Thermochimica Acta, 210 (1992) 171–183
Elsevier Science Publishers B.V., Amsterdam

Characterization of chemically modified chemithermomechanical pulp by thermal analysis. Part 2. Treatment with isocyanates

H.P. Rensch and B. Riedl

Centre de Recherche en Science et Ingénierie des Macromolécules, Département des Sciences du Bois, Faculté de Foresterie et de Géomatique, Université Laval, Sainte-Foy, Quebec G1K 7P4 (Canada)

(Received 15 February 1992)

Abstract

Chemithermomechanical pulp (CTMP) was chemically treated with different mono-, di-, and polyisocyanates in dimethylformamide as solvent without any catalyst. Gravimetrical and thermoanalytical methods (differential scanning calorimetry and thermogravimetry) were used to determine hydrophilicity and thermal stability of the modified CTMP. Aliphatic isocyanates, such as *n*-butylisocyanate and hexamethylenediisocyanate, showed a low potential of reaction with CTMP, compared to aromatic isocyanates with equal functionality like phenylisocyanate and diphenylmethane diisocyanate. The use of diphenylmethane diisocyanate and its oligomeric modification poly(methylene(polyphenylisocyanate)) as coupling agent did yield an increased thermal stability of the modified pulp compared to untreated pulp. CTMP treated with either one of these two components exhibited identical thermoanalytical behavior. Treatment with the aromatic diisocyanate MDI, however, resulted in an increased reduction of water uptake. FT-IR studies of the isocyanate-modified pulps showed urethane formation as being the main component of these chemical pulp modification processes.

The use of phenylisocyanate at high concentration for pulp modification did alter markedly the differential scanning calorimetrical and thermogravimetrical pattern of the CTMP compared to the same treatment with low concentration of phenylisocyanate. The presence of an intense endothermic peak in DSC experiments indicates that in addition to the urethane formation, at least one more reaction component is formed. This might be due either to a secondary reaction between isocyanate and humidity which yields urea or to an isocyanate trimerization product, an isocyanurate. The presence of this secondary reaction component is linked with a high reduction in water uptake of the modified pulp. Model reactions between CTMP and phenylisocyanate under varied reaction conditions confirmed the adsorption or inclusion of a secondary reaction product.

Correspondence to: B. Riedl, Centre de Recherche en Science et Ingénierie des Macromolecules, Département des Sciences du Bois, Faculté de Foresterie et de Géomatique, Université Laval, Sainte-Foy, Québec G1K 7P4, Canada.

INTRODUCTION

Treatment with isocyanates

Isocyanates are known in wood chemistry as wood binders with successful application in particleboard manufacture [1]. Their high reactivity in the formation of isocyanate–polyol reaction products and the absence of by-products also give them an interesting potential as wood and wood-pulp modifying agents. In particular, the use of isocyanates which can polymerize and yield higher treatment levels than single-site reactions (such as the anhydride modification) is of industrial interest. However the chemical toxicity of most isocyanates and a multitude of possible reactions, due to their high reactivity, are detrimental to their application.

Early studies in the fifties and sixties on the reaction of veneers with phenylisocyanate and alkylisocyanates in dimethylformamide (DMF) indicated their great potential in the reduction of water uptake and the increase in mechanical strength of the wood [2, 3]. More recent investigations on the reaction of cellulose and lignin with isocyanates and prepolymers containing isocyanate groups have been reviewed by Reichelt and Poller [4]. The authors compare different methods of cellulose and lignin modification processes with a variety of isocyanates and describe possible applications of the modified cellulose. Isocyanates as wood binders and the chemistry of isocyanate reactions with wood have been reviewed by Johns [1]. In particular, the chemistry of 4,4′-diphenylmethane diisocyanate (MDI), the preferred type of diisocyanate for particleboard manufacturers, is discussed.

