Variation in Rubber Chemistry and Dynamic Mechanical Properties of the Milking Liner Barrel with Age

D. Boast,* M. Hale,* D. Turner,† and J. E. Hillerton‡1
*Avon Rubber, Materials Development Centre, Brook Lane Industrial Estate, Westbury, BA13 4EP, United Kingdom
†Bathford, Bath, United Kingdom
‡DairyNZ, Hamilton, New Zealand

ABSTRACT

The milking liner is the interface between the milking machine and the cow. Liner properties important to milking performance were investigated for liners of different ages using discriminating tests rather than the normal, rubber-industry quality control-based tests. Large variations in the liner mechanical properties occurred depending on where the sample was taken; stiffness increased 4-fold 40 to 50 mm below the top of the liner. This was related to changes in the chemistry of the rubber created by absorption of milk-derived products (MDP) into the rubber and losses of formulation components, particularly 50% of the plasticizer and all of the antidegradent 40 to 50 mm below the top of the liner, with age and use. The presence of MDP leads to calcium and phosphate deposits on the inner surface of the liner barrel where the MDP was absorbed. The detailed liner properties can be used to explain the forces on the cow’s teat and its reactions and effects on milk flow behavior, and to guide future liner development.

Key words: liner, teat, rubber, chemical and mechanical properties

INTRODUCTION

Most of the tests used to develop rubber formulations come from national and international standards, which are important as quality control tests to check that the rubber has been processed correctly. Often product specifications are defined by these tests. A more enlightened approach to rubber testing was discussed by Gent (1992) and Whear (2003), including agreement that the commonly used tensile test is not sufficiently discerning to show the important changes to liners that control their performance.

The forces on the teat of a cow during machine milking result from the liner vacuum, milk flow, and loading by the liner during pulsation. Liners have a recommended maximum life depending on the rubber formulation of usually 1,000 to 2,500 milkings. Degeneration of the rubber is progressive, but no useful descriptions are available on the processes, speed, or the threshold beyond which liner action becomes unacceptable.

Initial measurements on used liners showed large variations in the properties depending on the part of the liner sampled. Used liner rubber contains milk-derived products (MDP). The MDP were first found to be absorbed from butterfat when natural rubber was used for liners (Gardner and Berridge, 1952; Cooper and Gardner, 1955). The presence of butterfat causes many of the changes in the rubber. Nitrile liners, the most common type in current use, absorb some milk fat progressively with exposure to milk. The butterfat swell mechanism and the swelling of the rubber itself are more complicated than simple, single-value volume swell or mass uptake tests show because of the nature of permeation and the range of temperatures involved in the milking process (ambient to hot wash temperatures). These mechanisms need to be analyzed carefully to understand their effect on product and milking performance. Some of the important changes, rather than the bulk rubber properties, are dimensional changes resulting from creep and relaxation of the material and the structure.

The general conditions of liner use will alter the details of the liner changes; the conditions will vary from farm to farm and from time to time. The responses of the teats to milking with liners of different ages, a subset of the work reported here, was described by Hillerton et al. (2004). The objectives were to describe degeneration of rubber and to examine the barrels of aged liners to map out systematic variation of rubber properties. The mechanism of how the MDP gets from milk to rubber was investigated by in vitro tests to measure liner properties important for performance during milking, especially how this may vary with age. Complementary work is underway on the changes to the mouth-
piece, which has quite different structural and mechanical functions.

**MATERIALS AND METHODS**

Only European-style nitrile rubber liners have been considered; they have a recommended life of 2,500 milkings. A batch of DeLaval 960000-01 liners (DeLaval, Cymbran, UK) was fitted into HC150 DeLaval clusters in a double-8 DeLaval milking parlor operating at 47 kPa plant vacuum, pulsation of 60 pulses/min, and 60:40 ratio. Automatic cluster take-off was initiated at a milk flow threshold of 400 mL/min with a 2-s delay. A herd of approximately 230 cows was milked twice daily. All operating conditions were monitored including circulation cleaning of the milking equipment using the supplier’s recommended hot wash (minimum 80 °C) with a detergent, DeLaval C6 extra. After 1,500 milkings the liners were retensioned as recommended by the supplier.

