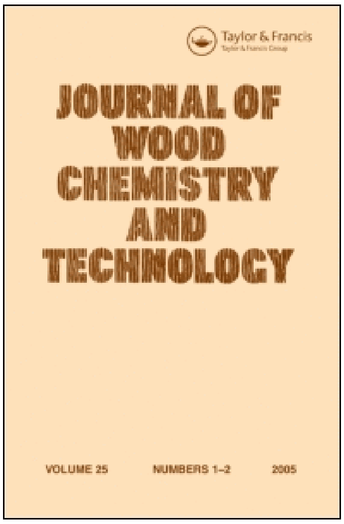

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Donatien P. Kamdem[a]; Bernard Riedl[a]
[a] Départment des sciences du bois Faculté de foresterie et de géomatique, Centre de recherche en science et ingénierie des macromolécules, Sainte-Foy, Québec, CANADA

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IGC CHARACTERIZATION OF PMMA GRAFTED ONTO CTMP FIBER

Donatien P. Kamdem and Bernard Riedl
Centre de recherche en sciences et ingénierie des macromolécules
Département des sciences du bois
Faculté de foresterie et de géomatique
Université Laval
Sainte-Foy (Québec) G1K 7P4 CANADA

ABSTRACT

Inverse Gas Chromatography (IGC) was used to characterize chemithermomechanical pulp (CTMP) wood fiber surfaces modified by polymer grafting. From the retention times at infinite dilution over a range of temperatures, the differential heat of adsorption, ΔH^{o}_{A}, the standard free energy, ΔG^{o}_{A}, and the standard entropy of adsorption, ΔS^{o}_{A}, have been determined for the n-alkanes vapors C_8-C_{11} on CTMP wood fibers grafted with poly(methylmethacrylate) (PMMA) at various polymer loadings (PL). The dispersive component of the surface free energy γ^{L}_{S} (London) has also been calculated by using a method based on the increment of ΔG^{o}_{A} per CH_2 group. Comparison of results for the original material, CTMP and PMMA, with those of the grafted fibers has allowed the evaluation of surface modification. Grafted samples at high PL show values of ΔH^{o}_{A}, ΔG^{o}_{A}, and γ^{L}_{S} approaching those of the pure PMMA indicating a high density of polymer chains grafts on the CTMP wood fiber.

INTRODUCTION

Intense research and development have been done in the area of thermoset and thermoplastic composites during the last decade. Various fibers such as carbon, Kevlar, glass fiber, and cellulosic derivatives have been used as reinforcement and/or filler agent[1-4]. These fibers are incorporated within a polymeric matrix to yield an engineering material with high performance. Several studies suggested use of wood fibers in the form of pulp, sawdust and chips, because they are readily available, renewable and cheap[1-5].

However, polarity of lignocellulosic materials and polymer matrix are somewhat different. Cellulosic fibers are hydrophilic while the polymeric matrix is hydrophobic. Thus, adhesion between reinforcing and/or filler agent and polymeric matrix is poor. The performance of a composite material is highly dependent on the fiber/matrix adhesion. In order to improve the adhesion between the wood fibers and the matrix, several researchers suggested the surface modification of wood fibers or polymeric matrix surface by different chemical or physical treatment such as the use of coupling agents, an increase of the matrix polarity by grafting or adding a polymer on the fiber surface[3-6].

The aim of this work is to characterize the modification occuring at the wood fiber surface due to polymer grafting in order to well understand phenomena at the fiber/polymeric matrix interface. The BET (Brunauer, Emmett and Teller)[7] method for surface area measurement and SEM (Scanning Electron Microscope) were used to monitor the surface area modification and the morphological changes on fibers after grafting. IGC (Inverse Gas Chromatography) has been widely used to study solid surfaces such as cellulose, cellophane, glass fibers, textiles, wood, cotton, carbon, Kevlar, silica, paper and polymers[8]. In general, this technique has been used for thermodynamic measurements[9]. It has partly replaced traditional static methods for the adsorption process, because it is less time consuming, it does not require elaborate apparatus or a vacuum, and it is accurate at low concentration. Measurements can also be conducted over a wide range of temperatures, and adsorption can also be measured for corrosive substances containing fluorine and sulfur. IGC allows the determination of heats and entropies of adsorption, specific surfaces, adsorption isotherms, and the London component of the surface free energy, γ^L_S[10-14].