Extensive experimental work on the application of isocyanates as coupling agents for different types of cellulosic materials and polymers has been carried out by Kokta and coworkers. Composites were manufactured with cellulosic material which was either pre-coated with an isocyanate/polymer mixture or the isocyanate was added directly to the mixture of fiber and polymer [5, 6]. It was shown that isocyanate treatment of wood pulp improves the dispersion of the fibers in the polymer and the mechanical properties of the resulting composites with polystyrene [7]. The highest mechanical composite properties were achieved with PMPPIC as coupling agent [5, 8], a commercial product which consists of MDI and its oligomeric modification. The experimental results of Kokta and coworkers show that in many cases, isocyanates as coupling agents are superior to the application of silanes or polymer coatings [5]. The use of isocyanate-treated cellulosic fibers, therefore, can result in a material which is not only competitive in mechanical properties with mica- or glass-fiber-reinforced thermoplastics, but is even more cost effective [9].

Despite a knowledge of the reactions between isocyanates and cellulosic material, questions still remain. Although it is clear that the modification of cellulose with certain isocyanates reduces their swelling, it is still not known, if this is mainly due to a chemical reaction between cellulose and isocyanates which crosslinks the cellulosic chains, or to an adsorption or inclusion of the additive and its reaction products. Most authors support the theory of direct covalent bonds (urethane linkage) between cellulose and lignin hydroxyls and isocyanate groups [4, 10, 11]. Their hypothesis is supported by the results of numerous experiments which show that the use of isocyanates as wood binders not only reduces the swelling of the cellulose but also increases the mechanical properties of the resulting composites with different thermoplastic polymers. In contrast, authors like Johns [1], Frieser [12] and Kramer [13] propose the formation of polyurea and polyisocyanurates as the main reaction of the isocyanates, urethane linkage playing only a minor role. They argue that in the presence of even traces of humidity, which can hardly be avoided, isocyanates will react preferably with the water instead of with the hydroxyl groups of the cellulose. The result will be symmetrically disubstituted ureas on the fiber surface. Due to their basicity they can react easily with further isocyanates which results in side chains, that are not bonded to the hydroxyl groups of the cellulose. The main reaction of the isocyanates, therefore, consists of inclusion or adhesion of alkyl or aryl ureas and their further reaction products with isocyanates. A comparable adhesion or inclusion mechanism can be assumed for phenylisocyanurate, a trimerization product of phenylisocyanate, which is developed at high reaction temperature.

Supporters of this theory indicate that a reduction in swelling of a cellulosic material after isocyanate treatment does not prove a chemical linkage because a reduced swelling of cellulose can also be induced by inclusion of synthetic resins [12].

A knowledge of the true reaction mechanism between the isocyanate coupling agent and the cellulosic material may facilitate the optimization of this cellulose modification process and enable the detrimental side reaction to be controlled. Therefore we wish to investigate the influence of different types of isocyanates on the cellulosic surface chemistry. This paper gives the results of a screening test on the influence of a variety of different isocyanates on CTMP and its thermoanalytical behavior. Further work will be done to examine the modified fiber surface by spectroscopic means, based on FT-IR and ESCA techniques. In order to examine the interaction of the modified cellulosic fiber with a reinforcing polymer (LLDPE), investigations on composites with selected isocyanate-treated CTMP are also planned.

EXPERIMENTAL

Materials

Chemithermomechanical pulp composed of 45% spruce, 45% fir and 10% poplar from Stone Consolidated Inc. Bathurst Div. (Bathurst, New Brunswick, Canada) was used as the cellulosic material. After defibration and grinding the pulp was sieved to mesh size 30. The isocyanates used for fiber modification were *n*-butylisocyanate (BUI), phenylisocyanate (PHI), hexamethylenediisocyanate (HMDI), 4,4′-diphenylmethane diisocyanate (MDI) and poly(methylene(polyphenyl isocyanate)) (PMPPIC). The isocyanates, used for chemical modification of CTMP, differ in functionality (mono-, di- and polyisocyanates) as well as in their chemical structure (aromatic or aliphatic) as shown in Fig. 1. They were supplied by Polysciences Inc., with a purity of at least 98%. PMPPIC consists of a mixture with more than 50% of poly(methylene(polyphenyl isocyanate)) as oligomer and less than 50% diphenylmethane diisocyanate. Dimethylformamide was used as solvent for the chemical modification processes due to its high boiling point (152°C) and its good solubility for isocyanates. Its high potential of swelling cellulose should enable an intimate contact between the wood surface and the isocyanates in order to promote the formation of polar polyurethanes [14]. DMF and xylene were supplied by Aldrich in ACS grade.

