RESEARCH ARTICLE

Grease material properties from first principles thermodynamics

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Abstract

Thermodynamics has historically been used to derive characteristic material properties. In this study, fundamental thermodynamics is applied to grease. First-principle formulations of existing material properties—heat capacity and storage modulus—and new properties—thermal strain and stress coefficients, chemical resistance and thermo-chemical decay coefficient—are derived, some of which are experimentally determined. A new group of Maxwell relations is introduced by replacing the classical compression work PdV with the grease shearing work $V\tau d\gamma$. The physical interpretations and implications of these properties on grease behaviour and performance are presented. Experimental measurements of the derived properties are performed in accordance with the theoretical formulations. Six different grease types are studied. Obtained results are shown to conform with anticipated, observed and established grease behaviours. The proposed properties can be used in grease performance and degradation analyses, as well as grease selection for lubrication applications.

KEYWORDS

grease life, grease properties, lubricating grease, rolling bearings, thermodynamics

1 | INTRODUCTION

Most rolling bearings are lubricated with grease, a significant percentage of which run under conditions where bearing fatigue life is very long. Thus, the service life of these bearings is limited by the life of the grease. The lubricating ability of a grease is finite, mainly because of the gradual reduction of the EHL (Elasto-Hydrodynamic Lubrication) film thickness, a consequence of the loss of base oil in the raceways and the loss of "lubricity" of the base oil.[1] This decrease is caused by continuous evaporation and leakage, in combination with progressive

decrease in oil release (or bleed) rate and oxidation.[2] The bleed rate decrease is not primarily caused by a reduction in oil content in the grease, but by the change in the thickener microstructure. Oxidation impacts grease microstructure and lubricity. Oxidation also accelerates evaporation. The transformation process can be described by a change in the thermodynamic material properties. The basic principle is that the transformation of grease from state A to state B corresponds to a change in its thermodynamic potential or free energy, evaluated as a change in energy or entropy. These changes induce (and are induced by) material responses to physical (e.g., heat,

work) and chemical (oxidation) interactions. The responses to active interactions–or resistances against the transformations–yield specific grease properties, and are the focus of this paper.

It has been shown that the optimum way to measure grease degradation is by running bearings to failure, as done in R0F test rigs[3–5] or FE9.[6–8] However, these tests require long durations and only measure the total life. Reasonable test times can only be obtained by running at high temperatures. Extrapolating test results to operating conditions where actual lubrication or failure modes are different is not trivial. A purely physical model is therefore preferred. Unfortunately, such a model does not exist today. However, there are relatively simple measurements/tests that are used to qualify a grease for performance and life, many of which have been standardised. These tests measure the change in grease material properties while aging the grease. With respect to (thermo-) mechanical grease degradation, the shear stability (measured using a grease worker[9,10]) and roll stability (using a roll stability test[11]) are typical. The changes are quantified using the 'penetration depth' according to DIN ISO 2137[12] and/or yield stress.[13] For resistance to oxidation, the oxidation induction time–measured by Pressure Differential Scanning Calorimetry[14]–is used. To apply the results of these degradation tests to real life bearing operation, we need a general degradation theory for lubricating grease. The second law of thermodynamics is the basis of this: energy transformations are accompanied by material disorganisation, as prescribed by the increase in entropy principle.[15–17]

Over the past three decades, several studies using thermodynamic energies and entropies to analyse grease transformation have emerged. Earlier works[18] by Kuhn define a rheological energy density, which includes material properties and loading conditions, while more recent works by the first author[16,17] employ entropy to include temperature. Rezasoltani and Khonsari[19] correlated Prigogine's minimum entropy generation[15] with shear stress and obtained empirical models for time-based shear stress changes in grease. Including the effects of microstructural and temperature changes, Osara and Bryant[17] showed, using the Degradation-Entropy Generation (DEG) theorem, a planar transformation of grease shear stress in a three-dimensional (3D) space. The authors presented thermodynamic evaluation of grease in-operation transformation using" free" entropy generation (entropy generation based on the thermodynamic free energies, Helmholtz and Gibbs), while deriving grease material properties from thermodynamic entropy. In this study, we extend the prior work to generalised thermodynamic analysis of lubricating greases, verifying existing properties and introducing new properties—via a manipulation

of the well-known Maxwell relations—that consistently characterise changes in grease microstructure due to external and internal interactions. These can replace consistency and yield stress for adequately describing grease behaviour and degradation in the standardised tests and during real-time machinery operation. Experimental measurements on six different grease types are performed and presented herein.

2 | FORMULATIONS

When work or heat is applied onto grease, the grease changes from one state to another. This change could be *reversible*, as in the case of moderate isothermal compression of the grease. It could also be *irreversible*, wherein the grease degrades. The grease in the above-mentioned compressed state has *free energy* that is, energy that can be released (and used) to perform work. The *free energy* is therefore a potential. This is essentially different from the *internal energy U*, which is the energy that was needed to create the grease and bring it into the compressed state. A portion of the internal energy may be free energy (oxidation and mechanical shear will change the internal energy, hence part of it is free or available). While actual internal energy U cannot be measured, change dU can be measured. This change in internal energy is given by the first law of thermodynamics as

$$dU = \delta Q - \delta W + \mu dN, \tag{1}$$

where, for grease, Q is the heat into the grease (J); W is the work by the grease on its surroundings (Nm), for example, bearing balls, raceways, shoulders, and so forth; μ is the chemical potential; and N is the number of moles of active species.

The change in *free energy* can be measured via either the Gibbs or the Helmholtz free energy. The Gibbs free energy G is the free energy obtainable at constant temperature T and pressure P (or shear stress for grease):

$$G = U + PV - TS. \tag{2}$$

where V is volume and S is *entropy*. The Helmholtz free energy F is the free energy obtainable at constant temperature,

$$F = U - TS. \tag{3}$$

Here, U is still the *internal energy*, T is the temperature and S is the entropy. For internal changes in grease composition and strength without external work, the Gibbs formulation and its properties present a complete

characterisation of the grease. In the presence of external work, as in a bearing application, the Helmholtz formulation and its properties present a more convenient and complete characterisation of the grease. Similar to the earlier work by Osara and Bryant,[17] this study will use the Helmholtz formulation as it encompasses the more commonly encountered grease-in-bearing interaction.