CTMP wood fibers has been modified by radical polymer grafting at different polymer loadings level. These modified fibers, as well a pure polymer and CTMP fibers, are used as the stationary phase in a gas chromatography column. Its surface is characterized by vapour adsorption of n-alkanes (C_8-C_{11}) in the zero coverage region or at infinite dilution in order to respect Henry's law. The retention time of the probes injected at very low concentration are studied as a function of the column's stationary phase, the column temperature and the probe injected.

EXPERIMENTAL

CTMP Wood Fiber

The substrate is a CTMP wood fiber from both softwood and hardwood (50% spruce and 50% balsam fir). The pulp yield is 90% and the lignin[15] content is 30%. The CTMP is made of 70% holocellulose, 60% cellulose, 17% hemicellulose[16] and 0.3% sulphonate[16] (CPPA). The degree of polymerization of cellulose determined by the CED test (Cupri-ethylene-diamine) according to the standard[16] NFT12-005 is 717.

The characteristics of the pulps are: drainage index (CSF), 125 ml; breaking length, 4.5 km; tear index, 7.50 mN.m^2/g; burst index, 2.8 kPa.m^2/g; bulk, 2.5 cc/g; shives (Sommerville), 0.03%; average fiber length, 0.75 mm; pH, 6.2 and the stretch about 2.10%. The pulp properties were performed according to the CPPA (Canadian pulp and paper association) technical section standard method. These pulps fibers were dried in a circulating air oven at 80 ± 5°C during 48 hours prior to the determination of the moisture content.

Modification Of CTMP Fiber And Support Surfaces

The experimental procedure used for modifying wood fiber surface is graft copolymerization, similar to those previously published[17]. The xanthate method of grafting is initiated in this case by using H_2O_2/Fe^{2+} redox system to graft methyl methacrylate onto CTMP wood fibers. The procedure of pulp conditioning and the xanthate method of graft polymerization have been described in a previous paper by Kokta et al[18]. The percentages of grafting, as of polymer loadings, are determined gravimetrically after Soxhlet extraction for 8 hours with acetone using the following equation:

$$PL^* (\%) = 100 * \frac{A - B}{A} \quad (1)$$

where A is the weight after polymerization, grafting and extraction in grams,

B is the initial pulp weight in grams,

PL* is the polymer loading in percentage compared to the grafted fiber.

The standard error on PL* is about 3% according to combined balance error, loss during washing, filtering and extraction steps. This value is estimated by blank tests.

Methyl methacrylate from Kodak, used as monomer, was purified by distillation after removing inhibitors with sodium hydroxide and stored in dark bottles in a refrigerator. All others chemicals were analytical grade and used as supplied by the manufacturers.

Grafted and initial ungrafted CTMP fiber was dried, first in air and afterwards in an air oven at 70-80°C for 48 hours prior for column packing. As a reference, PMMA from Polyscience Inc. was first dissolved in acetone in a beaker (50% weight/volume PMMA in solvent). A weighted quantity of support material was added to the polymer solution and the mixture agitated to insure that all of the support was covered by the solution. The mixture was placed in a hood and the acetone evaporated with continued agitation. The support chosen for these studies were glass beads from Chromatographic Specialties. The percent loadings were calculated by the ashing method (8.0 ± 0.1%) which were the same values as calculated by weighting the initial products. This method consists of placing coated and uncoated support in an oven for 12 hours at 450°C. The support is weighted before and after the process to determine the percent loading:

$$L^* = \frac{W_a - W_b}{W_a} \times 100 \tag{2}$$

W_a, weight after the process,
W_b, weight before the process.

Surface Area Measurement

Surface areas of various adsorbents were measured by the BET adsorption isotherm model, using Krypton as adsorbate. The apparatus used was a Micromeritics, Model Accusorb 2100E. The adsorption was determined at 77°K and at a low partial pressure (p/p_o, 0.02-0.3). The values used to calculate the surface area by the BET method[7] were $p_o = 2.51$ mm, the saturated pressure of Krypton at 77°K and $A = 21 Å^2$, the surface of a Krypton atom. Gurnagul and Gray[19] found that Krypton adsorption at 77°K yields more accurate surface areas than nitrogen for relatively small areas (5 to 1 m^2/g) due to the low saturated vapour pressure of Krypton[20]. Table II contains the surface area of various samples, and it can be seen that this parameter varies with the grafting level PL*.

