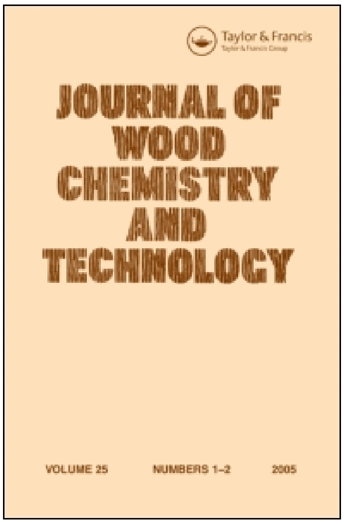

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An Infrared Spectroscopic Study of Chemically Modified Chemithermomechanical Pulp

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AN INFRARED SPECTROSCOPIC STUDY OF CHEMICALLY MODIFIED CHEMITHERMOMECHANICAL PULP

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ABSTRACT

FT-IR spectroscopy was used to characterize chemically modified wood pulp and to judge the efficiency of different pulp modification processes. Treatment of wood pulp with aliphatic anhydrides was shown to be more effective in a polar solvent such as DMF compared to a non-polar one typified by xylene. The esterification of hydroxyl group associated with the cellulosic material was indicated by the characteristic absorption bands of the resulting cellulosic esters; the degree of hydroxyl conversion was determined by the ratio of peak intensity of hydroxyl and carbonyl stretching vibrations. The so-called "Infrared Acetyl Index" was shown to give a linear correlation with the gravimetrically determined anhydride uptake. Isocyanate modification of wood pulp yielded more complex infrared spectra, because of various secondary reactions of the reactive isocyanate component. Various aromatic isocyanates, used for chemical treatment of the wood pulp, led mainly to urethane formation, as evidenced by the spectra of the modified pulp. The presence of polyurea or urea as the main reaction product of aromatic isocyanates, postulated by a number of authors, could not be confirmed. Nevertheless, phenylisocyanate treatment, at high concentration of isocyanate and without purification of the modified pulp, led to the appearance of at least one more reaction product in the pulp spectra, which is presumed to be either triphenylisocyanurate, the trimerization product of phenylisocyanate, or carbanilide.

INTRODUCTION

Cellulosic fibres, a cheap and renewable raw material, show a high potential for application in fibre-reinforced composites, especially thermoplastics. To achieve a good compatibility between the polar cellulosic fibre and less polar polymers, a variety of modification processes of the fibre and, to a lesser extent, of the matrix polymer are being investigated. One method for introducing polarity into the host polymer is to crosslink the polymer with thermolabile free radical formers in the presence of cellulosic fibres[1]. More familiar methods for optimizing composite properties involve physical or chemical modifications of the cellulosic fibre itself[2].

Treatment of Cellulosic Material with Anhydrides

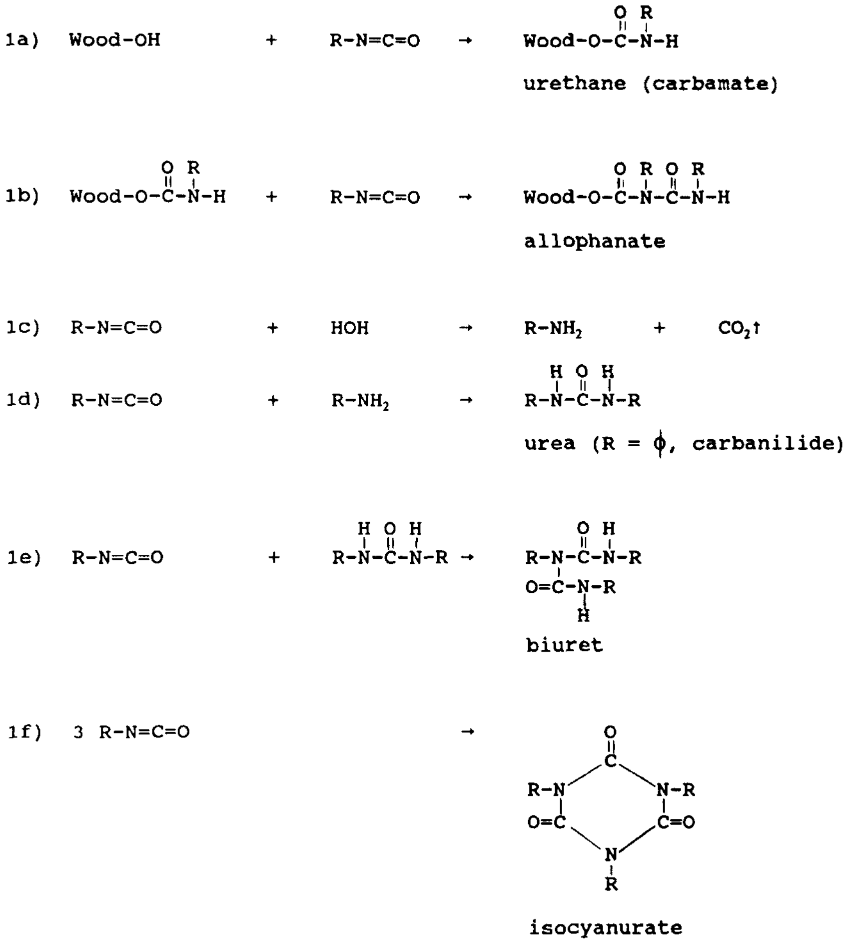
The treatment of CTMP with anhydrides is a single site reaction which leads to ester formation with the hydroxyl groups of cellulose and lignin and an acid as by-product. Acetylation is one of the most common methods to reduce the hydrophilicity of cellulosic material. The degree of acetylation can be estimated in infrared spectroscopy by the intensity of the carbonyl (C=O) stretching vibrations[3,4]. Another method, used to compare cellulosic fibres at different degrees of acetylation, is to determine their "Infrared Acetyl Index"[5,] the ratio of absorbance of the carbonyl stretching band (at about 1750 cm^{-1}) to hydroxyl stretching band (at about 3400 cm^{-1}). This method is suitable for comparing acetates made from different pulps. It can also be used for samples which show differences in their dispersion behavior in the halide in the potassium bromide pellet sampling technique[3]. The application of the Infrared Acetyl Index also eliminates errors due to differences in the amount of sample exposed to the spectrophotometer light source.

