

Kinetic analysis and modelling of the ageing process for Kraft paper aged in natural ester dielectric fluid

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Abstract: This paper describes briefly various different degradation kinetic models of cellulose and paper insulation in the literature and presents a new cumulative degradation kinetic model for loss of tensile strength of cellulose and paper insulation. Applying this model, the predicted loss of tensile strength has been compared with accelerated ageing data of Kraft paper obtained from the publications of McShane et al. of Cooper Power System. McShane et al. conducted the ageing of Kraft paper in both mineral oil and natural ester in sealed tube at elevated temperatures. It is shown that the cumulative degradation kinetic model for loss of tensile strength of paper insulation can give an excellent description of the ageing process of Kraft paper insulation in both natural ester dielectric fluid and mineral transformer oil.

Introduction

In recent years there has been increasing interests in biodegradable dielectric fluids as alternatives to insulating mineral oil. McShane et al. [1-3] have reported a comparative experimental investigation on the ageing of Kraft paper insulation in both natural (vegetable oil) ester dielectric fluid and conventional mineral transformer oil using sealed tube accelerated ageing technique. The results show that, under identical conditions, Kraft paper insulation ages significantly slower in natural ester fluid than in mineral oil. Multiple and interrelated mechanisms have been proposed to explain the increase in paper insulation life [1], however, there has been little discussion on the kinetics of ageing process of Kraft paper. On the other hand, there is not yet an entirely reliable kinetic rate equation model for the ageing of cellulose although existing kinetic models have considerably improved our understanding of the phenomena at play.

In this paper, we first examine various kinetic models of cellulose degradation in the literature, then develop a new cumulative degradation kinetic model for loss of tensile strength of paper insulation, and finally test the validity of the new model by comparing with accelerated ageing data of McShane et al. [1-3].

Overview of degradation kinetic models of cellulose and paper insulation

Extensive efforts at modeling the degradation processes of cellulose and paper have resulted in the development of a number of kinetic rate equation models. The complexity of the phenomena which arise during the (thermal) ageing of the various substances can be rarely described by a single reaction kinetic equation. As a consequence, sophisticated models with several unknown parameters have to be developed. The determination of the unknown parameters and the validation of the models require the simultaneous evaluation of the whole series of experiments. A model and its parameters can be accepted only if a reasonable fit can be achieved by several experiments carried out at different experimental conditions.

One of the earliest Kraft paper insulation degradation kinetic approaches was probably the empirical relationship developed by researchers at Weidmann® [4] for loss of tensile strength (TS) of paper insulation as

$$TS = TS_0 e^{-C_{TS}(T)t} \quad (1)$$

Where TS_0 and TS are the tensile strength values before and after an ageing time respectively, $C_{TS}(T)$ is the coefficient of ageing and t is the duration of ageing. Equation (1) has the advantage of requiring fewer data points, but can only be applied to long-term ageing.

Emsley and Stevens [5] reported that the majority of accelerated ageing data of cellulose and paper in the literature could be fitted by an Ekenstam relationship derived for a first-order chain-scission process as

$$\frac{1}{DP} - \frac{1}{DP_0} = kt \quad (2)$$

Where DP_0 and DP are the number average degree of polymerization of cellulose in the time of 0 and t respectively, and k is the reaction rate constant. However, Emsley and Heywood et al. [6] have subsequently reported that (2) is fairly invalid when the DP approaches the critical value of about 200, the so-called leveling-off degree of polymerization (LODP) in the literature; they then introduced an additional assumption that k in (1) is not a constant but decreases with ageing time, and finally gave a model as

$$\frac{1}{DP} - \frac{1}{DP_0} = \frac{k_{10}}{k_2} [1 - \exp(-k_2 t)] \quad (3)$$

where k_{10} is the initial value of k_1 , and k_{10} and k_2 are constants. In order to derive a relationship for loss of tensile strength with time, Emsley and Heywood et al. [6] made a further assumption that the relationship of tensile strength to the degree of polymerization of aged Kraft paper could be described by the following differential equation

$$\frac{dTS}{dt} = -k_1 k_3 + k_4 \cdot DP \quad (4)$$

Combining (3) and (4) gives

$$TS - TS_0 = K_1 e^{-k_2 t} + K_2 \left[\ln(e^{k_2 t} - K_3) \right] - K_4 \quad (5)$$

