Reinhard Heinrich Fechter[1] / Carl Sandrock[1] / Frederick Johannes Willem Jacobus Labuschagne[1]

Modelling the Thermal Degradation and Stabilisation of PVC in a Torque Rheometer

[1] Department of Chemical Engineering, University of Pretoria, Pretoria, South Africa, E-mail: reinhard.fechter@gmail.com, carl.sandrock@up.ac.za, johan.labuschagne@up.ac.za. http://orcid.org/0000-0002-4820-4585.

Abstract:
A novel method for simulating the torque and temperature curves from a torque rheometer thermal stability test on poly(vinyl chloride) (PVC) was developed. A mathematical model was proposed which combines the chemical kinetics involved in the thermal degradation and stabilisation process of PVC with heat transfer and viscosity relationships within the torque rheometer. The model coefficients were fitted to data obtained from previous experiments with a program written in the Python programming language using the Levenberg-Marquardt Algorithm (LMA) with multiple starts. The mathematical model fits the torque rheometer data successfully depending on the characteristics of the torque curve. The model fit is successful when the torque curve follows the expected behaviour. An unsuccessful model fit occurs when the torque curve deviates from the expected shape in a very specific way. In the degradation phase the torque curve increases to a local maximum, decreases to a local minimum and then increases again. The exact reason for the dip in torque is unknown.

1   Introduction

Poly(vinyl chloride) (PVC) is a commercially significant and versatile thermoplastic. Unfortunately PVC is susceptible to thermal degradation at processing temperatures leading to a loss of colour and mechanical properties. This is an important problem in the PVC industry [1, 2]. It is well documented that during the thermal degradation of PVC, hydrogen chloride (HCl) is released forming unwanted polyene sequences on the polymer chain and cross linking between polymer molecules [3]. If the HCl released during the dehydrochlorination remains in the system, it has a catalytic effect on the degradation. The autocatalytic effect of the HCl influences both the propagation and initiation of polyene sequences [4]. The exact mechanism for the HCl autocatalysis is not fully understood due to the difficulties in the measuring techniques involved [5]. This is also true for the overall thermal degradation process which is well understood but where the exact chemical mechanisms of the individual steps are a matter of debate [3]. To prevent thermal degradation, heat stabilisers are added to PVC [4].

PVC stabilisers are grouped in two basic categories: primary and secondary stabilisers. To obtain PVC with short and long term stability primary and secondary stabilisers are combined. Primary stabilisers react with allylic chlorides preventing the propagation of polyene sequences. Due to the autocatalytic nature of the degradation once the process is initiated it accelerates very quickly and therefore the primary stabilisers are essential for the inhibition of the initial step to maintain early stability and colour. A number of primary stabilisers are available commercially including mixed metal stabilisers, organotins and pure organics [6].

Secondary stabilisers are substances which have the ability to scavenge HCl. The removal of HCl cannot prevent the initial degradation step but inhibits the auto-catalytic degradation. This means that a secondary stabiliser used in isolation cannot give short term and colour stability, but provides some long term stability [6].

An example of a secondary stabiliser are Layered Double Hydroxides (LDHs). LDHs are clay like materials that have a wide range of chemical compositions. The general structure of an LDH involves cationic layers with brucite like crystalline structure that are connected with crystal water and anions intercalated in between the cationic layers to maintain the electro neutrality of the complete structure (as shown in Figure 1). LDH is relatively simple to manufacture in a laboratory or for industrial applications [7].

Frederick Johannes Willem Jacobus Labuschagne is the corresponding author.
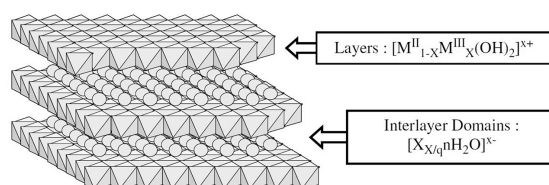
Figure 1: General LDH Structure [7].

Several different mechanisms are proposed for the HCl scavenging ability of LDH but currently the most probable of these is the adsorption of HCl into the pores and onto the surface of the LDH [1, 8, 9]. This is shown for one of the most commonly used LDHs, hydrotalcite (Mg-Al-CO$_3$), in Figure 2.
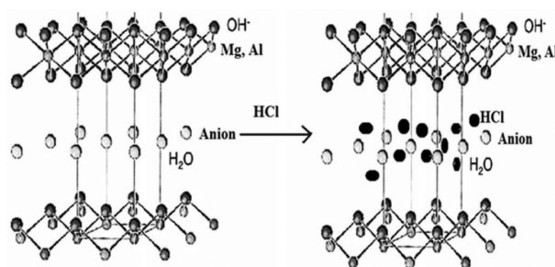

Figure 2: Adsorption of HCl into the anionic interlayer of hydrotalcite [1].

