Transesterification Reaction Between Acetylated Wood and Trialkoxysilane Coupling Agents

Nilgül Özmen,[1] Nihat Sami Çetin,[1] Philippe Tingaut,[2] Gilles Sèbe[2]

[1]Faculty of Forestry, Kahramanmaraş Sütçü İmam University, Kahramanmaraş, Turkey
[2]Laboratoire de Chimie des Substances Végétales, Université Bordeaux 1, Talence, France

ABSTRACT: A novel dibutyltin oxide-catalyzed transesterification reaction between acetylated maritime pine sapwood (*Pinus pinaster* Soland) and methyltrimethoxysilane (MTMS) was studied. The transesterification exchange between the acetyl moities and MTMS was confirmed by weight percent gain calculations, Fourier-transform infrared spectroscopy, as well as solid state ^{13}C and ^{29}Si cross-polarization with magic-angle spinning nuclear magnetic resonance spectroscopy. The silicon atoms in the MTMS-transesterified wood were found to exist in the form of more or less condensed structures, concurrently formed by condensation between neighboring $Si(OMe)_3$ groups. An increase in the acetyl/MTMS exchange rate was also noted when the catalyst amount, temperature, or reaction time were increased. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 570–575, 2007

Key words: acetylation; maritime pine; methyltrimethoxysilane; transesterification; dibutyltin oxide

INTRODUCTION

Wood–plastic Composites (WPC) have gained significant popularity in the last decade. More and more products are now found in the market place but more research is also required to further develop this material. For instance, when WPCs are used in outdoor environments, they are subjected to various degradations due to fungal exposure,[1,2] UV light irradiation,[3–7] or freeze-thaw cycling.[8,9] In most cases, the wood filler was found to be responsible for the composite deterioration, because of its propensity to decay, photodegrade, and absorb water. Another critical drawback is the lack of adhesion between the hydrophilic lignocellulosic fibers and the hydrophobic polymers, which limits the strength performances and require the use of coupling agents.[10–14]

It has been reported that wood properties could be considerably improved by chemical modification of the lignocellulosic polymers;[15,16] therefore, this approach could be also applied to enhance the WPC's performances further. In particular, acetylation was found to improve the wood resistance to decay, as well as its photostability.[15,17–21] The water absorption by acetylated wood was also found to decrease. Varied nonwood lignocellulosic fibers have been acetylated and incorporated into plastic matrices, with the objective to improve interfacial adhesion.[22–26] Results indicated that the hydrophobized fibers were more easily wetted and dispersed into the polymer matrix. However, coupling agents such as maleic anhydride-grafted polymers were found to be generally more effective.[27]

It is thus believed that the combination of acetylation and coupling agent addition could further enhance the WPC's performances. While acetylation could improve the wetting by the polymer, the particles dispersion, the dimensional stability, decay resistance, and photostability, the coupling agent could strengthen the interfacial region and improve mechanical properties. At present, maleic anhydride-grafted polyolefins or organofunctional trialkoxysilanes $[R—Si(OR')_3]$ are the most commonly used coupling agents; these compounds are reported to react with the hydroxyl groups at the wood surface via the anhydride or trialkoxysilane functions, and interact with the polymer matrix via the polyolefin or R functional group (polymer chain entanglement, crosslinking or strong secondary interactions),[11–13] but in acetylated wood, the number of accessible hydroxyl groups is much reduced (most of them being acetylated), and the reaction with the coupling agent is very unlikely. In this context, a transesterification reaction between the acetyl groups at the wood surface and trialkoxysilane coupling agents could be envisaged (exchange between the acetate and alkoxysilane functions). The feasibility of such an exchange reaction has

Correspondence to: N. Özmen (nilgulozmen@hotmail.com) or G. Sèbe (g.sebe@lcsv.u-bordeaux1.fr).

been demonstrated with tetramethoxysilane (TMOS), in presence of dibutyltin oxide as a catalyst,[28] but trialkoxysilanes are much less reactive than tetraalkoxysilanes[29] and their reactivity toward acetylated wood needs to be explored.