Preparation For SEM

The different samples prepared for microscopic studies are described in Table I. A scanning electron microscope (S.E.M.),

TABLE I
Sample Treatments

Sample	Description	Sample preparation
A	Chemi-Thermo-Mechanical Pulp (CTMP) wood fibers	Intact dried CTMP wood fibers
B	CTMP grafted at 0%	H_2O_2 treated CTMP fibers
C	CTMP grafted at 30%	PMMA grafted onto CTMP fibers at 30% PL*(a)
D	CTMP grafted at 50%	PMMA grafted onto CTMP fibers at 50% PL*
E	CTMP grafted at 60%	PMMA grafted onto CTMP fibers at 60% PL*
F	Poly (Methyl Methacrylate) (PMMA)	PMMA coated onto glass beads 60/80 mesh at 8% L*(b)

(a) Percentage of PMMA based on the weight of the grafted fibers after extraction of the homopolymer, from equation 1. 28.1, 48.7 and 62.6% were the exact value corresponding to 30, 50 and 60% PL*, respectively. Since the standard error is about 3%, 30, 50 and 60% were adopted as rounded figures.

(b) PMMA powder dissolved in acetone and coated onto glass heads, L* calculated according to Equation 2.

TABLE II
Column Description

Columns[a] no	Samples Non-mobile phase	Samples loadings (g)	Pressure drop P_i/P_o	Surface area[b] (m^2/g) Kr Sorption
1	A	1.70	1.04	1.58
2	B	1.80	1.10	1.72
3	C	2.02	1.04	2.21
4	D	1.33	1.04	2.20
5	E	1.85	1.03	1.83
6	F	1.50	1.04	0.09

(a) 120 cm long, 6.35 mm interior diameter copper column.

(b) Surface area determined by BET theory using Krypton (Kr) sorption.

Model JSM-25SIII, JEOL, was employed to study the fine structure of modified fibers. Platinum and thereafter gold were deposited onto the surface of samples by using a Spotter-Cutter, Model Technics, in the usual way. Electron micrographs, presented in Figure 1, clearly demonstrate that CTMP wood fiber surfaces have been modified by grafting.

IGC Measurement

Apparatus And Measurement

A Hewlett Packard 5700A gas chromatograph, equipped with dual hydrogen flame ionization detectors maintained at 300°C, is used for the measurements. The injection ports of the chromatograph are maintained at 300°C, which is 50°C above the highest boiling point of the alkanes sorbates to ensure flash vaporization at each injection. The ends of the column are equipped with finned transistor heat sinks in order to minimize the temperature gradient in the columns caused by the detector and the injector operating at higher temperature than the column.

A circulating water bath from Julabo (U.C. model UC-5b) is used to keep the temperature of the column constant. This column temperature is controlled within ± 0.5°C and monitored with an Omega digital thermometer (model 2165A, Copper/Constantan thermocouple). The gas chromatograph is interfaced with a Hewlett Packard model 3380A Integrator. The integrator is used to control instrument conditions such as the base lines, to store the retention times and to record the peaks after each injection. A 1 μl Hamilton syringe is used to inject small volumes, ranging from 0.02 to 1 μl, of sorbate. The highest sensitivity range of the chromatograph and the detector are used to detect much small amounts.

Linde prepurified nitrogen is used as carrier gas. This nitrogen is passed through a 5Å molecular sieve trap from

Chromatographic Specialties Inc. before entering the column, in order to eliminate all the remaining impurities. The flowrate is 30 ml/min at room temperature, measured at the outlet of the column and corrected for the presence of water in the soap bubble flowmeter. Corrections are made for the pressure drop between the inlet and outlet of the column, and the difference between column and flowmeter temperature[9].

The pressure drop is determined from a mercury manometer connected at the inlet of the column to a precision of 0.067 $kN.m^{-2}$ during the flowrate measurement. The outlet pressure of the column is atmospheric and it is measured with a mercury manometer (the pressure drop across the various packed column was in the range of 1 to 5 $kN.m^{-2}$). The column temperature is determined by measuring bath temperature with a digital copper/Constantan thermocouple with ± 0.5°C of precision, and the flowmeter temperature is taken as the room temperature.

Columns were prepared by using PMMA coated glass beads and CTMP wood fibers grafted with polymer at various loading levels (PL*) as stationnary phase. Table 1 gives the description of the columns. The non-mobile phases were introduced under vacuum to facilitate packing into a 4 mm I.D. and 1.2 meter long copper tubing that had been previously washed with methanol and rinsed with acetone. The packed columns were conditionned at 60°C in a stream of nitrogen for 24 hours to remove any volatile impurities prior to use.

