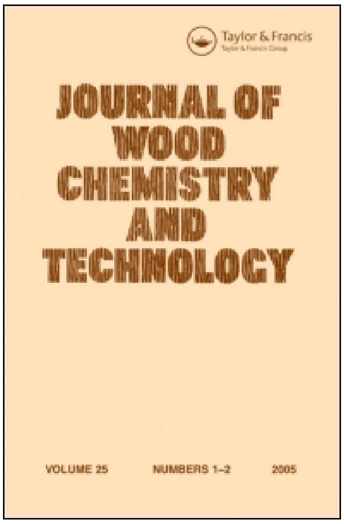

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# The Activation of Wood Fibre for Thermoplastic Coupling, the Reaction of Wood With a Potential Coupling Agent

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# THE ACTIVATION OF WOOD FIBRE FOR THERMOPLASTIC COUPLING, THE REACTION OF WOOD WITH A POTENTIAL COUPLING AGENT.

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## ABSTRACT

The reaction of *pinus sylvestris* with an unsaturated aliphatic isocyanate, TMI, was studied. Using six different solvent/swelling systems, the weight percent gains (WPG) of solid wood blocks was investigated. TMI was found to react readily with wood & WPG's of up to 74% were recorded. The modification of the wood improved the dimensional stability, with high anti shrink efficiency (ASE) values up to 90% and low weight losses recorded over two 7 day water soak cycles. This evidence strongly suggests modification of cell wall polymers.

The reacted blocks were characterised by FT-IR and the spectra showed good evidence of a reaction between the -NCO and wood -OH with the introduction of a carbonyl group at 1710 - 1720 $cm^{-1}$. There was no evidence of polymerisation of TMI, indeed the spectra indicated the continued presence of C=C, possibly 1,1 disubstituted ethylene functionality.

The activation energy of the reaction was determined by measuring the WPG at 4 temperatures. This was found to be 54 kJ/mol., comparable to that of butyl -NCO with wood.

## INTRODUCTION

An aim of much recent research in the area of biomass utilisation has been to convert wood waste and high yield fibre into a high value product.[1]

The use of thermoplastics and composites thereof has also increased tremendously for packing, building, electronics and other applications.[2] The great advantage of thermoplastic polymers is their ability to be tailor-made to suit each end use.[3] Indeed, a three fold increase in demand is forecast for lightweight, strong and reliable thermoplastic products.[4,5,6]

To increase the strength and toughness properties, fibres and fillers are added. Most commercially important composites are based on glass fibre.[7] In fact, about 93% of all industrial fibre reinforcing material is glass fibre.[8,9] Fillers have also been added to reduce the cost of production. But the high energy costs of producing synthetic fibre has forced researchers into looking for cheaper renewable alternatives. One possibility is to use natural, lignocellulosic based fibre material.

Performance of a fibre reinforced composite depends largely on the strength of the interfacial bond between the fibre and the matrix.[10] A major problem therefore is the incompatibility between natural fibre and thermoplastic polymers. Three main problems have been identified :

1. Poor dispersion of the fibre due to fibre/fibre hydrogen bonding.[11]
2. Wide polarity differences of the surfaces, preventing efficient matrix - fibre bonding.[12]
3. The hydrophilic nature of organic fibre.[4,5]

Ways of overcoming the limitations of resin systems in wood composites, such as the lack of covalent bond formation between wood and resin,[13] have also been sought. For example:

1. Cross linking by difunctional molecules e.g. diisocyanates.
2. Surface modifications allowing particle surface chemical reaction.
3. Surface plasticisation.[14]

The ultimate aim is to produce a wood composite with the advantages of thermoplastic forming properties, having efficient covalent bonding between fibre and matrix. The use of coupling agents has proved relatively successful in this area e.g. silanes[15] and isocyanates.[12,16]

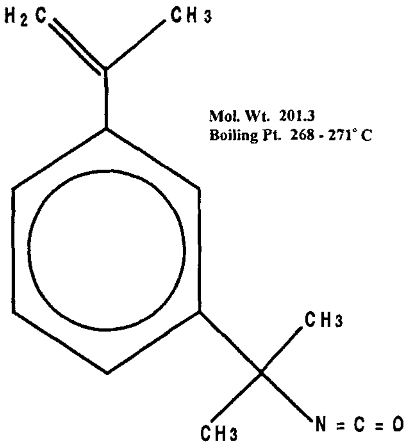


FIGURE 1. The molecular structure of dimethyl m-isopropenyl benzyl isocyanate (TMI).