The chemical composition of the cationic layer and the intercalated anionic domain has an influence on the HCl adsorption ability of an LDH. It is of great importance to the PVC stabilisation industry to identify the type of LDHs which have the best HCl adsorption ability leading to a significant amount of research done in this direction [1, 7, 10–15].

The dynamic thermal stability of PVC is measured using a torque rheometer. A torque rheometer consists of two intermeshing rotors that are situated in a thermostatically controlled chamber (as is shown in Figure 3) [3].
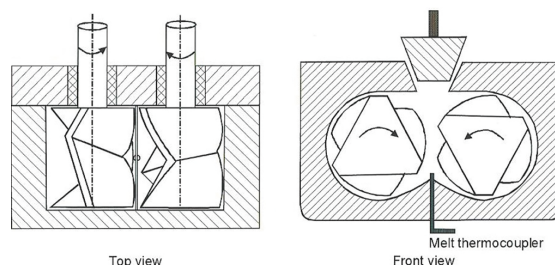

Figure 3: Torque rheometer structure [4].

A torque rheometer measures the torque applied to the rotors, which turn at constant rpm, and the temperature of the plastic in the block [4]. A typical torque curve for flexible grade PVC is shown in Figure 4
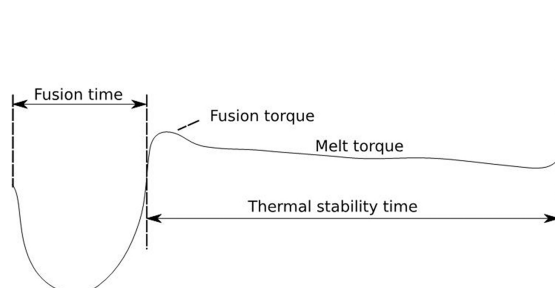

Figure 4: Typical torque curve measured by a torque rheometer for a flexible grade PVC taken from ASTM D2538–02.

Besides giving information about the dynamic thermal stability of a PVC compound, the torque curve also gives information on the viscosity and general flow behaviour of the PVC. The combination of all this information makes the torque rheometer an excellent instrument for gaining insight into the processing behaviour of PVC compounds [16–19].

However, the current method used to analyse the torque curve from a torque rheometer is very limited; a thermal stability time is determined (as per ASTM D2538–02) which can be defined in a number of ways and is, therefore, not an effective way to analyse the stabilising ability of LDH or any other stabilisers.

The purpose of this investigation was to design a model describing the thermal degradation process of the PVC inside the torque rheometer and fitting the model to torque and temperature curves from laboratory experiments done with different LDHs. A good model allows for a more detailed analysis of the degradation and stabilisation process.

The model was designed using the chemistry involved in the thermal degradation and stabilisation process of the PVC as well as heat transfer and viscosity relationships. The model was fitted to experimental data with a program written in Python using the Levenberg-Marquardt Algorithm (LMA) [20, 21] to minimise the sum of the square of the residuals.

2 Model

The model that is developed calculates the torque and temperature curves of a PVC thermal stability test generated using a torque rheometer. The equations used to describe the behaviour of the degradation process of PVC are derived from the chemistry involved, heat transfer relationships and viscosity characteristics.

2.1 Chemical Reactions

The kinetics are described with the following chemical reactions. The HCl released during the thermal degradation of PVC has an autocatalytic effect on the degradation process. This is modelled with the chemical reaction

$$\text{HCl + polymer active site} \rightarrow \text{2HCl + radical} \tag{1}$$
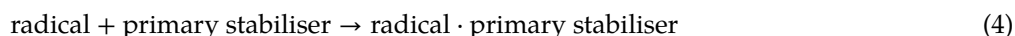
The polymer active site refers to any part of the chain where an HCl molecule can be released which is either a chain defect, a normal monomer or an allylic chloride. The different levels of reactivity of the different polymer active sites are not taken into account to simplify the model. The radical is a construct of the model and would not exist for any appreciable amount of time in reality. The initiation of the degradation process by the polymer defects is modelled with an initiation reaction for the autocatalytic dehydrochlorination reaction

$$\text{polymer active site} \rightarrow \text{HCl + radical} \tag{2}$$

with a rate constant that is orders of magnitude smaller than the autocatalytic reaction. The HCl scavenging by the secondary stabiliser LDH is modelled with the reaction

$$\text{nHCl + LDH} \rightarrow \text{LDH} \cdot \text{nHCl} \tag{3}$$

where n is a positive integer included because one LDH molecule has the capacity to scavenge a number of HCl molecules. The primary stabilisation is modelled with the following reaction

$$\text{radical + primary stabiliser} \rightarrow \text{radical} \cdot \text{primary stabiliser} \tag{4}$$

where the primary stabiliser blocks the propagation of the degradation reaction by reacting with the radical formed in eq. (1). If the primary stabiliser does not attach itself to the radical the polymer will degrade by the formation of double bonds. This is modelled with the reaction

$$\text{radical} \rightarrow \text{degraded polymer} \tag{5}$$

The polymer can further degrade by forming cross-links between polymer chains. This is modelled with the reaction

$$\text{2radical} \rightarrow \text{cross} - \text{link} \tag{6}$$

It is assumed that the reaction between two radicals happens exclusively between two separate molecules and not between radicals on the same molecule.

