

Author response to the comments by P. Calvini regarding the article “On the degradation evolution equations of cellulose” by H.-Z. Ding and Z. D. Wang

H.-Z. Ding · Z. D. Wang

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The viewpoints of Ding and Wang (2007) and Calvini (2007) can be briefly summarized. The article by Ding & Wang seeks to develop the degradation evolution equations of cellulose that will closely track experimental results over a long-time period under practical operating conditions; while Calvini seeks to develop a kinetic model based on purely theoretical grounds of degradation of linear polymers without any reference to experimental results. In brief, Ding & Wang wish to modify the kinetic theory of degradation of linear polymers to fit experimental results of cellulose degradation while Calvini appears to aim for the converse. Calvini has asserted that there is nothing new in the kinetic model developed in the paper and even suggests that the degradation evolution equations are incorrect. This is manifestly untrue, for in the paper it is quite clear that the degradation evolution equations developed track exceedingly closely the experimental results. Consequently, this assertion by Calvini is totally unsubstantiated.

There then follows the comment that “the new degradation evolution equation of cellulose proposed by Ding and Wang is a worrying exhumation of old

misleading kinetic statements”. This again is far from the truth. The new degradation evolution equation developed is certainly based on fundamental kinetic theory of polymer degradation, which is then developed to fully represent experimental results over an extended time period. This it does with great accuracy. Theory and practicality are brought together and it is hoped will indeed form the basis for further developments in the kinetic theory of cellulose degradation.

The following notes deal in detail with Calvini’s comments and it will be seen further reinforce the replies to Calvini’s comments just given.

The central issue

The central point at issue is about the characterization of cellulose degradation. In brief, Ding & Wang propose in the paper that the degradation of cellulose can be best characterized in terms of the percentage DP loss (i.e., ω_{DP} function) and the degradation evolution equation of cellulose can be best described by a first-order kinetic equation as

$$\omega_{DP} \equiv 1 - \frac{DP}{DP_0} = \omega_{DP}^* (1 - e^{-k_{DP}t}) \quad (1)$$

where DP_0 and DP are the degree of polymerization before and after the degradation, k_{DP} is the DP degradation reaction rate constant and ω_{DP}^* can be determined by introducing the constraint

H.-Z. Ding (✉) · Z. D. Wang
School of Electrical and Electronic Engineering, The
University of Manchester, P O Box 88, Sackville Street,
Manchester M60 1QD, UK
e-mail: hongzhi.ding@manchester.ac.uk

condition: $\omega_{DP}(t = t_f) = 1$, where t_f is the time to failure. However, Calvini appears to think that the degradation of cellulose must be characterized by a function of the reciprocal of DP and the rate of cellulose degradation can be one of the following four equations:

$$\frac{1}{DP} - \frac{1}{DP_0} = \left(1 - \frac{1}{DP_0}\right)(1 - e^{-kt}) \quad (2)$$

$$\frac{DP_0}{DP} - 1 = (DP_0 - 1)(1 - e^{-kt}) \quad (3)$$

$$\frac{1}{DP} - \frac{1}{DP_0} = \left(\frac{1}{LODP} - \frac{1}{DP_0}\right)(1 - e^{-kt}) \quad (4)$$

$$\frac{DP_0}{DP} - 1 = \left(\frac{DP_0}{LODP} - 1\right)(1 - e^{-kt}) \quad (5)$$

Calvini claims that Eqs. 2 and 3 “correspond to the first order kinetics settled in the literature and satisfy the *asymptotic* condition $DP = 1$ ”; Eqs. 4 and 5 “take into account the *asymptotic limit* due to levelling-off degree of polymerization (LODP)” and “fulfil the dimensional analysis”.

The Calvini approach: real or spurious?

At first sight the Calvini approach appears reasonable, because he not only claims that his approach recalls “the ground of the kinetic theory of polymer degradation”, but also claims that in the first-order kinetics his approach obtains the equation

$$\frac{d(DP)}{dt} = -k(DP^2 - DP) \quad (6)$$

and “yields Eq. 3 after integration”. However, further study will find that there is essential difference between the Calvini approach and the classical kinetic theory of degradation of linear polymers, and the Calvini approach together with his Eqs. 2–5 are certainly questionable.