Accordingly, the possibility of a transesterification reaction between acetylated wood and trialkoxysilane coupling agents has been studied and is reported herein. Reactions were performed on acetylated maritime pine sapwood, with methyltrimethoxysilane chosen as a model trialkoxysilane. The chemical modifications were characterized by Fourier-transform infrared spectroscopy (FTIR) as well as ^{13}C and ^{29}Si crosspolarization magic angle spinning (CP-MAS) NMR spectroscopy.

MATERIAL AND METHODS

Preparation of wood flour

Maritime pine sapwood was ground using a hammer mill and sieved to a size of 40 mesh. The wood flour (WF) was Soxhlet-extracted with a standard toluene:acetone:ethanol mixture (4 : 1 : 1 v/v/v) for 8 h, then with deionized water for an additional 8 h, to remove the extractives. Extracted WF was oven-dried at 105°C overnight, transferred to a desiccator containing phosphorous pentoxide, and allowed to cool to room temperature.

Chemicals

Methyltrimethoxysilane (MTMS), pyridine (Py), dimethylformamide (DMF), acetic anhydride (AA), and dibutyltin oxide (DBTO) were supplied from Aldrich and used without further purification. Chemical reactants were characterized by NMR spectroscopy and their carbons were assigned as followed (Fig. 1): AA: ^{13}C NMR (100.6 MHz, CDCl$_3$), 21.5 (b') and 166.1 (a') ppm. MTMS: ^{13}C NMR (100.6 MHz, CDCl$_3$), −8.7 (c') and 50.4 (d') ppm; ^{29}Si NMR (39.7 MHz, CDCl$_3$, with chromium(III) acetylacetonate as a relaxing agent): −38 ppm.
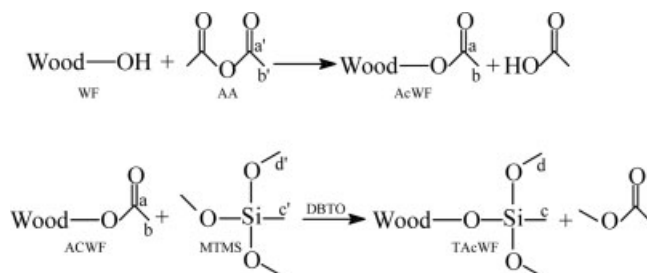

Figure 1 (a) Acetylation of wood with acetic anhydride (AcWF); (b) Transesterification reaction between AcWF and MTMS (TAcWF).

Acetylation of wood flour

In a round bottom flask equipped with a condenser and a magnetic stirrer, 50 g of sawdust (WF), 7 mmol Py/g dry wood, 14 mmol AA/g dry wood, and 200 mL of DMF were introduced. The reaction mixture was heated at 100°C for 6 h. The amount of reactant used (14 mmol/g dry wood) corresponds to an estimation of the concentration of OH groups in maritime pine, calculated with a formula reported in a previous article.[30] At the end of the reaction, the modified samples were Soxhlet-extracted with the toluene:acetone:ethanol mixture (4 : 1 : 1 v/v/v) for 8 h, to remove the unreacted chemicals and by-products formed. Samples were subsequently oven-dried overnight at 105°C, transferred into a desiccator containing phosphorus pentoxide until cool then weighed. The weight percentage gain (WPG) was then calculated as follows: $WPG(\%) = \frac{Wt_1 - Wt_0}{Wt_0} \times 100$, where Wt_0 and Wt_1 are the oven dry weights of the sample, before and after acetylation. A WPG of 27% was found in the conditions of the reaction.

Transesterification reaction

For transesterification studies, oven-dry acetylated WF (AcWF) was used as a starting material. In a round bottom flask equipped with a condenser and a magnetic stirrer, 1 g of AcWF, 0.04 mmol DBTO/g dry wood, required amounts of MTMS, and 10 mL DMF were introduced. The amount of MTMS used for each reaction was calculated from an estimation of the number of acetyl groups in AcWF: MTMS amount = [4 × (weight gains in gram after acetylation/molecular weight of adduct)]. Varied temperatures (105, 125, or 150°C), catalyst amounts (0, 0.04, or 0.08 mmol/g dry wood) and reaction times (2, 4, or 6 h) were investigated.