In this study, monofunctional aliphatic anhydrides were used to modify the pulp. The application of acetic, propionic and butyric anhydrides made it possible to examine the influence of increasing chain length and therefore the effect of increasing hydrophilicity of the modifying agent on pulp properties. The absorbance ratio (1750 cm^{-1} / 3400 cm^{-1}) was applied to estimate the efficiency of different anhydride treatments of CTMP.

Treatment of Cellulosic Material with Isocyanates

Isocyanates react with many kinds of materials having reactive hydrogen atoms such as alcohols, amines, carboxylic acids and water. Because they show a great variety of modification possibilities, isocyanates are an interesting modifying agent for cellulosic materials[6-8]. Reaction schemes are shown in Figure 1. Since cellulose and lignin both carry hydroxyl groups, they are potential reaction partners with isocyanates for the formation of a nitrogen-containing ester (urethane) (Figure 1a). The high reactivity of the isocyanates may lead to a variety of additional reaction products. Thus, an excess of isocyanate can react with the urethanes to form thermally less stable allophanates (Figure 1b). The reaction with water, present mostly as adsorbed humidity or in the water vapor form, proceeds through an amine intermediate (Figure 1c) to a derivative of urea (Figure 1d) and, with an excess of isocyanate, to biurets (Figure 1e). At high temperatures homopolymerization to cyclic dimer and trimer (Figure 1f), takes place.

Dimer formation (uretidinediones) arises only from aromatic isocyanates and is inhibited by ortho substituents. The slow dimerisation of 4,4' diphenylmethane diisocyanate (MDI) is uncommon, even at room temperature. At higher temperatures insoluble polymeric materials are formed[6,7]. The formation of the trimer (isocyanurate), which takes place when aliphatic and aromatic isocyanates are heated, is more important because of its excellent thermal stability relative to that of the dimer. Isocyanurate formation in polyurethane manufacture yields very stable branch points for crosslinking networks. Unlike the reactions leading to the formation of uretinedione, biuret, allophanate and urethane linkages, this reaction cannot be reversed easily. For example, isocyanurate foams prepared from MDI



thermal stability:

isocyanurate 〉 urea 〉 urethane 〉 biuret 〉 allophanate

FIGURE 1. Reactions of isocyanates

show little degradation below 270 °C[6]. In contrast, biurets and allophanates decompose at temperatures as low as 100 °C[7]. At higher temperatures, there also exists an increased potential for reaction between isocyanate and isocyanate derivatives, such as urethane and urea, yielding such products as polyureas.

Differences in the reaction scheme and reaction products are dependent on the chemical structure and the number of functional groups of the isocyanate used as modifying agent. Some results found in the literature are referenced later.

Monoisocyanates

The reaction between monoisocyanates and cellulose leads to urethanes (carbamates) and an excess of monoisocyanates can lead to allophanates as reaction products. Reichelt and Poller[8] have described the reaction of phenylisocyanate with various kinds of cellulose in DMF without a catalyst (1 hour, 110 °C) which led to a weight increase of 5.7 % of the treated material. Further treatments of cellulosic material with phenylisocyanate in pyridine and benzene as solvents are also described in this article. Phenylisocyanate has been shown to react easily with lignin model substances such as guaiacol and creosol, to form thermally stable, solid compounds[8].