Where K_1, K_2, K_3 and K_4 are constants, which incorporate the fundamental constants k_{10}, k_2, k_3, k_4 and DP_0 . Note that equation (5) was initially developed using air-aged results [6] and has been applied equally to oil-aged paper [7]. One difficulty with this model is the relative complexity of tensile strength loss equation.

Very recently, Ding and Wang [8] have presented a new model of ageing of cellulose and paper insulation, using the concept of degradation accumulation. According to this model, the fractional loss in degree of polymerization, from an initial value of DP_0 to DP at time t can be determined by

$$1 - \frac{DP}{DP_0} = \frac{k_0}{k} \left(1 - e^{-kt} \right) \quad (6)$$

The left side of (6) represents the degree of degradation that is a cumulative quantity, k is the reaction rate constant and k_0 is a rate coefficient of paper ageing. Equation (6) has been applied to explain well the accelerated ageing data of Kraft paper by several experiments carried out at different conditions over a wide ageing temperature range from 60°C to 160°C. In this paper, we will continue to use the similar concepts to develop a cumulative degradation kinetic model for loss of tensile strength of paper insulation.

A cumulative degradation kinetic model for loss of tensile strength of paper insulation

Note that there is a well-documented connection between loss of tensile strength and the severity of degradation conditions of cellulose based paper insulation [9, 10]. IEEE Std C57.92 [9] has been using tensile strength retention values of paper insulation as the end of transformer insulation life. The concept of degradation accumulation may therefore be used as a

more suitable approach to predict the remaining tensile strength and lifetime of cellulose and paper insulation.

In the present approach, cumulative degradation parameter ω at time t is defined as the fractional loss in tensile strength, from an initial value of the tensile strength TS_0 to the current tensile strength TS ,

$$\omega \equiv \frac{TS_0 - TS}{TS_0} = 1 - \frac{TS}{TS_0} \quad (7)$$

which results in a value with a theoretical range of 0 to 1 and grows monotonically. From the definition of (7) it is clear that the cumulative degradation ω at time t depends on the choice of the initial TS_0 . The degree of degradation is 0 for new paper and 0.75 for 25% retained tensile strength of paper insulation.

On the other hand, remember that the main feature of tensile strength loss of cellulose and paper insulation is the *successive* chain scission in cellulose fibre. Accelerated ageing of pure cellulose papers in air [11] and Kraft papers in transformer oil [7] have demonstrated that the loss of tensile strength during ageing is due to a decrease in fibre strength and not bond strength loss; and the decrease in fibre strength is due to depolymerization of the cellulose caused by acid-catalysed hydrolysis. Hence, we postulate a differential equation describing the degradation rate according to

$$\frac{d\omega}{dt} \equiv \omega_0 n, \quad \omega(t=0) = 0 \quad (8)$$

The above differential equation relates the rate of change of the cumulative degradation parameter (ω) with time to the number of unbroken bonds available (n) times the rate coefficient ω_0 . The initial condition implies that paper insulation has undergone no previous degradation.

