Studies of the reaction of carboxylic acid anhydrides with wood. Experimental determination and modelling of kinetic profiles

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Studies of the reaction of carboxylic acid anhydrides with wood. Experimental determination and modelling of kinetic profiles

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Kinetic profiles have been determined for the pyridine catalysed reaction of Corsican pine (*Pinus nigra*) sapwood, with an homologous series of linear chain carboxylic acid anhydrides. A model based upon percolation theory has been developed to explain the observed reaction profiles. The model is described, and the results from this are compared with experimental data. By considering the combined effects of diffusion of reagent on a porous network and rate of reaction at sites within the network, the observed experimental kinetic curves have been reproduced. It has been found that the reaction profiles can be reproduced by varying one parameter in the model, which represents the rate of reaction of molecules with active sites located in the network. The kinetics of the reaction of acetic anhydride with whole wood is diffusion controlled throughout. This indicates that wood chemically modified by this reagent will be reacted to different extents, depending upon the local density of the substrate.

Introduction

Although wood continues to remain a popular material due to its excellent material properties, it has a number of disadvantages such as dimensional instability in the presence of moisture and susceptibility to decay organisms. These deficiencies are due to the nature of the cell wall polymers, which contain an abundance of hydroxy groups. Yet the presence of these functional groups allows for the possibility of exploiting their reactive chemistry in order to alter the material properties, a process referred to as chemical modification. Chemical modification has been studied for over fifty years, with most interest being directed at acetylation using acetic anhydride.[1–3] It is likely that such a process will be commercially developed in the near future.[4] Although the material properties of modified wood have been extensively studied, there has been little attempt to investigate the reaction kinetics of the process.[5] In part, this perceived reluctance may be due to the complex nature of the substrate.

The wood cell wall exhibits considerable heterogeneity in its ultrastructure. A typical softwood cell (tracheid) may be considered as a hollow tube, the hollow interior being referred to as the lumen. This is shown schematically in Fig. 1. Tracheids are typically 10–70 µm in diameter, the cell walls of which vary from 2 to 6 µm in thickness. Earlywood (formed at the start of the growing season) has thinner cell walls, and a larger diameter lumen, to facilitate the transport of sap and nutrients. Towards the end of the growth period, latewood is created, which has thick cell walls and a narrow lumen, imparting strength to the wood. Tracheid lengths vary from 1 to 5 mm. The cell wall is composed of several layers, of which the majority of the volume is contained within the S_2 layer. This consists of many layers of spiral wound microfibrils which are themselves composed of crystalline cellulose.[6,7] Attached to the surface of the microfibrils are the hemicelluloses, which act as an interfacial coupling agent between the highly ordered cellulose of the microfibrils and lignin which is an amorphous hetero-polymer composed of phenolic units. Although the hemicelluloses are (like cellulose) polysaccharides, they differ in that they are composed of many different sugar residues, have a lower molecular weight, and generally exhibit an amorphous structure. The lignin, which is highly crosslinked, provides stiffness to the cell wall and additionally acts to bond cell walls together *via* the middle-lamella.

Within the cell wall, there are regions between the cell wall polymers which constitute the cell wall pore structure. The detailed geometry of this cell wall void network is not known with any certainty, although there have been many studies using solute exclusion,[8–10] NMR[11] (pulsed gradient spin echo), and sorption isotherm techniques.[12] Mercury porosimetry, which has been used to determine the macro-pore structure of wood,[13] is not suitable for studies of the cell wall pore structures, since such pores have radii smaller than the limit of resolution of this technique. The majority of the reactive OH sites of the cell wall are located within the interior; thus in order for reagent to react with these sites it is necessary for the molecules to travel *via* the pore network. It is suggested in this paper, that the mechanism for such a transport process is diffusion, driven by the concentration gradient between the surface of the cell wall (that exposed to the lumen) and the interior.

Any attempt to explain the nature of kinetic processes operating during wood modification may therefore have to take
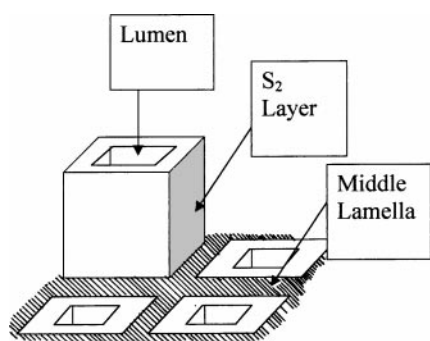

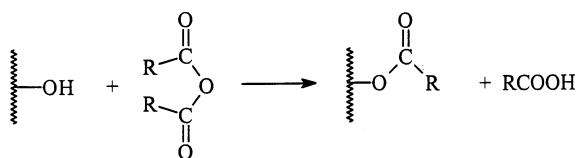**Fig. 1** Schematic representation of the structure of softwood.

Fig. 2 Reaction scheme referred to in text (R = CH$_3$ acetic, R = C$_2$H$_5$ propionic, R = C$_3$H$_7$ butyric, R = C$_4$H$_9$ valeric, R = C$_5$H$_{11}$ hexanoic, R = C$_6$H$_{13}$ heptanoic anhydride).

account of a number of factors: (i) Differences between bulk and surface reactive sites. (ii) Differences in the chemical reactivities of the various hydroxy groups (*e.g.* primary and secondary alcoholic, phenolic). (iii) Various steric effects due to the different environments encountered in the material. (iv) The complex porous nature of the cell wall.