The second law of thermodynamics states that the change in entropy dS for a reversible process that is, a process where no degradation takes place, is related to heat δQ and temperature T, according to:

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{reversible process}}. \tag{4}$$

Very slow heating or imposing a stress in the linear visco-elastic regime is quasi-reversible and will not lead to (observable) degradation, even though energy is transferred to the grease. In such cases, Equation (4) approximately applies. However, when more energy is added, degradation, a spontaneously irreversible process, will take place. This *irreversibility* is characterised by entropy generation S', a measure of grease microstructural disorganisation which, via the second law, is the difference between entropy change dS and entropy transfer $\delta Q/T$:

$$\underbrace{\delta S'}_{\text{generation}} = \underbrace{dS}_{\text{change}} - \underbrace{\frac{\delta Q}{T}}_{\text{transfer}} \geq 0. \tag{5}$$

The entropy transfer is given by heat transfer δQ into the system at temperature T. Note that while entropy generation is always positive irrespective of process direction (energy addition or depletion), entropy change dS and entropy transfer $\delta Q/T$ can be negative or positive. For a reversible (i.e., ideal, with no degradation) process, the entropy generation $\delta S' = 0$. Grease degradation can therefore be quantified using the generated entropy $\delta S'$. Combining with the first law's energy balance for grease undergoing heat transfer, mechanical shearing and chemical degradation,

$$\underbrace{dU = dU_{rev}}_{\text{int. energy change}} = \underbrace{\delta Q}_{\text{heat transfer}} - \underbrace{V\tau_w d\gamma}_{\text{shear work}} + \underbrace{\mu dN}_{\text{chem. reaction}} \tag{6}$$

yields

$$\delta S' = dS - \frac{V\tau_w d\gamma}{T} + \frac{\mu dN}{T} - \frac{dU_{\text{rev}}}{T}, \tag{7}$$

where V is the sheared volume, τ_w is the shear stress as a result of work done by the grease on its surroundings (e.g., grease resisting shear in a rheometer or grease worker) and γ is the shear strain, conjugating to define the (external) shear work by the grease $\delta W = V\tau_w d\gamma$. The subscript rev in the last term indicates the reversible (perfect, no degradation) form of the energy change.

The change in the Helmholtz free energy is equal to the maximum work (or load) obtainable from (or applicable to) the grease. Differentiating the Helmholtz free energy and combining with Equation (7) yields the Helmholtz free energy-based entropy generation.[16,17]

$$\delta S' = \left[-\frac{SdT}{T} - \frac{V\tau_w d\gamma}{T} + \frac{\mu dN}{T}\right] - \frac{dF_{\text{rev}}}{T} \tag{8}$$

derived from the grease's available useful (free) energy for external/boundary work. The first right-hand side term in Equation (8) has been termed the Microstructurothermal (MST) entropy describing the internal material response to active interactions, and is non-zero for anisothermal and transient processes, which are prevalent in grease in rolling bearings. Equation (8) is the grease-shearing form of the recently named irreversible Massieu functions,[20] and implies that dF_{rev} is a negative extremum and must be greater in magnitude than the sums of the other terms–in the square brackets–in the equation describing active processes (ideal available energy is always greater than actual available energy in any real system), to conform with the second law's requirement of $\delta S' \geq 0$. Note that $d\gamma > 0$ indicates a strain accumulation when work is done on the grease (or grease is loaded/stressed). Here, $dN < 0$ for chemical degradation such as grease oxidation at high temperatures, and can also include grease leakage and evaporation when the latter two are significant. Equation (8) includes the simultaneous dissipative effects of heat, work and compositional changes. This study focuses on the parameters that make up the microstructurothermal (MST) entropy SdT/T and their significance in grease characterisation.

3 | GREASE MATERIAL PROPERTIES

Applying Maxwell's approach and Callen's[21] derivatives reduction technique to the three independent second partial free energy derivatives of a loaded system, Osara and Bryant[17,20,22] presented generalised characteristics-defining material properties for performance and degradation analysis. Here, the formulations are adapted to grease, deriving existing and new grease material properties. The derived parameters define the response of grease to active processes. Examples of existing properties are

storage and loss moduli in the linear visco-elastic regime, specific heat capacity, viscosity and so on.

Setting $\delta S' = 0$ (no entropy generation, indicating a reversible process without degradation) in Equation (8) and rearranging gives

$$dF = -SdT - V\tau_w d\gamma + \mu dN, \qquad (9)$$

where the subscript rev has been dropped for convenience in the derivations in this section. Since true reversibility is not achievable in reality, Equation (9) approximately defines quasi-reversible (very slow) processes which are typically laboratory-controlled. Hence, it is suitable for determining material properties but does not describe active nonlinear and dissipative transformations encountered in typical rolling bearings applications, for which $\delta S' > 0$. Equation (9) indicates that the Helmholtz free energy $F = F(T, \gamma, N)$ is a function of temperature T, strain γ and amount of active species N.

In terms of the partial derivatives of its independent variables, the grease Helmholtz energy change is

$$dF = \frac{\partial F}{\partial T}dT + \frac{\partial F}{\partial \gamma}d\gamma + \frac{\partial F}{\partial N}dN. \qquad (10)$$

Direct comparison of Equations (9) and (10) suggests

$$\left.\frac{\partial F}{\partial T}\right|_{\gamma,N} = -S; \left.\frac{\partial F}{\partial \gamma}\right|_{T,N} = -V\tau_w; \left.\frac{\partial F}{\partial N}\right|_{T,\gamma} = \mu. \qquad (11)$$

In Equation (11), the subscripted variables $|_{i,j}$ are constant (i and j are any two of γ, T and N). In the following sections, partial derivatives of Equation (11) will be used to establish the material properties that constitute entropy content S for evaluating the MST energy change $-SdT$.

3.1 | Heat capacity C

The heat capacity

$$C = \delta Q/dT \qquad (12)$$

is an established material property which measures the amount of heat a component or system can absorb before experiencing a degree rise in its temperature.

Taking the partial derivative of the first equality in Equation (11) with respect to temperature yields

$$\frac{\partial^2 F}{\partial T^2} = -\frac{\partial S}{\partial T} = -\frac{C}{T} \leq 0, \qquad (13)$$

which is rearranged to give the grease heat capacity at constant low strain (or strain rate)

$$C = T\left.\frac{\partial S}{\partial T}\right|_{\gamma,N} \geq 0. \qquad (14)$$

Equation (14) implies that the grease entropy content S increases in response to increase in temperature. Note that Equation (14) indicates a constant strain and number of active molecules as entropy is increased. This is only asymptotically achievable in reality via slow heating, hence the subscripts γ and N can be dropped. In other words, in reality, when grease is heated, strain is not constant and slight evaporation could occur. Assuming the entropy rise is the result of heat addition alone, substituting Equation (4) into (14) gives the well-known form in Equation (12). As a material property, the specific heat capacity $c = C/m$, where m is mass, is used.