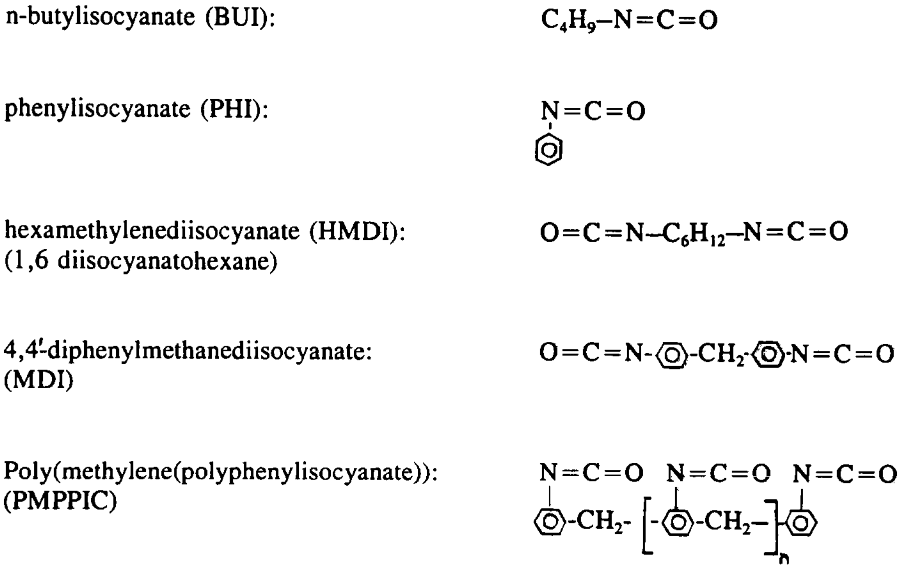

Fig. 1. Isocyanates used for modification of CTMP.

Modification of CTMP with isocyanates

Oven-dry CTMP was allowed to swell 30 min in DMF and was treated with the isocyanate without use of any catalyst. Identical process conditions were chosen for the chemical treatment of the CTMP (Table 1), except for the *n*-butylisocyanate treatment which was at lower temperature, due to its boiling point of 115°C. After the chemical treatment of the CTMP, the samples were dispersed twice in hot DMF and washed thoroughly before being dried at 105°C under air convection. For comparison CTMP was treated under identical process conditions in DMF without any isocyanate addition (sample B). To compare mono- and bifunctional isocyanates on an equal reactivity basis, the former were used in a concentration twice as high as the latter. In the case of sample F2, a strongly elevated isocyanate concentration (PhI) was used for the chemical modification of the pulp and no washing was done after the chemical treatment process.

Apparatus and operating conditions

For the thermoanalytical studies, a Mettler TA4000 thermal analysis system with DSC 20 and TG 50 was used. DSC and TG measurements were carried out with 6.5–7.5 mg of the sample at a heating rate of $20°C\,min^{-1}$. Dynamic measurements took place under nitrogen flow; isothermal TG measurements were made in static air. Further parameters of the thermoanalytical studies and the analytical procedures for the determination of water uptake and degree of degradation from thermoanalytical data are described in Part 1 of this study [15].