The detailed study involved liners from new to 5,800 milkings of use. Every 2 wk (approximately 400 milkings), 1 whole cluster was removed to an experimental milking parlor (Butler et al., 1990), where the same operating conditions were used for detailed observations on milking performance and teat condition. A sub-sample of 8 cows, the same group used throughout the study, was accustomed to the experimental conditions at one afternoon milking and, at 0900 h the following day, was milked using the liners of progressively increasing age, still within the same cluster.

All 4 liners, still in their shells, were removed to the Avon Rubber Materials Development Centre (Westbury, UK) where key dimensions were measured 30 min after removal of the liners from the shells. Samples from the liners were then examined by 1) dynamic mechanical thermal analysis to measure changes in the mechanical properties of the rubber; 2) thermogravimetric analysis to determine large-scale compositional changes such as removal of plasticizer and fat uptake (solvent extraction was used to determine the amount of soluble matter in the rubber); 3) GC to determine the dioctyl phthalate plasticizer (DOP) content, the antidegradant N,N′-1,3 dimethylbutyl-N′phenylparaphenylenediamine (6PPD), and MDP, and 4) scanning electron microscopy and energy dispersive x-ray spectrometry (EDAX) to examine the surface of the liner and the surface residue remaining after extraction for thermogravimetric analysis. The repeatability of the position of sample removal from the liner was controlled between liners by measurement of distance from the base of the mouthpiece chamber.

Butterfat was deposited on the liner surface by mechanical attrition of the milk. The mechanism of the liner closing on the teat was similar to a wheel rolling on the rubber. A test machine was built to roll a nylon wheel (diameter 20 mm, stroke 50 mm) over rubber coated in whole milk using a load approximating 50 kPa at 35 °C in bouts to approximate 200 milkings (400 h). Significant amounts of butterfat were deposited after a short time, but only where the wheel rolled.

**RESULTS AND DISCUSSION**

**Dimensional Changes**

The barrel was typically 3% longer after 2,500 milkings (Figure 1). These liners are nominally circular in cross section. Because of inevitable variations in manufacture and storage conditions all circular liners have some initial ovality; thus, they always collapse in the same plane. The ovality of the liners (the difference between the major axis and the minor axis of collapse) was approximately 4 mm after 2,500 milkings. The liner must first buckle before proceeding to bend and close. The ovality was significant because the buckling pressure was controlled by the largest radius (at the narrowest part of the oval liner bore). The largest radius increased as the liner became more oval.

The buckling pressure for a liner is given by the relationship

\[ P_{\text{crit}} = k \times (1/4) \times [E \times (1 - v^2)] \times (t/r)^3 \]

where \( P_{\text{crit}} \) is the barrel buckling pressure, \( k \) is a constant (generally about 0.5), \( E \) is the Young modulus, \( v \) is the Poisson ratio for the rubber, \( t \) is the liner wall thickness, and \( r \) is the liner barrel radius (largest radius of the oval). The value of Poisson ratio was the low...
strain value of 0.5 (Turner and Brennan, 1990). The modulus used should also be the low strain modulus.

The bending of a liner involves large changes in the rubber geometry, and the full treatment would involve large strain elasticity concepts. The forces applied by the teat to bend the rubber are small compared with the massage contact pressure. Small strain theory was found adequate to show the important variables. Small strain theory of bending gives

\[ F \propto E \times I / R \]  \hspace{1cm} [2]

where \( F \) is the force needed to bend the rubber, \( E \) the Young modulus of the rubber, \( I \) the moment of inertia, and \( R \) the change in radius. The change in radius of an oval liner is less than for a circular liner. When the pressure difference across the liner exceeds the buckling pressure, the liner closes rapidly to a point determined by the bending stiffness. The touch point pressure (TPP), the pressure across the liner wall so that the opposite sides just touch, is affected by the change in modulus and the ovality, and is mainly a measure of the bending stiffness of a liner. The TPP is not a useful tool to determine the massage or contact pressure on the teat, which is more properly governed by the tension in the liner and the bending radius in the axial direction. Nevertheless, the TPP can be a useful guide to check for changes in the liner.