3.2 | Storage modulus G'

The grease storage modulus G' at constant temperature, a widely used grease rheological parameter, is defined as[23]:

$$G' = \left.\frac{\tau_y}{\gamma_y}\right|_T > 0, \qquad (15)$$

where τ_y is yield stress and γ_y the yield or cross-over strain, both marking the limit of elasticity, beyond which viscous phenomena activate. The second partial derivative of the Helmholtz free energy with respect to shear strain γ can be written in terms of G'. Taking the partial derivative of the second equality in Equation (11) with respect to strain yields

$$\left.\frac{\partial^2 F}{\partial \gamma^2}\right|_{T,N} = -V\left.\frac{\partial \tau_w}{\partial \gamma}\right|_{T,N} = VG' \geq 0. \qquad (16)$$

To accord with the conventions in mechanics and rheology wherein a positive increase in stress imposed from an external source results in a positive increase in strain, substitute $\partial \tau = -\partial \tau_w$ into Equation (16) as the shear stress imposed by the surrounding solid boundaries—for example, rheometer plates—onto the grease (recall earlier definition of τ_w as stress from grease to surroundings) and rearrange to obtain

$$G' = -\left.\frac{\partial \tau_w}{\partial \gamma}\right|_T = \left.\frac{\partial \tau}{\partial \gamma}\right|_T > 0. \qquad (17)$$

Plasticity generates heat and, hence, is anisothermal. The isothermal constraint on Equation (17) therefore imposes the elastic constraint, making Equations (17)

and (15) equivalent expressions. Note that subscript N was dropped in Equation (17) as the requirement of constant number of moles is trivial for rheological parameters such as G'.

3.3 | Thermal strain coefficient α_γ and thermal stress coefficient β

When the heat generated in or transferred into the grease is sufficient enough to raise the grease temperature—the amount of heat required determined by the grease heat capacity—the grease microstructure begins to respond to the increasing temperature (in the absence of mechanical load via shear or otherwise). Most matter will expand in response to temperature increase, the amount of which is determined by material composition via the volumetric thermal expansion coefficient $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\big|_P$, a material property. For stress-loaded systems such as grease, this property, derived from a manipulation of the Gibbs free energy partial derivatives (see Appendix A), is hereby termed the thermal strain coefficient

$$\alpha_\gamma = \frac{\partial \gamma}{\partial T}\bigg|_\tau \tag{18}$$

to indicate the essential and characteristic microstructural strain response of the grease to temperature change at constant stress. Further research into the physical mechanisms of grease thermal strain may be considered in the future. At this point, it is noted that this phenomenon involves thermally energised kinetic interactions.

The mixed second partial derivative of the Helmholtz free energy with respect to temperature T and shear strain γ defines the thermal stress coefficient β. Taking the partial derivative of the first equality in Equation (11) with respect to strain to obtain a mixed second partial Helmholtz derivative, then substituting Equations (17) and (18), with $\partial \tau = -\partial \tau_w$, gives

$$\frac{\partial^2 F}{\partial T \partial \gamma} = -\frac{\partial S}{\partial \gamma} = V\frac{\partial \tau}{\partial T} = -V\frac{\partial \gamma/\partial T}{\partial \gamma/\partial \tau} = -V\alpha_\gamma G' = -V\beta \leq 0. \tag{19}$$

Rearrange to define the grease thermal stress coefficient

$$\beta = \alpha_\gamma G' > 0, \tag{20}$$

the stress induced in the grease by a degree rise in temperature at constant low shear strain (or strain rate). Equation (19) implies that grease entropy content S must increase in response to increase in shear strain γ for

process continuity. It also implies that the stress spontaneously increases as temperature increases, according with expected behaviour.

3.4 | Isothermal chemical (or oxidation) resistance R_N

Similar to the electrical resistance, the resistance of grease to chemical reaction (typically oxidation) can be quantified. The second partial derivative of the Helmholtz free energy with respect to the number of moles (or amount) of the reactive species (or anti-oxidants) N defines the chemical (or oxidation) resistance at constant temperature R_{N_i} of the grease. Taking the partial derivative of the third equality in Equation (11) with respect to number of moles of reactive species N yields

$$\frac{\partial^2 F}{\partial N^2} = \frac{\partial \mu}{\partial N}\bigg|_{T,\gamma} = R_N \geq 0, \tag{21}$$

a measure of grease resistance to chemical reactions such as oxidation.

3.5 | Thermal decay (oxidation) coefficient λ

The impact of temperature on grease oxidation is well documented. Here, we define a grease coefficient of thermal decay (or oxidation) λ via the mixed second partial derivative of the Helmholtz free energy with respect to temperature T and amount of reactive (or anti-oxidant) species N. Taking the partial derivative of the first equality in Equation (11) with respect to number of moles of reactive species N to obtain a mixed second partial Helmholtz derivative yields

$$\frac{\partial^2 F}{\partial T \partial N} = -\frac{\partial S}{\partial N} = \frac{\partial \mu}{\partial T}\bigg|_\gamma = \lambda \geq 0, \tag{22}$$

rearranged to give the grease thermal oxidation coefficient at low constant strain

$$\lambda = \frac{\partial \mu}{\partial T}\bigg|_\gamma > 0, \tag{23}$$

a measure of decay/oxidation level (or anti-oxidant depletion) per degree rise in temperature.

Both the oxidation resistance R_N and thermal oxidation coefficient λ can be obtained from existing experimental data in the literature. Chemical degradation of grease occurs via depletion of the anti-oxidant additive. Rhee[24] developed a method to evaluate grease oxidation

by measuring the time duration for 99% of the additives to be consumed. Standardised experiments, such as the Pressure Differential Scanning Calorimetry (PDSC), are used to determine this" oxidation induction time". Thermogravimetric Analysis (TGA) is also often used to measure grease oxidation.

The exponential decay of the antioxidants depends on the reaction rate constant k given by the Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}} \tag{24}$$

where A is Arrhenius frequency factor, E_a is activation energy, R is universal gas constant and T is temperature.

The chemical potential μ for a reactive mixture[15] (such as grease) can be estimated as

$$\mu = \mu_0 + RT \ln(fx_i), \tag{25}$$

where μ_0 is reference/standard chemical potential, R is universal gas constant, T is temperature, f is activity coefficient, representing the deviation from ideal behaviour and x_i is the fractional amount of anti-oxidant additive in the grease: $x_i = \frac{N_i}{N}$ where N_i is the amount of anti-oxidant and N is the total amount of active species in the grease. From Equation (24),

$$RT = \frac{-E_a}{\ln \frac{k}{A}}. \tag{26}$$

Substitute (26) into Equation (25) to get

$$\mu - \mu_0 = \frac{-E_a}{\ln \frac{k}{A}} \ln(fx_i). \tag{27}$$

The grease oxidation resistance, Equation (21), recalling that $x_i = N_i/N$ is then computed as

$$R_N = \frac{\partial \mu}{\partial N_i} = \frac{\partial \mu}{N \partial x_i} = \frac{-E_a}{N_i \ln \frac{k}{A}}. \tag{28}$$

Values of reaction rate constant k, Arrhenius frequency factor A, activation energy E_a for various greases are available in the literature or can be obtained for any grease using the PDSC experiment. Note that values obtained from the PDSC method[14] are for pure oxygen and high pressure, and can be translated to 21% oxygen (as found in air) and ambient pressure via the method by Osara et al.[25]

Similarly, the thermal oxidation coefficient can be evaluated from Equation (25) thus:

$$\lambda = \frac{d\mu}{dT} = R \ln(fx_i) \tag{29}$$

In Equation (27), k is a function of temperature via Equation (24).