RESULTS

Gravimetry

Table 1 lists the weight increases of CTMP after different isocyanate treatments in DMF. With aromatic mono- (sample F), di- (sample C), and polyisocyanates (sample D), at a concentration of $0.027–0.054\,mol\,l^{-1}$, weight increases between 7.2 and 12.0 wt.% were achieved. Aliphatic mono- (sample E) and diisocyanates (sample G), under similar process conditions, yielded only minor weight increases. As a consequence of the isocyanate treatment, aromatic-isocyanate-modified pulp, exposed to a constant humidity of 67% r.h., shows a moderate reduction in its water uptake, compared to untreated CTMP. Phenylisocyanate modification of CTMP (sample F) yields a reduction in water uptake by one fifth. Less efficient in water reduction, in decreasing order, are MDI, PMPPIC and BUI, with almost no effect for HMDI-modified pulp. In contrast, CTMP

TABLE 1

Influence of isocyanate modifications on the humidity uptake of the modified pulp

Sample	Modifying agent	Process conditions	Weight gain [a] (wt.%)	Isocyanate uptake (per NCO-unit) (10^{-4} mol (g CTMP)$^{-1}$)	Water uptake [b] (wt.%)	$\Delta H^{\mathrm{humid}}$ [c] (J g^{-1})
A	–	Untreated	–	–	9.8	224
B	–	DMF, 125°C, 1 h	0.0	–	11.1	250
C	MDI	0.027 *m*, DMF, 125°C, 1 h	12.0	9.6	8.5	191
D	PMPPIC	40 wt.%, DMF, 125°C, 1 h	8.7	6.5	8.8	210
E	BUI	0.054 *m*, DMF, 115°C, 1 h	0.1	0.1	9.1	213
F	PHI	0.054 *m*, DMF, 125°C, 1 h	7.2	6.0	7.7	172
G	HMDI	0.027 *m*, DMF, 125°C, 1 h	2.0	2.4	9.6	215
F2	PHI	0.26 *m*, DMF, 125°C, 1 h	70.5	59.2	3.4	62

[a] Of the oven-dry sample. [b] Difference in weight between oven-dry and humid (67% r.h.) sample. [c] Enthalpy of the endothermic peak of the humid (67% r.h.) sample between 35 and 140°C measured by DSC.

treated in DMF without any isocyanate shows a significant increase in water uptake (sample B). This is possibly due to a partial extraction of lignin which leads to a more hydrophilic pulp surface (confirmed by ESCA measurements).

Treatment of CTMP with phenylisocyanate, at a concentration of 0.26 mol l^{-1} without additional cleaning of the reaction products (sample F2), yields a very high weight increase of 70.5 wt.% and a reduction in water uptake of two thirds.

Differential scanning calorimetry

Dynamic DSC measurements in nitrogen of CTMP treated with PMPPIC (sample D), BUI (sample E) and PHI (sample F) are compared to untreated CTMP (sample A) in Fig. 2. The endothermic peak between 35 and 140°C can be related to the humidity uptake of the sample and its enthalpy correlates with the gravimetric results as can be seen in Table 1. A more distinct difference in the DSC pattern of these isocyanate-treated samples is obvious when we compare the temperature region ($T > 180$°C) in which their dynamic degradation takes place (shown in Fig. 2). Isocyanate treatments with PMPPIC (sample D in Fig. 2), MDI and HMDI (not shown in Fig. 2) effect an increase in the first exothermic degradation step compared to the untreated CTMP. MDI-treated CTMP shows exactly the same DSC pattern as PMPPIC-treated samples, only differ-