The injection of the smallest amount of probe is achieved by using the splitting injection technique as described by Munk[21]. This technique consists of emptying about 3 to 4 times the syringe and to inject only the amount remaining in the syringe needle, or to inject the needle into a hot false injection port, to evaporate most of the probe and then inject the remaining vapour amount into the real port.

The retention time is measured at the peak maximum. For large volume injections (1 μl), the retention time varies, but remains constant with volumes of 0.5 μl or less to a precision of 3%. The adsorption peak became more assymetric with large volume injection and the retention time also increased. Thus, only small amounts of sample where the retention time is constant ($\leq$ 0.5 μl) were used in the study. The dead volume in the columns was determined from the peak maxima retention volumes of methane.

Experiments were performed in the temperature region from 293 to 323°K. Chromatographically pure alkane probes ranging from n-octane to n-undecane were purchased from Aldrich and checked out for purity by G.C. (Gas Chromatography) prior to use. Purity was better than 99% in all cases. For each probe, in each column, the retention time was measured as the mean of 10 to 12 injections.

Data Reduction

The main data obtained by the IGC is the time of retention, t_R, of the probe through the non-mobile phase. By assuming that the dominant retention mechanism is only a surface adsorption, the net retention volume is defined by the following equations[9]:

$$V_N = K_S \cdot A \qquad (3)$$

$$V_N = Q \cdot (t_R - t_m) \qquad (4)$$

where K_S is the surface partition coefficient between the non-mobile and mobile phase,

A, the total surface area of the stationary phase determined by using Krypton adsorption BET theory[7],

t_R, the retention time of the injected probe,

t_m, the retention time of methane,

Q, the corrected flowrate of the carrier gas at column temperature and at 760 mm obtained as follows[9]:

$$Q = Q_o \cdot J \cdot \frac{T_c}{T_a} \cdot 1 - \frac{P_w}{P_a} \qquad (5)$$

where Q_o is the flowrate measured from the end of the column in mL/minute,

J, the James-Martin correction factor for gas compressibility[22],

T_c, the column temperature,

T_a, the ambient temperature,

P_w, the water pressure in mm Hg at T_a,

P_a, the atmospheric pressure in mm Hg.

The specific net retention volume $V^o{}_g$ at 0°C and per gram of adsorbent is calculated by using the following expression[23]:

$$V^o{}_g = \frac{273.15}{T_c} \cdot \frac{1}{W} \cdot V_N \qquad (6)$$

where W is the amount in grams of the adsorbent in the column.

The standard molar enthalpy, $\Delta H^o{}_A$, standard free energy, $\Delta G^o{}_A$, and standard entropy, $\Delta S^o{}_A$, of adsorption are calculated from gas chromatography data, the net retention volumes, by using the well known equations suggested by Dorris and Gray[11-12]:

$$\Delta H^o{}_A = -q_d = -R \frac{d(\ln V^o{}_g)}{d(1/T)} \qquad (7)$$

$$\Delta G^o{}_A = -RT \ln (K_S \cdot P_{s,g}/\Pi_s) \qquad (8)$$

$$\Delta S^o{}_A = -(q_d + \Delta G^o{}_A)/T \qquad (9)$$

where q_d is the differential heat of adsorption of the injected probe, in kJ/mol,

R, the gas constant, in Joule/mol. °K,

T, the column temperature, in °K,

$P_{s,g}$, the adsorbate vapour pressure in the gaseous standard state[13] equal to 101 $KN.m^{-2}$,

Π_s, the reference two-dimensional surface pressure whose standard state is 0.338 $mN.m^{-1}$, defined by De Boer[13].

The work of adhesion, W_A, between a nonpolar liquid and a surface is expressed by the following equation[24]:

$$W_A = 2(\gamma_l \cdot \gamma^L{}_s)^{1/2} \qquad (10)$$

where γ_l is the surface tension of the nonpolar liquid,

$\gamma^L{}_s$ is the London Component of the solid surface tension.