4 | ENTROPY CONTENT S

The microstructurothermal MST energy ($-SdT$, see Equation (9)), the energy dissipation observed via increase in temperature as the grease is loaded, includes the effects of internal heat generation and external source heating. The temperature change dT is driven by entropy content S. As with the free energy, the Helmholtz free entropy $S = S(T, \gamma, N)$ is a function of temperature T, shear strain γ and amount of active species N. In terms of partial derivatives with respect to its variables, the total differential of entropy is

$$dS = \frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial \gamma}d\gamma + \frac{\partial S}{\partial N}dN. \tag{30}$$

Substituting Equations (13), (19) and (22) into Equation (30) yields

$$dS = \frac{C}{T}dT + V\alpha_\gamma G'd\gamma - \lambda dN. \tag{31}$$

Dividing through by incremental time dt (to express in rate terms) and integrating from an initial reference time $t = t_0$ where $S = S_0 = 0$ for fresh grease at reference temperature $T = T_0$, shear $\gamma = 0$ and active species $N = N_0$, to the present state, the Helmholtz entropy content is

$$S = \underbrace{C \ln \frac{T}{T_0}}_{\text{thermal}} + \underbrace{V\alpha_\gamma G'\gamma}_{\text{thermo-mechanical}} - \underbrace{\lambda(N - N_0)}_{\text{chemical}} \tag{32}$$

a function of grease heat capacity C, coefficient of thermal strain α_γ, storage modulus G', thermochemical decay coefficient λ, and operational state variables: temperature T, volumetric strain γ and amount of active species N. While the state response variables (T, γ, τ, N) are directly dependent on active interaction rates (e.g., shear rates), loads and conditions (e.g., external source heating or cooling), the material properties $(C, \alpha_\gamma, G', \lambda)$ can be assumed steady over a wide range of values of the state variables, to simplify practical implementation. In reality, the material properties would vary with changing state variables, but this variation is minimal in stable operational grease, for example, grease in a bearing with no

thermal and chemical discontinuities such as phase changes and severe oxidation.

4.1 | Grease yield entropy content

Equation (32) indicates that process-dependent parameters: temperature, stress or strain, and amount of active species, are required to obtain a grease's entropy content. However, for greases in rolling bearings, these are usually unknown. For such a prevalent case, we hereby propose a simplified version of Equation (32), which can be evaluated before and after grease operation/working, based on the yield stress τ_y and yield (or cross-over) strain γ_y.

The yield stress and strain determine the transition from a reversible to irreversible state and are typically evaluated in the linear elastic response region at low applied shear rates and near-constant temperature. They are related via the storage modulus—Equation (15)—as[26,27] $\tau_y = \gamma_y G'$. If we further assume that no oxidation occurs (hence, $N - N_0 = 0$), we can substitute γ_y into Equation (32) to obtain

$$S_y = C \ln \frac{T}{T_0} + V \alpha_\gamma G' \gamma_y, \tag{33}$$

from which, via $\gamma_y = \tau_y / G'$ and dividing through by volume V, we define the yield entropy content density

$$s_y = S_y / V = \rho c \ln \frac{T}{T_0} + \alpha_\gamma \tau_y, \tag{34}$$

where ρ is grease density, c is the specific heat capacity and $T \approx T_0$. Yield entropy content density, Equation (34),

TABLE 1 Summary of the Helmholtz energy-based material properties.

Category	Property	Equation
Thermal	Heat capacity C	$\delta Q / dT$ (Equation 12)
Mechanical	Elastic shear (storage) modulus G'	$\partial \tau / \partial \gamma$ (Equation 17)
Thermo-mechanical	Thermal strain coefficient[a] α_γ	$\partial \gamma / \partial T$ (Equation 18)
Thermo-mechanical	Thermal stress coefficient $\beta = \alpha_\gamma G'$	$\partial \tau / \partial T$ (Equation 20)
Chemical	Chemical resistance R_N	$\partial \mu / \partial N$ (Equation 21)
Thermo-chemical	Thermal decay coefficient λ	$\partial \mu / \partial T$ (Equation 23)

[a]The thermal strain coefficient $\alpha_\gamma = \partial \gamma / \partial T$ is a Gibbs energy-based parameter (see Appendix A).

with units of Pa/K, can be used to compute entropy content based on material properties and yield stress. Table 1 presents a summary of the various relevant grease parameters. In subsequent sections, we shall elucidate the practical implications and connotations in Equation (34), and evaluate s_y using measured properties of six fresh greases.

5 | MATERIAL PROPERTIES AND GREASE DEGRADATION

Recall that the microstructurothermal MST energy change, $-SdT$, the first term in Equation (9), reduces the available useful (or free) energy F when temperature increases. Therefore, an increasing entropy content S would further increase the impact of this term on the available energy. However, for the same level of MST energy change, the combination of high entropy content S and low temperature increase dT is desired. To wit, if two greases show the same level of MST energy change, the grease with lower temperature rise is likely to degrade slower. This deduction obtains from Equations (33) and (34) which show that high heat capacity C and storage modulus G' (or yield stress τ_y) would yield high entropy content S_y. However, a high thermal strain coefficient α_γ could be adverse in an application in which the grease undergoes significant temperature rise. This indicates that while" high-entropy" greases could be desired in high-shear and/or high-temperature environments, they may not necessarily perform better at low shear. In addition, given the different materials—thickeners, base oils, additives—and their proportions that make up different greases, a grease's entropy content may be dominated by heat capacity, which means it may not be suitable for high shear notwithstanding its high entropy. Similar" mixed" behaviour has been reported for high-entropy alloys which, like grease, are mixtures of constituent materials that contribute to the final overall material properties. Hence, entropy content should not be interpreted as a standalone variable, but resolved into its components to better understand which properties dominate. In addition, where available, temperature changes during grease working should be combined with entropy content to obtain the MST energy and entropy which give more complete descriptions of the energy dissipation in the grease, reducing its available energy for lubrication and hence, inducing grease degradation. Table 2 summarises the conceptual meanings of the grease properties and their overall impact.

The above breakdown accords with anticipated grease behaviour and the transformation of the grease properties in response to various loads and interactions.

Experimental verification of herein discussions follows subsequently.

6 | MEASURING GREASE MATERIAL PROPERTIES

In this section, six different grease types—PE2.5C, PP3.5C, PE2C, LM3C, LM2L and LM3L—made from different thickeners and base oil types, are used to verify and demonstrate the above formulations. Table 3 lists the compositions and rheological properties of the greases studied in this work. Measuring oxidation (for chemical resistance R_N and thermal decay coefficient λ) is beyond the scope of the current study. For more on grease oxidation, please refer to.[25]

Experimental results are presented in Table 4. Plots are used to visualise the properties evaluation methods and data trends (to compare different greases).