Di- and Polyisocyanates

Non-catalytic reactions of hexamethylene diisocyanate (HMDI) with different cellulosic materials in solvents such as toluene, DMF and benzene and in the gas phase are reported to produce weight gains of up to 23 wt %[8]. HMDI reacts more slowly with lignin model substances than does phenylisocyanate (PHI). Another type of diisocyanate normally used for particleboard manufacture is 4-4' diphenylmethane diisocyanate or MDI. It is the diisocyanate with the highest volume consumption in polyurethane manufacture and is mainly applied in its oligomeric form (known as PMPPIC, polymeric methylene diisocyante or PMDI), in various compositions and with varying contents of reactive isocyanate groups[6]· MDI previously has been shown to be an effective binder for wood[9].

However, the question of how isocyanates react in presence of cellulosic material is still unresolved. The importance of the formation of the polyurethane and polyurea in the bonding of wood[9,10] is controversial. Most authors believe that the use of diisocyanates leads to a crosslinking of cellulosic chains[8,11] by direct covalent bonding of isocyanates with the reactive hydroxyl groups of cellulose and lignin (urethane formation). There are also indications that the reduction in swelling can be caused by the inclusion of the additive or its reaction products in the cellulosic material[12]. Besides the formation of urea, another secondary reaction which leads to isocyanurates is hypothesized. This reaction could also lead to a crosslinked network which might contribute to the structural strength of the composite[7].

In our previous studies, anhydride[13] and isocyanate treatments[14] of chemithermomechanical pulp (CTMP) were used to modify pulp properties to reduce hydrophilicity. These chemical modification processes can alter significantly the amount of water uptake and the thermal stability of the cellulosic fibres as demonstrated by thermoanalytical methods. In this present study, infrared spectroscopy has been applied to obtain information about the nature of these chemical modifications. Also, the extent of the chemical modification of cellulosic fibres after different treatment processes has been estimated by their infrared spectra and compared with gravimetric data. A knowledge of the chemical composition of the pulp should provide a tool to predict possible interactions with the polymer matrix.

EXPERIMENTAL

Materials

Chemithermomechanical pulp, composed of 45 % spruce, 45 % fir and 10 % poplar supplied by Stone Consolidated Inc, Bathurst Div., was defibrated, ground, and sieved to mesh size 30. The CTMP was modified with various anhydrides and isocyanates under similiar reaction conditions without any catalyst (Tables 1 and 2). Anhydrides used for modification in xylene and DMF were

TABLE 1

Influence of Anhydride Modification on the Physical and Chemical Properties of CTMP

sample	modifying agent	process conditions	weight gain[1] [wt %]	anhydride uptake [10^{-4} mol/g CTMP]	water uptake[2] [wt %]	integrated peak area (FT-IR)		
						3350 cm^{-1}	1746 cm^{-1}	1746cm^{-1}/3350cm^{-1}
CTMP	---	untreated	---	---	9.8	117	3.4	0.030
A0	---	xylene, 125°C, 2 hrs	0.0	---	10.4	---	---	---
A1	acetic anhydride	2.65 M, xylene, 125°C, 2 hrs	11.1	10.9	5.1	108	18.0	0.170
A11	acetic anhydride	A1 + water extraction	7.3	7.5	6.1	98	16.1	0.164
A2	propionic anhydride	2.65 M, xylene, 125°C, 2 hrs	0.8	0.6	7.9	116	5.9	0.051
B0	---	DMF, 125°C, 1 hr	0.0	---	11.1	119	3.4	0.029
B1	acetic anhydride	2.65 M, DMF, 125°C, 1 hr	17.9	17.5	5.0	84	20.4	0.253
B2	propionic anhydride	2.65 M, DMF, 125°C, 1 hr	20.0	15.4	3.9	79	16.6	0.215
B3	butyric anhydride	2.65 M, DMF, 125°C, 1 hr	18.8	11.9	3.5	75	14.3	0.189

Key: 1- of the ovendry sample
2- difference in weight between ovendry and moist (67% r.h.) sample

TABLE 2

Influence of Isocyanate Modification on the Physical and Chemical Properties of CTMP

sample	modifying agent[1]	process conditions	weight gain[2] [wt %]	isocyanate uptake (per NCO - unit) [10^{-4} mol/g CTMP]	water uptake[3] [wt %]	integrated peak area (FT-IR)		
						3350 cm^{-1}	1729 cm^{-1}	1729cm^{-1}/3350cm^{-1}
CTMP	---	untreated	---	---	9.8	117	3.4	0.030
BO	---	DMF, 125°C, 1 hr	0.0	---	11.1	119	3.4	0.029
C	MDI	0.027 M, DMF, 125°C, 1hr	12.0	9.6	8.5	141	12.7	0.090
D	PMPPIC	40 wt%, DMF, 125°C, 1 hr	8.7	6.5	8.8	104	9.8	0.094
E	BUI	0.054 M, DMF, 115°C, 1 hr	0.1	0.1	9.1			
F	PHI	0.054 M, DMF, 125°C, 1 hr	7.2	6.0	7.7	98	9.3	0.096
G	HMDI	0.027 M, DMF, 125°C, 1 hr	2.0	2.4	9.6	61	5.0	0.082
F2	PHI	0.26 M, DMF, 125°C, 1 hr	70.5	59.2	3.4	55	20.6	0.357