Transesterified WF (TAcWF) was filtered into a Soxhlet thimble, washed with excess acetone, then Soxhlet-extracted with a toluene:acetone mixture (2 : 1, v/v) for 8 h (elimination of the unreacted MTMS). An additional 4 h extraction was performed with dichloromethane, to remove any silicone polymers that could be formed as by-products (condensation between MTMS molecules). Samples were subsequently oven-dried overnight at 105°C, transferred into a desiccator containing phosphorus pentoxide until cool then weighed. The weight percentage gain (WPG) was then calculated as follows: $WPG_t(\%) = \frac{Wt_2 - Wt_1}{Wt_1} \times 100$, where Wt_1 and Wt_2 are the oven dry weights of the sample, before and after the transesterification reaction.

Infrared spectroscopy

Infrared absorption spectra of transesterified, acetylated, and unmodified WF were obtained with the

potassium bromide technique, using a Perkin–Elmer Paragon 1000 FTIR spectrometer, at a resolution of 4 cm^{-1} (50 scans). In each case, 1% w/w of dry WF was dispersed in a matrix of KBr and pressed to form pellets.

^{13}C and ^{29}Si NMR CP-MAS analysis

Solid state ^{13}C and ^{29}Si CP-MAS (crosspolarization-magic angle spinning) NMR spectra of maritime pine WF were performed at room temperature on a Brüker DPX-400 NMR spectrometer, using MAS rates of 4–8 kHz, at a frequency of 100.6 MHz for ^{13}C NMR and 79.49 MHz for ^{29}Si NMR. Samples were packed in MAS 4 mm diameter zirconia rotors. All the spectra were run for 15 h (25,000 scans).

RESULTS AND DISCUSSION

Transesterification reaction between acetylated wood and MTMS

In the current study, maritime pine sapwood flour was first esterified with AA [Fig. 1(a)] and the acetylated wood obtained (AcWF, WPG = 27%) was used as a starting material for the transesterification investigations. With DBTO as a catalyst, an exchange reaction between the pendant ester groups of acetylated wood and MTMS (chosen as a model trialkoxysilane) is expected to occur according to the equation in Figure 1(b). Since AcWF was fully characterized in our previous article,[28] the acetylation reaction has not been discussed here.

The first experiments were performed in a standard set of conditions inspired from our preliminary work with tetramethoxysilane[28]: i.e., in DMF (solvent), at 125°C, for 6 h and with 0.04 mmol of DBTO/g dry wood (catalyst). In these conditions, a WPG of 8.3% was measured, indicating that some alkoxysilane molecules remained bounded in wood after reaction, despite the extensive extractions with appropriate solvents. Since a concomitant weight loss due to the release of methyl acetate is also expected [Fig. 1(b)], this WPG does not directly correlate with the number of MTMS molecules that were actually exchanged.

The transesterified WF (TAcWF) was characterized by FTIR and solid NMR spectroscopy (^{13}C and ^{29}Si). The FTIR spectra of WF, AcWF, and TAcWF are shown in Figure 2. The bands of the grafted acetyl moieties in AcWF (spectrum b) were identified at 2942 cm^{-1} (ν_{C-H}), 1750 cm^{-1} ($\nu_{C=O}$), 1376 cm^{-1} (δ_{C-H}), 1241 cm^{-1} (ν_{C-O}), 900 cm^{-1} (γ_{C-H}), and 604 cm^{-1}.[28] A decrease in the intensity of these bands was obviously observed after the transesterification reaction with MTMS (spectrum c), indicating that acetyl groups were cleaved during the transesterification treatment. In addition, characteristic bands of the
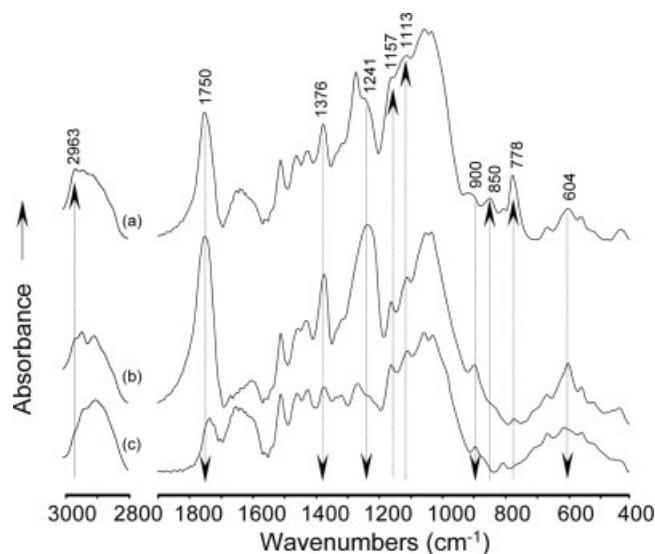
Figure 2 FTIR spectra of (a) unmodified wood flour (WF), (b) acetylated WF (AcWF, WPG = 27%), and (c) MTMS-transesterified WF (TAcWF, WPG = 8.3%).