Dorris and Gray[10-11], have proposed an useful empirical expression to estimate the London Component $\gamma^L{}_s$ of the surface free energy of the adsorbent based on the incremental change in $\Delta G^o{}_A$ per $-CH_2-$ group for a series of alkanes. This relation assumes that W_A, the work of adhesion between an alkane and an adsorbent is equal to the free energy of adsorption per mole of methylene $-CH_2-$ group:

$$\gamma^L{}_s = \frac{1}{4} \cdot \frac{1}{\gamma_{CH_2}} \cdot \left[\frac{\Delta G(-CH_2-)}{N.a}\right]^2 \qquad (11)$$

where N is Avogadro's number,

a, the area occupied by a $-CH_2-$ group[10], 0.06 nm^2,

γ_{CH_2}, the surface tension of a surface of only $-CH_2-$ groups[10], 35.5 $mN.m^{-1}$ at 20°C,

$\gamma^L{}_s$ depends upon the differential $\Delta G(-CH_2-)$, and it is independent of the surface area A of the adsorbent, and therefore is a fundamental parameter.

This method, then, provides a route to surface free energies which avoids some problems of contact angle measurements on fiber due to the roughness, porosity and heterogeneity on the wood fiber surface.

RESULTS

Micrographs of samples from SEM at magnification of 2500X, 4000X, 6000X and 8000X are presented in Figure 1. Table I describes the different samples prepared for this study. Table II shows the surface area of samples, increasing from 0.09 up to 2.20 m^2/g. The retention volumes of the n-alkanes from n-octane to n-undecane have been measured on the various fibers. This series of alkanes was chosen since the n-hexane and n-heptane have shown very short retention times for adsorption and the n-dodecane presented excessive times for adsorption in the temperature range of this study. The retention volumes of adsorption were investigated in the zero coverage region, where the mobile phase concentration injected is so low that all mobile phase molecules behave independently. This agreement with Henry's law was confirmed by the symmetrical shape of the elution peaks and the constancy of the net retention volume over a significant range of adsorbate sizes injected (0.1 to 0.6 μl), and with the carrier gas flow rate variation (30 ± 5 ml/min). The proportional area of the elution peak to the amount of the injected probe vapour at the highest sensitivity of the FID detector indicates that the adsorption isotherm were in the linear region. Figure 2 shows chromatograms of n-decane on CTMP fiber at 25°C, illustrating the symmetry and surface area proportionality to the injected probe vapour. Figure 3 presents the adsorption isotherms of n-decane at 20, 25, 40 and 50°C and indicates that they are linear in the study region.

Within the temperature range of this study (20-40°C), the plots of ln V^o_g versus 1/T for all mobile and non-mobile phases are linear, confirming the validity of equation 7. Figures 4 and 5 show typical results for various samples. The slopes of these curves were obtained from least squares and their standard

Fig. 1 Scanning electron micrography of:
a) the untreated CTMP control (sample A) (x 2500), b) H_2O_2 treated CTMP (sample B) (x 4000), c) the 30% CTMP-PMMA grafted sample (sample C) (x 8000), d) the 50% CTMP-PMMA grafted sample (sample D) (x 8000), e) the 60% CTMP-PMMA grafted sample (sample E) (x 6000)

deviations were about 3 to 4%. The differential heats of adsorption, q_d, were computed from these slopes according to equation 7. The results for samples A through F are given in Table III. The standard free energies of adsorption, $\Delta G^o{}_A$, were calculated from equation 8 by using the surface area determined by the method of Kr adsorption through BET theory[19] and the De Boer[25] standard state for spreading pressure. The difference between $\Delta G^o{}_A$ and $-q_d$ gives the standard entropies of adsorption at zero