In the literature, the kinetic approach for the random degradation of linear polymers generally assumes that the depolymerization process is a first-order reaction. If n is the number of unbroken bonds remaining in the polymer at time t , k is the reaction rate constant, then the rate of scission, dn/dt , can be determined by

$$-\frac{dn}{dt} = kn \quad (9)$$

Assuming the total number of bonds at the initial is n_0 and integrating (9) gives

$$n = n_0 e^{-kt} \quad (10)$$

Substituting (10) into (8) finally gives

$$\frac{d\omega}{dt} = \omega_0 n_0 e^{-kt} \equiv k_0 e^{-kt} \quad (11)$$

Here $k_0 \equiv \omega_0 n_0$ is a degradation rate coefficient that incorporates the fundamental constants ω_0 and n_0 . Integrating (11) we have

$$1 - \frac{TS}{TS_0} = \frac{k_0}{k} (1 - e^{-kt}) \quad (12)$$

Or, written as a different expression as

$$\frac{TS}{TS_0} = \left(1 - \frac{k_0}{k}\right) + \frac{k_0}{k} e^{-kt} \quad (13)$$

This is the kinetic equation for loss of tensile strength of cellulose and paper insulation derived from the concept of degradation accumulation. The following section of the paper will discuss how well the new model fits with the data of Kraft paper aged in both natural ester dielectric fluid and mineral transformer oil.

Model application and comparison with data of Kraft paper aged in natural ester and in mineral transformer oil

Figure 1 shows the plot of the retained tensile strength versus accelerated ageing time for results of Kraft paper sealed tube aged at 150°C in mineral oil and natural ester obtained from [2] along with the corresponding regression fit made with equations (1) and (13). Figures 2 and 3 show plots of the retained tensile strength versus accelerated ageing time for results of thermally upgraded Kraft paper sealed tube aged at 160°C and 170°C in mineral oil and natural ester obtained from [3] along with the corresponding regression fit made with (1) and (13). All regression analyses and graphing were performed using Origin 6.0 software and a minimum chi-square (χ^2) algorithm to obtain best-fit parameters for (1) and (13). All ageing parameters fitting (1) and (13) to the corresponding data of Figures 1-3 as well as the statistical error parameters χ^2 and R^2 are summarized in Tables 1 and 2.

Clearly, Figures 1-3 show that the Weidmann approach (1) deviates from the data of accelerated ageing and is fairly invalid for predicting paper insulation ageing performance in natural ester. It is important to note that the excellent agreement observed on Figures 1-3 were obtained according to the current model (13) with two ageing parameters, which are much less than five parameters in Emsley and Heywood et al.'s model (5). Emsley et al.'s model is not used in the present comparison due to insufficient data available to obtain a solution.

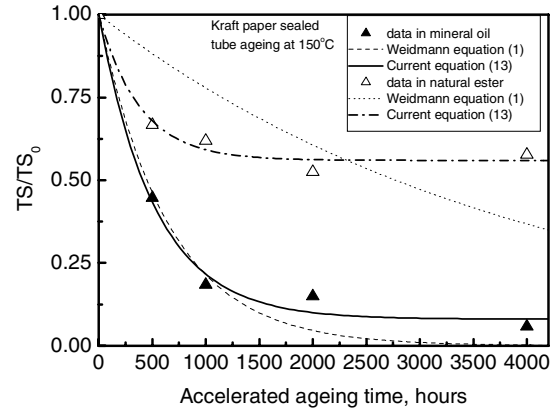


Figure 1: A plot of TS/TS_0 versus ageing time: Experimental data [2] of Kraft paper at 150°C and regression analysis fit of (1) and (13).

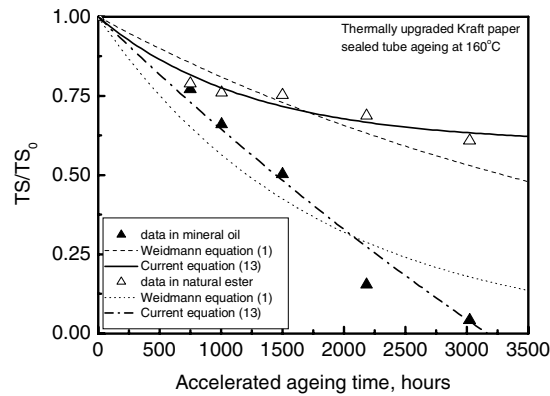


Figure 2: A plot of TS/TS_0 versus ageing time: Experimental data [3] of thermally upgraded Kraft paper at 160°C and regression analysis fit of (1) and (13).