2.2 Chemical Species Kinetics

The dynamics of each of the important species involved are described by a set of differential equations expressed in matrix form below

$$\dot{c} = \alpha^T r \tag{7}$$

Where

$$\dot{c} = \frac{d}{dt} \begin{bmatrix} \text{HCl} \\ \text{LDH} \\ \text{polymer active site} \\ \text{radical} \\ \text{primary stabiliser} \\ \text{degraded polymer} \\ \text{cross} - \text{link} \end{bmatrix} \tag{8}$$

α is the stoichiometric matrix which for the 6 reactions given above is

$$\alpha = \begin{bmatrix} -n & -1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & -1 & 1 & 0 & 0 & 0 \\ 1 & 0 & -1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & -2 & 0 & 0 & 1 \end{bmatrix} \tag{9}$$

and r is the reaction rate vector

$$r = \begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \\ r_6 \end{bmatrix} = \begin{bmatrix} k_3 \, [\text{HCl}] \, [\text{LDH}] \\ k_4 \, [\text{HCl}] \, [\text{polymer active site}] \\ k_5 \, [\text{polymer active site}] \\ k_6 \, [\text{radical}] \, [\text{primary stabiliser}] \\ k_7 \, [\text{radical}] \\ k_8 \, [\text{radical}] \end{bmatrix} \tag{10}$$

2.3 Viscosity and Temperature

The temperature T dependence of the viscosity μ is taken as an Arrhenius expression

$$\mu = \mu_0 e^{\left(\frac{-E}{RT} \right)} \tag{11}$$

where μ_0 is the pre-exponential constant and E is the activation energy. The viscosity is directly proportional to the concentration of degraded polymer because the double bonds that constitute the degraded polymer cannot rotate freely like a saturated bond. This is expressed as

$$\mu = k_9 \, [\text{degraded polymer}] \tag{12}$$

Cross-linking has a greater effect on the viscosity because it increases the molecular mass of the molecules. This effect is expressed using a power law

$$\mu = k_{10} [\text{cross} - \text{link}]^q \tag{13}$$

Combining eqs. (17), (18) and (19) gives an expression for the viscosity of the PVC in the torque rheometer

$$\mu = \mu_0 e^{\left(\frac{-E}{RT}\right)} + k_9 \, [\text{degraded polymer}] + k_{10}[\text{cross} - \text{link}]^q \tag{14}$$

The torque rheometer block is assumed to be at a constant temperature T_∞. For the experiments in this study $T_\infty = 200\,°\mathrm{C}$ was used. The energy balance can be expressed using the following equation

$$mC_p \frac{dT}{dt} = UA\,(T_\infty - T) \tag{15}$$

where U is the overall heat transfer coefficient, A is the surface area for heat transfer, m is the mass of the PVC added to the rheometer and C_p is the heat capacity of PVC assumed to stay constant over the temperature range that the torque rheometer operates. The left hand side of equation 21 describes the energy change of the PVC as it is heated and the right hand side gives the heat transfer rate from the block to the PVC.

 The PVC temperature T is influenced by the mechanical work exerted by the mixers on the PVC. The mechanical work is assumed to be directly proportional to the viscosity μ giving the following equation

$$\frac{dT}{dt} = \frac{UA}{mC_p}\,(T_\infty - T) + k_{11}\mu \tag{16}$$

The torque rheometer uses a thermocouple to measure the temperature of the PVC which is shown in Figure 3. It is assumed that the thermocouple has first order dynamics giving the following differential equation

$$\frac{dT_m}{dt} = k_2\,(T_m - T) \tag{17}$$

where T_m is the temperature measured by the thermocouple. The final model equation describes the direct proportionality between torque τ and viscosity μ which is

$$\tau = k_1\mu \tag{18}$$

3   Results and Discussion

The model uses eqs. (13) to 25 to produce the torque and measured temperature curves which can be fitted to data obtained from a torque rheometer test. A number of torque rheometer tests were conducted by students of the University of Pretoria.

 The code that fits the model parameters to the data is written in Python programming language using Jupyter [22]. All the code used to fit the model to the data and all the versions generated in the development of the code are available online at https://github.com/reinhardfechter/CSCDataMining.