This paper reports an assessment of the reaction of a potential isocyanate coupling agent and wood

TMI is potentially an excellent coupling agent (see Figure 1). The isocyanate group (-NCO) is well documented in reactions with wood.[17,18,19] Kinetics of the reaction between butyl -NCO and wood has also been studied in some depth.[20,21] The unsaturated α-methyl styrene type monomer functionality has potential for grafting other unsaturated monomers such as styrene and methyl methacrylate to the surface of wood or plant fibres.

## EXPERIMENTAL

Wood specimens were of clear scots pine sapwood 15 x 15 x 5 mm (radial x tangential x longitudinal), extracted for 5 hrs in 4:1:1 (vol:vol) toluene : acetone : IMS mixture. Blocks were dried at 105°C prior to use.

### Swelling Study

6 solvent ratios were used. Pyridine 100% (swelling solvent); 65:35 pyridine:toluene; 50;50; 40:60; 35:65 and 100% toluene (non swelling solvent).

Solvents were dried, pyridine stored over KOH as traces of water in solvents increase wood swelling.[22] Moisture was excluded from the system with a silica gel moisture trap. Reaction temperatures of 20,50,90 & 114°C were used in the study. Blocks were removed from the solvents at timed intervals and the dimensions recorded (±0.05mm) until equilibrium was reached.

### TMI Modification

The solvent mixtures described above were used and an excess of TMI was added. Two reactions were carried out, one in an oxygen atmosphere and the other under a positive pressure of argon. Both reactions took place in the dark at 114°C in sealed reaction tubes. The reaction was stopped by washing the blocks in cold acetone followed by 90 min reflux in acetone/chloroform. Blocks were dried and weighed.

### Dimensional Stability

A water soak method was used to determine the dimensional stability of the reacted wood blocks. The method was developed by Rowell & Gutzmer[23] and fully described by Rowell & Ellis.[24] Initial volumes were calculated and the blocks were then subjected to two 7 day water soak cycles. ASE and weight losses were recorded after re drying at the end of each 7 day period.

Anti shrink efficiency (ASE) is calculated as follows:

$$\text{Volumetric swelling coefficient (S)} = \frac{V_2 - V_1}{V_1}$$

Where $V_2$ = wood volume after wetting with water.
$V_1$ = wood volume of oven dried sample before wetting.

$$\text{Anti shrink efficiency (ASE)} = \frac{S_2 - S_1}{S_1}$$

Where $S_1$ = treated volumetric swelling coefficient
$S_2$ = untreated volumetric swelling coefficient

### FT-IR Characterisation

Wood samples were sliced and cooled in liquid nitrogen before being powdered in a micro dismembrator. KBr disks containing 1% sample were pressed and scanned.

### Activation Energy of the Reaction

Pre swollen blocks were added to a pre heated reaction mixture containing ≈ 3 times excess of TMI (calculated from available -OH in wood). Reactions were carried out at the following temperatures, 50, 70, 90 & 110°C. The reaction was stopped and the specimens cleaned up was as above. The WPG's were recorded.

## RESULTS AND DISCUSSION

### Swelling Study

The interesting points to come out of this preliminary study were the effects of temperature on behaviour of blocks. As expected, increasing the volume of pyridine in the reaction mixture lead to increased absolute volumetric swelling of the samples. However, increasing the temperature does increase the rate of wood swelling to equilibrium, but does not seem to increase the absolute volume attained, e.g. in 100% pyridine, the results are summarised in Table 1.

West[21] studied the swelling of wood in a mixture of pyridine and toluene. The swelling profile was found to be a classic sigmoid curve supporting the theory that wood has 'layers' of -OH available for swelling. The swelling to saturation of the first 'mono' layer causes the first part of the curve, followed by swelling of multi layers causing the sharp increase in the latter part of the curve.

The data give an indication of how -OH sites become available as pyridine swells wood. Swelling of the blocks will be important to allow TMI (a large molecule) access to these -OH groups As pyridine also acts as a base catalyst for the -NCO wood reaction, the modification reaction was carried out with the same solvents as used in the preliminary swelling study.

### Modification with TMI

The WPG of modified wood increases as swelling and catalyst content increases (Figure 2). A similar reaction was carried out in an argon atmosphere to reduce further the possibility of free radical formation (and possible polymerisation of TMI) in the reaction system. The results of this experiment were similar to the first system (see Table 2).

