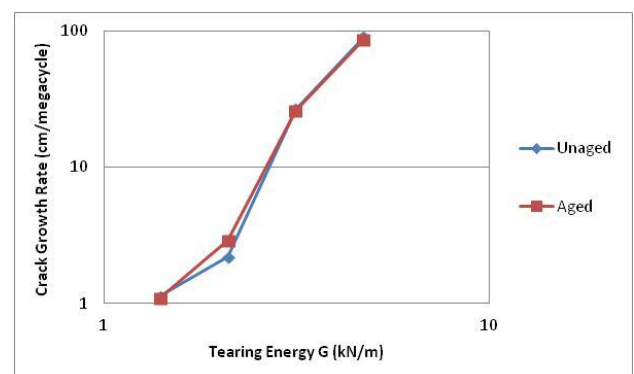

Figure 10: NAS Cured NR/BR Blend Before and After Shelf Ageing 1 Year at 21 °C

The work covered in this document was conducted on model compounds and was intended for publication. Work on shelf age-stiffening has been underway for years at LORD Corporation and the NAS cure system has been compared to the actual formulations and cure systems routinely used for making rotorcraft parts. Figure 11 shows the results of 6 years of monitoring a conventional production compound versus the same compound with the NAS technology when aged at 21 °C.
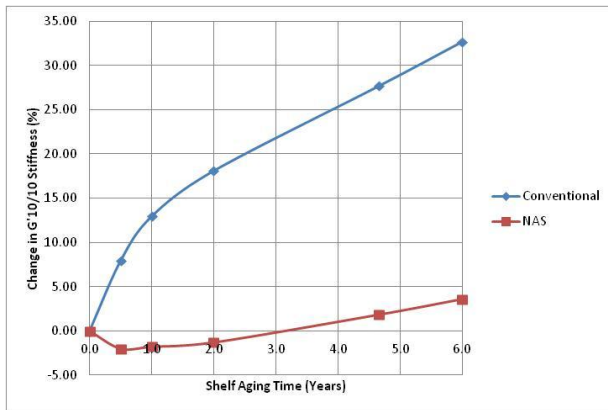
Figure 11: Shelf Age-Stiffening of NR/BR Blends, Conventional versus NAS Technology

4. SUMMARY AND CONCLUSIONS

Shelf age-stiffening occurs in all conventional natural rubber and polybutadiene compounds. An increase in G'10/10 (±10% shear strain, 10 Hz) of 8% to 12% in six months at room temperature is not out of the ordinary for a typical NR/BR blend. A proprietary chemistry that significantly reduces the magnitude of age-stiffening has been discovered. Although the chemistry is not disclosed, it demonstrates that it is possible to greatly reduce or eliminate the observed phenomenon. The proprietary cure and stabilization system imparts both improved heat resistance and improved fatigue resistance to the compounds.

References

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