 The data for seven different LDHs at five initial concentrations are used to fit the model. The seven LDHs include three commercial products; Pyrosorb 911, Alcamizer 1 and Actilox CAHC and four laboratory synthesised LDHs (Mg-Zn-Al-CO$_3$, Mg-Fe-Al-CO$_3$, Mg-Cu-Al-CO$_3$ and Ca-Al-CO$_3$). The five different initial concentrations are 0.3, 0.5, 1, 2 and 5 phr. For every combination of LDH type and initial concentration there are three data sets.

 Before the model can be fitted, the data must be trimmed based on the torque curve to remove the zero measurements at the start of the run and the final dip in the torque that is observed in all of the torque curves. The first cut where the zero torque measurements are removed is achieved by finding the maximum of the first half of the data and ignoring all the data points that precede the maximum. The second cut is achieved by finding the maximum torque value in the second half of the data and only using those data points up to the point in time where the torque exceeds a value of 2 N·m less than the maximum. The value of 2 N·m less than the maximum is chosen to increase the probability that any decrease in the gradient of the torque curve in the degradation phase is rejected. A typical torque curve with cut points is shown in Figure 5.
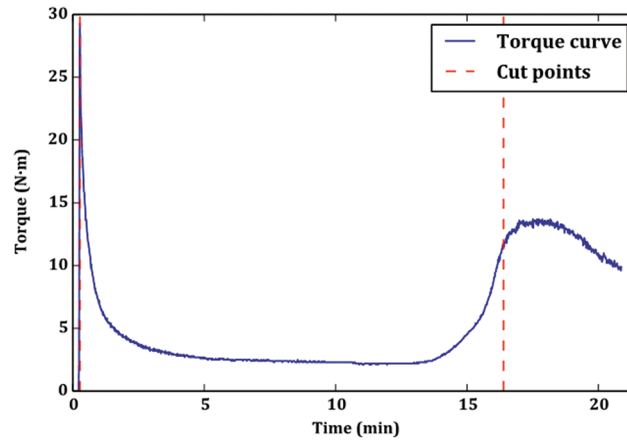
Figure 5: Torque curve with cut points for PVC with 0.3 phr Alcamizer.

It is necessary to remove the decrease in torque, which happens after a time of 17 minutes in Figure 5, because the model is not designed to accommodate any decrease in the torque after the initial decrease where the PVC is melting. The temperature data points corresponding to the ignored torque data points are also ignored for the purposes of the model fitting.

The LMA [20, 21] is used to fit the torque and the temperature curves simultaneously. However the numerical values of the temperature data are roughly one order of magnitude greater than the torque values which means that the LMA will place more emphasis on minimising the numerically greater errors on the temperature data. This is solved by numerically equalising the two curves by applying the following formula to each torque and temperature data point

$$x_{eq} = \frac{x - \bar{x}}{\sigma} \tag{19}$$

where x is a torque or temperature data point, x_{eq} is the equalised data point, $\bar{x}$ and σ are the average and standard deviation of all the data points of every data set that is analysed for either the torque or the temperature respectively. The model is programmed to apply equation 26 using the same torque and temperature $\bar{x}$ and σ for all the data sets.

The multiple start method is used to reduce the chance of finding poor local minima. It is implemented by generating a random value for each of the varied model parameters, between upper and lower limits specific to each parameter, and then fitting the model. This process is repeated 10 times for each data set. The limits are obtained by a gradual process of fitting the data with reasonable initial guesses, finding the mean and standard deviation for each parameter and setting the upper and lower limits to approximately two standard deviations above and below the mean. This process is repeated to remove as many outliers as possible. The limits of the varied model parameters are given in Table 1

Table 1: Upper and lower limits of varied model parameters.

Parameter	Description	Lower Limit	Upper Limit
k_1	viscosity torque relationship	1.6	2.1
k_2	thermocouple dynamics	8	46
k_3	LDH HCl scavanging	0	6
k_4	auto-catalytic dehydrochlorination	0	2.1
k_5	initiation for dehydrochlorination	0	0.03
k_6	primary stabilisation	0	39
k_7	radical to degraded polymer	0	2.7
k_8	radical to cross-link	0	7.9
k_9	degraded polymer effect on viscosity	0	13.1

k_{10}	cross-linking effect on viscosity	0.2	10.9
k_{11}	mechanical work	2	3.6
UA	heat transfer	275	402

All the other model parameters are not varied. The model parameter fixed values are summarised in Table 2.

Table 2: Model parameter fixed values.

Parameter	Description	Value	Units
E	arrhenius activation energy	6208.6	J/mol
R	gas constant	8.314	J/(K·mol)
μ_0	arrhenius pre-exponential constant	0.0372	kg/(m·s)
q	cross-linking effect on viscosity power	2.5	1
m	mass	0.5	kg
C_p	heat capacity	900	J/(kg·K)
T_∞	torque rheometer block temperature	200	°C

Note that the units for all the set parameters other than the temperature T_∞ are not very significant because the units are effectively absorbed by the varied model parameters. The mass m and heat capacity C_p are estimated and the power q is found by allowing it to vary and choosing roughly the mean of the fitted values. The Arrhenius constants E and μ_0 are determined using the initial part of the torque curve which is the same for all the data sets. This is shown in Figure 6 where it is clear that the initial decrease in torque for all the 40 representative torque curves is identical.