TABLE 1

Effect of Temperature on Rate and Absolute Volumetric Swelling of Wood.

| TEMP (°C) | Vol. Swelling (%) | Time to Eqm. (mins) |
|---|---|---|
| 20 | 19.7 | 720 |
| 50 | 19.2 | 180 |
| 90 | 19.3 | 120 |
| 114 | 19.0 | 120 |

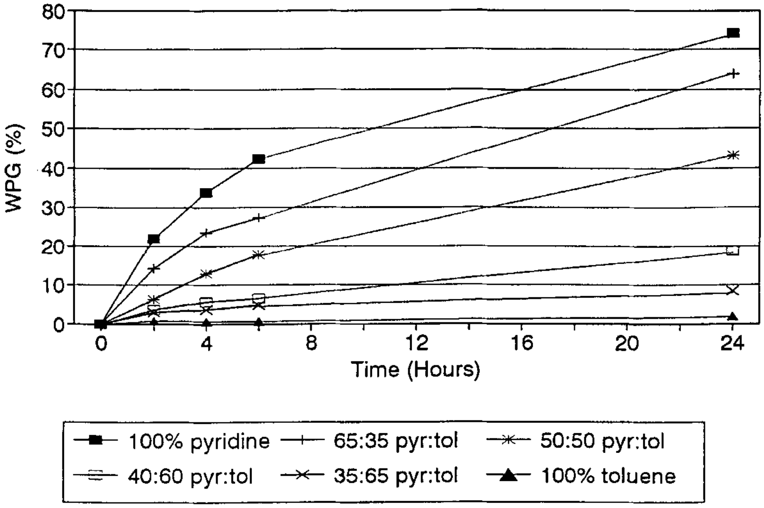


FIGURE 2. WPG profiles for modified wood samples at 114°C

In an argon atmosphere and in the dark, free radical initiation is most unlikely to occur. Hence no route for homopolymerisation can be easily perceived. Even in the presence of oxygen it seems that no polymer is formed.

Rowell[18] investigated the wood / -NCO reaction and found that lignin underwent a higher degree of chemical substitution than the polysaccharide component. West & Banks[25] found that butyl -NCO reacted more rapidly towards lignin, but to a lesser extent over an extended period than the polysaccharides.

TABLE 2

Comparison of WPG Data for Oxygen and Argon Atmosphere System at 114°C

| | **Reaction** | **Conditions & WPG (%)** |
|---|---|---|
| **Time (hrs.)** | 100 % pyridine, $O_2$ | 100 % pyridine, argon |
| 2 | 21.9 (1.0) | 22.5 (0.8) |
| 4 | 33.9 (1.2) | 32.2 (0.8) |
| 6 | 42.2 (0.5) | 37.5 (1.1) |
| 24 | 74.1 (1.9) | 74.0 (3.1) |

parentheses = standard deviations; N°of replicates = 5

So far the assumption has been made that the modification is taking place in the cell wall. A simple calculation can be made which compares the degree of wood swelling with the calculated volume of added chemical.

$$\text{Volume} = \frac{\text{Mass add on (g)}}{\text{Density TMI (g/ml)}}$$

If the reaction occurs mainly in the cell wall, then the volume of added chemical should correspond to the increase in volume of the wood. Whereas, a polymerisation type reaction in the lumen would lead to high WPG but lower volumetric swelling. A sample of blocks were taken and the comparison made, the results are shown in Table 3.

The comparison of the two suggests good correlation between the calculated add on volume of TMI and the increase in volume of the wood blocks. This is further evidence that a reaction is taking place in the cell wall.

Determination of Dimensional Stability

Rowell & Ellis[24] investigated wood stability in an experiment designed to show differences between wood cell lumen and cell wall reactions. The results obtained from TMI modified blocks are displayed in Figure 3.

Small reductions in weight were associated with the water soak procedures. These are summarised below.