grafted MTMS emerged at 2963 cm^{-1} (ν_{Si-CH}), 850 cm^{-1} (ν_{Si-O}), and 778 cm^{-1} (ν_{Si-C}).[31-33] Two additional bands were identified at 1157 and 1113 cm^{-1} and were assigned to the stretching bands of some siloxane bridges ($\nu_{Si-O-Si}$).[34-36] These siloxane structures were probably formed by condensation between neighboring MTMS molecules (see the ^{29}Si CP-MAS NMR results below). Similar condensations have been noted in our previous study with tetramethoxysilane.[28]

The ^{13}C CP-MAS NMR spectra of WF, AcWF, and TAcWF are presented in Figure 3. The carbons of the acetyl groups in AcWF appear clearly at 171 and 21 ppm [carbons *a* and *b*, respectively, according to the nomenclature in Fig. 1(a)]. As expected, the intensity of these two chemical shifts decreased after the transesterification exchange (spectrum c), confirming that a cleavage of the acetyl moieties occurred. The grafted MTMS was identified in the form of a strong signal at 0 ppm and a smaller one at 52 ppm [carbons *c* and *d*, respectively, according to the nomenclature in Fig. 1(b)]. The low intensity noted for carbon *d* indicates most of the Si—OMe bonds were cleaved during the transesterification process. The two signals at 14 and 27 ppm were assigned to traces of the DBTO catalyst (DBTO is hardly soluble in most organic solvents).

The MTMS-transesterified sample (TAcWF) was further characterized by ^{29}Si CP-MAS NMR spectroscopy (Fig. 4). Four signals were detected at −44, −53, −62, and −70 ppm, indicating that the silicon atoms in TAcWF existed in the form of four different structures, with four different electronic environments around the silicon atom. It has been reported that the condensa-
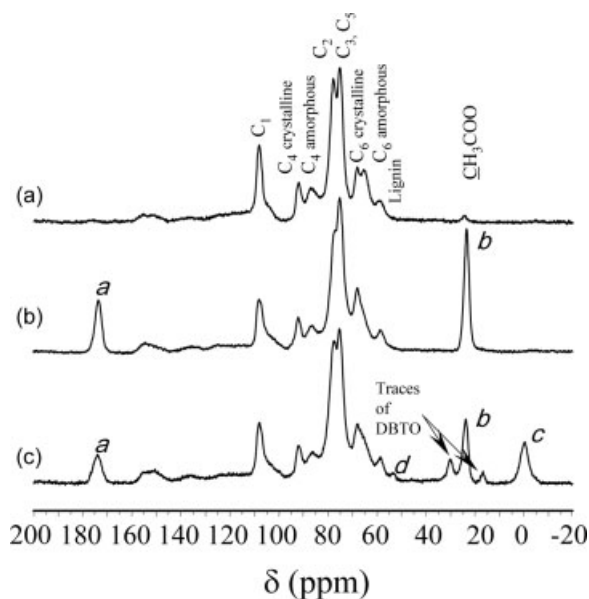
Figure 3 CP-MAS ^{13}C-NMR spectra of (a) unmodified wood flour (WF), (b) acetylated WF (AcWF, WPG = 27%), and (c) MTMS-transesterified WF (TAcWF, WPG = 8.3%).