There are *two* reasons why we think the contribution found by Calvini is spurious. Firstly, seeing and thinking mathematically, the integrated form of Eq. 6 is the well-known Ekenstam equation in the form of

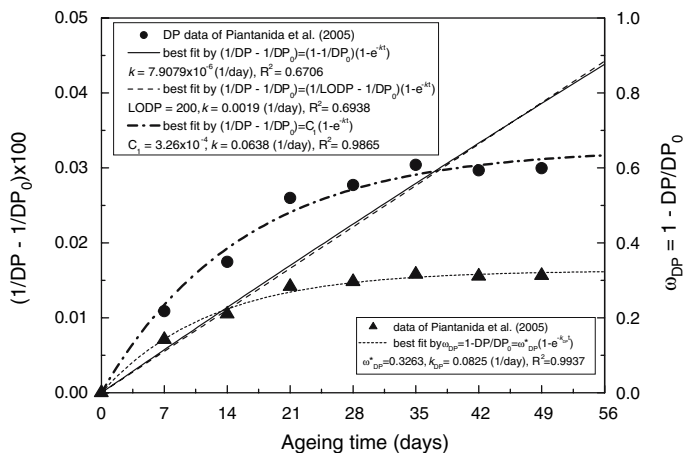
$$\ln\left(1 - \frac{1}{DP_0}\right) - \ln\left(1 - \frac{1}{DP}\right) = kt \quad (7)$$

This equation has been reported in the literature of degradation of high polymers many decades ago (Casassa 1949; Jellinek 1949) and has appeared in a large number of literatures of cellulose degradation. Bearing in mind the definition of natural logarithm function (i.e., the variable x in $\ln(x)$ must be a positive real number), the Ekenstam equation (7) holds *only* for $DP > 1$. This is because $DP = 1$ in Eq. 7 implies that the time $t = \infty$, in other words: the time to failure of cellulose goes to infinite; but we know that such a situation is physically unrealistic! Recalling the Calvini claim that after simple mathematical transformation equation (7) yields the Calvini equation (3); and keeping in mind the fact that Calvini does obtain the Eqs. 2 and 3 using the asymptotic condition $DP = 1$. We could, fairly, argue that the Calvini equations (2) and (3) are developed for “ideal” cellulose that the true failure time is infinite, certainly not for real cellulose with a finite failure time.

Secondly, seeing and thinking experimentally, there is no present experimental evidence in support the asymptotic approach developed by Calvini. Work carried out by Heywood et al. (Emsley et al. 1997; Heywood et al. 1999) for the degradation of Kraft paper aged in air at 120 °C for 10,000 h has already shown that the first order kinetic equation (7) does not hold at low DPs (i.e., $DP \sim 200$, see detailed experimental data in Fig. 1 of the Heywood et al. (1999) paper).

On the other hand, the best way to recognize that the Calvini equations (2–5) are incorrect is to apply them to fit the real experimental data of cellulose and paper degradation. The reader of this rebuttal may use any real experimental result or any experimental data that utilised in the Ding & Wang article to make a test. As an example, Fig. 1 shows a quantitative comparison of plots of $(1/DP - 1/DP_0)$ and $(1 - DP/DP_0)$ versus ageing time during accelerated ageing of pure cellulose paper (Whatman no. 1) in a climatic chamber (80 °C + 65%RH), together with the corresponding predictions by Eqs. 1, 2 and 4. The DP experimental data are originally reported by Piantanida et al. (2005). The values of the regression coefficients for best fitting are $R^2 = 0.9937$ for Ding & Wang equation (1), $R^2 = 0.6706$ for Calvini equation (2), and $R^2 = 0.6938$ (assuming $LODP = 200$)

Fig. 1 Plots of $(1/DP - 1/DP_0)$ and $(1 - DP/DP_0)$ versus ageing time for the accelerated ageing data of Whatman no. 1 pure cellulose paper in a climatic chamber (80 °C + 65%RH); experimental data of DP after Piantanida et al. (2005)



for Calvini equation (4). Similarly, as shown in Fig. 2, the same DP data used in Fig. 1 has been re-plotted by $(DP_0/DP - 1)$ versus ageing time, together with the corresponding predictions by Eqs. 3 and 5. The best fit shows $R^2 = 0.6706$ for Eq. 3, and $R^2 = 0.6938$ (LODP = 200) for Eq. 5. It is shown clearly from Figs. 1 and 2 that while Ding & Wang equation (1) works well ($R^2 = 0.9937$), all Calvini equations (2–5) are fairly poor ($R^2 < 0.7$) in explaining the data of pure cellulose paper.

