

Why Does Chewing Gum Stick To Hair and What Does This Have to Do With Lignocellulosic Structural Composite Adhesion?

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Abstract

The development of structure/property relationships for polymeric diphenylmethane diisocyanate (pMDI) bonded wood composites can be achieved by understanding the nature of the adhesion process and by understanding the changes in molecular motions and molecular ordering of the adhesive, the wood and the interaction zone. Efforts to understand these phenomena are reported in this paper. A range of techniques have been used to understand the mode of adhesion by which isocyanates bond wood and to characterise the physical and chemical nature of the adhering zone.

The techniques include optical and x-ray microscopy which show the locus and extent of resin penetration into wood. Solid state and inversion recovery cross polarisation NMR investigations, have been employed which show how the molecular mobilities of lignin and hemicellulose, but not cellulose, are changed in the presence of isocyanate resin. Diffusion studies were conducted which showed that the isocyanates induce a morphological change in the wood. These effects are related to microscopic visco-elastic phenomena, which were investigated using dynamic mechanical thermal analytical studies of pMDI bonded wood composites. A direct correlation between the changes in molecular mobilities and loss moduli can be realised.

A diffusion interphase mode of adhesion is concluded from this work which exhibits distinct visco-elastic properties and which is responsible for the final property set of the composite including strength and water interaction characteristics.

Introduction

The use of lignocellulosic composites for structural applications has grown dramatically in the past twenty years. The continued growth and introduction of these composites into new engineering applications necessitates a clear understanding of the adhesion mechanisms contributing to composite performance.

The object of these studies is therefore to determine the nature of isocyanate based resin adhesion to wood and to understand how the molecular nature of substrate and the resin impact/control the large scale physico-mechanical properties of the derived composites. Understanding these aspects will allow for future product improvements both in terms of processing and final property sets.

For adhesion of any kind to occur it is vital that the adhesive wets the substrate surface well. Wetting can be affected by numerous parameters including temperature, surface energies, surface roughness, pH, relative humidity, viscosity and so on. If good wetting is achieved, then the adhesive needs to establish an adhesive link to the substrate. There are many theories as to why things stick, these include

- the formation of chemical bonds (covalent or ionic bond formation),
- the formation of secondary bonds (hydrogen bonds, Van der Waals forces and so on),
- mechanical interlocking, in which the adhesive flows into cracks and crevices of the substrate and then hardens, physically locking the adhesive to the substrate,

- establishment of a diffusion interphase, which is, at a simple level molecular entanglement between the adhesive and the substrate. This can almost be seen as a mechanical interlocking but at the molecular level, and
- electrostatic forces, when two bodies are in close contact, electrons may transfer from one to the other generating positive and negative charges.

Many studies have been carried out attempting to determine the nature of adhesion between various resins and wood. These studies usually attempt to prove or disprove the existence of one of the possible modes of adhesion listed above (4,6,8,20,21). The approach taken in the current study has been to assess the adhesive-substrate interactions using a range of techniques, and interpreting the results collectively to determine the mode of adhesion. Some of these studies are reported below along with the overall conclusions of the work.

The investigation goes further, using NMR and thermal analytical tools to investigate the molecular and microscopic visco-elastic behaviour of the adhering materials in an attempt to explain the macroscopic composite performance.

Experimental

Polymeric methylene di-phenyl di-isocyanate, pMDI, used in these studies was Rubinate[®] Binder-1840 manufactured by Huntsman Polyurethanes. The pMDI resin had an Isocyanate Equivalent Weight of 135, NCO content of 31.2%, and viscosity at 25°C was 250cps.

Solid State NMR

Harvested logs of Aspen wood (*Populus tremoides* Michx.) were obtained from a forest-product structural panel manufacturer. A representative log was cross-sectioned. The cross sections were further cut in a tangential direction into veneers of approximate size 100 x 60 x 1mm. The veneers were conditioned in a 110°C forced air oven for one hour. After oven drying, the veneers were equilibrated to 8% moisture content in an environmental chamber. Moisture contents were determined using a Wagner Moisture Meter[®] Model-L606. The measurements were obtained from stacked veneers to ensure proper sampling depth.