TABLE 3

Comparison of Block Swelling And Calculated Add On of TMI

| Conditions/Time | WPG | Vol. swell (cm$^3$) | Chemical Addn. (cm$^3$) |
|---|---|---|---|
| 35:65 pyr : tol 6 hrs | 4.7 | 0.03 | 0.03 |
| 40:60 pyr : tol 6 hrs | 6.4 | 0.04 | 0.03 |
| 50:50 pyr : tol 4 hrs | 12.9 | 0.08 | 0.07 |
| 65:35 pyr : tol 4 hrs | 23.4 | 0.16 | 0.15 |
| 50:50 pyr : tol 24 hrs | 43.0 | 0.24 | 0.22 |
| 100 % Pyr 24 hrs | 74.1 | 0.53 | 0.47 |

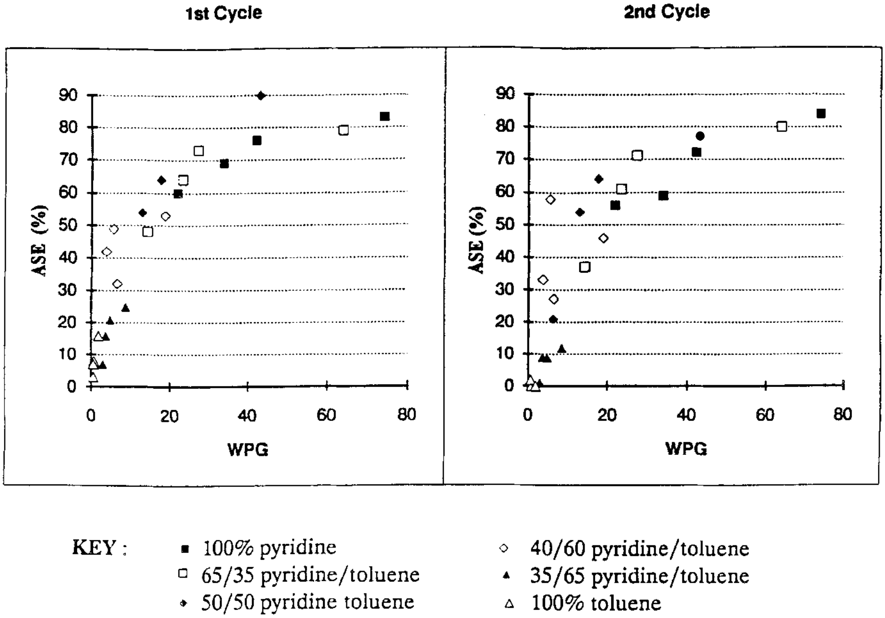


FIGURE 3. Comparison of anti-shrink efficiency vs. WPG over 2 cycles of water soaking.

Average for the 1st 7 days : 1.6 % (± 0.9) Control 1%

Average for the 2nd 7 days : 0.2 % (± 0.16) Control 0.4%

Modification of the wood leads to irreversible swelling and a reduction of the number of -OH groups. This imparts a significant dimensional stability. There are two useful comparisons to be made from the data. One is how the level of modification (WPG) affects the ASE. Figure 3 shows a clear trend of increasing ASE as the WPG increases. There is also a small but consistent drop in ASE after the second 7 day cycle. Rowell & Ellis[24] suggested that a small loss of adduct is the cause. The small weight losses reported above support this view.

The levelling off of ASE at high WPG's is interesting. Rowell et. al.[26] found that the ASE can be reduced at very high WPG's. This was attributed to the cell wall beginning to rupture exposing fresh -OH sites. Table 4 compares the ASE values for methyl -NCO modified wood[17] to that of TMI.

Table 4 shows that both TMI and methyl -NCO modification imparts a similar level of dimensional stability at a similar WPG. Though for TMI there is not the large reduction in the ASE values above 40 % WPG exhibited by methyl -NCO and associated by Rowell et. al.[26] with exposure of fresh -OH sites. TMI is a large molecule (Mol. wt. 201.3) compared with methyl-NCO (Mol. wt. 57). The effect of this is made clear in Figure 4. At a given mole % gain (WPG / Mol. wt.) the ASE of TMI modified wood is higher than methyl -NCO modified samples. But Figure 4 also shows that a much higher degree of substitution of -OH groups is reached by methyl -NCO modification. At ≈ 0.5 mole % gain the ASE is at its maximum.

This suggests that the higher ASE values for TMI are due to a greater cell wall bulking effect and the levels of modification required to cause cell wall rupture are not reached. The ASE values may therefore be associated with a combination of both bulking and -OH removal effects.