In practice, the liner is stretched in the shell to put the liner barrel rubber under tension. The liners were retensioned after 1,500 milkings; the supplier’s recommended practice with this type of liner. The effect of retensioning is to reduce the liner bore by about 1 mm in diameter for every 10 mm of liner stretch. The change in bore diameter is a geometrical effect and only a function of the stretch. Any reduction in tension as the rubber creeps in response to the load during pulsation does not cause changes in the bore diameter. A retensioned liner, one that is stretched slightly further in the shell after a predetermined number of milkings, could have a bore diameter 2 mm smaller than a new liner. This follows from equation [3]:

\[ \text{Barrel diameter} \times [1 - (1 + \text{barrel strain})^{1/2}] = \]  \hspace{1cm} [3]

change in barrel diameter

A further reduction in bore diameter occurs when the liner closes as the strain, and therefore the tension, increases when the liner stretches round the teat. The amount a liner can be retensioned is limited as the bore reduction becomes excessive, thus reducing the liner’s ability to close.

![Diagram](image)

**Figure 2.** Variation in proportion of weight (%) of the dioctyl phthalate (DOP) plasticizer, the \( N^\prime\)-1,3 dimethylbutyl-\( N^\prime\) phenylpara-phenylene diamine antidegradent (6PPD), and milk-derived products (MDP) along the length of the liner after 2,500 milkings. The area 40 to 60 mm below the mouthpiece is the part that wraps around the teat end during liner collapse.

**Chemical Composition of the Rubber**

Thermogravimetric analysis showed that the carbon black content expressed as a ratio of the polymer and the polymer content itself did not change with the age of the liners, yet additional extractable matter was being accumulated. Figure 2 shows a considerable amount of MDP (butterfat) extractable by solvent from aged liners. Other calcium-rich material on the liner surface was also found (Figures 3, 4, and 5).

A systematic study of liner composition by GC, with sample positions carefully controlled, showed the relative 6PPD, DOP, and MDP content, extracted by solvent, at different positions down the liner bore (Figure 2). The antidegradant 6PPD protects the rubber to stop environmental damage causing cracks. At approximately 50 mm from the liner mouthpiece, the 6PPD locally in the barrel was entirely removed. When 6PPD is removed the liners quickly fail by classical ozone cracking. This was a highly localized effect and may be an extreme value because no liners failed in the trial, but it was evidence of the limited life of a liner. Removal of the plasticizer DOP stiffens the rubber.

The greatest concentrations of MDP in the barrel occurred 40 to 60 mm from the bottom of the mouthpiece where the teat ends touched the liner (Figure 2). No MDP was detected in the rubber more than 120 mm below the top of the liner. The GC was not calibrated for MDP, so the levels shown were indicative of the relative concentrations.
Figure 3 shows the mass uptake of material into an unused liner from the swell tests in butterfat. This mass uptake test paid particular attention to recording information a few hours relative to liner age; see Figure 6. Temperature had a large effect and was relevant because the liner operated over a temperature range. Three relevant temperatures—ambient when the machine is running but not milking (generally 5 to 35°C), milk temperature applicable during milking (35°C), and wash temperature (up to 90°C)—were considered. The initial reduction in mass (Figure 6) was due to extraction of DOP and possibly of 6PPD. Extraction of materials from the rubber and diffusion of materials into the rubber occurred simultaneously, with MDP diffusing into the rubber much more slowly than material was extracted from the rubber. Permeation and extraction were governed by the diffusivity and the solubility constants for the rubber and swelling agent. The mass flow rate through a liner is governed by equation [4]:

\[
\text{Mass} = \text{permeability} \times (c_2 - c_1) \times \frac{\text{time}}{\text{rubber thickness}}
\]

where \(c_1\) and \(c_2\) are the concentrations of swelling media on either side of the rubber and permeability = solubility \(\times\) diffusivity. Both solubility and permeability are highly dependent on temperature, but vary for each of the components involved.