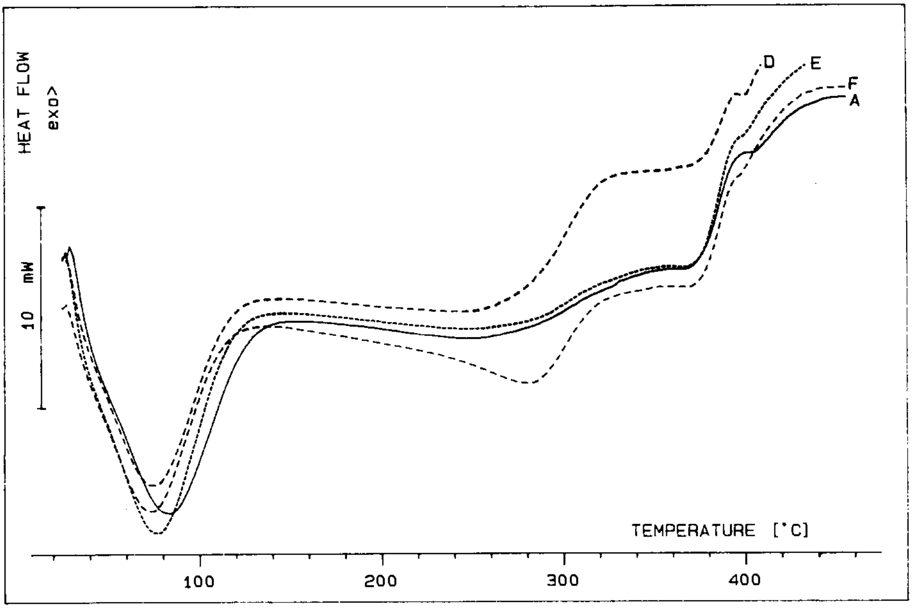

Fig. 2. Dynamic DSC pattern (20°C $\min^{-1}$, nitrogen) of CTMP modified with different isocyanates, as identified in Table 1.

ing in the enthalpy of the dehydration peak. This indicates a change in the thermal reactivity of the isocyanate-modified pulp compared to untreated CTMP.

Phenylisocyanate modification of CTMP (sample F in Fig. 2) results in an additional endothermic peak at 280°C prior to the degradation step, compared to untreated CTMP (sample A). A five-fold increase in phenylisocyanate concentration (sample F2) effects an even more intense endothermic peak at 278°C (Fig. 3c). Simultaneously the water uptake of this sample is reduced by two thirds (Table 1). Because FT-IR investigations show the presence of urethane bonds for all isocyanate-modified samples [16], this endothermic peak in phenylisocyanate-modified pulp might be correlated with an additional reaction component. Its degradation temperature (278–280°C, at a heating rate of 20°C min^{-1}) suggests the presence of a thermally stable product such as carbanilide (m.p.: 235–240°C; b.p. 262°C) or triphenylisocyanurate (m.p. 280°C). Extraction of the phenylisocyanate-modified CTMP (sample F and F2) in acetone