Further complications arise since the substrate swells as modification proceeds, thus the structure alters and additional reactive sites may become available as a consequence. In addition, extensive hydrogen bonding networks exist within the cell wall and it is necessary for such bonds to be broken before reaction may proceed. The situation considered in these experiments is one in which the wood is already fully swollen with solvent before the reagent is added.

There have been relatively few investigations of the kinetics of modification of wood with anhydride reagents. It has been shown that the reactivity of the cell wall polymers to acetylation decreases in the order lignin > hemicelluloses > cellulose.[14] Scanning electron microscopy electron diffuse X-ray analysis (SEM-EDXA) of wood reacted with chloroacetic anhydride, indicates that at short reaction times the S$_2$ layer is substituted to much higher levels than the middle lamella. At extended reaction times, the middle lamella exhibits the highest levels of reaction.[14] This has also been found for reaction of chloroacetic anhydride with oil-palm and coir fibre.[15] The middle lamella region consists almost entirely of lignin, and has a higher density than the S$_2$ layer. These SEM-EDXA observations suggest that diffusion has a significant influence upon the reaction mechanism.

The kinetics of acetylation of jute and cotton fibre with acetic anhydride have been studied.[16] Acetylation was performed in both non-swelling and swelling media, in the presence of perchloric acid catalyst. It was found that the chemical reaction was so rapid, that diffusion alone was the rate controlling process. Diffusion plots exhibited a sigmoidal relationship, indicating anomalous diffusion, which was attributed to history dependent diffusion. A study of the perchloric acid catalysed acetylation of cellulose derived from wood pulp, found that the reaction followed pseudo first-order rate laws.[17] However, a study of the acetylation of cotton linters using acetic acid found that the reaction profile was best described in terms of a surface and bulk reaction. The bulk reaction was considered to be controlled by diffusion.[18]

This paper reports upon investigations aimed at attempting to understand the relative importance of the various factors affecting the anhydride modification of whole wood. In attempting to model the process, the diffusion of reagent molecules through a porous network has been considered. This network is a representation of the cell wall pore structure. A computer model has been developed which is based in part upon percolation theory. Percolation theory was first described by Flory in 1941[19] to describe the polymerisation of multiply branched monomers. Broadbent and Hammersley[20] introduced percolation in order to describe the flow of fluids through random porous media. It has since proved very useful in this context. Many examples of its applications in modelling, for example catalyst deactivation and transport through fractured rock have been described by Sahimi *et al.*[21−23] This appears to be the first application of the theory to wood. Due

to the importance of acetylation in wood modification, it was decided to investigate carboxylic anhydride reactions. For this purpose, the reaction of an homologous series of anhydride reagents (Fig. 2, R = CH$_3$ to R = C$_6$H$_{13}$) with Corsican pine sapwood was studied. The results of these experimental studies are compared with the model.

Experimental

All chemicals were obtained from Aldrich and used as supplied, pyridine was stored over KOH. Corsican pine (*Pinus nigra*) sapwood was selected for this study. Sample sizes of 20 mm × 20 mm × 5 mm (radial × tangential × longitudinal) were cut from kiln-dried wood, extracted with a solvent system consisting of toluene : methanol : acetone (4 : 1 : 1, by volume) in a Soxhlet apparatus for six hours, then oven-dried at 105 °C overnight. Prior to modification, samples were removed from the oven and allowed to cool to room temperature in a dessicator over silica gel, then weighed on a four figure balance. Pre-weighed samples were vacuum impregnated with dry pyridine (over KOH) using a rotary vacuum pump for a total of six cycles, then added to a flask containing 100 ml dry pyridine set in a oil bath at the desired temperature. A condenser and drying tube (filled with CaCl$_2$) were fitted and the wood samples left for one hour to equilibrate with the solvent. To the flask was then added a pre-heated equimolar solution of the anhydride in pyridine (total volume 25 ml), based upon an estimate of the number of OH groups in the sample (calculated on the basis of 14.9 mmol OH groups per gram of oven dry wood).[5] At the termination of the reaction, the pyridine was decanted off and the blocks added to acetone to quench the reaction. The blocks were left to stand for one hour in the acetone, transferred to a Soxhlet for extraction as previously, then oven dried overnight at 105 °C. Such a treatment was found adequate to remove all traces of solvent, reactant, and by-product. Samples were then re-weighed to determine weight gain due to modification.

Results and discussion

This investigation is concerned with the reaction of anhydride molecules with the wood cell wall polymeric hydroxy groups (Fig. 2). The reaction uses pyridine as a solvent, which is necessary since the longer chain anhydrides do not react with wood otherwise. Pyridine acts as a catalyst for the reaction, and additionally serves to swell the wood thus facilitating access of reagent to active sites, and ensuring that as the reaction proceeds no additional swelling occurs. Wood contains a certain percentage by weight of solvent extractable material, which is removed before the reaction. Since wood is a natural material, it is inevitable that some sample to sample variation will occur. In order to take some account of this variation, yet limit the experiment to a manageable number of samples, five replicates were used for each data point.

A series of reaction profiles for acetic (a), propionic (b) and butyric (c) anhydrides is shown in Fig. 3, and for valeric (a), hexanoic (b) and heptanoic (c) anhydrides in Fig. 4. All reactions shown here were performed at 100 °C. The error bars represent standard deviations of the five replicates. The reaction curves show an asymptotic profile, with lower rates of reaction and ultimate degree of substitution as size of anhydride increases. In order to understand the factors affecting the rate of reaction it is necessary to develop a conceptual model. The simplest description that can be applied is to consider the reaction of two types of site with the reagent, namely surface and bulk sites.