The mechanical attrition at the point of liner/teat contact breaks down the milk emulsion such that a fat phase is deposited on the liner surface. The amount of absorption and swell varied with the amount of butterfat and so differed for milking and washing, from cow to cow, and with stage of lactation. Swell contributed...
Figure 4. Variation in a) ratio of P to Ca and b) sulfur content (%) with liner length after 4,000 milkings determined by energy dispersive x-ray spectrometry.

Dynamic Mechanical Properties

Most strains on the liner during milking were low (Table 1). Normal tensile tests, including those used in International Standards Organization tests, are not sufficiently discriminating to show differences in properties affecting milking at these low strains (Figure 8). Local changes in the material caused by the absorption of MDP mean that normal dumbbell-shaped samples when taken from the barrel may contain significant material variation along the length of the test piece such that tensile tests can be very misleading because of the heterogeneity between positions on the liner (Figure 8). The dynamic mechanical properties, especially elastic modulus and hysteresis, dictate the responses of the liner to the loads imposed during milking. It is
Figure 5. Scanning electron micrographs of a) liner surface showing the calcium/phosphate deposits 30 mm from the top of the liner (bar = 100 μm) and b) liner surface showing calcium/phosphate deposits 100 mm from the top of the liner after 4,000 milkings (bar = 100 μm).

important to determine the dynamic properties of the rubber at the precise working temperature, frequency of loading, strain encountered, and position in the liner barrel. Dynamic mechanical thermal analysis measured the stiffness and hysteretic properties of small samples of rubber at different temperatures, frequencies, and amplitudes. It was especially useful at lower amplitudes typical in the operation of the liner (Gent, 1992; Boast et al., 2003). The rubber properties at the particular operating conditions for different parts of the liner can be used to understand the operation of the liner. The orientation of the sample and position were chosen with care, because the axial and circumferential stiffness in the barrel can vary by up to 40% because of polymer orientation during manufacture.

Figure 9 shows that the strain dependency of the rubber and this depends on the carbon black fillers in the rubber. The stiffness of the liner (E) depends on how much the liner is strained. Rubber exhibits other nonlinear effects at high strain, and the strain dependency should not be confused with these. The dynamic data (Figure 10) show that the elastic modulus increased with liner age. Tan delta and the viscous modulus also increased as the liner aged (data not shown). Figure 10 shows that the changes are most dramatic in the zone from 40 mm below the top of the liner.

Some softening of the rubber is likely with uptake of MDP, which acts as a plasticizer. This may be offset by local hardening from loss of DOP, the formulation plasticizer. Surface deposits contributed to the hardening of the rubber. When approximately 0.5 mm of the inner surface was removed there was a general softening in the bulk of the rubber, shown as changes in stiffness of the barrel rubber (Figure 11). The overall stiffening of the liner shown in Figure 10 appeared to be created mostly by the changes on and in the surface of the rubber, which more than counteracted the effects of swell.

The liner properties are also temperature dependent; Figure 12 shows that the stiffness (E) almost doubles between 35 and 0°C. Although the inner bore rubber will warm to body temperature during milking, the general liner temperature may be much lower at certain times of the year, especially at the start of each milking.

During milking the liner is forced closed by the pressure difference across the wall of the liner, created by atmospheric pressure in the pulsation chamber and milking vacuum inside the liner. The increase in liner stiffness and hysteresis with age both resist the closure of the liner. When the liner opens because of plant vacuum in the pulsation chamber, the tension in the liner (the sum of the original tension and the extra tension as the liner stretches round the teat) acts to reduce the rubber length and return the liner wall to its original straight shape, albeit stretched inside the teatcup. The increased tension due to stiffening will tend to speed the response of opening, but the increase in hysteresis (tan delta) tends to reduce the speed. A reduction in tension due to the stress relaxation of the liner in the teatcup also slows the opening of the liner. The net effect of these changes will vary with liner design and machine operating conditions, but opening of the liner will be slower with age, resulting in slower milking with older liners.
Scanning Electron Microscopy and EDAX of the Liner Surface