tion of Si—OR into a Si—OSi linkage results in an upfield shift of about 8–9 ppm for the silicon atom.[37,38] Accordingly, the four signals in Figure 4 were assigned to uncondensed, mono-, di-, and tri-condensed structures, concurrently formed by condensation among 0, 1, 2, or 3 neighboring $Si(OMe)_3$ groups, respectively. Such condensations in dry conditions have been noted in other studies,[28,37,39] but their mechanism has not been clarified yet. The relative intensities of the signals reveal that di- and tri-condensed structures are predominantly found in wood. The tri-condensed structures cannot have reacted with acetylated wood but they may be fixed via the mono- or di-condensed forms.
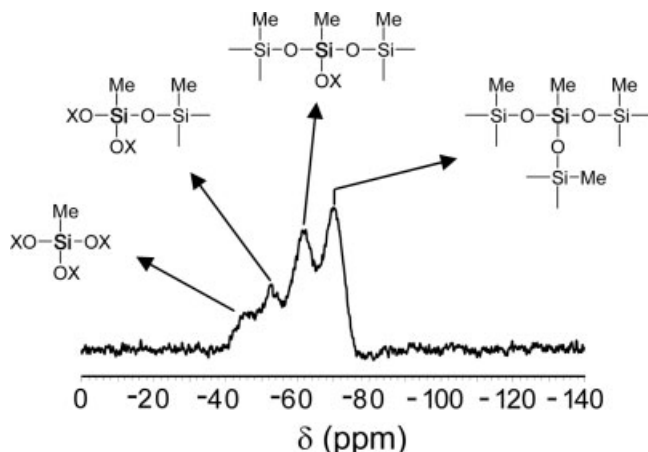

Figure 4 CP-MAS ^{29}Si NMR spectrum of MTMS-transesterified wood flour (TAcWF, WPG = 8.3%); X = wood and residual —CH_3.

To confirm that the transesterification exchange really occurred between the acetyl moieties in wood and MTMS (and not between wood hydroxyl groups and MTMS), a control experiment was performed in the same conditions, with unacetylated WF. As expected, neither weight gain nor spectroscopic signals were detected in that case.

Effect of reaction conditions on the transesterification exchange

The transesterification reaction between AcWF and MTMS was further studied as a function of catalyst amount, temperature, and reaction time. The WPGs obtained after reaction in these different conditions are presented in Table I and the infrared spectra in Figures 5–7. Changes in the characteristic FTIR vibrations previously assigned were then noted and used to discuss reaction efficiency (comparison of bands intensities). The new infrared vibration identified at 426 cm^{-1} (Figs. 5–7) was assigned to some bending vibrations of the siloxane bridges (δ_{O-Si-O}).[34]

No transesterification reaction was observed without catalyst, confirming the importance of DBTO in this reaction. A 3.3% weight loss was even noted in these conditions (4 h at 125°C, in DMF and without catalyst), indicating that the combination of relatively high temperature and solvent has a detrimental impact on the woody material (degradation of wood polymers and deacetylation).

The transesterification exchange was found to be increasingly more efficient when more catalyst was added: the WPG and FTIR vibrations of the silane

TABLE I
Weight Percentage Gains (WPG) After Transesterification Between AcWF and MTMS in Varied Conditions: Impact of the Catalyst Amount, Reaction Temperature, and Reaction Time

	WPG (%)
Catalyst amount (mmol/g dry wood)[a]	
0	−3.3
0.4	6.1
0.08	8.1
Reaction temperature (°C)[b]	
105	−0.2
125	5.7
150	11.4
Reaction time (h)[c]	
2	4.2
4	5.8
6	8.3