Surface reactions

Reaction at the surface may be considered to be affected by the concentration of the reagents only, whereas reaction in the bulk of the material requires that the reagent molecule reaches
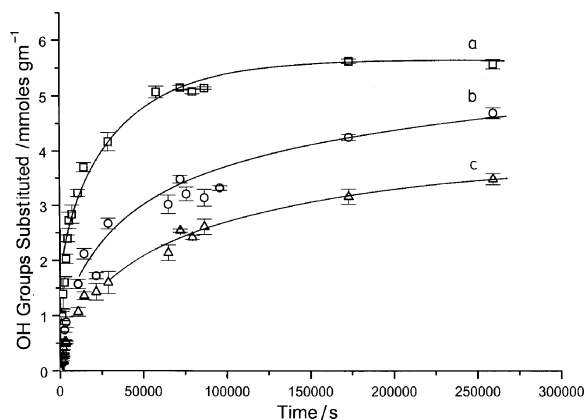
Fig. 3 Kinetic profiles for reaction of Corsican pine sapwood with acetic (a), butyric (b) and hexanoic (c) anhydride at 100 °C.

a reactive site before reaction can proceed. With reactions at the surface, the two reagents are the anhydride molecules, and the wood hydroxy groups. The reaction is thus described by second order kinetics. However, in the case where only the surface sites are considered, the reaction may be described as a pseudo first-order reaction, since the concentration of anhydride reactant is in large excess compared with the number of surface sites which represent a small proportion of the total OH group content. Thus in the initial stages of the reaction, it is to be expected that a first-order reaction profile will be observed. This can be determined from the following relationship:

$$\ln([OH]_t/[OH]_0) = -k't \qquad (1)$$

Where $[OH]_t$ and $[OH]_0$ are the concentrations of unsubstituted hydroxy groups at time $= t$ and time $= 0$ respectively, k' the pseudo first-order rate constant, and t the reaction time. Thus by plotting $\ln([OH]_t/[OH]_0)$ vs. t, a straight line relationship will be obtained, with a gradient equal to $-k'$ if first order kinetics are obeyed. The concentration of hydroxy groups is not a trivial value to determine. It is possible to calculate an approximate value which depends upon the chemical composition of the cell wall polymers (cellulose, hemicelluloses, lignin), but this takes no account of the hydroxy groups which are inaccessible to reagent. Hydroxy groups of the cellulosic component are categorised as amorphous or crystalline depending upon whether they are located on the surface or within the interior of the microfibril, respectively. Those in the latter category are not accessible to reagent. Similarly, some (or some parts) of the hemicelluloses are intimately associated with the microfibrils, and probably not accessible to reagent. In addition there are steric factors which will probably limit the accessibility of reagent to certain
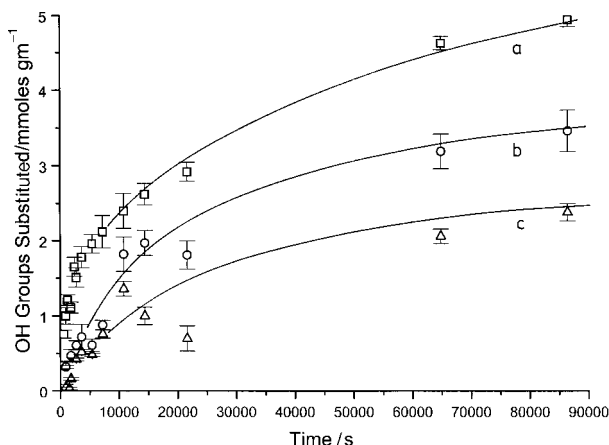
sites. Finally, the absolute hydroxy content (of the lignin especially) is not known with certainty, and will vary from species to species and within a wood sample. Thus any attempt to determine the accessible OH content will inevitably lead to an error. However, the number of OH groups substituted is readily determined, by measuring the weight gain of the wood due to modification, and dividing by the molecular weight of the adduct. This will then not allow a true estimate of the rate constant, but will nonetheless allow one to determine whether first-order kinetics are obeyed. An example is given for the reaction of propionic anhydride ($R = C_2H_5$) with wood at 90 °C, where it is observed that a linear relationship is indeed obtained ($R^2 = 0.947$), consistent with the hypothesis that first-order kinetics are dominant during the initial stages of the reaction (Fig. 5). Whether a linear relationship is obtained depends upon the nature of the reacting species with, for example, acetic anhydride ($R = CH_3$) showing no evidence of first-order kinetic processes, but with hexanoic anhydride ($R = C_5H_{11}$) a linear relationship is observed during the initial stages of the reaction (Fig. 6). Although it is not possible to show every rate curve for the reactions here, the following general observations have been made: (i) As reaction temperature decreases, first-order kinetics is observed over longer time periods. (ii) As reagent size increases, there is a greater likelihood of observing first-order kinetics during the initial part of the reaction.