NMR experiments were carried out using wood preparation as above with and without a resin loading of 10% Rubinate Binder (by weight of the wood). The resinated wood NMR samples were pre-cured in a forced air oven at 140°C for one hour.

¹³C cross polarisation magic angle spinning (CP/MAS) experiments were performed on a Varian Unity-200[®] solid state NMR spectrometer operating at a ¹³C resonance frequency of 50.77MHz. A proton de-coupling and spin locking field strength of 57kHz was utilised for all the experiments. Cross polarisation time constants, T_{CH}, were obtained using the inversion recovery cross polarisation (IRCP) pulse sequence seen in figure 1. In this experiment the initial CP contact time, t₁, was equivalent to the CP maxima obtained from a variable contact time experiment. Immediately following initial CP the proton spin reservoir was phase shifted 180° and held for an inversion time, τ. τ-Values of 0 to 10 000μs were employed. The IRCP data, relative carbon intensity vs. inversion time, were fit to the bi-exponential models of Parker, *et al.* (15).

DMTA studies

Freshly cut and moisture content conditioned wood veneers (25 x 13 x 1mm) were mounted in a TA Instruments 983[®] Dynamic Mechanical Analyser in low displacement (0.3mm) bending mode using 1Hz frequency. The modulus as a function of temperature (25 – 225°C with a heating rate of 10°C/min) was then recorded. A second piece of wood conditioned similarly to the first and coated with 5% by weight of Rubinate[®] Binder-1840 was then tested. Having been through the first heating cycles (heat #1), the samples were cooled re-conditioned to original moisture content and re-tested (heat #2). This two step experiment was devised to eliminate confounding of the

data due to natural variability between pieces of wood. In essence, heat #1 is a curing step and heat #2 defines the change in behaviour of the wood in the presence of cured binder after environmental equilibration.

Optical microscopy studies

Single drops of Rubinate[®] Binder-1840 (Huntsman Polyurethanes) were premixed with 0.2% Hostasol Red GG (Hoechst), a fluorescent dye and applied to a freshly cut surface of a single piece of Aspen (*Populus Tremoides* Michx. obtained from a forest-product structural panel manufacturer). The wood had previously been conditioned to a defined moisture content and the surface cut was selected to be either tangential or radial. A second similarly prepared piece of wood was then placed, with parallel grain, on top of the resinated wood piece. The assembly was then mounted in a press at 180°C for 10 minutes at 8-bar pressure. After allowing to cool, microtomed sections were cut from the transverse face of the assembly and observed under an Olympus BHS optical microscope using a mercury lamp. By observing consecutive sections, the cross grain and along grain spreads, as well as the depths of resin penetration could be observed and 3D images of the movement of resin could be reconstructed. From these, spreadability, maximum penetration depths, depth distribution, and penetration volume as well as shapes of penetrated resins could be determined.

Diffusion of isocyanates into wood

Pre-weighed, thin (0.1 – 0.2mm) sections of tangentially cut, moisture content controlled aspen and pine (*Pinus sylvestris* L.) were immersed in temperature controlled Rubinate[®] Binder-1840. The samples were removed periodically and after having removed residual surface resin 'contamination' by scraping with a knife, the samples were re-weighed. Plotting the weight as a function of square root time, and using Fick's second law of diffusion, the diffusion coefficients could be calculated for that temperature (3).

X-Ray Microscopic Studies

Single drops of Rubinate[®] Binder-1840 were applied to wood and cured as for the optical microscopy study. The sample was then embedded in LR White Methacrylate (Taab laboratories) by immersing the sample in the monomer for 21 days. After curing at 70°C for 12 hours, the block was then orientated, trimmed and sectioned with a diamond knife in an ultra-microtome to obtain 0.2 micron thick sections transverse to both the lumen and pMDI bonded surface interface. These sections (typically 1mm by 1mm) were then placed on a x-ray transmission membrane and placed in the scanning transmission x-ray microscope at the X1a beam line of the National Synchrotron light source at Brookhaven National Laboratory for imaging at atmospheric pressure. This work was carried out under the supervision or and in conjunction with Chris Buckley, King's College, University of London.