[a] Reaction time was 4 h and reaction temperature was 125°C.
[b] Reaction time was 4 h and catalyst amount was 0.04 mmol/g dry wood.
[c] Reaction temperature was 125°C and catalyst amount was 0.04 mmol/g dry wood.
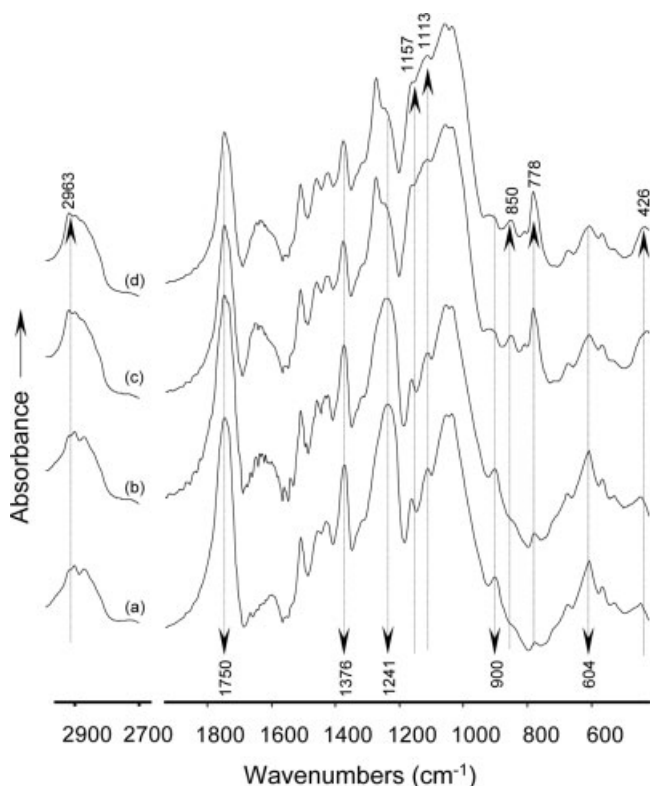
Figure 5 FTIR spectra of wood after transesterification with varied amounts of catalyst (4 h at 125°C): (a) AcWF before reaction with MTMS; (b) TAcWF without DBTO; (c) TAcWF with 0.04 mmol DBTO/g dry wood; (d) TAcWF with 0.08 mmol DBTO/g dry wood.

Figure 6 FTIR spectra of wood after transesterification with varied reaction temperatures (4 h with 0.04 mmol DBTO/g dry wood): (a) AcWF before reaction with MTMS; (b) TAcWF at 105°C; (c) TAcWF at 125°C; (d) TAcWF at 150°C.

gradually increased, while acetyl vibrations decreased. Previous work with alkoxysilanes and polymers bearing pendant ester groups showed that DBTO was not a catalyst in the common sense but was instead the precursor of dimeric difunctional tetraorganodistannoxanes, which are the true catalysts in the alkoxysilane–ester interchange reaction.[40–42] DBTO being hardly soluble in most organic solvents (because of its polymeric structure), the formation of such distannoxanes structures in wood was probably increasingly favored when more DBTO was added.