Bulk reactions

As reaction proceeds, the reagent will penetrate into the interior of the sample, and reaction with bulk sites will occur. The

Fig. 4 Kinetic profile for the reaction of Corsican pine sapwood with propionic (a), valeric (b) and heptanoic (c) anhydride at 100 °C.
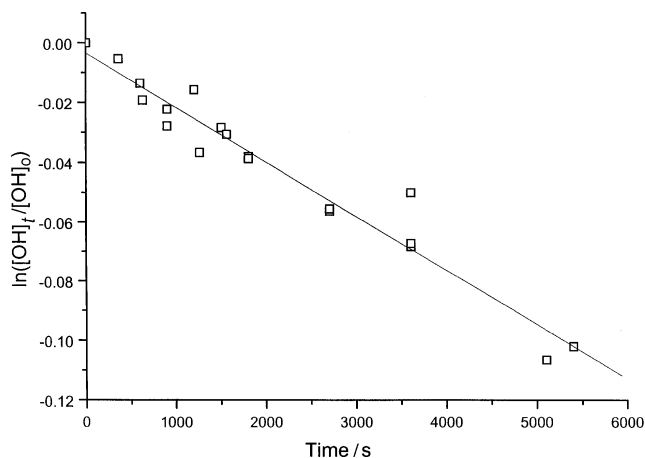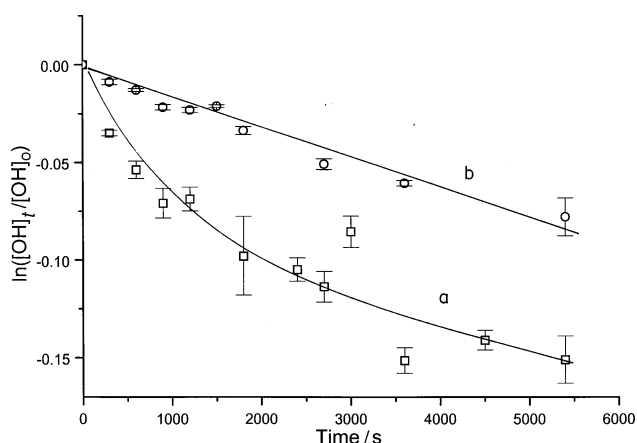

Fig. 6 First-order kinetic plot for reaction of acetic (a) and hexanoic (b) anhydride at 90 °C.

driving force for such a process is the difference in concentration between reagent molecules distributed in the pyridine at the surface of the cell wall, and the concentration of same within the cell wall. Thus it is probable that a diffusion mechanism will operate at this time. Many derivations[13,24,25] have been made where the mass change in a wood sample due to diffusion of a substance into the bulk has the form:

$$m = bt^{1/2} \qquad (2)$$

Where m is the mass change at time t, and b a constant which is related to the diffusion coefficient. A relationship of this form has also been demonstrated by Pannitier and Souchay[26] who considered the reaction kinetics of a diffusion controlled reaction on a heterogeneous substrate.

To calculate a diffusion coefficient for a reagent diffusing into the cell wall of wood is a major task, since there is considerable variation in the cell wall thickness between different cells, and between the early- and latewood particularly. However, a plot of mass change *versus* square root time will indicate that diffusion is a possible kinetic process, if a linear relationship is observed. For diffusion to be the dominant process, it is implicit that the rate of diffusion of a molecule to a reactive site is slow compared with the rate of reaction at that site. A plot of the number of OH groups substituted *versus* square root time is shown for the reaction of acetic (a), butyric (b) and hexanoic (c) anhydride with wood at a temperature of 100 °C (Fig. 7). It can be seen that for acetic anhydride a linear relationship is obtained ($R^2 = 0.987$) (although there is considerable scatter of the data due to the inherent variability of the substrate), implying that diffusion is the dominant process in this case. Furthermore, a linear fit passes through the origin, indicating that reactions associated with the surface sites are not observable.[27] Thus, in this case, it is apparent that the rate of chemical reaction is rapid compared with the rate of diffusion (*i.e.* that diffusion is the rate limiting step). A similar plot for the reaction of propionic (a), valeric (b) and heptanoic (c) anhydrides is shown in Fig. 8. In this instance, and also with butyric and hexanoic anhydride, it is observed that the profiles obtained are sigmoidal in nature. Furthermore, the form of this profile is influenced by temperature, as is illustrated for reaction of propionic anhydride in Fig. 9.

The existence of such sigmoidal relationships has been noted previously for reaction of acetic anhydride with jute fibres.[16] This result was explained in terms of history dependent diffusion.[28] Such relationships are often referred to as anomalous (non-Fickian) diffusion, and are commonly observed with diffusion experiments on glassy polymers. Such deviations from non-linearity are considered to be related to the finite time taken for such a polymer to change its structure in response to the ingress of penetrant molecules. An increase
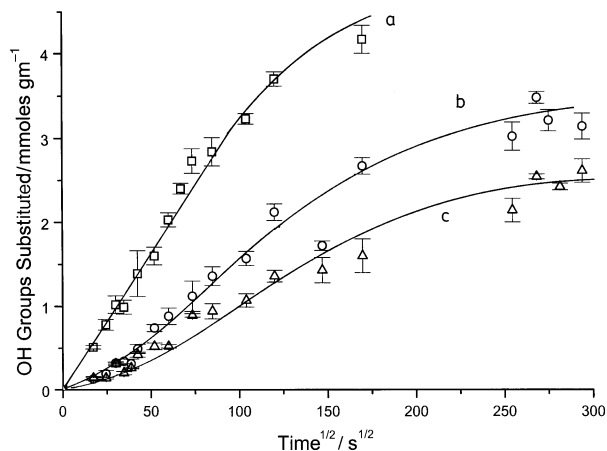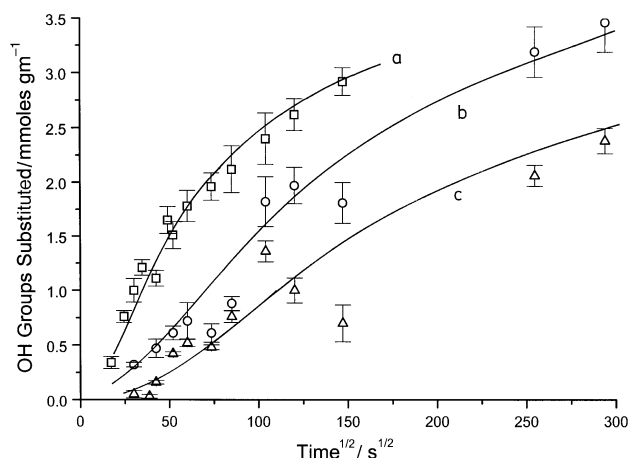
in the concentration of the penetrating molecules is assumed to lead to an increase in the local diffusion coefficient, which is then followed by a slow change to an equilibrium state as a result of a subsequent relaxation process. Thus, the value of the diffusion coefficient of an element of such a system depends upon the concentration history of that element. This, and other models which rely upon the hypothesis that structural rearrangement of the wood matrix occurs during modification, which then affects the diffusion coefficient locally, may thus explain the observed profiles. However, a number of factors should be borne in mind when such a model is considered.