Laser ionisation mass spectroscopic (LIMA) studies

Laser ionisation mass spectra of Rubinate[®] Binder-1840 impregnated wood as well as isolated resin and wood samples and resin model compounds (such as aromatic substituted ureas and ring-substituted anilines) were recorded. The work was conducted under the supervision of and in conjunction with A. Waddilove, Surface Science and Technology, University of Loughborough.

Results and Discussion

Solid State NMR

A true understanding of composite dynamics starts at the molecular level (19). NMR lends itself very well to the study of molecular dynamics and motions and molecular arrangements and

ordering at the molecular level (10,15). Once this is achieved, the molecular dynamics can be correlated to the macroscopic visco-elastic nature of the composite.

In a wood composite, if the number of molecular associations between adhesive molecules and wood molecules is large enough, we should expect to observe, by NMR, changes in at least some of the distributions of molecular mobility or changes in molecular arrangements when comparing the composite to neat wood. Differences will only be observable if the relaxation properties of the entire ensemble of observable nuclei are effected by the molecular interactions. Our investigations applied inversion recovery cross polarisation (IRCP) measurements as outlined in the experimental section, to probe the near static motional regimes of Aspen wood molecules in the presence and absence of pMDI.

Figure 1 illustrates the IRCP experiment and figure 2 represents a typical IRCP spectrum obtained for Aspen wood. The resonance assignments have been previously defined as 105 ppm for the C1 carbohydrate carbon, 73 ppm – 78 ppm for the C2, C3 and C5 carbons, 83 ppm – 89 ppm for the C4 carbon and 63 ppm – 66 ppm for the C6 carbon (7). The resonances at 21 ppm and 173 ppm can be attributed to $-CH_3$ and $-COOH$ of the acetate groups in hemicellulose. Despite the dominance of the carbohydrate resonances, lignin resonances are resolvable; in particular, the methoxy groups at 54 ppm and the aromatic carbons between 130 ppm and 160 ppm.

The morphological and motional features of polymers in general and wood specifically can be quite diverse. Therefore, in order to develop structure/property relationships and describe the macroscopic properties of polymers via microscopic or molecular level properties, we need to account for motional and morphological heterogeneity. It has been previously shown that IRCP measurements can be used to study morphological heterogeneity in solid polymers (2,12,13,14,16). IRCP allows one to deconvolute different components within a polymer by virtue of their different rates of cross polarisation, figure 2. These multiple components are seen as bi-exponential fits of the IRCP data. The accepted models for the CP process imply that cross polarisation time constants, T_{CH} , are sensitive to near static motions (22). This is in contrast to relaxation times like rotating frame spin lattice relaxations ($T_{1\rho}$), which are sensitive to kHz frequency motions. In addition, CP is a distance dependent phenomenon, with a $1/r^6$ dependence, where r is the inter-nuclear distance. Thus, when investigating a polymer, IRCP measurements can be used to probe local packing arrangements as well as motional components with long correlation times (16).

Table 1 illustrates the type of data obtained from an IRCP experiment. In this table we have carbon atoms representing the three main components of wood: cellulose, hemicellulose, and lignin. T_{CHA} represents the rapid cross polarising portions of those wood components and T_{CHB} represents the slower cross polarising carbons of those wood components. The fractional percentages of these components represents the weighting of those rapid and slower polarising components as derived from the bi-exponential fit of the data.

From the data it can be observed that lignin, hemicellulose, and cellulose all have different T_{CH} 's for the neat wood sample. The C1 cellulose carbon, 105 ppm, has the highest fractional percentage for T_{CHA} and the lowest T_{CHA} value. This is reasonable since cellulose is the most crystalline of the components and would therefore be expected to cross polarise rapidly. The data is self consistent when observing the T_{CHB} data for these cellulose carbons. That is, these cellulose carbons have the lowest T_{CHB} fractional percentage and lowest T_{CHB} values. What the data for the neat wood sample indicates is the 105 ppm carbon nuclei exist in at least two environments. A crystalline, rapidly cross polarising environment and a more disordered slower polarising environment. This multi-phase behaviour of these 105 ppm carbons for neat wood can be explained as arising from the crystalline and amorphous environments of cellulose. It might

further be explained by the fact, these types of carbon nuclei are found in both cellulose and hemicellulose environments.