The initial values for all the chemical species and the temperatures are given in Table 3.

Table 3: Initial values for chemical species and temperatures.

	Initial Value	Units
HCl	0	1
polymer active sites	5	1
radical	0	1
primary stabiliser	1.3	phr
degraded polymer	0	1
cross-link	0	1
T (PVC Temperature)	125	°C
T_m (measured temperature)	200	°C

The initial value for the polymer active sites is an assumed value and the initial value for the primary stabiliser is the amount that was used to obtain the data sets that are analysed. The initial LDH value which is not shown varies, as mentioned previously, depending on the data set. The value is recorded in the file name for each data set. The program responsible for fitting the model reads the value from each file name.

The model has resulted in two types of fits. The first type is where the model fits the torque curve exactly and very closely fits the temperature curve. These types of fits are indicative of a thermal degradation characteristic much like the torque curve shown in Figure 5. The torque first decreases according to Arrhenius eq. (17), then levels out exhibiting a stable region and finally increases exponentially when the polymer degrades. The torque curves for all the data sets with an initial LDH concentration of 0.3 phr and some of the data sets with 0.5 phr have the same basic shape as described above. An example of a successful fit is shown in Figure 7 and Figure 8. The concentrations over time of the chemical species involved in the successful fit are shown in Figure 9.
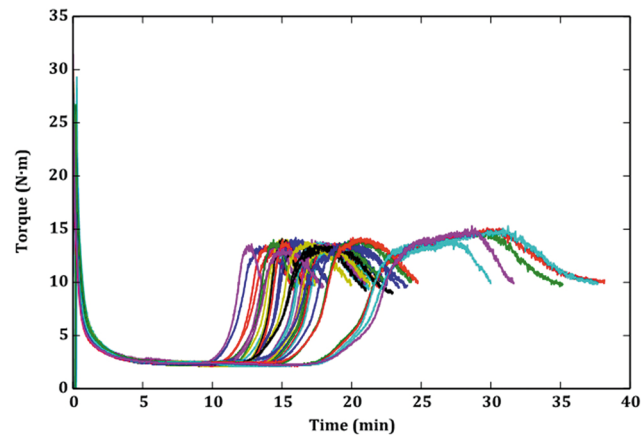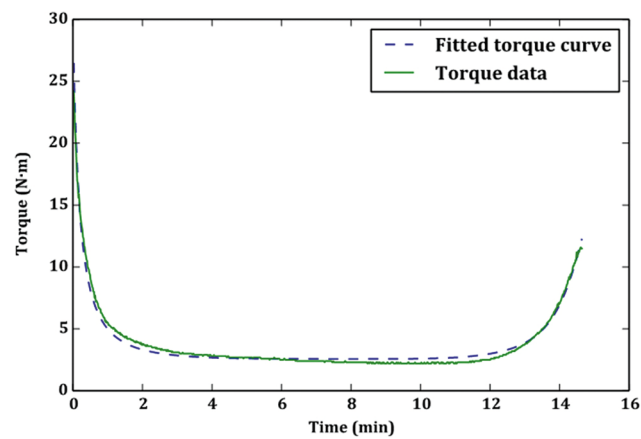
Figure 6: 40 representative torque curves.

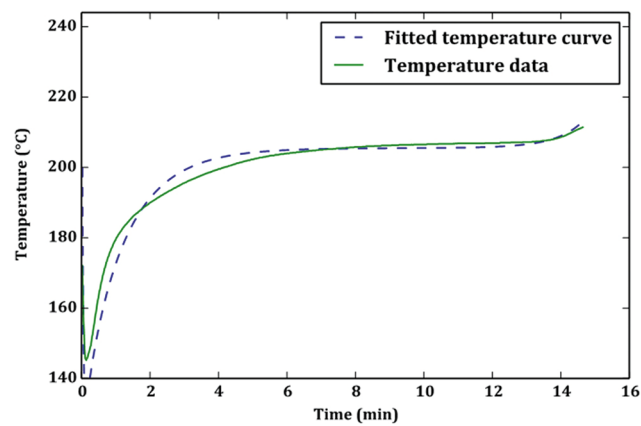**Figure 7:** Successful fit on torque curve for PVC with 0.3 phr Ca-Al-CO$_3$.