6.1 | Heat capacity C

As a material property, the specific heat capacity—heat capacity per unit mass, $c = \delta Q/mdT$—is typically used. The measurement apparatus is the Differential Scanning Calorimeter (DSC250) by TA Instruments, with heat transfer and temperature monitoring capabilities. For this work, TA Instruments Tzero aluminium pans with hermetic lids were used, following the manufacturer-recommended 3-run heat capacity analysis.

6.1.1 | Procedure

1. Weigh the empty DSC pan.
2. Place the grease sample in the pan and weigh the pan again. Subtract the empty pan weight to obtain the weight of the grease sample. Here, about 20 mg of grease was used for each measurement.
3. Seal the pan using the Tzero press and place it in the DSC machine.
4. While recording the heat flow and temperature, slowly heat up the grease from 30 to 40°C at 0.5°C/min.

A typical result is shown in Figure 1. The heat capacity is the slope of the heat flow vs temperature curve. For statistical significance, measurements for the specific heat capacities were performed twice, with the average values recorded in Table 4.

TABLE 2 Grease material properties and their generic conceptual interpretations.

Property	Physical interpretation	Favourable when
Heat capacity C	Grease's ability to withstand heat without an increase in temperature.	High
Thermal strain/ stress coefficients α_γ, β	Impact of temperature on shear strain/stress. Mechanical response to temperature change.	Low
Storage modulus G'	Elastic (mechanical) modulus of the elastic component of the grease.	High
Isothermal chemical/ oxidation resistance R_N	Grease's resistance to oxidation or chemical conversion of reactive species in the grease.	High
Thermal decay coefficient λ	Chemical response (e.g. oxidation and/or evaporation) to temperature change.	Low

TABLE 3 Composition and rheological properties of the greases tested in this study.

Property	Grease					
	LM2L	LM3L	LM3C	PE2C	PP3.5C	PE2.5C
Consistency class	2	3	3	2	3.5	2.5
Consistency	269	225	236	280	220	250
Thickener type	Li	Li	Li	DiU	DiU	PolyU
Base oil type	Min	Min	Min	Ester	PAO	Ester
Oil viscosity at 40°C (mm^2/s)	100	100	98.9	81.6	47.6	72
Yield stress at 40°C (Pa)	34	74	68	109.5	18.7	78
Density (kg/m^3)	900	900	900	960	850	960
Churning temperature (°C)	110	125	110	110	125	110
Churning behaviour[28]	Peak	Plateau	Peak	Peak	Plateau	Peak

TABLE 4 Measured properties of all six greases studied.

Grease	c (kJ/kg K)	G' (kPa)	α_γ (1/K)	β (kPa/K)
PP3.5C	2.215	42.29	0.054	2.318
PE2.5C	1.947	69.97	0.042	2.913
PE2C	2.026	24.46	0.092	2.277
LM3C	2.088	85.59	0.044	3.793
LM2L	2.566	15.56	0.107	1.677
LM3L	2.170	35.52	0.048	1.677

FIGURE 2 Measured storage modulus over time, the average of which is used in this study.

FIGURE 1 Heat flow versus temperature, the slope of which gives the heat capacity of the grease sample.

6.2 | Storage modulus G'

The storage modulus G' is a well-established material property. Descriptions can be found in rheology textbooks, such as Barnes et al.[29] In grease analysis, the storage modulus is typically obtained from oscillatory rheometric measurements. Here, we used TA Instruments' rheometer DHR2 with plate-plate geometry.

6.2.1 | Procedure

1. Load 0.5 g of grease onto the lower rheometer plate. Trim off the excess grease using a micro spatula after lowering the upper plate down to a gap of 0.525 mm.
2. Pre-shear the grease sample at a rate of 10 1/s for 30 s as prescribed in.[30]
3. Allow the grease to settle for 30 mins at the test temperature of 40°C.
4. Apply oscillatory shear stress of 10 Pa at a frequency of 1 Hz while recording the storage modulus for about 2 h.

Figure 2 shows that the storage modulus G' changes in time due to the thixotropic character of grease (the

thickener fibres slowly orient themselves in the direction of shear). Here, we used the time-average value, recorded in Table 4.

6.3 | Thermal strain coefficient α_γ

The measurement of $\alpha_\gamma = \left.\frac{\partial \gamma}{\partial T}\right|_\tau$ is performed in a TA Instruments' heated rheometer DHR2 with plate-plate geometry in stress-controlled mode at very low shear stress. Continuous shear stress induces wall slip.[23] Therefore, oscillatory shear stress was used.

6.3.1 | Procedure

1. Load 0.5 g of grease onto the lower rheometer plate. Trim off the excess grease using a micro spatula after lowering the upper plate down to a gap of 0.525 mm.
2. Pre-shear the grease sample at a rate of 100 1/s for 60 s as prescribed in.[30]
3. Allow the grease to settle for 30 min at the test start temperature of 40°C.
4. Apply low oscillatory shear stress of 0.1 Pa at a frequency of 1 Hz, while slowly heating the grease up at a rate of 0.5 or 1°C/min from 40°C to about 100°C. This is well below the High Temperature Performance Limit of all rolling bearing greases.[23]

α_γ is the slope of the plot of accumulated strain

$$\gamma = \int_0^t \dot{\gamma} dt \qquad (35)$$

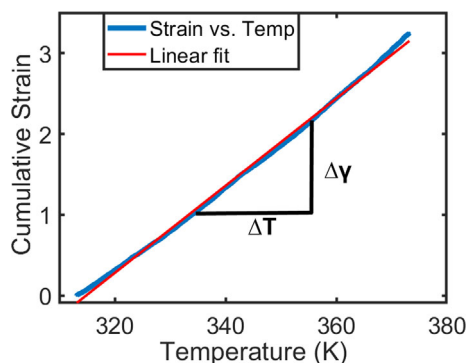versus temperature, see Figure 3. Values obtained for all the greases are compiled in Table 4.

FIGURE 3 Cumulative strain versus temperature, the slope of which yields the thermal strain coefficient.

6.4 | Thermal stress coefficient β

The thermal stress coefficient is measured similar to the thermal strain coefficient, but in strain-controlled mode at very low shear strain. In this study, β was not measured but simply obtained as $\alpha_\gamma G'$, the product of the thermal strain coefficient and the storage modulus.

6.5 | Yield stress

The yield stress is needed to calculate the grease yield entropy content, Equation (34). Like the storage modulus, the yield stress is an established rheological property. The measurement procedure, performed on a TA Instruments' rheometer DHR2 with plate- plate geometry, can be found in[26] where the yield stress is described as the stress at which the stress–strain relation deviates from linearity.

6.5.1 | Procedure

1. Load 0.5 g of grease onto the lower rheometer plate. Trim off the excess grease using a micro spatula after lowering the upper plate down to a gap of 0.525 mm.