Liners of different ages were examined, with a detailed study made on a liner used for 4,000 milkings. An initial visual inspection revealed a textured surface inside the liner barrel. This has often been described as some sort of surface degradation and erosion of the rubber, generally attributed to the cleaning regimen. Analysis using scanning electron microscopy and EDAX showed that this surface was coated with calcium, phosphorus, and some organic material (Figures 3, 4, and 5). The surface was not eroded, but coated with milkstone.

The levels of calcium and phosphate peaked at 40 to 60 mm from the top of the liner and then decreased further along the liner barrel, away from the mouthpiece (Figure 3) with the ratio of calcium to phosphorus remaining roughly constant along the liner barrel (Figure 4a). The analysis could not determine the exact relationship between the 2 inorganic components, but it was likely that the material was calcium phosphate. The levels of sulfur in the liner (Figure 4b) decreased toward the top of the liner (to almost zero). Sulfur is used to crosslink the rubber, and the presence of sulfur indicates that rubber can be detected. The surface of the rubber in the region of the teat end was entirely covered by the calcium and phosphorus layer, masking the detection of rubber. This was confirmed by detecting zinc and chlorine that were available in free liner surfaces.

The region 40 to 60 mm from the top of the liner, where the maximum changes in chemical and physical properties occurred, produced a low number of counts in the EDAX analysis. This suggests that there was a...
Table 1. Typical operating strains of different parts of the liner

<table>
<thead>
<tr>
<th>Strain</th>
<th>Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial prestrain</td>
<td>10–20</td>
</tr>
<tr>
<td>Axial strain during collapse (additional to the axial prestrain)</td>
<td>10</td>
</tr>
<tr>
<td>Surface strain at crease during collapse</td>
<td>40</td>
</tr>
<tr>
<td>Orifice strain</td>
<td>5</td>
</tr>
</tbody>
</table>

large amount of organic matter, which was not detectable on the surface of this region (Figure 5a). The surface roughness peaked 40 to 50 mm from the top of the liner. The roughness generally decreased down the liner. In the roughest area, there were both circumferential and longitudinal cracks in the layer. At about 30 mm from the top there were diagonal cracks, possibly due to flexing of the liner, as it was pulled at an angle by the cluster. At 80 to 100 mm from the mouthpiece, the liner surface morphology was more organized with longitudinal cracking predominating and becoming more finely spaced (Figure 5b), with a general reduction in feature size.

The nature of the surface changed markedly during the life of the liner. Initially, as the teat contacts the virgin rubber, the level of friction against the teat will be high. The friction decreases as the cleaning process progressively chlorinates the rubber surface. A chlorinated surface has a silky, low-friction texture. Once significant amounts of the calcium and phosphorus-based deposits are present, the friction will increase to a high level where the teat contacts the rough milkstone surface.

**Tension in the Barrel**

Two mechanisms resist the closure of the liner in 2 different planes. In the plane of the liner diameter, the liner first buckles and then bends (equations 1 and 2). In the plane of the liner axis, the liner tension as the liner bends around the teat produces the massage pressure. The contact pressure of the liner on the teat was mainly a function of the bending radius at the teat end (Figure 13) and the tensions in the liner. These are related by the membrane equation of pressure = tension/radius (equation [5]). Note that the radius is the deformed radius of the teat. Equation 5 brings together the tension from the liner and the radius, which will vary with the teat size and shape.

In this analysis the liner was treated as a membrane with no bending stiffness, because the pressure that was exerted on the rubber to bend it was small compared with the pressure created by the liner bending around the teat under axial tension. The contact forces due to pressure on the teat are dominated by the membrane. The contact pressure with the teat obeys the membrane equation (equation [5]). For typical barrel tensions and a local radius of 20 mm, the contact pressure due to the liner as a membrane will be 50 kPa. These contact forces will increase with greater tension in the liner and when the teat is locally firm.