Acetic anhydride does not exhibit this behaviour with whole wood, nor when reaction is performed on separated wood fibres. However, it has been observed in these laboratories that when wood flour is reacted, the sigmoidal behaviour is observed. This suggests that the phenomenon in the case of wood modification at least, is related to the surface area to volume ratio. Other studies on the non-catalysed reaction of acetic anhydride with Jute (*Corchorus capsularis*) fibres performed in this laboratory, have shown that a linear square root time dependence of the reaction profile is obtained, except at lower temperatures, where a sigmoidal relationship is observed. In addition, as previously noted, the reactions with whole wood are performed in the presence of pyridine. This is chosen since it acts not only as a catalyst for the reaction, but additionally serves to swell the wood structure. Since the wood is already pre-swollen then additional changes in the structure should not occur as a consequence of the modification process. Any theory that relies upon structural changes in the wood is therefore considered unlikely, in this case. The
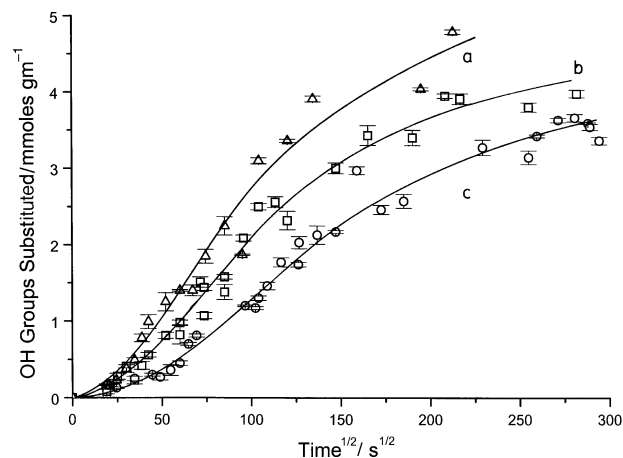

Fig. 8 Diffusion profile for reaction of propionic (a), valeric (b) and heptanoic anhydride (c) at 100 °C.

Fig. 7 Diffusion profile for reaction of acetic (a), butyric (b) and hexanoic anhydride (c) at 100 °C.

Fig. 9 Diffusion plot for reaction of propionic anhydride at 120 °C (triangles, a) 90 °C (squares, b) and 60 °C (circles, c).
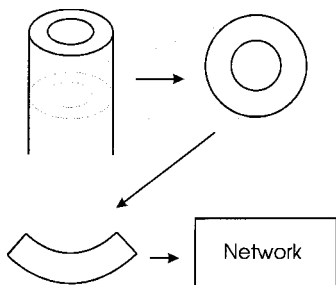
Fig. 10 Representation of cell wall using network.

intention of this paper is to show that such profiles can be explained by considering the relative rates of diffusion of reagent molecules on a porous network, and the rate of reaction of such molecules with active sites located within this network.

Percolation theory and description of the model

The model used to describe the reaction kinetics considers the reaction of molecules with reactive sites located within the cell wall. For this purpose, a slice is taken through a portion of the cell wall (Fig. 10), the molecular scale pore network is then created on this lattice. Consider a square lattice each square of which is filled with a black dot with probability p. Thus in a lattice containing n elements there are pn filled sites and $(1-p)n$ unfilled sites. The 4 neighbours of a given cell are defined to be those cells that share a vertical or horizontal line with it. Given this definition, groups of neighbouring filled squares are termed clusters. The idea is that, on larger lattices than in this example, transport of reactant molecules is allowed on clusters. In Fig. 11, 60×20 lattices are shown for three different values of p: $p = 0.4$, 0.6, and 0.8, where cluster sizes are compared for the three lattices. In Fig. 11(a) ($p = 0.4$) the clusters are very small compared to the overall lattice size, whereas in Fig. 11(b) and (c) there is a cluster which spans the lattice (that is, it extends from top to bottom and from left to right).