The other useful comparison is to look at the ASE of wood at similar WPG's achieved in different conditions. The fact that the reactions were carried out in different swelling conditions could possibly lead to uneven distributions of adduct in the cell wall in some of the lower swelling reactions. The ASE of such a sample could be lower than that of a comparable sample in which increased swelling lead to a more even penetration of chemical in the cell wall. A level of ≈ 20 % WPG was chosen and the ASE compared in Figure 5.

The evidence for uneven distribution and subsequent reduction in ASE is not strong. Figure 5 shows a similar ASE value is obtained at similar WPG. The

TABLE 4
Comparison of the Dimensional Stability of TMI and Methyl Isocyanate Chemically Modified Wood.

| Methyl Isocyanate | | TMI | |
|---|---|---|---|
| **WPG(%)** | **ASE (%)** | **WPG(%)** | **ASE(%)** |
| 11.3 | 47.7 | 12.9 | 54 |
| 16.3 | 68.0 | 17.6 | 64 |
| 25.0 | 72.0 | 23.4 | 64 |
| 28.6 | 74.5 | 27.7 | 73 |
| 40.4 | 76.3 | 42.2 | 76 |
| 47.7 | 70.8 | 63.9 | 79 |
| 52.7 | 57.3 | 74.1 | 83 |

Methyl Isocyanate data from Rowel & Ellis[17]

slightly lower ASE attained with the lowest swelling system (40/60 vol/vol pyridine/toluene) may be due to some thermal degradation occurring over the long (24 hr) reaction time needed to obtain the weight gain required.

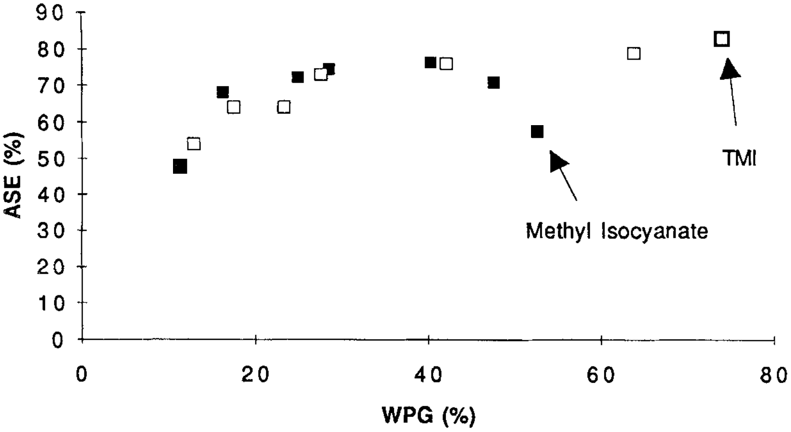
Overall, these results have shown the bond formed during the reaction of TMI with wood to be hydrolytically stable and that the TMI adduct is not readily leached from the wood. It appears to matter little whether the reaction is carried out in a full or partial cell wall swelling solvent

## FT-IR Characterisation

The major difference between the spectra obtained for modified and unmodified wood samples (Figure 6) is the presence of a carbonyl C=O peak at 1710 - 1720 $cm^{-1}$. This is consistent with a -NCO / wood -OH reaction yielding a carbamate ester product. The peak increases in intensity as WPG increases, whilst there is no evidence of unreacted -NCO groups (2200 $cm^{-1}$) indicating that the clean up procedure is efficient.

There are absorptions at 1600 - 1650 $cm^{-1}$ and 895 $cm^{-1}$. These are consistent with C=C, of a 1,1 disubstituted ethylene type.

There is also an interesting peak at about 1250 $cm^{-1}$, which appears at 15 % WPG and continues to grow. Rowell[18] found evidence of a band at



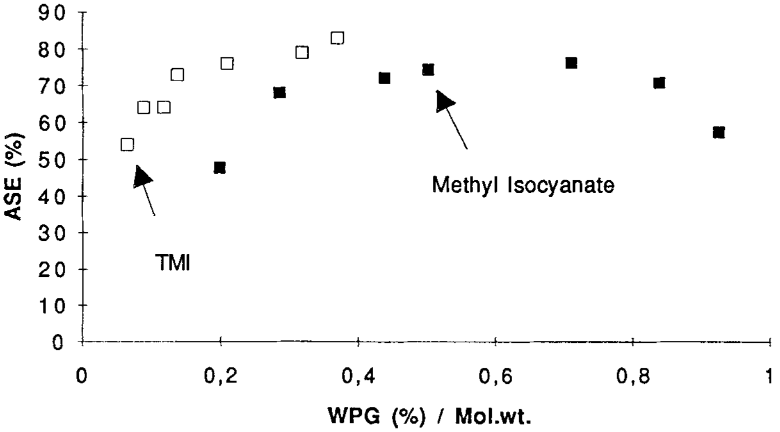


FIGURE 4. The effect of molecular weight of the modifying molecule on ASE. A Comparison of WPG and mole % gain methods for calculation of reaction.