The most likely explanation for the poor fit for Calvini equations (2–5) almost certainly lies in deficiencies in the Calvini approach rather than in the quality of the fit to experimental data. This then leads to the question what is wrong with Calvini’s theoretical analysis. In the opinion of the authors,

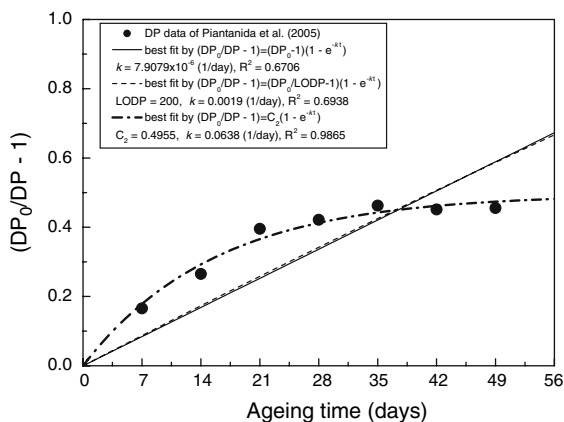


Fig. 2 Plot of $(DP_0/DP - 1)$ versus ageing time for the accelerated ageing data of Whatman no. 1 pure cellulose paper in a climatic chamber (80 °C + 65%RH); experimental data of DP after Piantanida et al. (2005)

Calvini has misused *asymptotic* notation when he argues that “S starts from $S = 0$ and ends asymptotically with $S = n^0$, when all the scissile bonds have been broken”, which brings the results that the Calvini equations are strictly applicable only in the circumstance of the true failure time being infinite. Really, both the first-order kinetic equation $dS/dt = k(n^0 - S)$ and the solution $S = n^0(1 - e^{-kt})$ used by Calvini are subjected to the constraint condition of a finite failure time. In other words, the degradation of cellulose, which involves accumulation of chain scissions up to a critical value of S , starts from degradation time $t = 0$ and ends with $t =$ the failure time of cellulose under given operating conditions instead of “ends asymptotically with $S = n^0$ ”. Bearing this premise in mind it can be easily shown that the rate equations (2–5) should be corrected to the following form of

$$\frac{1}{DP} - \frac{1}{DP_0} = C_1(1 - e^{-kt}) \tag{8}$$

$$\frac{DP_0}{DP} - 1 = C_2(1 - e^{-kt}) \tag{9}$$

Where C_1 and C_2 are constants to be determined by fitting experimental data. Applications of Eqs. 8 and 9 have been included in Figs. 1 and 2 respectively, and the results of best fitting are $C_1 = 3.26 \times 10^{-4}$, $k = 0.0638$ (1/day) and $R^2 = 0.9865$ for Eq. 8; and $C_2 = 0.4955$, $k = 0.0638$ (1/day) and $R^2 = 0.9865$ for Eq. 9.

Calvini also claims that both Eqs. 2 and 4 can be approximated to the Ekenstam equation and therefore “allows the evaluation of the activation energy from short time analysis”. We would like to remind the

reader that even if both Eqs. 2 and 4 could be developed in Taylor series at the beginning of degradation and approximated to the Ekenstam equation (i.e., $1/DP - 1/DP_0 = \alpha kt$), it would still be wrong to claim that “the unknown parameter α of different cellulose samples contributes only to the pre-exponential frequency factor A ”.