The axial tension in the liner reduces over time (stress relaxation). Swelling of the liner is one mechanism of the aging process that reduces the axial tension. The decrease in tension will decrease the rubber/teat contact pressure and so make massage less effective.

![Figure 8](image)

*Figure 8.* Tensile behavior of new (0 milkings) and used (4,400 milkings) liners.

![Figure 9](image)

*Figure 9.* Variation in elastic modulus (E) and hysteresis (tan delta) of unused liner rubber for strain sweeps (% double-strain amplitude, DSA) at 10 Hz and 40°C determined by dynamic mechanical thermal analysis.
The effects will dominate any overall increase in rubber stiffness.

The wash cycle of the milking machine is important, because the high temperature used increases the rate of liner swelling and accelerates stress relaxation. The dynamic relaxation rates in rubber are greater when the product is being flexed than in static relaxation rates. Static relaxation testing should be used with caution.

Farmers often report that liners take time to “bed in.” This is probably because the initial tension in the liner is high, but decays quickly; with time, the rate of decay in the tension reduces. This work did not investigate the changes that occur in the first few days after fitting, although some of the changes are likely large. To reduce the high initial tension, the liners could be run at wash temperatures for some hours.

**Effect on Milking Performance and Teats**

The effects of liner age on milking performance and teats were reported previously (Hillerton et al., 2004) and are summarized here. The same average flow rate was sustained for 2,800 milkings, slightly longer than the recommended liner life of 2,500 milkings, only becoming lower after 4,000 milkings. The most noticeable change was in the proportion of individual quarters that contained a measurable strip yield after cluster removal. This proportion increased before the reduction

---

**Figure 10.** Variation in rubber stiffness (E) along the barrel for liners of different age at 10 Hz and 40°C determined by dynamic mechanical thermal analysis on rubber with 0.5 mm of the inner rubber surface removed.

**Figure 11.** Variation in rubber stiffness (E) along the barrel of a liner (distance from mouthpiece) used for 4,000 milkings relative to a new liner (value = 100) determined by dynamic mechanical thermal analysis.

**Figure 12.** Variation of liner rubber stiffness (E) and loss modulus (E”) with temperature; strain 0.13% determined by dynamic mechanical thermal analysis.

**Figure 13.** Model of forces imposed on the teat considering the liner as a membrane; R1 = radius of the teat apex; R2 = radius of collapsed liner on teat.

Journal of Dairy Science Vol. 91 No. 6, 2008
in milk flow rate occurred. A measurable reduction in the completeness of milking had occurred before the liners were 3,000 milkings old.

The proportion of discolored teats increased such that by 5,000 milkings significantly more teats were blue or red on cluster removal. Discoloration of teats after milking can be caused by several milking factors including over-milking (Hillerton et al., 2000). There was no evidence of over-milking in this study. Good milk let down was ensured, cluster take-off was highly efficient, and strip yield increased with liner age. The effects on milking performance and teats were consistent with impaired pulsation; that is, inadequate liner wall movement. The change was gradual with liner age.

CONCLUSIONS

Liners generally fail to perform correctly when they age such that their key properties move outside normal operating limits. Some of the changes to the key properties have been determined. The basic mechanism of butterfat deposition on and into the liner was described. This resulted in uneven changes in rubber chemistry and the liner’s mechanical properties. The surface changes were localized including deposition of inorganic material, not degeneration of the surface as described previously. Liner dimension changes affect the forces on the teat. Overall, it is clear that conventional rubber testing using common swell and tensile tests were not sufficiently discriminatory to evaluate liner action. This work forms the basis for future materials development and mathematical modeling of milk flow and the forces on the teat.

ACKNOWLEDGMENTS

Grateful thanks are due to Nicola Middleton for the milking experiments, Leah King for chemical analyses, Nick Cook for advice on rubber formulations, and Derek Davies and Ian Ohnstad for useful discussions on milking systems.

REFERENCES