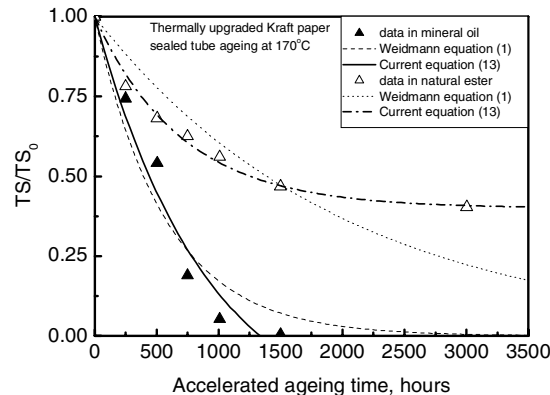


Figure 3: A plot of TS/TS_0 versus ageing time: Experimental data [3] of thermally upgraded Kraft paper at 170°C and regression analysis fit of (1) and (13).

Table 1: Ageing parameters for fitting equation (13) to the retained TS vs. ageing time data in mineral oil and in natural ester as shown in Figures 1-3.

Temperature	In mineral oil	In natural ester
150°C	$k = 0.00191 \text{ hrs}^{-1}$ $k_0 = 0.00176 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.00104$ $\text{R}^2 = 0.99288$	$k = 0.00261 \text{ hrs}^{-1}$ $k_0 = 0.00115 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.00062$ $\text{R}^2 = 0.98238$
160°C	$k = 0.00011 \text{ hrs}^{-1}$ $k_0 = 0.00037 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.00296$ $\text{R}^2 = 0.97805$	$k = 0.00082 \text{ hrs}^{-1}$ $k_0 = 0.00033 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.00067$ $\text{R}^2 = 0.96129$
170°C	$k = 0.0011 \text{ hrs}^{-1}$ $k_0 = 0.00143 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.00549$ $\text{R}^2 = 0.9664$	$k = 0.00143 \text{ hrs}^{-1}$ $k_0 = 0.00086 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.00038$ $\text{R}^2 = 0.99058$

Table 2: Ageing parameters for fitting equation (1) to the retained TS vs. ageing time data as shown in Figures 1-3.

Temperature	In mineral oil	In natural ester
150°C	$C_{\text{TS}}(T) = 0.00154 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.00376$ $\text{R}^2 = 0.97423$	$C_{\text{TS}}(T) = 0.00025 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.03046$ $\text{R}^2 = 0.1342$
160°C	$C_{\text{TS}}(T) = 0.00057 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.01313$ $\text{R}^2 = 0.90274$	$C_{\text{TS}}(T) = 0.00021 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.00393$ $\text{R}^2 = 0.80149$
170°C	$C_{\text{TS}}(T) = 0.00176 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.01019$ $\text{R}^2 = 0.93761$	$C_{\text{TS}}(T) = 0.0005 \text{ hrs}^{-1}$ $\text{Chi}^2 = 0.00961$ $\text{R}^2 = 0.76288$

Conclusions

1. A brief overview of various kinetic models of cellulose and paper insulation has been presented and the emphasis is focused on that a model and its parameters can be accepted only if a reasonable fit can be achieved with several experiments carried out at different experimental conditions.
2. A new cumulative degradation kinetic model for loss of tensile strength of paper insulation used in power transformers has been developed.
3. The model has been applied to predict the ageing process and compared with the accelerated aged data of Kraft paper sealed tube aged at 150°C and thermally upgraded Kraft paper sealed tube aged at 160°C and 170°C in mineral oil and in natural ester, obtained from the publications of McShane et al. in Cooper Power System. The results indicate that the model gives an excellent description of the ageing process for Kraft paper insulation aged in natural ester dielectric fluid and in conventional mineral transformer oil.

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