We would also like to remind the reader that the erroneous Calvini equations (2–5) have appeared in his previous publications (Calvini 2005; Calvini and Gorassini 2006) without comparison with any real data of cellulose degradation. It should be noted that Calvin (2005) declares that his Eq. 4 is “the same formal result of Emsley et al. (1997), ..., without introducing a change in rate constant as the reaction proceeds”. However, a quantitative comparison can show that such a declaration is simply untrue. If Calvini equation (4) is equivalent to Emsley and Heywood et al.’s equation:

$$\frac{1}{DP} - \frac{1}{DP_0} = \frac{k_{10}}{k_2} (1 - e^{-k_2 t}) \quad (10)$$

where k_{10} and k_2 are rate constants, then the following relationship must hold:

$$\frac{1}{LODP} - \frac{1}{DP_0} = \frac{k_{10}}{k_2} \quad (11)$$

In their article, Emsley et al. (1997) use Eq. 10 to fit the degradation data of Kraft paper aged in air at 120 °C for 10,000 h ($DP_0 = 1,250$, $LODP \sim 200$), and using $k_{10} = 1.78 \times 10^{-6}$ and $k_2 = 2.33 \times 10^{-4}$ respectively to obtain the best fit with $R^2 = 0.9930$. Applying these data to Eq. 11 can estimate $LODP = 118$, which is fairly smaller than the experimental value of $LODP \sim 200$. Moreover, if we look at the scale of degradation times, approximately, $DP \sim 200$ occurs after 3,000 h and $DP \sim 118$ occurs after 10,000 h, which implies that using Calvini equation (4) could yield an error up to approximately 7,000 h in estimating the remaining life of the Kraft paper. Heywood et al. (1999) have correctly pointed out: “It is at these low DPs that the strength of the paper becomes critical in calculating the remaining life and it is therefore important to be able to estimate them accurately”. We could, fairly, argue that the *asymptotic approach* developed by Calvini cannot be accepted to describe the kinetics of cellulose degradation and certainly cannot be applied for interpreting real experimental data.

The relationship between carbonyl and scission production: linear or nonlinear?

Calvini attempts to claim that “the increase of carbonyl end groups should increase linearly with the increase of the number of scissions, whatever it is the kinetic law of hydrolysis”, i.e.,

$$[CO] - [CO]_0 \propto \left(\frac{1}{DP} - \frac{1}{DP_0} \right) \quad (12)$$

He argues that Eq. 12 has been verified by Daruwalla and Narsian (1966) and Whitmore and Bogaard (1994). Actually these authors did obtain a linear relationship between carbonyl and scission production in *acid-treated* cellulose. However, there are no present experimental evidence in support that Eq. 12 is a universal relationship between carbonyl and scission production in *non-acid-treated* cellulose and paper particularly over a long-time period under practical operating conditions.

Figure 3 shows plot of carbonyl versus the percentage of the bond broken during oven ageing of unoxidized Whatman no. 42 filter paper under conditions of 80 °C and 65%RH. The experimental data are originally reported by Whitmore and Bogaard (1995). As shown clearly in Fig. 3, to the utmost, Eq. 12 is valid only in the initial stage of degradation ($DP > 595$); and similar result has also been reported by the same authors in a study on the

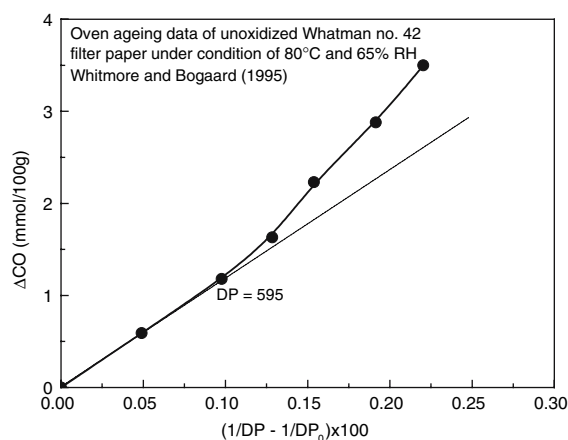


Fig. 3 Carbonyl versus the percentage of the bond broken during oven ageing of unoxidized Whatman no. 42 filter paper under conditions of 80 °C and 65%RH; experimental data after Whitmore and Bogaard (1995)

role of humidity fluctuations in the deterioration of paper (Bogaard and Whitmore 2002).