If we compare the T_{CH} 's for hemicellulose and lignin carbons, 21 ppm and 54 ppm respectively, we observe a lower fractional percentage for T_{CHA} and higher T_{CHB} values compared to those observed for cellulose. These trends are reasonable since hemicellulose is much less crystalline than cellulose and lignin is an amorphous network polymer. In addition, these carbons also exhibit two phase behaviour indicating they are found in more than one type of environment.

If we now compare what happens to these wood resonances in the presence of cured pMDI based adhesive we observe little or no change in the fractional percentages for all the resonances and a decrease in both T_{CHA} and T_{CHB} for both lignin and hemicellulose carbons. The lack of change in the cellulose resonance is not surprising because of the crystalline nature of cellulose. The changes in the lignin and hemicellulose cross polarisation rates can possibly be explained as changes in molecular mobility. Since these particular carbons have attached protons the distance between cross polarising protons and carbons should not be a factor and therefore, the changes must arise due to motional differences.

Why such changes in motion occur can be attributed to a number of possible causes – the heat treatment of the wood; the intimate proximity of the isocyanate adhesive; a reaction to the isocyanate adhesive; loss of associated components by for instance leaching of material from the wood into the continuous resin liquid phase prior to cure; dehydration phenomena; intra-wood component cross-linking induced by the presence of isocyanate resins.

Many of these possibilities can be eliminated through controlled experimentation. Hence, the application of heat to the wood can be neglected, further, by NMR and FTIR, chemical reactions between the isocyanate and wood components can be also essentially neglected. However, physical intimacy, leaching of associated components and induced chemical changes of that component by the presence of the isocyanate (e.g. cross-linking reactions, dehydration etc.) have not been fully eliminated as possible causes.

Some 2D NMR studies were also conducted, representative images are shown in figure 3. These images show that the cured resin in the composite is dominated by urea and biuret groups and that these are associated with lignin and hemicellulose.

DMTA studies

If the above data and interpretations are reasonable, we should be able to see the changes in molecular level dynamics manifested in microscopic dynamic measurements like dynamic storage or loss moduli measurements. Dynamic loss moduli (E'') were taken as the response of choice due to their sensitivity to energy dissipation caused by changes in molecular mobility or distributions of motion. The dynamic loss moduli curves for neat wood and wood coated with 5% pMDI based adhesive can be seen in Figure 4. The data in figure 4 was obtained using the multiple step methodology described in the experimental section. From the data we observe a larger heat #1 loss peak for the sample treated with pMDI than was observed for the neat wood sample. As will be seen below, the depth of resin penetration into wood is large. This volume of isocyanate 'modified' wood has different compression hardness properties compared to that of neat wood (11) and these two effects could result in a larger heat #1 loss peak for the pMDI coated sample as compared to the neat Aspen wood sample.

However, we must be certain the difference in loss moduli between neat Aspen and Rubinate Binder coated Aspen is not a result of differences between the two pieces of wood themselves. It

is precisely this concern of wood heterogeneity confounding our data that led us to develop our two step DMA methodology. In the two step method, we eliminate sample to sample variability by investigating only the changes occurring within the same sample. Thus, if we compare the differences between heat #1 and heat #2 E" data we observe little change in the loss peak for neat wood and a large decrease in the loss peak for the Rubinate-1840 coated wood. This large change indicates a reduction in viscous energy dissipation. A low loss modulus is typical for composites and polymers exhibiting reduced molecular mobility as a result of good adhesion or increased cross link density. These findings are consistent with those observed by IRCP NMR.