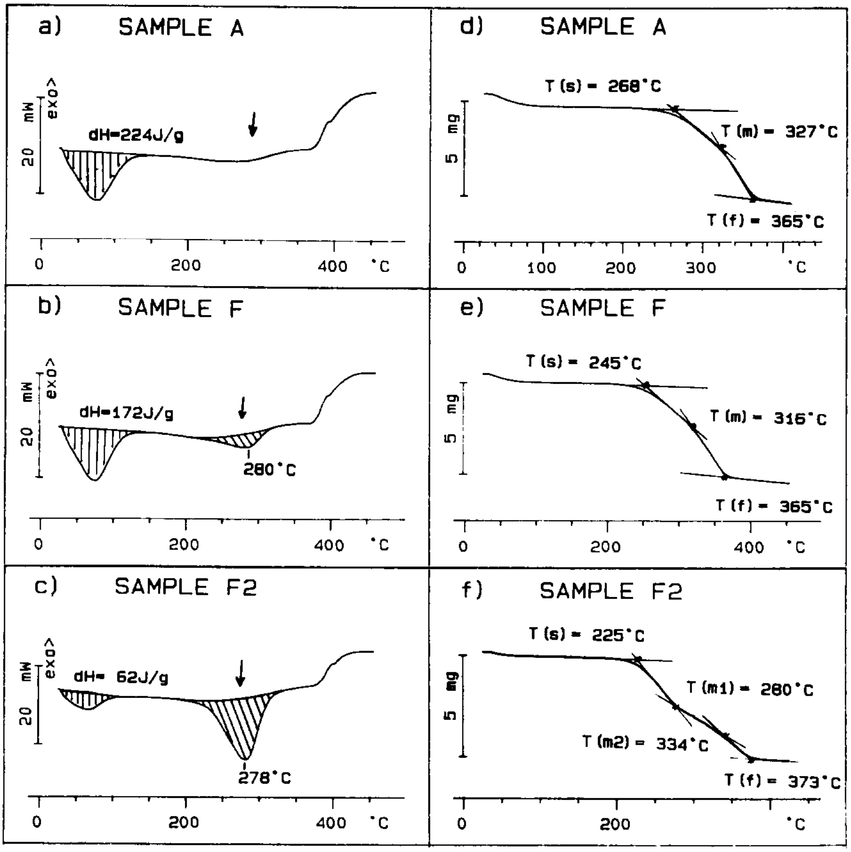

Fig. 3. Dynamic DSC and TG pattern (20°C min^{-1}, nitrogen) of CTMP modified with phenylisocyanate at different concentrations.

yielded only a minor reduction in the enthalpy of the endothermic peak at 280°C, which excludes a pure physical adsorption of a secondary product on the fiber.

The differences in the degradation behavior of the isocyanate-treated CTMP can no longer be found when the DSC experiments are done in static air. In oxidizing atmosphere, the start of the degradation reaction is shifted to lower temperatures and a more uniform degradation pattern appears. In contrast, the enthalpy of the dehydration peak is not influenced significantly by change in the purge gas.

In order to examine the influence of humidity, reaction temperature and phenylisocyanate concentration on the thermoanalytical pattern we carried out a variety of model reactions and examined their reaction products by DSC. As a result, we could show that the isocyanate treatment reduces moderately the water uptake of the modified pulp, without changing its DSC pattern (in nitrogen). If we do not clean the isocyanate-modified pulp before drying or if we use a DMF solution from an earlier isocyanate treatment as solvent, we find the endothermic effect at about 280°C, combined with a reduction in water uptake which is more than twice as high as in the former case. The endothermic effect can be correlated to a component isolated from the residue of a DMF solution after the phenylisocyanate treatment of CTMP at 125°C. We conclude, therefore, that a secondary reaction product of the phenylisocyanate, is responsible for a pulp modification which strongly influences its water uptake.

Thermogravimetry

Thermogravimetric studies show the same tendency for the weight losses up to 140°C (due to water desorption) as the gravimetric and DSC measurements, but differ in their absolute values (Table 2). This might be due to the influence of conditioning the humid sample in the thermobalance prior to measurement (2–3 min), which results in an undetermined loss in humidity compared to the gravimetric method.

Dynamic TG studies (not presented here) show the influence of isocyanate modification on the thermal stability of the pulp. In dynamic TG experiments, MDI and PMPPIC treatment shift the starting temperature of the degradation in nitrogen to higher values. Also the overall weight loss, between 180 and 400°C, is significantly lower than for untreated CTMP (Table 2). All other isocyanate modifications show a decrease in the starting temperature of the degradation. Phenylisocyanate treatment at high concentration (sample F2) results in a different degradation behavior, due to the additional endothermic effect at 280°C (shown in Fig. 3f). The derivative signal of the weight loss (not shown

TABLE 2

Influence of isocyanate treatment of CTMP on thermogravimetric results, for samples as identified in Table 1: dynamic TG in nitrogen at 20°C min^{-1} and isothermal TG in air

Sample	Dynamic TG Weight loss[a] (wt.%)		Isothermal TG Weight loss[b] (wt.%) at 220°C, 1 h, in air
	40–140°C	180–400°C	
A	8.5	66.0	14.2
B	8.6	66.5	14.4
C	7.5	56.9	12.4
D	7.8	58.3	12.5
E	8.4	67.2	18.1
F	6.3	69.6	17.1
G	8.2	63.7	15.8
FR	4.3	82.0[c]	35.8

[a] Of the humid (67% r.h.) sample. [b] Of the oven-dry sample. [c] Different degradation pattern.