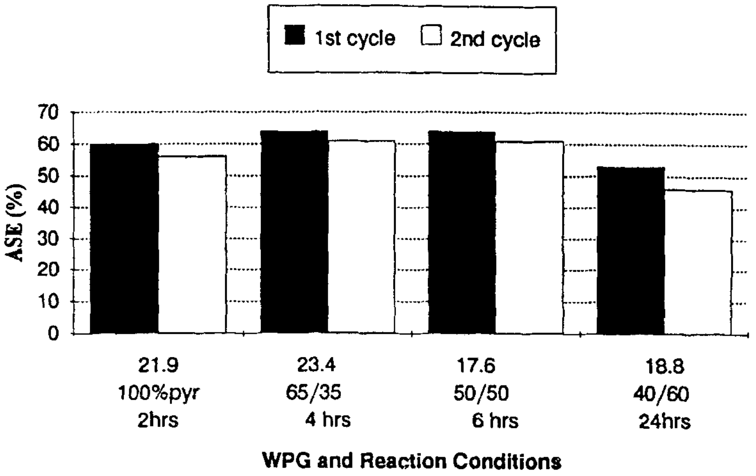


FIGURE 5. Comparison of the ASE of wood blocks of similar WPG, reacted for different times and in different conditions.

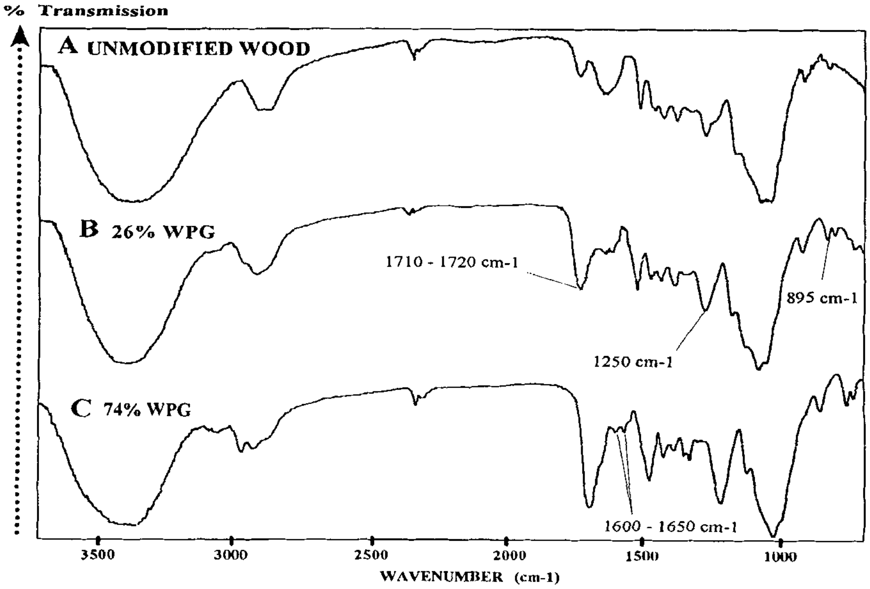


FIGURE 6. FT-IR spectra of unmodified and modified wood samples.

1270 $cm^{-1}$ which was attributed to C-N vibrations of disubstituted amines. Rensch & Reidl[27] studied the FT-IR spectra of -NCO modified chemi-thermomechanical pulp (CTMP). The presence of urethane C=O bonds was detected at 1725 - 1729 $cm^{-1}$. There was also a band at 1233 - 1218 $cm^{-1}$ which was considered again to indicate urethane as the major product.

The spectra of the samples reacted in an argon atmosphere were not significantly different to the reactions carried out in air. It is known that the C=C bond in TMI is stable to auto-oxidation.

The data again suggest strongly that TMI has reacted with wood and especially important is the evidence that the C=C bond on TMI has remained intact after the modification.