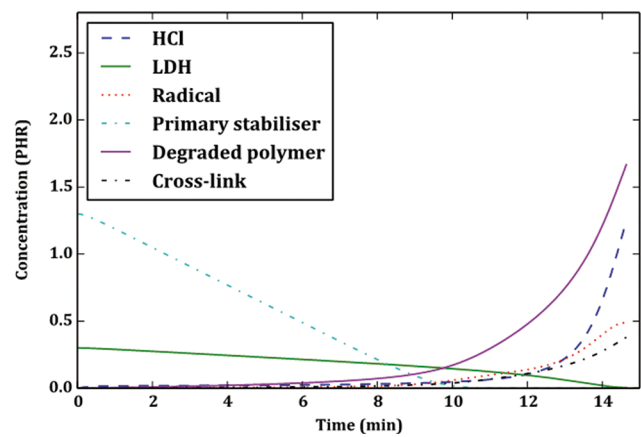**Figure 8:** Successful fit on temperature for PVC with 0.3 phr Ca-Al-CO$_3$.

Figure 9: Concentration over time of chemical species involved for PVC with 0.3 phr Ca-Al-CO$_3$.

The second type of fit is where the model fails to fit the data because the shape of the torque curve deviates significantly from the type of behaviour the model is designed to describe (as shown in Figure 7). These torque curves have the same initial behaviour as the curve shown in Figure 7 but deviate from the typical shape after the onset of polymer degradation. After a period of thermal stability the torque increases, reaches a local maximum, stays constant or decreases for a short period of time and then increases again. The model fails to fit the data sets that exhibit the characteristic described above because the reason for the dip in torque is not known. There is no equation included in the model that will lead to a decrease in the torque of the system once degradation of the polymer has started. Many of the data sets with an initial LDH concentration greater than 1 phr exhibit the dip in torque described above. The shape and size of the dip varies considerably between data sets for different LDH types and initial concentrations. The most pronounced dips in torque are exhibited by the data sets for two commercial LDHs, Alcamizer and Pyrosorb at an initial concentration greater than 1 phr and for the Ca-Al-CO$_3$ LDH at an initial concentration of 2 phr. An example of an unsuccessful fit is shown in Figure 10 and Figure 11.
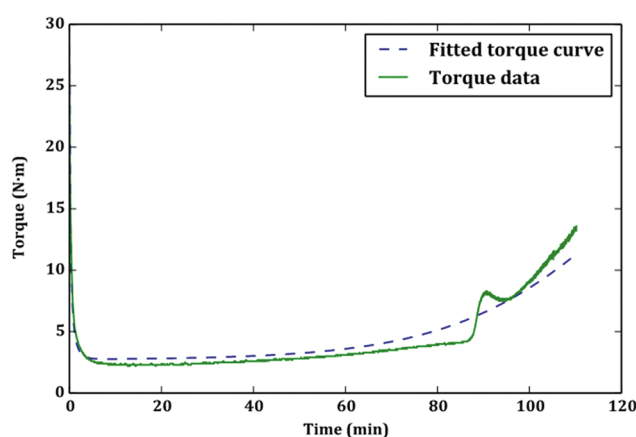

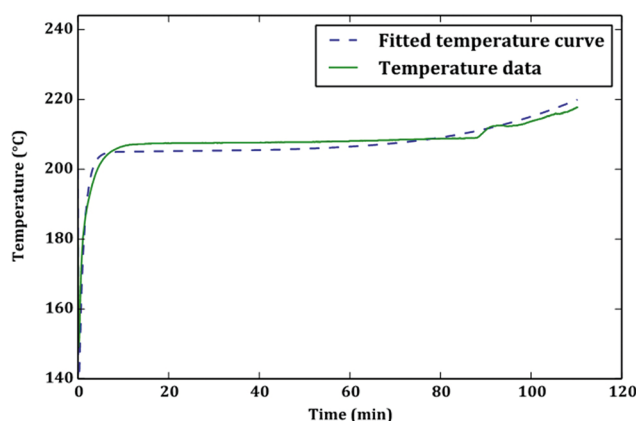**Figure 10:** Unsuccessful fit on torque curve for PVC with 5 phr Alcamizer.

Figure 11: Unsuccessful fit on temperature curve for PVC with 5 phr Alcamizer.

The effect of the two types of fit on the success of the model is clearly visible when examining the integral of the absolute error (IAE) of the torque curve for all the data sets. The IAE is a good indication of how successful the model was fitted to a given data set. A histogram of the IAE is shown in Figure 12.
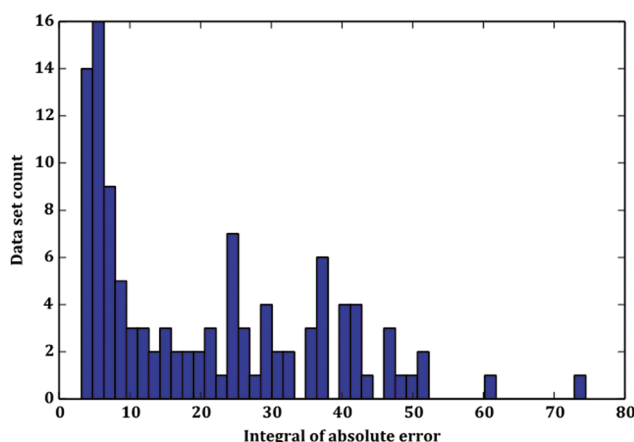
Figure 12: Histogram of the integral of the absolute error for all torque curves.