The other results in Table I and Figures 6 and 7 indicate that the efficiency of the transesterification exchange also increased with increasing temperature and reaction time. However, since a weight loss was already noted at 125°C (−3.3% in Table I), an increasing wood degradation is also very likely when the temperature is augmented. No weight gain was measured at 105°C, but the infrared data indicate that transesterification has partially occurred (spectrum b in Fig. 6). In that particular case, the weight gain induced by MTMS was probably exactly counterbalanced by the weight loss due to the release of methyl acetate (no wood deterioration is
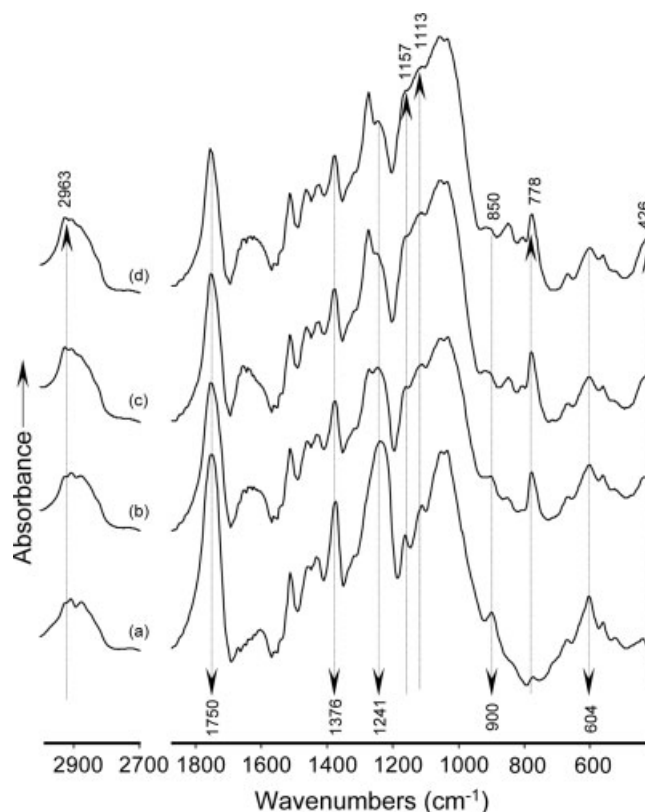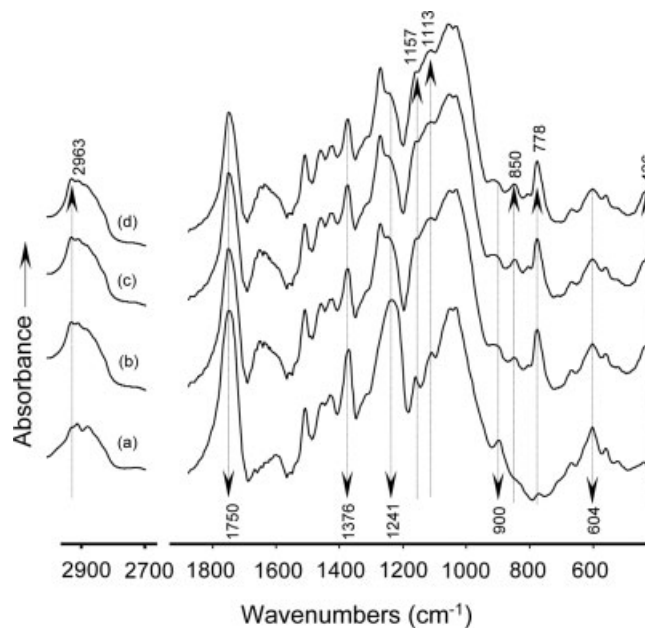

Figure 7 FTIR spectra of wood after transesterification with varied reaction times (at 125°C with 0.04 mmol DBTO/g dry wood): (a) AcWF before reaction with MTMS; (b) TAcWF after 2 h; (c) TAcWF after 4 h; (d) TAcWF after 6 h.

expected at this temperature). In our previous study with tetraethoxysilane,[28] a 6% weight gain was noted at 105°C. The current result with MTMS is hence in agreement with the lower reactivity generally noted for trialkoxysilanes compared with tetralkoxysilanes.

CONCLUSIONS

The objective of this article was to investigate the possibility of using transesterification as a chemical pathway to graft trialkoxysilane coupling agents at the surface of acetylated wood, to improve the strength performances of wood–plastic composites. The acetyl/alkoxysilane interchange reaction between acetylated wood and trialkoxysilanes was accordingly studied, with methyltrimethoxysilane (MTMS) chosen as a model trialkoxysilane. The concomitant cleavage of acetyl moieties and grafting of MTMS molecules has been confirmed by WPG calculations, FTIR spectroscopy, and ^{13}C CP-MAS NMR analysis, but the ^{29}Si CP-MAS NMR results indicated that concurrent condensations between neighboring Si(OMe)$_3$ groups also occurred in wood, via a mechanism that is not understood at this stage of the study. Control experiments performed with unacetylated sawdust and without catalyst confirmed that the reaction involved the acetyl moieties in wood, and required the presence of DBTO in the reaction medium. An increase in the acetyl/MTMS exchange rate was observed when the catalyst amount, temperature, or reaction time were augmented, but a degradation of wood (and maybe deacetylation) was also noted from 125°C. Finally, the trialkoxysilane molecule (MTMS) was confirmed to be less reactive than tetramethoxysilane.

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