Figure 4 shows plot of carbonyl versus the percentage of the bond broken during thermal ageing of Whatman no. 1 pure cellulose paper in a climatic chamber of air environment of 80 °C and 65%RH. The experimental data are originally reported by Piantanida et al. (2005). As shown clearly in Fig. 4, a linear relationship between carbonyl and scission production *cannot* be established and Eq. 12 does not hold.

In regard to the application of the ω_{DP} function to the data of HCl hydrolysis of cellulose (as shown in Fig. 1 in Calvini's commentary), Calvini argues that “where an apparent strong increase of carbonyl groups occurs, and this increase is obviously questionable”. This, in fact, indicates that Calvini does not really understand the ω_{DP} function. Actually the reason for an apparent strong increase of carbonyl group occurring is that ω_{DP} is an accumulated function in terms of the percentage DP loss, and when the DP value is closing to the LODP, the accumulated degradation has the tendency to vertically level-off, similar to the phenomenon that occurs in Fig. 4.

The ω_{DP} function: a step back or a step ahead?

It is a certain fact that $1/DP$ instead of DP being plotted as a function of degradation time has been accepted in the field of cellulose research for many decades as a traditional approach to the kinetics of

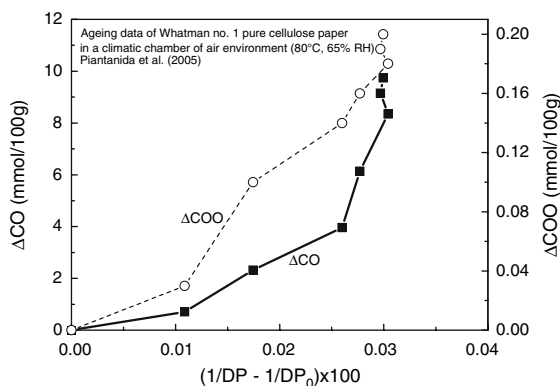


Fig. 4 Carbonyl and carboxyl versus the percentage of the bond broken during thermal ageing of Whatman no. 1 pure cellulose paper in a climatic chamber of air environment of 80 °C and 65%RH; experimental data after Piantanida et al. (2005)

cellulose degradation. However, it is also important to recognize that Ding & Wang's approach to characterizing cellulose degradation by ω_{DP} in terms of the percentage DP loss does not simply mean “the direct plot of DP as a function of time”.

Let us first refer to the original statements made by Bryce and Greenwood (1957) and Sharples (1971). In their kinetic analysis of the degradation of high polymers (time scales are about 100 min and 200 h), Bryce and Greenwood (1957) argues “the correct formulation for measuring degradation can be obtained following the method of Ekenstam (1936) ... for either a zero- or first-order reaction, the degradation rate constant in the initial stages is proportional not to DP but to DP^{-1} , and DP^{-1} versus t will be linear. For large amounts of degradation, this relationship will still hold for a zero-order reaction, but $\ln(1 - DP^{-1})$ versus t is necessary for a first-order reaction as higher terms in the expansion are then required”. Clearly, according to Bryce and Greenwood the linear relationship between $1/DP$ and the time t is valid only *in the initial stage* as an essential premise. Sharples (1971) states that “a rectilinear plot is obtained if the reciprocal of DP is plotted as a function of the time; while the direct plot of DP as a function of time takes the form of a rectangular hyperbola which is considered to be obviously misleading”. Obviously, according to Sharples “the direct plot of DP as a function of time is misleading from a kinetic standpoint” presupposed that “a rectilinear plot is obtained if the reciprocal of DP is plotted as a function of the time” (i.e., $1/DP$ versus t plot is straight line). It is essential to recognize that this was the situation as of 1957 and 1971; certainly, a different verdict could be given today. It is now well established in literature that a rectilinear plot cannot be obtained even if $1/DP$ is plotted as a function of the time (e.g. Daruwalla and Narsian 1966; Whitmore and Bogaard 1994, 1995; Emsley et al. 1997; Strlič et al. 2001; McShane et al. 2003; Piantanida et al. 2005). Also, despite ongoing debates in literature on the evolution equation of cellulose degradation, consensus has slowly emerged on at least one point: whatever the experimental conditions and the cellulose materials, when the DP approaches the LODP, the zero/first order Ekenstam equations are fairly invalid (e.g. Emsley et al. 1997; Heywood et al. 1999). Returning now to Calvini's claim, the essential prerequisite to Sharples'

argument in 1971 has become invalid. In the opinion of the authors, it is not unreasonable to deemphasize the Sharples (1971) argument today and develop an alternative approach to characterizing cellulose degradation based on experimental results. Following simply and blindly the traditional approach may not only mislead the reader but also obstruct research on the kinetics of cellulose degradation.