FIG. 1b

FIG. 1c

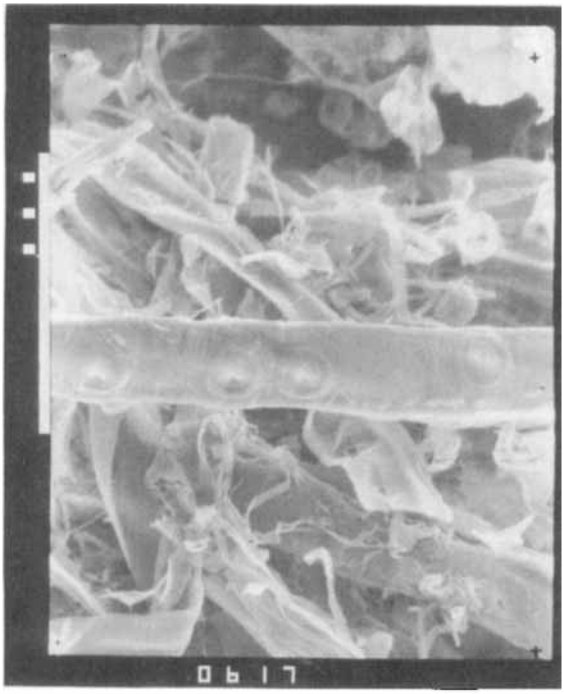

FIG. 1d

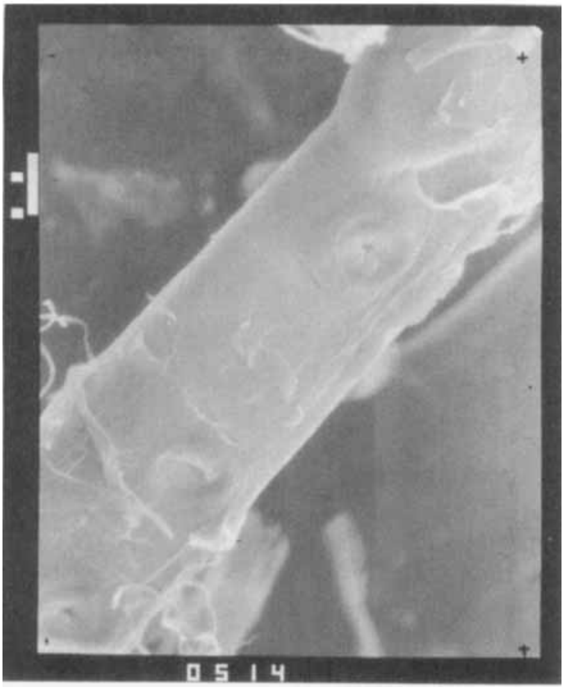

FIG. 1e

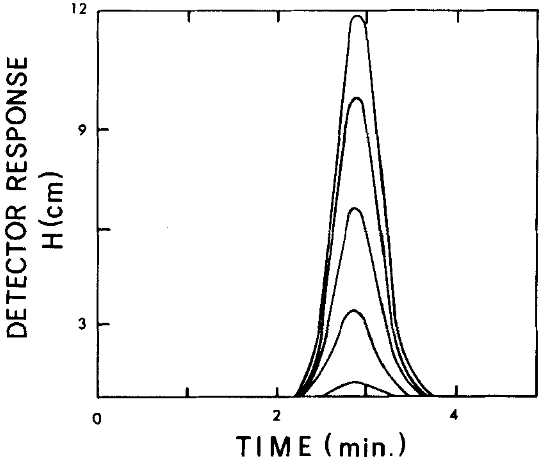

Fig. 2 Chromatogram of n-decane on CTMP fibers at 298.15°K. The peak is recorded at very high sensitivity of the chromatograph (1x1) and the detector (1x2), and corresponds to partial pressures smaller than 1 $N.m^{-2}$.

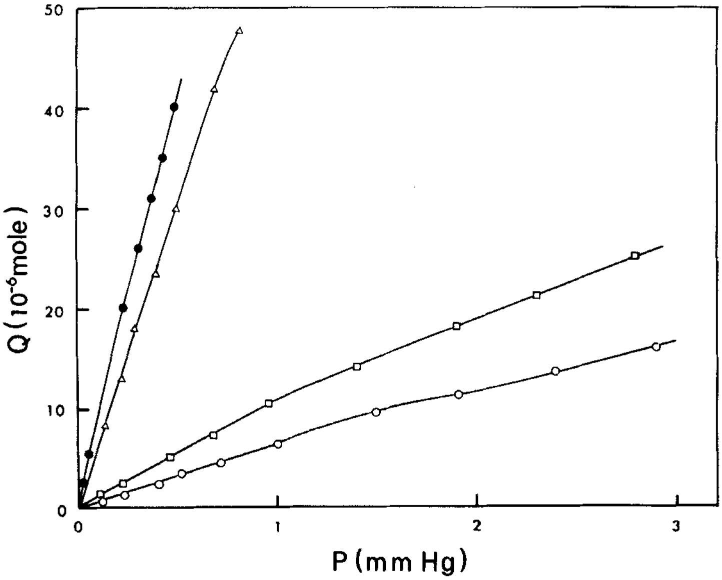

Fig. 3 Adsorption isotherm of n-decane on CTMP at 293.15°K (●), 298.15°K (△), 313.15°K (□) and 323.15°K (○)