In this model, a finite, two-dimensional square lattice is first generated as an array. The lattice is an attempt to model a cross-section of the cell wall, with the top edge of the lattice representing the surface of the cell wall closest to the lumen. Boundary conditions apply on the left and right sides of this
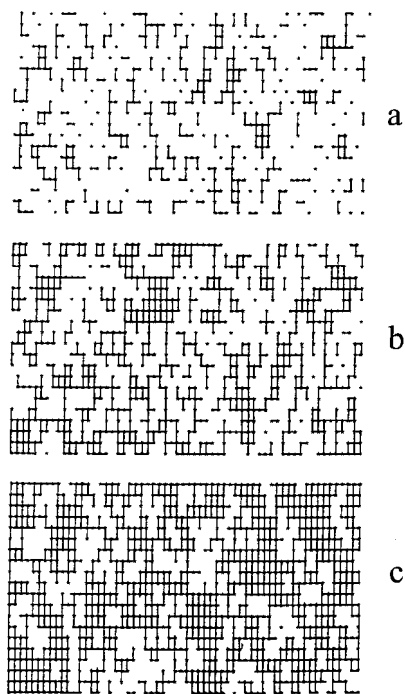

Fig. 11 Examples of percolation networks with values of p of 0.4 (a), 0.6 (b), and 0.8 (c).

lattice so that the neighbour of a site on the right hand edge of the lattice is defined to be the site nearest to the left hand edge of the next row down. Having generated the lattice, the vertices (sites) of the lattice are labelled available with probability p, and unavailable with probability $1 - p$. The average size of a cluster in the lattice is dependent on the value of the parameter p. The other parameters used in the model are r, which is used to represent the reaction probability, and d which is the depth of the lattice (number of rows).

Transport of reactant molecules is now allowed on clusters as follows. Reactant molecules enter the lattice on one edge (the top edge), occupying only available sites on this edge. At each of these sites a reaction is allowed to occur with probability r (achieved by generating a pseudo-random number between 0 and 1 and comparing it with the pre-set value of r). This takes a total of one time step. If, at a given site, a reaction has occurred then the site is said to be reacted. In the next step, reactant molecules in the lattice which have not reacted then attempt to move at random to adjacent sites. If the site chosen is itself already occupied by a reactant molecule or if the site is unavailable then this move is not allowed. Following this, at each occupied unreacted site the reaction is again allowed to occur with probability r. After this, all available sites on the top edge again become occupied (replacing the molecules which have moved to other sites or reacted). All the above occupies another time step and this step is repeated until every available site belonging to a cluster which is connected to the top edge has reacted. The time at which the process finishes is called t_{end}. The boundary conditions mentioned in the previous paragraph ensure that molecules do not 'leak' out of the sides of the lattice. For example a molecule that jumps off the right hand edge of the lattice will re-enter at an appropriate point on the opposite edge.

For a given lattice the existence of what is known as the percolation threshold is well known in percolation theory. Consider a lattice (in this case two dimensional) which has infinite linear length. For low values of p only small finite clusters exist. For large values of p an infinite cluster exists which spans the lattice from top to bottom and from left to right. In fact, there exists a value p_c, the percolation threshold, such that, for all $p < p_c$ only finite clusters exists, and for all $p \geqslant p_c$ an infinite spanning cluster exists. In the case of the two dimensional square lattice used here $p_c \approx 0.5927$.[29] With the chosen value for the parameter p, is associated a correlation length ξ which has value 0 at $p = 0$, and at $p = 1$, and tends to infinity as p approaches p_c from above and from below. If $p > p_c$ then, on a scale larger than ξ clusters are homogeneous, whereas on scales smaller than ξ clusters are heterogeneous. This leads to two different types of observed behaviour for diffusion on the infinite cluster ($p \geqslant p_c$), depending on whether the average distance travelled by diffusing molecules, $A(t)$, is of the order greater or less than ξ.

If $A(t)$ is of order greater than ξ then it has been observed that, in general, single diffusing molecules obey the law $A(t) \propto t^{1/2}$. If however, $A(t)$ is of order less than ξ, then it has been found that anomalous diffusion occurs, so that the law $A(t) \propto t^n$ applies with $n \approx 0.33$.[30] Returning to this model, it has been found that for large enough lattices, with $r = 1$ and $p \gg p_c$, a standard diffusion process dominates throughout, excepting a very small initial period, i.e. in general, it is observed that:

$$M \propto t^{1/2} \qquad (3)$$

where M is the number of reacted sites. For $p \approx p_c$ ($r = 1$ still), it has been observed that:

$$M \propto t^n \qquad (4)$$

where $0.30 \leqslant n \leqslant 1/2$, in the early and middle stages of the process when the lattice is large enough for significant diffusion to occur. In the later stages, diffusion is affected by the
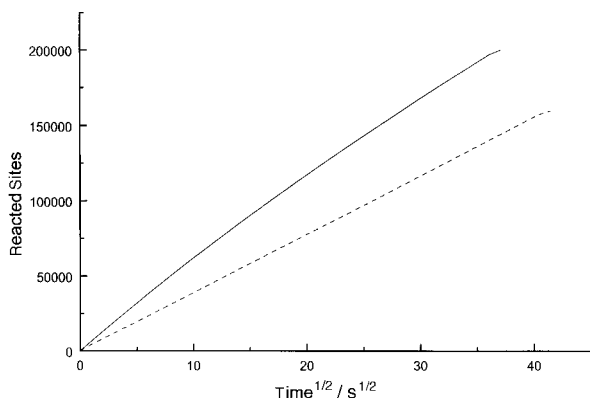
Fig. 12 Results of simulation on a network for values of $r = 1$, $p = 1$ (continuous line), and $p = 0.8$ (dashed line).