We have also observed corroborative changes in microscopic dynamic measurements like dynamic moduli.

Optical microscopy studies

Figure 5 shows a typical optical micrograph image of resin penetration into aspen wood. As can be seen, the resin penetrates deeply into the wood, reaching depths of more than 1mm. It has been found, by increasing the resin droplet size applied to the wood surface, that a maximum depth of penetration is reached, beyond which further penetration does not occur. In these instances, as the amount of resin is increased further, spread of resin, both across and along the grain increases and the total volume of wood impregnation increases.

By observing consecutive sections cut from a single sample of glued wood, the total resin spread, depth distribution (as well as maximum depth and average depth), total penetration volume and even the shape of penetrated resin can be deduced. In this way, the influence of the quality of the wood (species, cut, moisture content, growth rate etc.), the influence of the quality of resin (viscosity, reactivity, surface tension etc.) as well as the influence of prevailing conditions (relative humidity, temperature etc.) on penetration characteristics can be studied. Many of the subtleties of the influences are beyond the scope of this paper, however, it is important to note that penetration is both very rapid and very deep as exemplified in table 2. This results in large volumes of modified wood.

In order to understand composite performance and the nature of adhesion, it is of great importance to understand the nature of this modified wood zone, whether it is more compressible or stiffer, whether it increases or decreases moisture ingress and so on. It is also important to determine whether the observed penetration is beneficial or detrimental for adhesion. The physicochemical effect of the large penetration was seen with the NMR and DMA work. A large volume of wood is affected which exhibits changes in the microscopic damping and molecular mobility.

Further, it has been found that the penetration parameters can be correlated to the macroscopic properties such as thickness swell and tensile strengths:

- (i) There is a critical penetration depth required for good mechanical properties. This depth is approximately equal to three cell thicknesses.
- (ii) The shape of the penetrated volume controls the stress distribution when loads are applied and that therefore, depending on the nature and orientation of applied loads, there is different preferences with regard to the shape.
- (iii) The greater the spread and the greater the volume of penetration, the better the thickness swell performance.

Examples of these points are illustrated graphically in figures 6 – 7 (17). The performance of isocyanate bonded wood composites can therefore be optimised by controlling the locus of resin penetration.

Diffusion of isocyanates into wood

It was mentioned above, the rate of movement of resin into wood is rapid. This rate has been measured by diffusion as described in the experimental section. Diffusion coefficients, as calculated by Fick's second law (3), were found to be of the order of $3.5 \times 10^{-4} \text{ mm}^2 \text{ s}^{-1}$ at room temperature, which are higher than the coefficients of diffusion of water into wood.

But rather more important than the rate of diffusion, is the pMDI uptake profile, an example of which is shown in figure 8. The uptake profile is initially conventional, in that mass increase is immediate and linear with respect to the square root of immersion time and after a certain period an equilibrium mass is reached. However, after prolonged immersion, a second mass increase stage is seen and this is followed by a subsequent mass loss of the sample.

This type of profile is usually associated with a morphological change in the sample, which is induced by the presence of the diffusant material. Hence, having diffused into the wood, the concentration of pMDI in the wood at the first equilibrium mass level, causes a change in the structure of wood, which allows even more isocyanate to diffuse into the matrix. To date it is unclear what this change is, whether it is beneficial to adhesion and whether it is beneficial to the derived property set of the composite, although from the NMR study, if related, would suggest that this is of benefit to property development.

It can be argued that although this morphological change does occur, it only does so, at relatively high concentrations of isocyanate and is therefore irrelevant for the purposes of industrial panel performances, which only use 1.5 – 6% resin loadings. However, it should be realised that within the penetrated volume of wood, described above, the concentration of resin will be high and within that volume of wood, this observed morphological change could be occurring.

The second uptake stage is followed by a mass loss. This indicates either leaching of material from the wood matrix or loss of mass due to the evolution of carbon dioxide, the formation of which is possible from isocyanate/water (or acid) reactions. However, the extent of mass loss is often larger than the total possible carbon dioxide mass (if all the isocyanate reacts with water). The observed mass loss is therefore assumed to be due to the leaching of material. Supporting this assumption are the observations that less resinous and lower extractive content woods show less mass loss and the isocyanate reservoir in which the wood is immersed increases in viscosity and eventually becomes solid (even when atmospheric moisture is excluded).