2. Pre-shear the grease sample at a rate of 100 1/s for 60 s as prescribed in Reference [30].

3. Allow the grease to settle for 30 min at the test temperature of 40°C.

4. Apply oscillatory shear strain sweep in the range of 0.001%–1000% at a frequency of 1 Hz on all samples using the strain-controlled rheometer. The yield stress is the point where the stress deviates from linear response to strain by 0.5%.

Yield stress values for the studied greases are shown in Table 5.

TABLE 5 Grease yield stress τ_y and yield entropy content density s_y for the six greases.

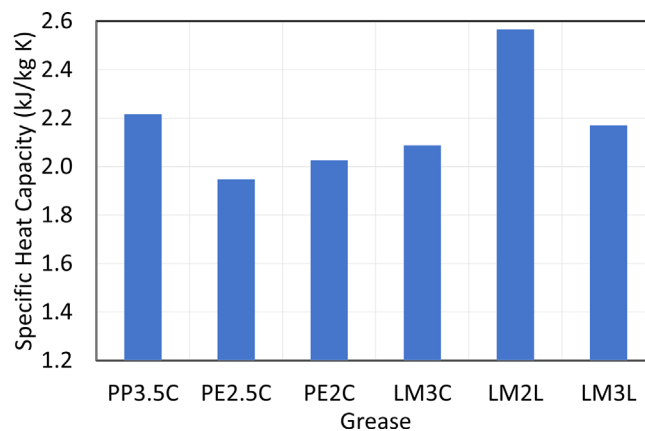| Grease	τ_y (Pa)	s_y (J/m^3/K)
PP3.5C	18.7	1.61
PE2.5C	78.0	3.86
PE2C	109.5	10.75
LM3C	68.0	3.60
LM2L	34.0	4.38
LM3L	74.0	4.15

FIGURE 4 Specific heat capacity c of all six greases.

7 | COMPARING DIFFERENT GREASES

This section interprets and discusses the values of the various properties obtained for the six greases studied.

7.1 | Specific heat capacity c

The specific heat capacities are plotted in Figure 4. Of the six greases, LM2L has the highest specific heat capacity while PE2.5C has the lowest. Overall, the specific heat capacities of all the greases are comparable.

7.2 | Storage or elastic shear modulus G'

Values of storage modulus G' are plotted in Figure 5. LM3C has the highest G' of 85.59 kPa while LM2L has the lowest value of 15.56 kPa. See Table 4.

7.3 | Thermal strain coefficient α_γ

Figure 6 plots the thermal strain coefficients α_γ of the various greases. PE2.5C has the lowest α_γ of 0.042 1/K,
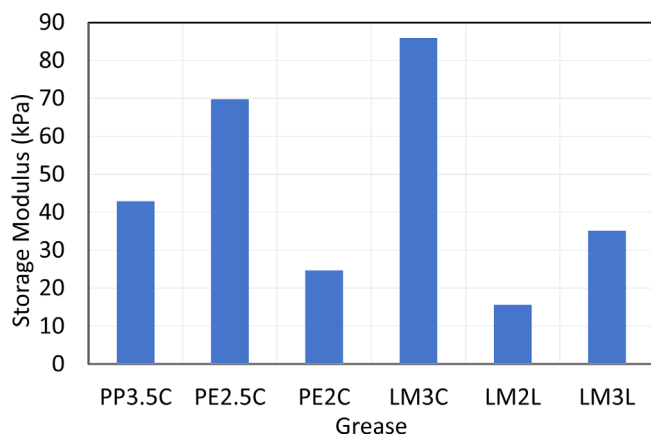
FIGURE 5 Storage modulus G' of the six greases.
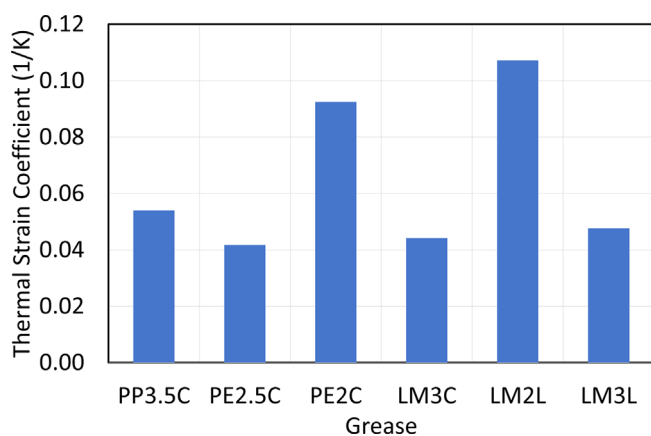
FIGURE 6 Thermal strain coefficient α_γ of all six greases.
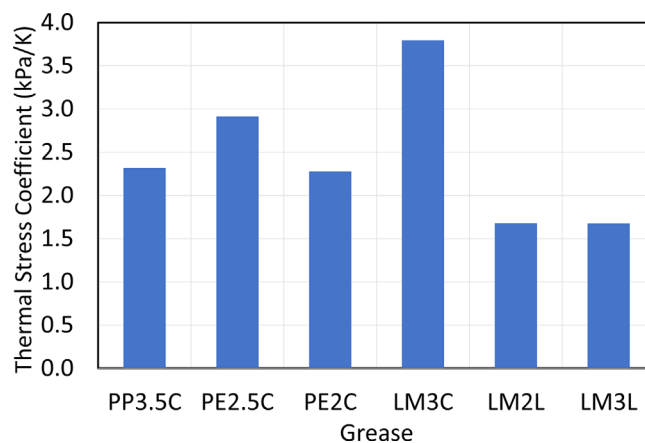

FIGURE 7 Thermal stress coefficient $\beta = \alpha_\gamma G'$ for all six greases.
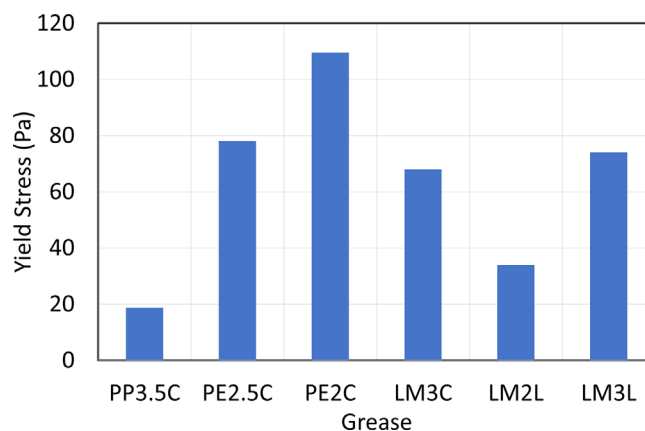
FIGURE 8 Measured yield stress τ_y values.