Key: 1- MDI: 4, 4' diphenylmethane diisocyanate
PMPPIC: poly(methylene (polyphenyl isocyanate))
BUI: n-butylisocyanate
HMDI: hexamethylene diisocyanate
PHI: phenylisocyanate
2- of the ovendry sample
3- difference in weight between ovendry and moist (67% r.h.) sample

acetic (ACA), propionic (PRA) and n-butyric (BUA), supplied by Aldrich in ACS grade. Isocyanates used for modification in DMF were phenylisocyanate (PHI), n-butylisocyanate (BUI), hexamethylenediisocyanate (HMDI), 4,4'- diphenylmethane diisocyanate (MDI) and poly(methylene(polyphenyl isocyanate)) (PMPPIC), supplied by Polyscience Inc. The isocyanates differ in functionality (mono-, di-, and polyisocyanates) and in their chemical structure (aromatic and aliphatic). Reaction conditions and procedures are described in detail in former publications[13,14]. Sample abbreviations (CTMP modified by the different chemicals) are listed in Tables 1 and 2.

Infrared Spectra

Measurements were made using a Sirius 100 Mattson spectrometer. CTMP and modified CTMP samples were characterized using the potassium bromide pellet sampling technique. Great attention was given to avoid water contamination and achieving a uniform dispersion of the wood fibre in the pellet. Exactly 2 mg of dry cellulosic fibers (mesh size 60), modified and unmodified, was mixed with 198 mg of dry potassium bromide. One hundred mg of the dry mixture was placed in a press and subjected to a load of 9000 kg to form a pellet. Prior to measurement, the pellets were dried in air at 100 °C and stored over phosphorus pentoxide. Absorption intensities of characteristic peaks, calculated after baseline correction with an integration program, were used to make a semi-quantitative comparison of the degree of chemical modification of different modified pulps.

RESULTS AND DISCUSSION

CTMP Modified by Anhydrides

The interpretation of cellulose or pulp spectra recorded using the potassium bromide pellet technique has been reviewed by many authors[3-5]. Therefore, only the changes in spectral characteristics of the modified CTMP will be discussed.

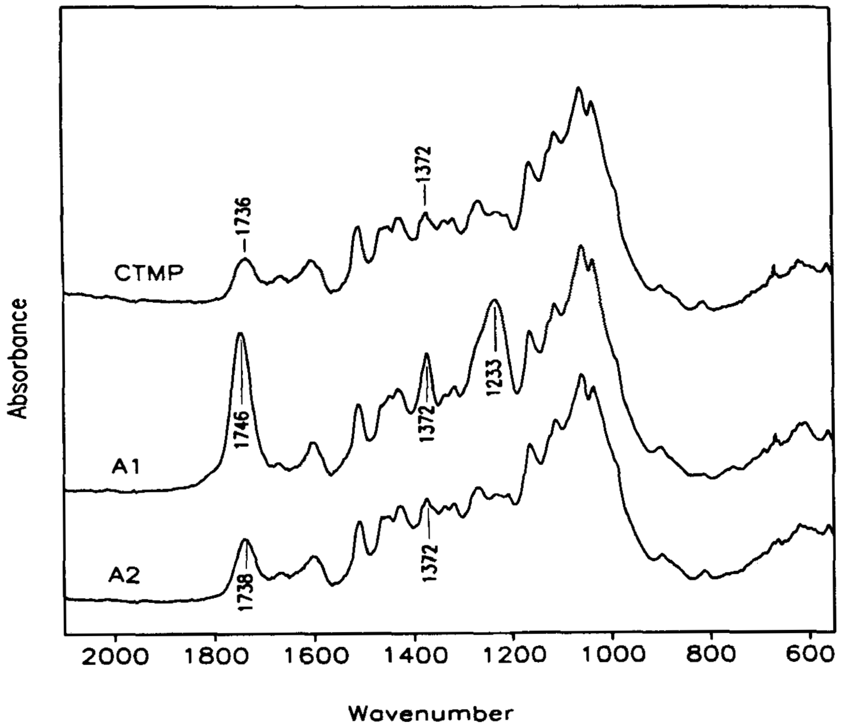


FIGURE 2. Infrared spectra of chemithermomechanical pulp modified by reaction with anhydrides in xylene