Calvini also argues that the ω_{DP} function causes a strong stretching of the experimental data plots that reduce even an autocatalytic (S-shaped) kinetics to a rough exponential pattern. It is not the place here to comment on the experimental finding of Zervos and Moropoulou (2005) and the autocatalytic (S-shaped) kinetics. However, based on literature data, autocatalytic degradation does not necessarily appear as S-shaped (sigmoid) kinetic curve, even the reciprocal of DP is plotted as a function of the time. Figure 5 shows plots of the percentage of the broken bonds during thermal ageing of thermally upgraded Kraft insulation paper in sealed metallic tubes at 160 and 170 °C with mineral transformer oil. These are typical autocatalytic degradation kinetic data reported by McShane et al. (2003) and obviously even when the value of DP has been decreased to far smaller than the value of LODP = 200 (comparing that in Zervos and Moropoulou (2005) the bending point in their S-shaped kinetic curve occurs at about DP = 257), the kinetic plots do not appear as the S-shaped curves.

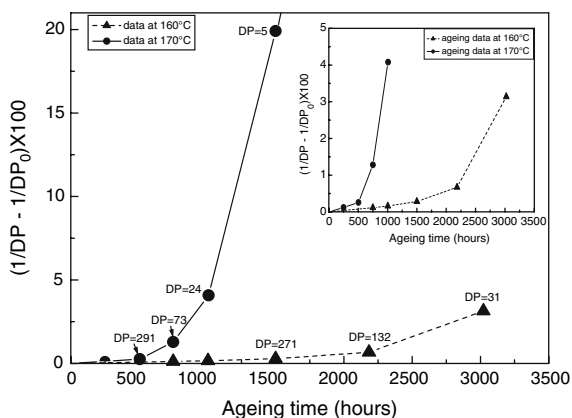


Fig. 5 Plots of the percentage of the broken bonds during thermal ageing of thermally upgraded Kraft insulation paper in sealed metallic tubes at 160 and 170 °C with mineral transformer oil; experimental data of DP after McShane et al. (2003)

Calvini further argues that the ω_{DP} function minimises the effect on the kinetic plots of the simultaneous occurrence of more than one single mechanism and this drawback represents a loss of precious information. As a matter of fact, this may be considered not a drawback but a remarkable merit for the life prediction of cellulose and paper, as have already been shown in the paper. This is because when plotting $1/DP$ as a function of the time, although the kinetics of cellulose degradation process could be arbitrarily divided into several distinguishable phases (e.g. Strlič et al. 2001) with differing rates of chain-scission that being characterized by the corresponding rate constants from Ekenstam equation, it also makes a complicated issue of cellulose degradation more complicate and difficult to yield a master equation representing the kinetics of cellulose degradation for a reliable life prediction.

While criticizing that the ω_{DP} function is a bad unit of measure, Calvini also claims that “the key unit of measure for the kinetics of degradation is the number of scissions S ” and S can be either the chain scission number ($CSN = DP_0/DP - 1$) or the scission fraction of cellulose unit ($SFCU = 1/DP - 1/DP_0$) as already discussed in the Introduction in the paper. Surprisingly, he appears ignorant of the argument made by himself that the SFCU concept is based on the *difference* between two reciprocal values of DP, and every experimental uncertainty about the actual values of DP_0 and DP is amplified in the determination of the number of scissions S (Calvini and Gorassini 2006); and the argument made by Chen and Lucia (2003) that the CSN concept is *not* suitable for characterizing the chain scission activity of cellulose, because the CSN of cellulose with a high DP value is greater than that of cellulose with a low DP value when the chain scission activity of cellulose is the same. He also appears ignorant of the facts that the ω_{DP} function, which is sensitive as the measure of molecular weight changes, seems well suited for explaining experimental data of cellulose degradation; and further, the success of the ω_{DP} function in fitting experimental data performed in different conditions (dry, moist and sealed-vessels ageing) can also give us some measure of confidence in applying this approach to characterizing the tensile strength loss of cellulose that are less well understood.