It thus seems that isocyanate enters wood, causes a morphological change, which allows increased diffusion of the resin. This in turn results in a continuous liquid phase through the wood matrix, providing a pathway for the removal of extractable materials.

Considering this result in light of the findings from the NMR work, it appears that intimacy between the adhesive and the wood does indeed occur but that the morphological change itself and/or the subsequent leaching of wood components, could also be responsible for the observed NMR relaxation time differences.

X-Ray Microscopic Studies

The penetration studies show that isocyanates access large volumes of wood and the NMR work shows that the isocyanate is intimately associated with lignin and hemicellulose. These results suggest that the isocyanate diffuses mainly into the middle lamellae between the wood cells, since, as can be seen in figure 9 (5) the highest concentrations of these components are in that layer of the wood. This interpretation is also supported by unpublished work by the authors, which show great affinity of the isocyanate to lignin and lignosic type materials and a very low affinity to cellulose and cellulose derivatives. To confirm this interpretation, the isocyanate modified wood zone was observed using x-ray microscopy. Figure 10 shows a typical composite image generated by x-ray microscopy; the isocyanate is shown as the bright areas. It is apparent that

the isocyanate is distributed in four principal areas: along the interface between the two pieces of wood; inside the ray cells; in some of the connecting pits between cells; and in the lumen on the inner cell wall surface of some of the large vessel cells. It is worth noting also where the isocyanate is not found. It is not found, in the smaller more abundant parenchyma and tracheid cells, in the middle lamella and finally, in the cell walls of the wood. Figure 11 shows more clearly a region of cell wall adjacent to resin, which has wetted the inner cell wall surface. In this instance, the isocyanate (or more specifically the aromatic content regions) is shown as the dark areas. Spot-spectra taken from the cell wall show x-ray absorbances consistent with that of lignin and cellulose. The spectrum is void of all the expected isocyanate type absorbances, except for a small shoulder at 286.6eV. Spot spectra of the middle lamella show typical lignin absorbancies only.

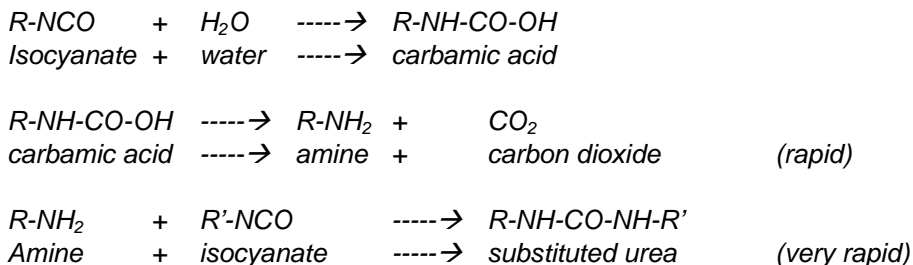
The isocyanate thus appears not to be accessing the middle lamellae. The shoulder in the cell wall spectrum could indicate the presence of isocyanate. However, since none of the other, stronger, isocyanate absorbance bands are seen, the presence of significant amounts of isocyanate in the cell walls is unlikely (1). From this work, it is difficult to see what the changes in NMR relaxation times and what the secondary uptake from the diffusion study are due to, since the isocyanate is not accessing the true wood matrix which could possibly result in the observed changes.

However, it should be noted that the pMDI model used in this work, was moisture-cured isocyanate, that is, the model was polyurea based on pMDI. Hence, the x-ray microscopic study reveals 'isocyanate' regions but only in the form of polyurea. Those areas identified as being void of isocyanate are actually therefore only void of polyurea. The shoulder at 286.6eV in the cell wall spectrum has not been identified. However, it does suggest the possibility of isocyanate, in some form other than polyurea, being present in the cell wall. Irrespective of what the nature of the possible cell wall isocyanate is, if truly present, this would explain the NMR and diffusion study results.