Treatment of CTMP with acetic anhydride (sample A1) in xylene results in a significant increase in peak intensity at 1746 cm^{-1}, 1372 cm^{-1} and 1233 cm^{-1} compared with the untreated CTMP as shown in Figure 2. Infrared spectra of cellulose acetate[4] have bands at 1750 cm^{-1} (C=O stretching), 1240 cm^{-1} (C-O stretching), and 1375 cm^{-1} ($C-CH_3$ symmetrical deformation). A comparison of the integrated peak areas of the C=O ($\simeq$1746 cm^{-1}) and O-H stretching vibrations (3100-3650 cm^{-1}, with a maximum at $\simeq$3350 cm^{-1}) is represented in Table 1. The resulting Infrared Acetyl Index of the acetylated pulp (sample A1) shows a 5-to 6-fold increase compared with the original pulp. On the other hand, bands associated with lignin components[15-17] at 1594 cm^{-1}, 1503 cm^{-1}, 1271 cm^{-1}, 660 cm^{-1} and 556 cm^{-1} are not influenced by acetylation or by propionic anhydride treatment in xylene (sample A2).

Treatment with propionic anhydride in xylene under identical process conditions as were used on acetylation, leads to minor differences in the pulp spectra compared to untreated CTMP (Figure 2). The only change which can be detected is a slight increase in the integrated intensity of the C=O stretching vibration at 1738 cm^{-1} (Table 1). Water extraction of acetylated CTMP (sample A11) causes only minor changes in the spectra (not shown here). A small reduction in peak intensity at 1746 cm^{-1}, 1372 cm^{-1}, and 1233 cm^{-1} takes place (Table 1), which can be due either to the extraction of remaining acetic acid as by-product or to partial hydrolysis of the ester.

The effects of CTMP treatment with acetic (sample B1), propionic (sample B2) and butyric anhydride (sample B3) in DMF are shown in Figure 3. After the different anhydride treatments, the modified CTMP shows in all cases a clear reduction in hydroxyl stretching vibrations between 3650 and 3100 cm^{-1} (Table 1). Simultaneously, the intensity of the C=O stretching band at 1742 - 1748 cm^{-1} increases 4 - 6 times compared to untreated CTMP.

A detailed examination of the peak area between 1750 and 1000 cm^{-1} reveals differences in the spectra of the modified CTMP that are dependent on the type of anhydride used for modification (Figure 3). At 1464 cm^{-1} the absorption increases for propionic and butyric anhydride-modified CTMP. This peak also appears in the spectra of pure propionic and butyric anhydride but is not present in that of pure acetic anhydride. It can be related to C-H deformation vibrations of the CH_2-groups[18]. CTMP, acetylated in DMF, shows an increased absorption at 1372 cm^{-1}, comparable to the behavior observed in xylene (Figure 3).

Propionic and butyric anhydrides do not show this strong effect attributable to C-CH_3 deformation. Also, characteristic of the acetylated CTMP is a strong absorption at 1233 cm^{-1}, which is not found in the propionic nor for butyric anhydride- treated CTMP. This peak can either be compared with one present at

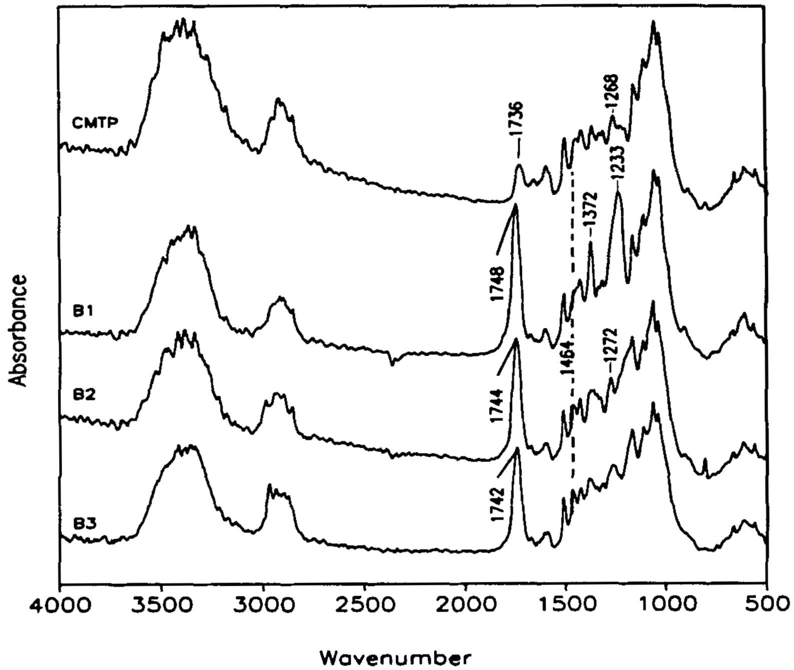


FIGURE 3. Overall infrared spectra of chemithermomechanical pulp modified by reaction with anhydrides in DMF

1226 cm^{-1} in the spectra of pure acetic anhydride (C-O stretching) or with the C-O-C asymmetric stretching vibration in cellulose and hemicelluloses[17]. For propionates and butyrates, the C-O stretching vibration is in the 1150-1200 cm^{-1} range. It is not possible to identify clearly these bands in Figure 3, since there is also a band at this frequency in untreated and acetic anhydride-treated CTMP.