Calvini also offers a comment that “even though the ω_{DP} function of Ding and Wang is based on a questionable physical ground, it can be considered as master curve that roughly approximates the Ekenstam’s equation”. However, the fact is that some data of cellulose degradation that hardly can be described by Ekenstam equation can be described fairly well by the ω_{DP} function and the Ding& Wang equation (1).

The Ding & Wang approach: does it bring about negative value of physical entities?

The article by Ding & Wang is crystal clear about the parameter ω_{DP}^* , which can be determined only by introducing the constraint condition: $\omega_{DP}(t = t_f) = 1$, where t_f is the time to failure of the test sample under specific experimental conditions. As a consequence, ω_{DP}^* in Eq. 1 can be either smaller than or equal to or larger than 1, depends on the experimental conditions. However, Calvini attributes to Ding & Wang that $\omega_{DP}^* = 1 - 1/DP_0$ by claiming that “a simple analysis of equation (i.e., $\omega_{DP} = (1 - DP/DP_0) = S/(M_0 + S)$ in his commentary) indicates that the maximum allowable value of ω_{DP}^* is $\omega_{DP}^* = 1 - 1/DP_0$ ” and “allowing values of $\omega_{DP}^* > 1 - 1/DP_0$ (corresponding to negative values of DP)”. The truth is that Ding & Wang never claim $\omega_{DP}^* = 1 - 1/DP_0$ in the paper, this is obtained by Calvini through an erroneous asymptotic analysis of his equation: $\omega_{DP} = (1 - DP/DP_0) = S/(M_0 + S)$. Figure 6 as an example shows plots of ω_{DP} versus

ageing time during thermal ageing of thermally upgraded Kraft insulation paper in sealed metallic tubes at 160 and 170 °C with mineral transformer oil (McShane et al. 2003), together with corresponding predictions by Eq. 1, which yields $\omega_{DP}^* = 0.9963$, $k_{DP} = 0.0011$ (1/h) and $R^2 = 0.9970$ for the data of 160 °C; and $\omega_{DP}^* = 1$, $k_{DP} = 0.0032$ (1/h) and $R^2 = 0.9937$ for the data of 170 °C. Bearing in mind that the experimentally measured DP values are DP = 31 after 3,022 h at 160 °C and DP = 1 after 3,002 h at 170 °C. In the case of ageing at 170 °C the value of ω_{DP}^* is $\omega_{DP}^* = 1 > 1 - 1/DP_0 = 0.9991$; however, as shown clearly in Fig. 6 that even for the whole degradation process of paper, Eq. 1 does not bring about negative values of DP.

Similarly, in regard to the new kinetic equation for loss of tensile strength (TS)

$$\omega_{TS} \equiv 1 - \frac{TS}{TS_0} = \omega_{TS}^* (1 - e^{-k_{TS}t}) \tag{13}$$

Calvini declares that “where ω_{TS}^* is led in some cases to negative asymptotic values of tensile strength”. This again is wrong. Throughout the paper it has been clearly noted that ω_{TS}^* is a parameter that may be determined by introducing the constraint condition: $\omega_{TS}(t = t_f) = 1$, t_f is the time to failure; and as a consequence, ω_{TS}^* can be either smaller than or equal to or larger than 1, depends on the experimental conditions. As an example, Fig. 7 shows plots of ω_{TS} versus ageing time during thermal ageing of thermally upgraded Kraft insulation paper in sealed metallic tubes at 160 and 170 °C with

Fig. 6 Degree of degradation change by percentage DP loss during thermal ageing of thermally upgraded Kraft insulation paper in sealed metallic tubes at 160 and 170 °C with mineral transformer oil; experimental data of DP after McShane et al. (2003)