Comparison of model with experimental data—effect of changing the reaction probability (r) and effect of lattice depth

Various lattices were generated of differing depths, while the widths were kept constant. Firstly the depth, d, was set to 200 and the effect of changing r and p separately was considered. Square root time plots are presented in Figs. 12 and 13 for both these changes. It is assumed that any straight line regions in square root time plots indicate that standard diffusion is dominating the reaction kinetics. Observe that in Fig. 12 where plots for differing values of p are compared (while r is fixed), both sets of data yield good straight lines throughout, indicating a process determined by standard diffusion. It is noted that for $p = 0.8$, although the same law, $M = Dt^{1/2}$, is observed, the value of D is lower than in the case where $p = 1$. This is due to the reduced connectivity in the lattice, so that although nearly all available sites are accessible, the path traversed by a molecule in reaching a given accessible site is more tortuous than in the case where $p = 1$. It has been further observed that, for values of p significantly greater than p_c, the reaction is completely controlled by standard diffusion, when the value of r is set at 1. It is only the value of the constant D which changes, with respect to p.

In Fig. 13, p is fixed at 1 and curves for two different values of r are plotted. It is observed in this instance that, for the case where $r = 0.0001$, the reaction is still almost completely controlled by standard diffusion (indicated again by the straight
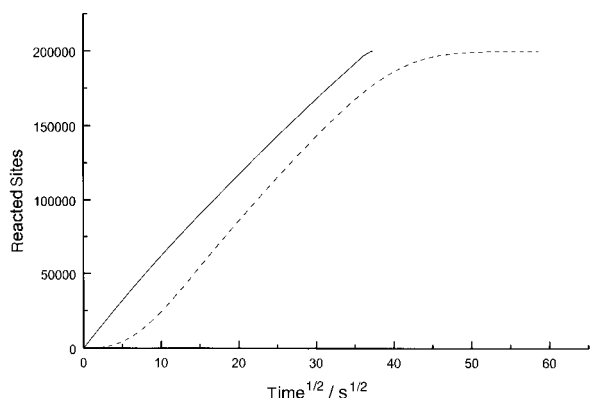
line region). The change in r appears to influence the reaction in the early and late stages. At the start of the reaction, sites become occupied very quickly (these are the accessible sites close to the top edge). This means that the value of r controls the kinetics, *i.e.* the rate of reaction is the rate determining step. This is also the case near the end of the reaction where the availability of readily accessible reaction sites is low, but all sites are occupied by reagent molecules (*i.e.* the sample is saturated). In this time frame we observe an exponential decay of the number of unreacted sites. In general the following rate law has been observed (p is constant).

$$dM/dt \propto rR \qquad (5)$$

where R is the number of occupied unreacted sites. This means that the rate of increase of reacted sites at a given time is proportional to the number of unreacted occupied sites (which can be well approximated by measuring the vertical distance between the two plots in Fig. 13).

The effect of altering the depth of the lattice is now considered. It is expected that an increase in d will result in an increase in the period of time during which the reaction is diffusion controlled. This is indeed the case, as is shown in Fig. 14. In this case, p and r have been fixed and lattices of two different depths have been compared. The results have been normalised so that the difference in the number of sites has been ignored and comparison of the shapes of the curves can more easily be made. It has been observed that, although the initial and final stages controlled by r are of comparable time spans, the diffusion dominated region when $d = 200$ is much larger than when $d = 30$. In fact the apparent straight line region in the $d = 30$ case is illusory, rates have been calculated for both plots and have been found never to be constant (which would represent a straight line region) when $d = 30$.

All of the above programs were run on lattices with high values of p. It has been found that, in general, these yield good straight line square root time plots. However, in some instances, in the very early and very late stages of the reaction, linear behaviour is not observed. This behaviour is not appropriate as a model for the aforementioned wood modification reactions since, in general, for longer chain anhydrides, linear square root time dependencies have not been observed with experimental data. However, if the model is set with values of p close to p_c a significantly different type of behaviour emerges (see Fig. 15). In this case, no straight line region in the square root time plot is found. What is happening is that some portions of the lattice have become extremely difficult to access. This results in an increase in the amount of time taken for reactant molecules to reach these sites, and accounts for the deviation from a square root time dependency. This kind of behaviour seems far more appropriate as regards the wood
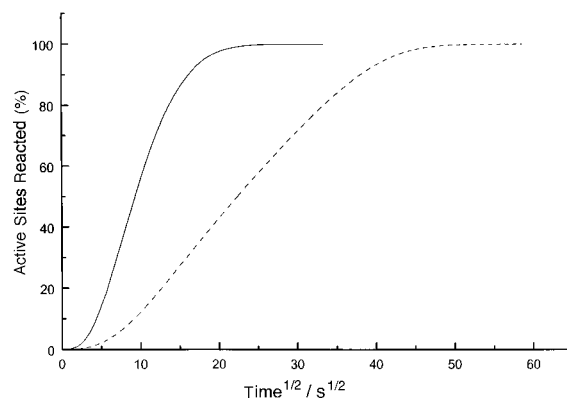
finite size of the cluster (which is due to the finite lattice size) so that the above law no longer holds. In other words, if the correlation length is small compared to the lattice size, a $t^{1/2}$ dependence is observed, whereas if the correlation length is large compared to the lattice size, then anomalous diffusion occurs throughout most of the reaction with a t^n dependency (where $0.3 \leqslant n \leqslant 0.5$).

Fig. 13 Effect of changing reaction probability (r), $r = 1$ (continuous line) and $r = 1 \times 10^{-4}$ (dashed line), $p = 1$.