The histogram in Figure 12 shows a bimodal distribution. The first peak region where IAE < 10 indicates the data sets where the fit was successful. The second peak region where 20 < IAE < 50 indicates the unsuccessful fits where the torque curve exhibits a dip in torque.

The model fails in another way that is not obvious when examining Figure 12. Due to the mathematics of the model the fitting algorithm can achieve a successful fit using only one of the two chemical species, degraded polymer and the cross-link, that directly cause an increase in the torque as described by eqs. (18) and (19). The fitting algorithm tends to set the rate constant for the reaction of one of the species to zero. This is very clear when the species dynamics (such as those shown in Figure 9) of the data sets with a successful fit are examined in more detail. A successful fit where only one of the two species is present is as common as a fit where both of the species are produced. This effect is also evident in Figure 13 where a histogram for each of the fitted model parameters is shown.
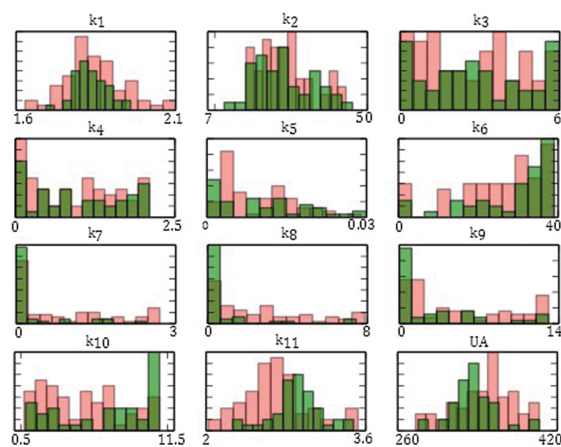

Figure 13: Histogram of fitted parameters with subset for data sets with IAE < 10 and subset for data sets with IAE > 10.

The rate constants for the degraded polymer and cross-link formation, k_7 and k_8, have a large number of successful fits where the parameter values are close to zero which is shown by the first bar of the histograms. The rest of the parameter values are evenly distributed which is evidence of the random nature by which the fitting algorithm alternates between using only one of the two species or both. The similarity between the shape of the k_7 and k_8 parameter histograms for the successful and unsuccessful fits shows that the model can fail in this way regardless of what shape any given torque curve has. This means that the parameters produced by the model with the current design are not reliable enough to be used to predict the behaviour of PVC with an initial LDH concentration different to that used in the data sets.

4   Conclusions and Recommendations

The model fitting on the torque rheometer results for PVC has resulted in two types of fits. The first type of fit is where the model achieves an exact fit for the torque curve and a very close fit for the temperature curve. All of the torque and temperature curves that the model successfully fits have the same basic shape. The torque

decreases exponentially, according to eq. (17), levels out for a time where the PVC is thermally stable and then increases exponentially when the PVC degrades (as shown in Figure 7).

The second type of fit is where the model fails to fit the torque curve because the torque curve has a shape that the model is not designed to fit. A torque curve of this type deviates from the shape described above in the thermal degradation phase of the curve. Instead of exhibiting a smooth exponential increase the torque increases reaching a local maximum, decreases again for a relatively short period of time and then increases again effectively making an unexpected dip in the torque during the degradation phase. The model is not designed to fit this type of torque curve because the reason for the dip in torque is unknown and consequently there are no equations included in the model to describe such behaviour.

The model fails in another way that is not connected to the shape of the torque curve but is a result of the mathematical design of the model equations. The model can be fitted to the data without using both of the chemical species that directly affect the torque, which are the degraded polymer and the cross-link. This means that the parameters fitted by the model are not sufficiently reliable to predict the thermal degradation behaviour of PVC with an initial LDH concentration different to those used to generate the data.

It is recommended that specific experiments be designed to determine the cause of the dip in torque. If the cause of the dip in torque is known it can be incorporated into the design of the model. It is also recommended that the model is reworked so that it is impossible for the fitting algorithm to exclude the degraded polymer or the crosslinking. This will improve the parameters generated by fitting the model to the data. One way to do this is to make the crosslinking a direct result of the amount of degraded polymer (polyene sequences), which follows a possible degradation mechanism, Diels Alder condensation, as proposed by Wilkest et al. [4].