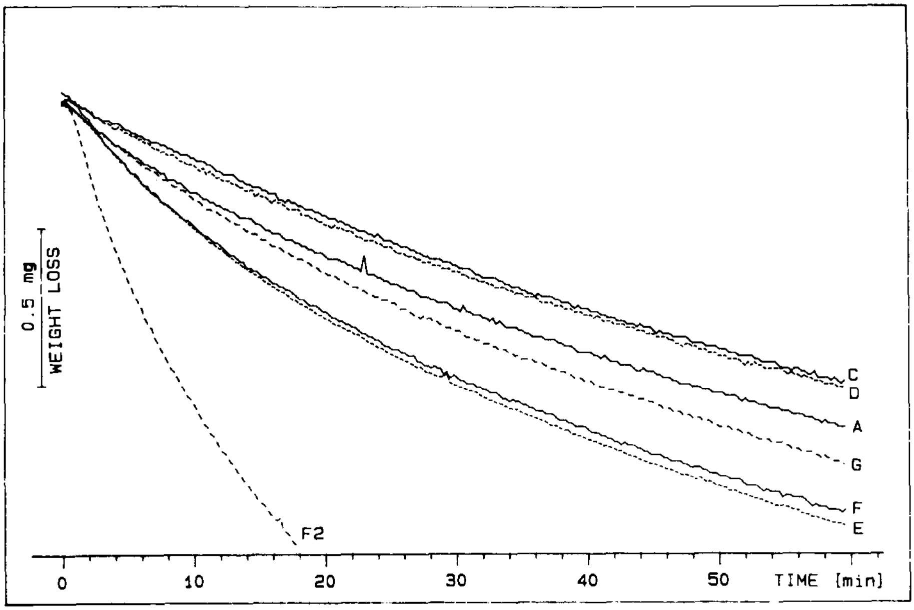

Fig. 4. Degradation behavior of CTMP modified by isocyanates, determined as weight loss by thermogravimetric analysis (isothermal, at 220°C in air); samples as identified in Table 1.

here) reveals a multistep degradation which is only partly consistent with the degradation pattern of untreated CTMP.

In order to quantify these differences in thermal stability, indicated by dynamic DSC and TG experiments, isothermal aging tests were made at 220°C in air. A static, oxidizing atmosphere was chosen for these tests, in order to achieve results on the degradation of the modified CTMP under experimental conditions which model a possible future composite processing. The results (Fig. 4 and Table 2) show an increased thermal stability for MDI- and PMPPIC-treated CTMP, but reduced thermal stability for HMDI, phenylisocyanate and butylisocyanate treatments in comparison to untreated CTMP. Sample F2 exhibits an extraordinary high weight loss and also differs in its degradation pattern in comparison to the other isocyanate-modified pulps.

CONCLUSION

CTMP was modified with various isocyanates in DMF, in the absence of any catalyst, and their effect on the thermoanalytical behavior of CTMP was investigated. In the case of aliphatic mono- (BUI) and diisocyanate (HMDI), used for the chemical modification of CTMP, only negligible weight increases were achieved. These treatments did not significantly affect the water uptake of the modified pulp. Furthermore the thermal stability of the modified samples in air was reduced slightly, compared to untreated CTMP. Phenylisocyanate treatment of CTMP, chosen as representative of aromatic monoisocyanates yielded moderate weight increase of 7.2 wt.% and a reduction in water uptake of the modified pulp by one fifth, compared to untreated pulp. The thermal stability of the reaction product was nevertheless lower than that of untreated pulp.

Treatment of CTMP with aromatic diiosocyanate (MDI) and polyisocyanate (PMPPIC) resulted in the highest weight increases, especially MDI with 12.0 wt.%. The water uptake of the modified pulp was slightly reduced and the thermal stability in air in both cases significantly increased compared to untreated CTMP. In general, all the isocyanate-modified pulps show the presence of urethane bonds, to varying extents, as detected by FT-IR [16].