## The Activation Energy (Ea) of the Reaction

The activation energy was calculated from the initial rate of reaction taken from a plot of the WPG profiles at 4 temperatures. The rate was expressed as WPG / hr. The method was used by West[21] when investigating the wood/butyl -NCO reaction.

The Arrhenius equation takes the form :

$$\text{(Rate) } K = A \exp(-Ea / RT)$$

Where A = Arrhenius pre exponential; Ea = the activation energy;
R = gas constant; T = temperature.

In logarithmic form the equation becomes :

$$\ln K = \frac{-Ea}{RT} + \ln A$$

Thus a plot of ln K vs. 1/T is of slope -Ea/R and Ea can be calculated. In this calculation ln K is synonymous with ln Ro which is the natural log of the initial rate of reaction. The data are plotted in Figure 7.

Regression analysis of a plot of the data (Figure 7) yields a slope of -6.478 and the activation energy is calculated to be 53.4 ± 2 kJ/mol .

The reaction is carried out in a heterogeneous system i.e. solid / liquid and the kinetics are therefore complex. However, the reagent TMI is kept in

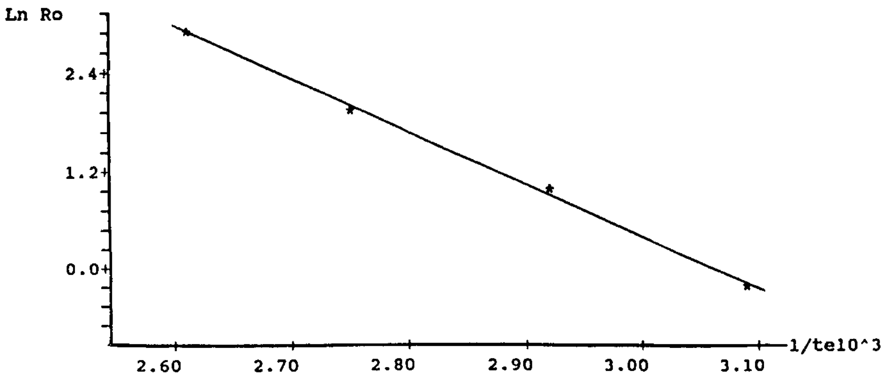


FIGURE 7. Arrhenius plot of the initial rate of reaction (Ro) of TMI modified wood.

excess. First order kinetics with respect to wood -OH groups are assumed. The data of Figure 7 give a remarkably good fit to this model.

The Ea for the TMI / wood reaction is very similar to that of butyl -NCO, found to be 57 kJ/mol.[21]. This suggests that the -NCO group has a relatively favourable orientation for reaction, projecting from the planar ring part of the molecule. This appears to allow favourable juxtaposition of the reagent and solid phase -OH groups to occur to allow easy reaction. The reagent is therefore a useful wood modifying molecule, giving rise to effective dimensional stabilisation and attaching a C=C bond which may allow grafting to occur by free radical addition. Systems concerning this possibility are being explored.

## CONCLUSIONS

The reaction of TMI with solid wood has been investigated. WPG data supported by water soak tests and FT-IR. indicate that TMI reacts with the wood cell wall. The Ea of the reaction show TMI to be very reactive compared to other -NCO's. A mechanism proposed by West[21] for the reaction of butyl -NCO with wood in a 3° amine catalyst showed that wood polymers are rapidly swollen by the solvent e.g. pyridine and a complex is formed between -NCO and amine.

The rate determining step, with an Ea of 57 kJ/mol for butyl -NCO and 54 kJ/mol for TMI was the formation of a transition state as the complex and -OH collide. It is perhaps here where the orientation of the reacting -NCO group and other steric factors become important. Finally, the formation of carbamate is rapid.

TMI it seems has satisfied one of the criteria for being a successful coupling agent, i.e. it is able to form stable covalent bonds with wood.

## LIST OF ABBREVIATIONS

| | | | |
|---|---|---|---|
| ASE | Anti shrink Efficiency | PYR | Pyridine |
| Ea | Activation Energy | TOL | Toluene |
| FT-IR | Fourier Transform Infra Red | TMI | Dimethyl m-Isopropenyl Benzyl Isocyanate |
| -NCO | Isocyanate group | | |
| -OH | Hydroxyl group | | |
| WPG | Weight Percent Gain $= \dfrac{\text{wt. after treatment - wt. before treatment}}{\text{weight before treatment}} \times 100$ | | |

## ACKNOWLEDGEMENTS

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