LIMA studies

Infra-red and NMR studies have revealed that during cure, the isocyanate is predominantly converted to polyurea via the reaction with water (reaction scheme 1) and that an appreciable amount of the polyurea groups react further with isocyanate to form biurets (reaction 2). There is very little evidence that isocyanates react with the abundant wood component hydroxyl groups to form urethane groups. The little evidence that has been found is with isolated extractives, which react with isocyanates to produce a number of reaction products including some limited urethane formation (17).

Reaction Scheme 1

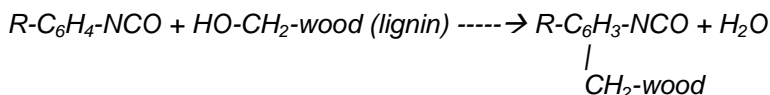


Reaction Scheme 2



Surface analytical studies, such as laser ionisation mass spectroscopy, of isocyanate/wood and model (e.g. isocyanate/lignin) samples gave rise to mass fragments consistent with ring substituted condensation reaction products of isocyanates with methylol wood component functionalities, as shown in reaction scheme 3.

Reaction Scheme 3



Isocyanate + methylol function on wood → ring substituted isocyanate, via methylene bridge

Equivalent fragments could be seen when substituted aromatic urea model compounds were heated with lignin or wood, but not when aromatic amine models were used.

The reaction shown in scheme 3 is rather unexpected in light of the hydroxyl reactivity with isocyanate functionalities. However, electronic modelling studies (9) have shown that such reactions would be feasible. Further, Pizzi has also identified such reaction products between isocyanate and wood (18).

Should such reaction products be produced in the cell walls of wood they would affect the NMR measurements, they could induce morphological changes, but they would not be observable by x-ray microscopy as it is currently done with polyurea being used as the reference for isocyanates. This will be checked during the next phase of the study.

Conclusions

Isocyanate adhesives rapidly and extensively diffuse and penetrate into wood. The resin locates in a number of anatomically distinct regions of the wood and there are indications that the reaction products formed are specific to the regions in which the resin has penetrated. Through a series of molecular level and microscopic level dynamic studies it has been shown that pMDI adhesives change the physical nature of wood. Specifically, the near static molecular dynamics observed by IRCP NMR show a decrease in molecular mobility for lignin and hemicellulose carbons. Further, diffusion studies have shown that morphological changes are induced within the wood in the presence of relatively high concentrations of the resins. These physical changes could be due to a number of effects, but as yet it is not possible to be conclusive as to which are really occurring. The possible effects are:

1. Primary bond formation via for instance methylene bridge formation to the aromatic ring of the isocyanate.
2. Secondary bond formation such as hydrogen bonding. Unpublished electronic modelling studies have shown the spatial and energetic possibilities of hydrogen bonding between polyurea and hemicellulosic fragments (9).
3. Isocyanate resin induced leaching of wood components.

These changes are responsible for an observed decrease in viscous energy dissipation in these pMDI/Aspen wood composites as seen by the microscopic level dynamics obtained via low frequency DMA show.

Since macroscopic composite properties are dependent upon microscopic and molecular level dynamics, this data provides a physicochemical basis for the high structural performance of pMDI bonded wood composites. Additional to the chemical effects impacting performance of the wood composite, the size, shape and distribution of resin penetrated wood regions have a significant influence on the derived mechanical and environmental property sets of the composites.

These results suggest that the mechanism of adhesion is one in which the isocyanate based resins form an 'anchored' diffusion interphase. In true diffusion interphases, there is a need for mutual inter-diffusion to occur between the two adhering phases. There is evidence that this indeed occurs, with the resin diffusing into the wood matrix and at least some wood components diffusing into the adhesive. The 'anchoring' referred to above refers to the possible covalent (methylene bridge formation from wood methylol groups to the isocyanate aromatic ring) and/or hydrogen bonding links (between polyurea and hemicellulose), which are probably occurring between the adhesive and the wood.

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