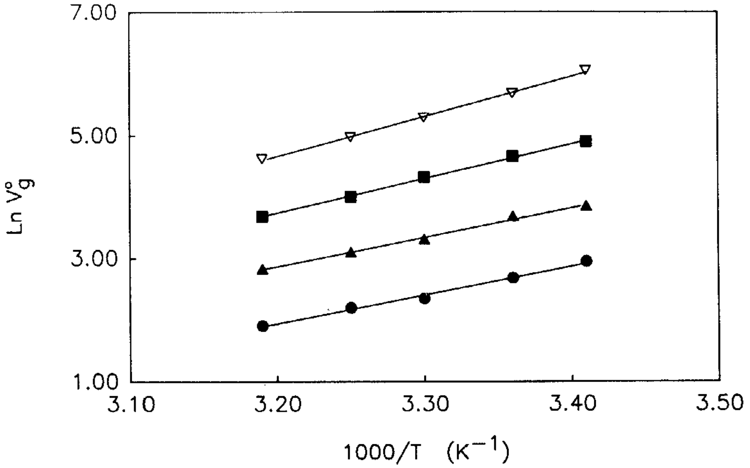

Fig. 4 Plot of ln(V°g) versus 1000/T for n-octane (●), n-nonane (▲), n-decane (■) and n-undecane and (▽) on untreated CTMP fibers (sample A).

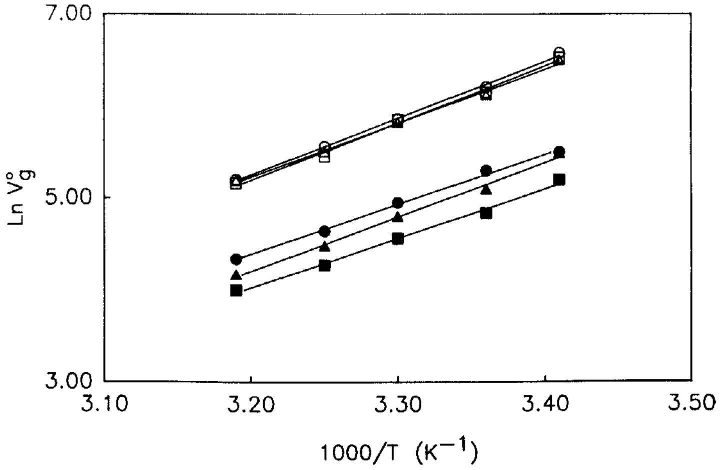

Fig. 5 Plot of ln(V°g) versus 1000/T for n-decane on samples A (■), B (□), C (△), D (O), E (▲) and F (●).

TABLE III
Standard Thermodynamic Functions for the Zero-coverage Adsorption of the N-alkanes at 298.15°k for the Various Samples

Non-mobile phase	Mobile phase	$q_d = -\Delta H^o_A$ (kJ/mole)	$-\Delta G^o_A$ (kJ/mole)	$-\Delta S^o_A$ (J/mole·K)
A	C_8	32.9	19.5	44.9
	C_9	39.7	22.3	58.4
	C_{10}	46.9	24.8	74.1
	C_{11}	53.9	27.3	89.2
B	C_8	39.2	21.3	60.0
	C_9	47.0	23.9	78.0
	C_{10}	53.5	26.5	90.0
	C_{11}	60.6	29.5	104.3
C	C_8	39.2	20.3	63.4
	C_9	47.1	23.1	80.5
	C_{10}	54.2	25.8	95.3
	C_{11}	61.3	28.6	109.7
D	C_8	39.2	19.0	67.5
	C_9	46.7	22.0	83.0
	C_{10}	54.1	26.0	95.0
	C_{11}	61.1	27.7	112.0
E	C_8	40.3	19.2	70.8
	C_9	48.0	21.4	89.2
	C_{10}	53.5	23.8	99.6
	C_{11}	61.6	26.5	117.7
F	C_8	38.0	27.0	36.9
	C_9	42.0	28.7	44.6
	C_{10}	47.1	31.7	53.7
	C_{11}	52.0	33.5	62.5

coverage by using equation 9. Table III presents complete results for various samples A to F at 298.15°K with the n-alkanes probes (C_8 - C_{11}). Table IV show the values of enthalpy, free energy and entropy of adsorption per mole of methylene group $-CH_2-$ obtained from the slope of $\Delta H^o{}_A$, $\Delta G^o{}_A$ and $\Delta S^o{}_A$ versus the number of carbon atoms of the n-alkane for the studied samples. The London nonpolar component of the surface free energy of various samples, $\gamma^L{}_S$, at 298.15°K were computed from equation 11 and the results are given in table V.