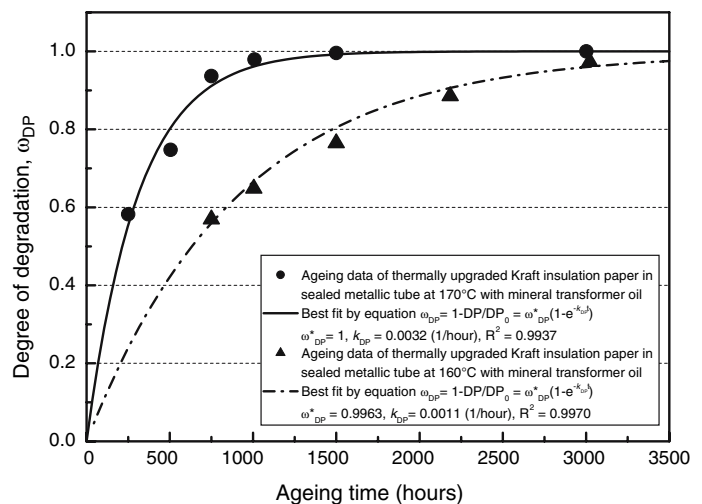
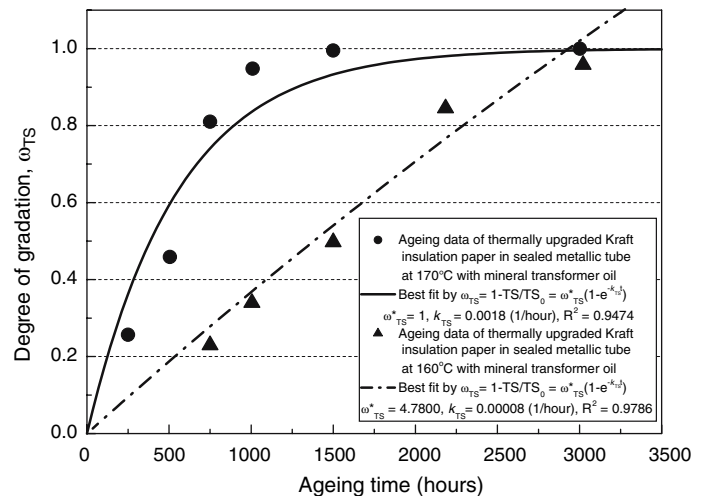


Fig. 7 Degree of degradation change by percentage TS loss during thermal ageing of thermally upgraded Kraft insulation paper in sealed metallic tubes at 160 and 170 °C with mineral transformer oil; experimental data of TS after McShane et al. (2003)



mineral transformer oil (McShane et al. 2003), together with corresponding predictions by Eq. 13, which yields $\omega_{TS}^* = 4.78$, $k_{TS} = 0.00008$ (1/h) and $R^2 = 0.9786$ for the data of 160 °C; and $\omega_{TS}^* = 1$, $k_{TS} = 0.0018$ (1/h) and $R^2 = 0.9474$ for the data of 170 °C. Bearing in mind that the experimentally measured TS values are TS = 6.2 MPa after 3,022 h at 160 °C and TS = 0 after 3,002 h at 170 °C. As shown clearly in Fig. 7 that even for the whole degradation process of paper, the value of ω_{TS}^* never leads to negative values of tensile strength.

Summary and concluding statement

To summarize, a full and detailed reply to all Calvini's comments has been presented and all his arguments refuted.

In conclusion, Ding & Wang would wish to emphasize that the Ding & Wang's approach while being firmly based on the fundamental kinetic theory of polymer degradation has made substantial improvement in the kinetics of cellulose degradation. Modifications to the kinetic theory model of polymer degradation have been made such that theory and experimental results have been brought together to more realistically represent practical conditions. This has not been done in Calvini's approach, which needs seriously revising to reflect the practical conditions under which cellulosic materials operate. The comment by Calvini that, "the new degradation evolution equation of cellulose proposed by Ding and Wang is

a worrying exhumation of old misleading kinetic statements", cannot be substantiated in any way. The Ding & Wang theory is one step ahead and marked development of the kinetic theory for predicting degradation of cellulosic materials over extended periods of time and under a varied of conditions including dry, moist, and sealed-vessels ageing.

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