The use of phenylisocyanate at a high concentration of 0.26 mol (g CTMP)$^{-1}$ without purification of the product (sample F2), reveals an additional endothermic effect in its dynamic DSC pattern and a multistep degradation in its dynamic thermogravimetric pattern (Fig. 3). The appearance of at least one more reaction product of the phenylisocyanate, compared to the reaction in a diluted solution (sample F), is linked with a severely decreased water uptake of the modified pulp. Model reactions show that the uptake of either urea or isocyanurate could be responsible for this effect. These secondary or by-products, which are not only physically adsorbed but strongly linked to the cellulosic material, seem to play an important role in the resulting physical and chemical pulp properties.

Compared to former anhydride treatments of the same type of CTMP under identical reaction conditions [15], the isocyanate modification leads (in a concentration of 0.026–0.054 mol (g CTMP)$^{-1}$) to only a moderate reduction in water uptake and increase in thermal stability. Only phenylisocyanate treatment at a concentration of 0.26 mol (g CTMP)$^{-1}$ yields a high reduction in water uptake of about two thirds compared to untreated CTMP. This is equivalent to the effect which was achieved with anhydride treatment at a ten-times higher concentration of modifying agent [15]. The minor potential of isocyanate modification of CTMP in order to achieve a more hydrophobic and thermally stable material, is in contrast to the results of Kokta and coworkers who improved thermoplastic composite properties of different pulps by use of isocyanates as coupling agents, added directly to the pulp before compounding or during compounding with the polymer. This suggests a possible additional reaction with the polymer during the compounding step, which influences the adhesion between pulp and polymer. In order to determine if the improvement of isocyanates as coupling agent is due to the chemical modification of the pulp or to an in situ reaction between isocyanate, pulp and polymer, comparative composite studies will be made.

ACKNOWLEDGMENTS

We thank The Natural Sciences and Engineering Research Council of Canada as well as the Fonds pour l'Aide à la Recherche of Québec (F.C.A.R.) and the Centre Québécois de la Valorisation de la Biomasse (C.Q.V.B.) for funding of DSC facilities and Stone Consolidated Inc. Bathurst Div. for the supply of cellulose pulp.

REFERENCES

1 W.E. Johns, J. Adhesion, 15 (1982) 59.
2 I.P. Clermont and F. Bender, Forest Prod. J., 7 (1957) 167.
3 B.R. Baird, Wood Fiber, 1 (1969) 54.
4 L. Reichelt and S. Poller, Acta Polymerica, 32(3) (1981) 172.
5 D. Maldas, B.V. Kokta, R.G. Raj and C. Daneault, Polymer, 29 (1988) 1255.
6 R.G. Raj, B.V. Kokta and C. Daneault, J. Mater. Sci., 25 (1990), 1851.
7 D. Maldas and B.V. Kokta, J. Reinforced Plastics and Composites, 8 (1990), 2.
8 D. Maldas, B.V. Kokta and C. Daneault, J. Appl. Polym. Sci., 37 (1989) 751.
9 R.G. Raj, B.V. Kokta, G. Grouleau and C. Daneault, Polym.-Plast. Technol. Eng., 29(4) (1990) 339.

10 S.E. Ellzey and C.H. Mack, Text. Res. J., 32 (1962) 1023.
11 A. Roussel, Cellulose Chem. Technol., 9 (1975) 247.
12 E.P. Frieser, Text.-Prax. Int., June (1965) 490.
13 M. Kramer, SVF Fachorgan Textilveredl., 12 (1957) 748.
14 O.H. Hsu and W.G. Glaser, Wood Science, 9(2) (1976) 97.
15 H.P. Rensch and B. Riedl, Thermochim. Acta, 205 (1992) 39.
16 H.P. Rensch and B. Riedl, J. Wood Chem. Technol., (1992), submitted.