Fig. 14 Effect of changing depth of lattice. Continuous line represents reaction profile for lattice depth of 30 (3×10^4 sites), dashed line is for lattice depth of 200 (2×10^5 sites), plots have been normalised to account for difference in number of sites ($p = 1$, $r = 1 \times 10^{-4}$).
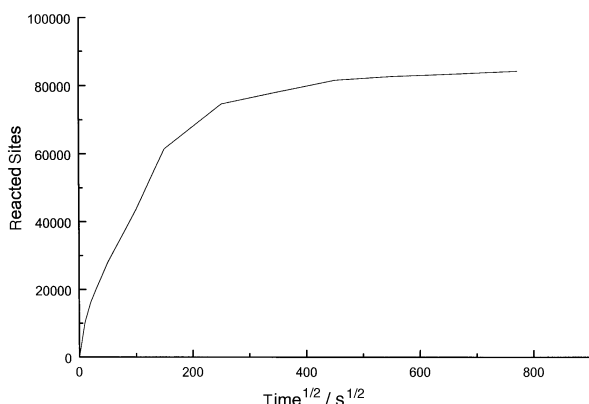
Fig. 15 Simulation performed on a network of depth 200, with $p = 0.6$ (close to percolation threshold) and $r = 1$ (instantaneous reaction).

modification reactions and hence in this context only values of p close to p_c will be considered.

Consider the reaction profiles displayed in Fig. 7, for wood modification by acetic, butyric, and hexanoic anhydride, with square root time plotted on the x-axis. Note that, for acetic anhydride, there is a no distinct initial period, whereas, for butyric and hexanoic anhydride there is. In order to model these reactions it is necessary to choose appropriate values for r, p, and d. In fact, for a lattice depth of 500, good matches with the data are obtained when $p = 0.6$ and r takes the values 1, 0.00033, and 0.00005 (see Fig. 16). No meaning is attached to the actual values of r, only perhaps to their relative values. We note that reactivity decreases with increased chain length in anhydrides and therefore it is expected that the lower values of r will correspond to the higher chain length anhydrides. The output from the model has again been normalised in order to take into account the relative OH accessibility for the different anhydrides, which are obtained from experimental data.

Conclusions

It has been shown that it is possible to model the kinetic profiles for the reaction of carboxylic acid anhydrides with wood by considering the relative rates of reaction and diffusion on a porous network. By running simulations of diffusion of molecules upon networks where p is close to the percolation threshold, the observed reaction profiles for reaction of a series of linear chain anhydrides with wood can be reproduced by varying one parameter (r), which represents the rate of reaction with sites located in the lattice. The profiles for both the reaction and the model are seen to have, in general, three
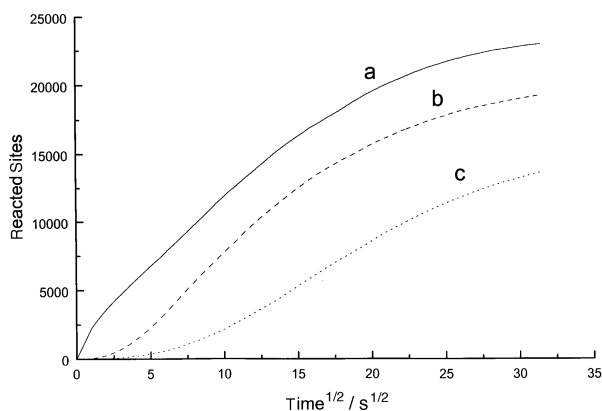

Fig. 16 Examples of kinetic profiles derived from the model for a lattice depth of 50, and $p = 0.6$, with the following values for the reaction probability: a ($r = 1.0$), b ($r = 3.3 \times 10^{-4}$), c ($r = 5.0 \times 10^{-5}$); plots have been normalised to account for different levels of ultimate OH substitution of acetic, butyric and hexanoic anhydrides.

distinct stages. The depth of the lattice affects the length of the later stage in relation to the middle and early stages, although the amount of effect is also controlled by the parameter p. The choice of r affects the shape of the plot in both the early and late stages. The action of r on the number of unreacted occupied sites is thought to be easily predicted (see above). Without the anomalous diffusion occurring for values of p close to the threshold these two factors do not suffice to model the reaction. For high values of p the middle section of the reaction is always proportional to $t^{1/2}$, suggesting a diffusion dominated process. As p decreases, areas of the lattice start to become inaccessible, and pathways to some accessible sites become very tortuous, thus altering shape of the plots in the middle regions so that they are a much better match to the experimentally determined reaction plots.

It is probable that for reaction of wood with acetic anhydride, a diffusion mechanism in such reaction processes is dominant. As a consequence the relative rate of reaction of reagent with various OH sites in the matrix is of no importance. Due to the dominance of diffusion, the rate of reaction will be a function of the density of the wood, which varies from region to region and in particular between earlywood and latewood. This has important implications regarding what levels of modification are required in order to ensure that protection of all of the substrate is achieved. With longer chain anhydrides, the rate of chemical reaction and diffusion both contribute to the reaction kinetics. It would be of interest to determine the effect of reagent size upon distribution of modificant within the cell wall, using a labelled anhydride and SEM-EDXA analysis. Although good approximations to the observed rate processes have been obtained, the modelling has thus far been restricted to small lattices and two dimensions due to limited computing power. Comparison of model with experimental data is based on empirical observation. Extension of the work to 3D lattices is now required in order to represent the cell wall pore space geometry more realistically. Attempts to determine the geometry of the cell wall pore network using mercury porosimetry were not successful, due to the high applied pressures leading to pore collapse. Nitrogen sorption isotherms may give the necessary information, however such experiments require the wood to be in a dry state (and hence unswollen). Information obtained using this method will hence not relate directly to the experiments performed here.

This is, as far as the authors are aware, the first study where percolation has been applied to any phenomenon connected with wood. It is likely that such studies may be applied to other areas of wood science such as flow and sorption.

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