References

[1] Gupta S, Dd A, Banerjee S. Thermal stabilization of poly(vinyl chloride) by hydrotalcites zeolites, and conventional stabilizers. J Vinyl Add Technol [Internet]. 2009 ;15(3):164–70 .

[2] Braun D. Poly(vinyl chloride) on the way from the 19th century to the 21st century. J Polymer Sci: Part A: Polymer Chem. 2004;42:578–86.

[3] Bacaloglu R, Fisch M. Degradation and stabilization of poly (vinyl chloride). V. Reaction mechanism of poly(vinyl chloride) degradation. Polymer Degrad Stabili [Internet]. 1995 ;47(1):33–57 .

[4] Wilkes CE, Summers JW, Daniels CA. PVC handbook. 1st ed. Munich: Hanser; 2005.

[5] Wypych G. PVC degradation & stabilization. 2nd ed. Toronto: ChemTec; 2008.

[6] Bacaloglu R, Fisch MH. Thermal Degradation and Stabilisation of PVC. Munich: Hanser; 2000.

[7] Forano T, Hibino T, Leroux F, Taviot-Gueho C. Layered double hydroxides. In: Bergaya F, Bkg T, Lagaly G, editor(s). Handbok of clay science. Amsterdam: Elsevier Ltd, 2006:1021–70.

[8] Lin Y, Wang J, Dg E, Li D. Layered and intercalated hydrotalcite-like materials as thermal stabilizers in PVC resin. J Phys Chem Solids [Internet]. 2006 ;67(5–6):998–1001 .

[9] van der ven L, Van Gemert M, Batenburg L, Keern J, Gielgens L, Koster T, et al. On the action of hydrotalcite-like clay materials as stabilizers in polyvinylchloride. Appl Clay Sci. 2000;17:25–34.

[10] Labuschagne FJWJJ, Molefe DM, Focke WW, Westhuizen I, van der Wright HC, Royeppen MD. Heat stabilising flexible PVC with layered double hydroxide derivatives. Polymer Degrad Stabili [Internet]. 2015 ;113:46–54 .

[11] Liu S, Zhang P, Yan K, Zhang Y, Ye Y, Chen X. Sb-intercalated layered double hydroxides–poly(vinyl chloride) nanocomposites: preparation, characterization, and thermal stability. J Appl Polym Sci. 2015 ;132(39). DOI: 10.1002/app.42524 .

[12] Yan J, Yang Z. Intercalated hydrotalcite-like materials and their application as thermal stabilizers in poly(vinyl chloride). J Appl Polym Sci. 2017 ;134(22). DOI: 10.1002/app.44896 .

[13] Yi S, Yang Z, Wang S-W, Liu D, Wang S-Q, Liu Q, et al. Effects of MgAlCe-CO_3 layered double hydroxides on the thermal stability of PVC resin. J Appl Polym Sci. 2010 ;119. DOI: 10.1002/app.32807 .

[14] Wang X, Zhang Q. Effect of hydrotalcite on the thermal stability, mechanical properties, rheology and flame retardance of poly(vinyl chloride). Polym Int. 2004;53:698–707.

[15] Yang H, Yang Z. The effect of sodium stearate-modified hydrocalumite on the thermal stability of poly(vinyl chloride). J Appl Polym Sci. 2017 ;135(4). DOI: 10.1002/app.45758 .

[16] Ari GA. Using a torque rheometer to characterize flow in poly(vinyl chloride) composites. New York: Plastics Research Online, 2010.

[17] Jin G, Zhao X, Wang M. Evaluation of rheological measurement of polymer blends melts in torque rheometer. Adv Mat Res. 2011 ;314–116:1424–29.

[18] Jazi S, Esfahany M, Bagheri R. Investigation of the addition of nano-$CaCO_3$ at dry mixing or onset of fusion on the dispersion, torque, and mechanical properties of compounded PVC. J Vinyl Additive Technol. 2012;18:153–60.

[19] Saeb M, Moghri M, Khonakdar H, Wagenknecht U, Heinrich G. Fusion level optimization of rigid PVC nanocompounds by using response surface methodology. J Vinyl Additive Technol. 2013;19(3):168–76.

[20] Levenberg K. A method for the solution of certain non-linear problems in least squares. Q Appl Math [Internet]. 1944 ;2(2):164–68 .

[21] Marquardt DW. An algorithm for least-squares estimation of nonlinear parameters. J Soc Ind Appl Math [Internet]. 1963 ;11(2):431–41 .

[22] Kluyver T, Ragan-Kelley B, Perez F, Granger B, Bussonnier M, Frederic J, et al. Jupyter notebooks—a publishing format for reproducible computational workflows. In: Loizides F, Schmidt B, editor(s). Positioning and power in academic publishing: players, agents and agendas. Amsterdam: IOS Press, 2016.