From the ratio of the absorbance of the C=O stretching band to the absorbance of the O-H stretching band it should be possible to estimate the efficiency of the chemical conversion of the CTMP. Table 1 shows that acetylation in DMF yields an higher Infrared Acetyl Index than does the same process (even after an extended reaction time) in xylene. Furthermore, the

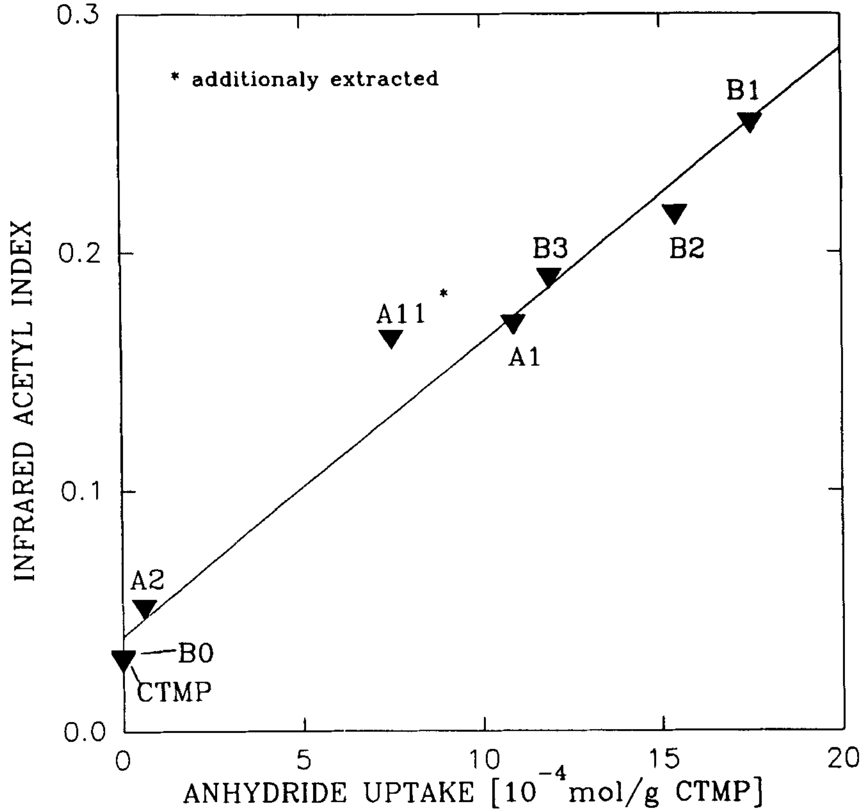


FIGURE 4. Correlation between gravimetrically determined anhydride uptake and the Infrared Acetyl Index of chemically modified CTMP

acetylation of CTMP in DMF seems to be more effective in forming ester bonds than does the reaction with propionic and butyric anhydrides. This agrees with former results from thermoanalytical analysis[13] which confirm that the extent of reaction decreases with increasing chain length of the anhydride. Comparison of the two treatments in xylene and DMF also show a reduction in the intensity of lignin-associated peaks (1499 cm^{-1} and 1599 cm^{-1}) with the more polar solvent. This can either be attributed to the enhanced solubility of the lignin in DMF (in

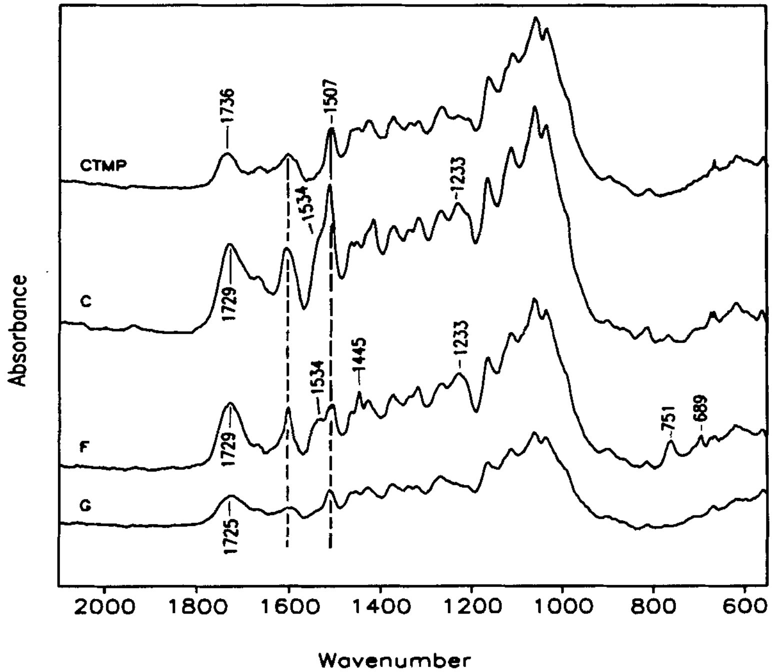


FIGURE 5. Infrared spectra of isocyanate modified chemithermomechanical pulp

the presence of the anhydride) or to an enhanced reactivity of the lignin towards the anhydride in DMF. The Infrared Acetyl Index of all samples examined by FT-IR correlates with the gravimetrically determined anhydride uptake as illustrated in Figure 4.