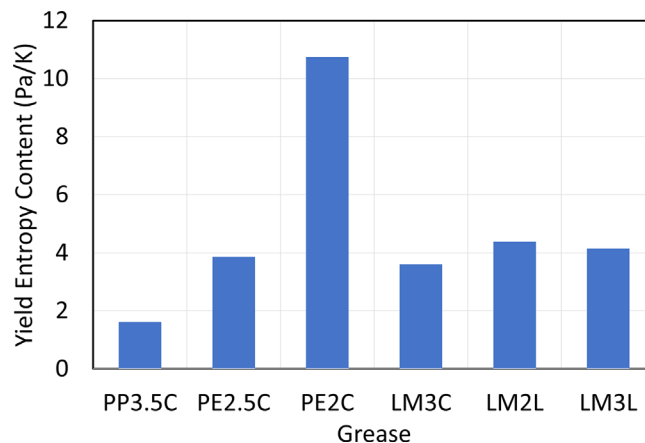

FIGURE 9 Yield entropy content density s_y values.

with LM3C a close second a 0.044 1/K, while LM2L has the highest α_γ of 0.107 1/K.

7.4 | Thermal stress coefficient β

With the thermal stress coefficient obtained as the product of the thermal strain coefficient and the storage modulus, $\beta = \alpha_\gamma G'$, values of thermal stress coefficient β show the combined effects of its constituent grease properties (α_γ and G'). A high G' can be the result of a high β, a low α_γ, or both. Figure 7 plots thermal stress coefficients of the various greases. Both LM2L and LM3L have the lowest value of 1.677 Pa/K, and LM3C the highest value of 3.793 Pa/K.

7.5 | Yield stress τ_y and yield entropy content density s_y

Measured yield stresses τ_y of the greases are presented in Figure 8 and Table 5. PE2C has the highest τ_y of 109.5 Pa and PP3.5C the lowest τ_y of 18.7 Pa.

Given this study focuses on grease material properties, we exclude the contribution of operating conditions (over time) in our definition and evaluation of the yield entropy content density s_y, hence $T \approx T_0$. Substituting the yield stress τ_y into Equation (34) then gives the yield

entropy content density s_y results plotted in Figure 9 and presented in the third column of Table 5. Of all six greases, PP3.5C has the lowest value of 1.61 J/m^3/K and PE2C has the highest value of 10.75 J/m^3/K.

With $T \approx T_0$, the *thermal* contribution $\rho c \ln \frac{T}{T_0}$ to yield entropy content s_y is dominated by density ρ which is several orders of magnitude higher than specific heat capacity c.

While the yield stress τ_y measures only mechanical response to load, yield entropy content density s_y measures a combination of thermal, thermo-mechanical, mechanical—and chemical, when applicable—responses to load as expressed in Equation (34).

8 | DISCUSSION, SUMMARY AND CONCLUSION

Lubricating greases should supply the EHL contacts in rolling bearings primarily with oil—via a process called bleed—as steadily as possible throughout the operation of the bearing. The bleed rate—the balance between a driving and retaining pressure—is given by the base oil-thickener affinity and the microstructure of the grease. It is desired that this microstructure be maintained throughout the life of the grease. In other words, grease degradation should be minimal. At low-to-medium temperatures, grease degradation is thermo-mechanical via shear onto the grease and heat generation/transfer. At high temperatures, chemical degradation occurs. Grease degradation process can be described using thermodynamics. The basis of this description is the free energy, a potential that is reduced by work, heat and material transfer/chemical reaction. This article described the change in grease free energy using the Helmholtz fundamental relation:

$$dF = -SdT - V\tau_w d\gamma + \mu dN, \quad (36)$$

which shows that the free energy change is a function of the grease properties that define the entropy content S (in the first right-hand side term in Equation (36)); the operating conditions, for example, temperature T, levels of stress τ_w and strain γ (which, including grease volume V, define the rheological work, the second right-hand side term); and the compositional changes defined by the chemical potential μ and number of moles of active/reactive constituents N (the last term). The entropy content is

$$S = C \ln \frac{T}{T_0} + V\alpha G'\gamma - \lambda N, \quad (37)$$

a function of heat capacity, temperature, rheological properties and chemical potential. For the low-to-medium temperature applications, where oxidation is considered minimal, this was simplified into a *yield entropy content density s_y* for which the parameters can be easily measured:

$$s_y = \rho c \ln \frac{T}{T_0} + \alpha_\gamma \tau_y, \quad (38)$$

where ρ is the grease density, c is the specific heat capacity, α_γ the thermal strain coefficient and τ_y the yield stress. Physical interpretations of the (old and new) grease properties were presented, including procedures for evaluating them.

Fresh samples of six different greases were studied, showing measured property values that accord with expected and observed behaviour, thereby demonstrating the universal applicability and validity of the thermodynamics-based properties in characterising grease transformations.

AUTHOR CONTRIBUTIONS

Conceptualization, design and data analysis were performed by Jude Osara. Data collection was performed by Sathwik Chatra. The first draft of the manuscript was written by all authors, who also commented on all versions of the manuscript. All authors read and approved the final manuscript.

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CONFLICT OF INTEREST STATEMENT

The authors have no relevant financial or non-financial interests to disclose.

DATA AVAILABILITY STATEMENT

Research data are not shared.

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APPENDIX A

A.1 | Thermal strain coefficient α_γ

Here, we derive the thermal strain coefficient given in Equation (18) from a manipulation of the Gibbs free energy.

Transforming the Gibbs free energy, Equation (2), yields the fundamental relation (recalling that $\partial \tau_w = -\partial \tau$)

$$dG = -SdT - V\gamma d\tau + \mu dN. \tag{A1}$$

Equation (A1) indicates that the Gibbs free energy $G = G(T, \tau, N)$ is a function of temperature T, shear stress τ and amount of active species N. In terms of the partial derivatives of its independent variables, the grease Gibbs energy change is

$$dG = \frac{\partial G}{\partial T}dT + \frac{\partial G}{\partial \tau}d\tau + \frac{\partial G}{\partial N}dN. \tag{A2}$$

Direct comparison of Equations (A1) and (A2) suggests

$$\left.\frac{\partial G}{\partial T}\right|_{\tau,N} = -S; \left.\frac{\partial G}{\partial \tau}\right|_{T,N} = -V\gamma; \left.\frac{\partial G}{\partial N}\right|_{T,\tau} = \mu. \tag{A3}$$

The mixed second partial derivative of the Gibbs free energy with respect to temperature T and shear stress τ defines the thermal strain coefficient α_γ of the grease obtained via the partial derivative of the first equality in Equation (A3) with respect to τ (which is equal to the

partial derivative of the second equality in Equation (A3) with respect to T):

$$\frac{\partial^2 G}{\partial T \partial \tau} = -\frac{\partial S}{\partial \tau} = -V\frac{\partial \gamma}{\partial T} = -V\alpha_\gamma \leq 0, \qquad (A4)$$

which is rearranged to yield the thermal strain coefficient

$$\alpha_\gamma = \frac{\partial \gamma}{\partial T} > 0, \qquad (A5)$$

defined as the amount of strain induced in the grease by an increase in temperature at constant low stress. Equation (A4) implies that grease entropy content S must increase in response to increase in stress τ for process continuity and grease stability. It also implies that the strain γ in the grease must spontaneously increase with increase in temperature to ensure stability.