CTMP Modified by Isocyanates

An overview of the infrared spectra of isocyanate modified CTMP (as identified in Table 2), is shown in Figure 5. In all cases an increase in peak intensity at about 1725 - 1729 cm^{-1} can be detected, which indicates the formation of urethane bonds[11,19]. In contrast to anhydride-modified CTMP, the position of the C=O stretching band is shifted to lower values compared with its position for untreated pulp (1736 cm^{-1}). Simultaneously, some of these C=O stretching bands become very broad which could signify the superimposition of two C=O stretching bands arising from different carbonyl groups in the modified pulp. Twin peaks, such as exist typically in allophanates[11], cannot be detected. Furthermore, none of these isocyanate treatments of CTMP (Figure 5) shows significant indications of the presence of pure urea[11] or polyurea bonds, which were identified by Farissey at 1650 cm^{-1} on isocyanate treated flakes[20].

The use of HMDI, an aliphatic diisocyanate, for wood pulp modification (sample G) leads to almost the same infrared absorption pattern as that for untreated pulp (Figure 5), the only variation being the intensities of hydroxyl and carbonyl stretching bands (Table 2). For the aromatic isocyanate-modified pulp, there are also increases in the peak areas at 1599 cm^{-1} and 1499 cm^{-1} attributable to C=C valence vibrations of the benzene ring. These bonds overlap with the aromatic ring signals in lignin. Therefore, the change in lignin content of the pulp, caused by the isocyanate treatment, cannot be judged by the intensity of these peaks as it was in the treatments with anhydrides. A decrease in lignin content, as was shown for the anhydride treatment, can still be hypothesized. Changes in the colour of the solvent after the treatment process support this supposition. UV-spectra of the solvents after isocyanate modification show the presence of aromatic components which can be traced to lignin.

CTMP's modified by MDI (sample C in Figure 5) and PMPPIC (not shown here) show almost identical infrared patterns, both of which differ significantly from the spectra of the untreated pulp. In both cases an intense new peak appears at about 1534 cm^{-1} which is not present in untreated CTMP. Phenylisocyanate-treated CTMP (sample F) also shows a very distinct infrared spectrum showing a variety of additional peaks compared with untreated CTMP (Figure 5).

In more detailed studies, the treatment of CTMP with phenylisocyanate was repeated with increased phenylisocyanate concentration (sample F2) and the modified CTMP was not purified by exhaustive washing. This was done to detect

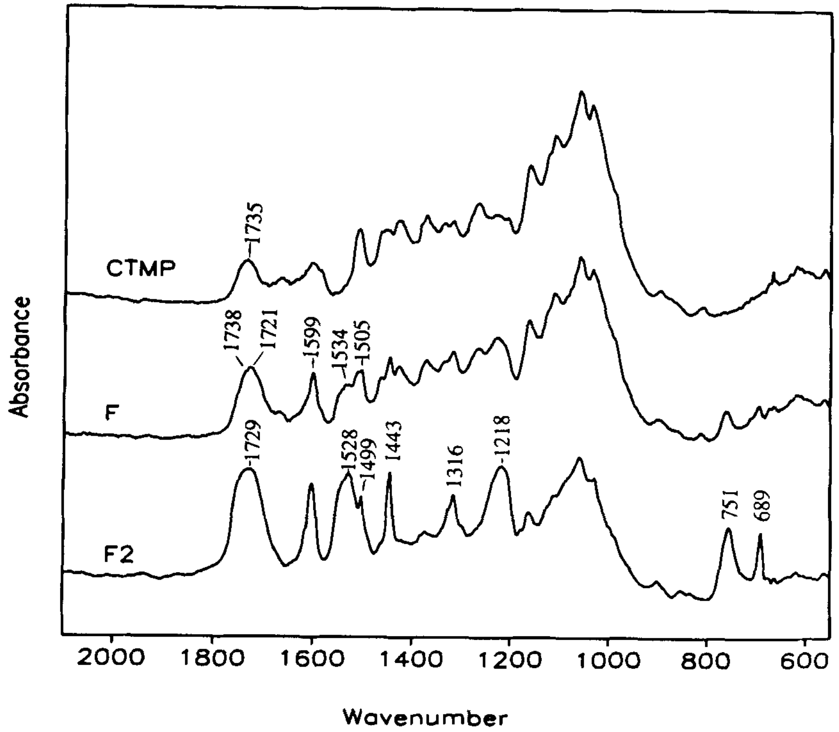


FIGURE 6. Infrared spectra of chemithermomechanical pulp modified by reaction with phenylisocyanate at different concentrations

more clearly peaks in the spectra attributable to potential by-products. Figure 6 shows the effect of the two different phenylisocyanate concentrations on the infrared spectra of the modified pulps. Both samples show an increase in peak intensity at 1729 cm^{-1} and 1599 cm^{-1} and new peaks at 1528 cm^{-1} (sample F2) and 1534 cm^{-1} (sample F) compared to untreated CTMP. These differences in the absorption of the untreated and phenylisocyanate-treated CTMP are already present at a low PHI concentration (sample F), but become major peaks in the spectra of the pulp treated at high PHI concentration (sample F2). In the literature this peak between 1528 cm^{-1} and 1534 cm^{-1} is assigned to an amide II group which can be found in monosubstituted amides and accompanies urethane formation[18]. A second new peak at 1240 - 1218 cm^{-1} (sample C and F at 1233 cm^{-1}, sample F2 at 1218 cm^{-1}) also indicates polyurethane bonds. Reichelt and Poller[8] describe polyurethane absorption bands at 1740 - 1720 cm^{-1}, 1560 cm^{-1} and 1220 cm^{-1} formed in the reaction of phenylisocyanate with lignin. These peak positions are comparable to those in our spectra with phenylisocyanate-treated CTMP (Figure 6). However, there are at least two additional new peaks with significant intensity at 1443 cm^{-1} and 1316 cm^{-1} (sample F2 in Figure 6) in phenylisocyanate-treated CTMP. The location of several peaks suggests the carbanilide or the triphenylisocyanurate as a possible reaction component, but in neither case is the identification certain.

A comparison of the efficiency of the isocyanate treatments by use of an intensity index (Table 2), as was done previously with anhydride-modified pulp, is questionable. On one hand, isocyanate reactions are in many cases not limited to single site reactions, as are anhydride modifications, but show a strong polymerization tendency. This means that the amount of hydroxyl groups blocked need not be directly proportional to the amount of isocyanate applied. On the other hand, it is not unequivocal to monitor the degree of O-H interaction by the absorption intensity between 3200 and 3600 cm^{-1} since N-H interaction occurs in the same spectra region. However, a qualitative interpretation of the intensities of carbonyl stretching vibrations (Table 2) should enable us at least to compare the different isocyanate treatments. HMDI treatment of wood pulp provides the smallest increase in the carbonyl stretching band intensity of all the isocyanate modification processes. PMPPIC and PHI produce about twice the amount in the carbonyl stretching band intensity as the HMDI treatment, when concentrations between 0.027 and 0.055 M are compared. MDI seems to be the most effective modifying agent in this concentration range if the C=O peak intensity is used as an index for comparison. Only PHI at a very high concentration without purification of the reaction product yields even higher values.

CONCLUSIONS

Acetylation of CTMP was successful in DMF and, to a lesser extent, in xylene. With increasing aliphatic chain length, the reactivity of anhydrides dropped more severely in xylene than in DMF. In contrast, all anhydride modifications of CTMP in DMF reduced significantly the amount of hydroxyl groups associated with the cellulosic material and was accompanied by an increase in intensity for the C=O and C-O stretching bonds. This is attributed to ester bonds formed during anhydride treatment of the CTMP. Additional water extraction of an acetylated sample did not alter its spectra significantly, indicating that no substantial amount of acetic acid was present as a by-product in the modified pulp. IR peak positions of the acetylated CTMP are comparable to those described for cellulose acetate in the literature. The application of the so-called Infrared Acetyl Index as an intensity ratio of the C=O stretch vibration and OH stretching bonds shows a linear correlation with gravimetrically determined anhydride uptake of the CTMP.

The FT-IR spectra of isocyanate-modified pulp are more complex than those of the acylated pulp and display increased peak width for the C=O stretching vibration. CTMP, modified by the aliphatic diisocyanate, HMDI, shows a slightly increased peak intensity at 1725 cm^{-1}, compared to untreated CTMP, but no other significant changes in its spectrum. The aromatic isocyanates, PHI, MDI and PMPPIC, also lead to increased peak intensities at 1725-1729 cm^{-1}, but, in addition, yield a multitude of new peaks. Adsorption at 1525-1534 cm^{-1}, 1218-1233 cm^{-1} and 1725-1729 cm^{-1} may indicate that urethanes are the main reaction products. The intensity and distinctiveness of the peaks at 1443 cm^{-1} and 1316 cm^{-1} indicate the presence of at least one additional reaction product. Thermoanalytical studies link this component to a secondary reaction product of phenylisocyanate which, being either strongly adsorbed at the surface or absorbed in bulk, effects a strong reduction in the water uptake of the modified pulp[14]. Several peak positions in the FT-IR spectra (sample F2) hint at the presence of carbanilide or triphenylisocyanurate. Further ESCA-studies should make it possible to differentiate between the two possibilities.

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