APPENDIX B

Plots of measured property values before and after aging in the grease worker are presented below in Figures B1–B6. 7200 strokes were applied to each grease at its churning temperature; see Table 3 for churning temperatures. In the plots, fresh greases are in blue and aged greases in orange.
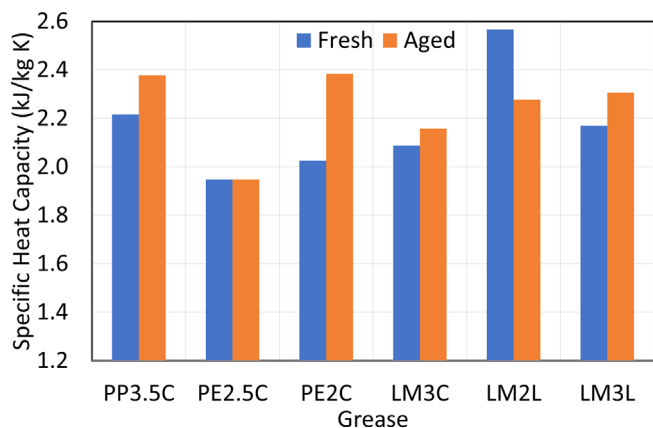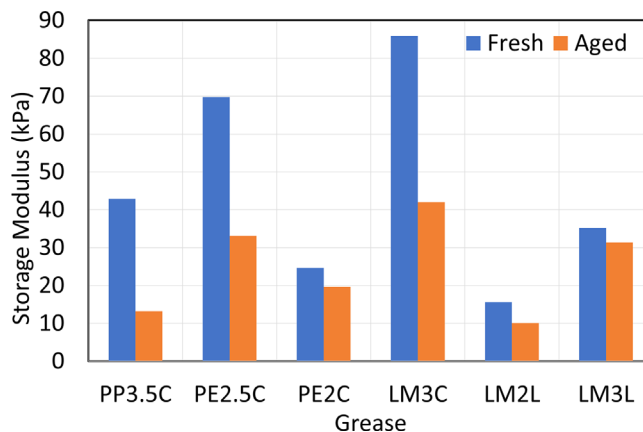

FIGURE B2 Storage modulus G' for the fresh (blue) and aged (orange) greases.

FIGURE B3 Thermal strain coefficient α_γ for the fresh (blue) and aged (orange) greases.
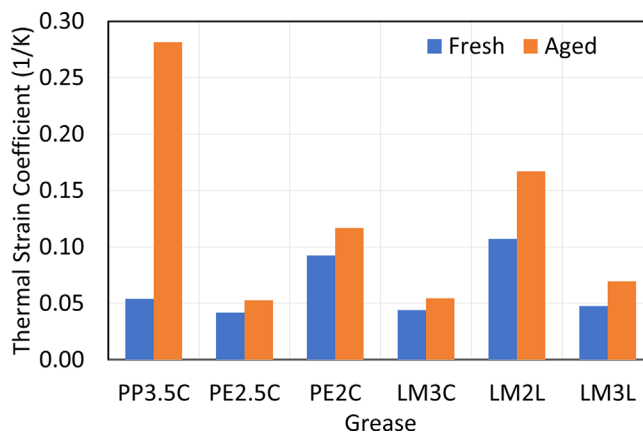

FIGURE B1 Specific heat capacity c for the fresh (blue) and aged (orange) greases.
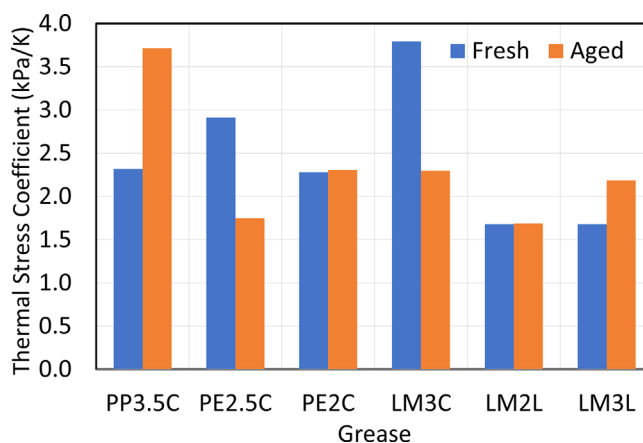

FIGURE B4 Thermal stress coefficient $\beta = \alpha_\gamma G'$ for the fresh (blue) and aged (orange) greases.
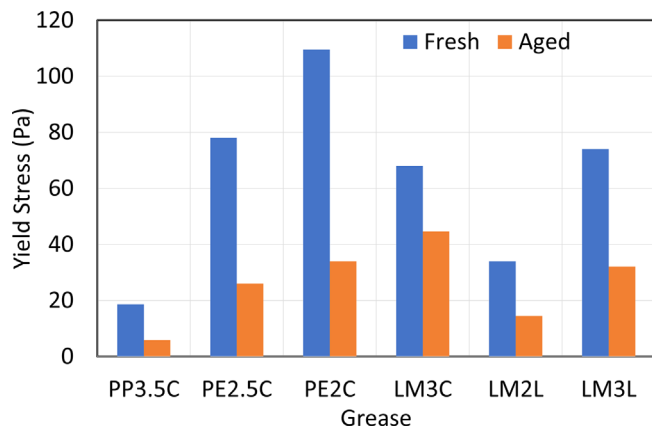
FIGURE B5   Measured yield stress τ_y values for the six fresh (blue) and aged (orange) greases.
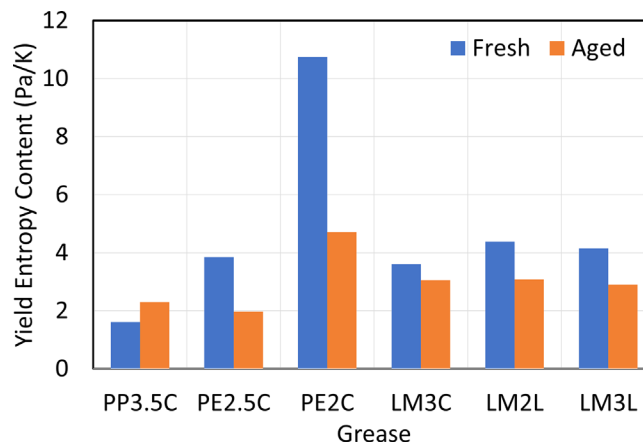
FIGURE B6   Yield entropy content density s_y values for the various fresh (blue) and aged (orange) greases.