DISCUSSION

Surface Area And Structure Of Wood Fiber

Tables I and II present the different samples treatment and their respective surface area measured by the BET adsorption isotherm using Krypton at 77°K. Initial CTMP has a surface area of 1.58 m^2/g, comparable of the TMP (Thermomechanical Pulp) value of 1.50 m^2/g reported by Dorris et al.[10] and 1.0 m^2/g as measured by Stone and Scallan[26] with the nitrogen based measurements. Gurnagul and Gray[19] found that, by using nitrogen instead of Krypton, with the same apparatus, the TMP gave an anomalously low surface area of 0.9 m^2/g compared to 1.50 m^2/g with Krypton. This is due to the very low surface energy of wood fiber and its surface area which is less than 5 m^2/g. Several researchers[19] reported that nitrogen is more adequate for studies of surfaces with specific surface area greater than 5 m^2/g.

H_2O_2 treated CTMP has a higher surface area than the initial pulp. The action of H_2O_2 on wood fiber have been studied by many researchers. Hornof and Puissant[27] have noted the oxidative degradation of cellulosic material by hydrogen peroxide and the breaking of intermolecular bonds of lignin and some wood components as well. Delignification has been reported by Lonikar[28] and an increase of surface area with the lignin removal percentage have also noted by Stone and Scallan[26]. ESCA

TABLE IV
Differential Heat of Adsorption, Standard Free Energy and Standard Entropy of Adsorption per Mole of Methylene Group on Various Non-mobile Phases at 298.15°k

Non-Mobile Phase	$-\Delta H^{o}_{A}(CH_2)$ (kJ/mole)	$-\Delta G^{o}_{A}(CH_2)$ (kJ/mole)	$-\Delta S^{o}_{A}(CH_2)$ (J/mole•K)
A	7.00	2.58	14.7
B	7.14	2.73	14.8
C	7.37	2.78	15.4
D	7.50	2.90	15.7
E	7.10	2.50	15.6
F	4.90	2.30	8.8

TABLE V

Dispersive Component of the Surface Free Energy, $\gamma^{1}{}_{S}$, at 298.15°k, and Thermodynamics Data for the Adsorption of n-decane on Samples A through F at 298.15°k

Non-mobile phase	A	B	C	D	E	F
$-q_d$ (kJ/mole)	46.9	53.3	54.2	54.1	53.5	47.1
$-\Delta G^{o}{}_{A}$ (kJ/mole)	24.8	26.5	25.8	26.0	23.8	31.1
$-\Delta S^{o}{}_{A}$ (J/mole.K)	74.1	90.0	95.3	95.0	99.6	53.7
$\gamma^{L}{}_{S}$ (mN.m^{-1})	36.4	40.1	42.3	46.0	34.2	29.0
$-q_{st}$ (kJ/mole)	49.4	55.8	56.7	56.6	56.0	49.6

techniques also showed that the O/C atomic ratio of H_2O_2 treated CTMP fiber is higher than that of the initial untreated, due to the increase of oxygen and/or the decrease of carbon on the surface[30]. The oxygen is essentially from polysaccharides whereas carbon is mainly from extractives and lignin. Therefore, H_2O_2 treatment contributed to the loss of some wood components and the creation of voids and pores in the cell wall, increasing the surface area of the initial fiber. Figures 1.a and 1.b show the micrographs of CTMP fibers before and after H_2O_2 treatment. After H_2O_2 treatment, the removal of some wood components contributed to increased pore and voids dimensions. The grafted samples have their external surface area higher than the initial pulp fiber, the PMMA and the H_2O_2 treated fiber (Table II).

The surface area changes can be interpreted as follows. Wood fiber swells in the aqueous medium and increases its specific surface. However, when the fiber dries, it collapses and regains its initial specific surface. After the grafting of a thermoplastic polymers such as PMMA, some of this swelling is "frozen in" and so, even after drying, the fiber does not return to its initial state, but retains a higher specific surface. Since the PMMA has a low specific surface (sample F), the specific surface decreases as more polymer is added. This would explain the low specific surface at higher PL*. Thus, values of specific surface of the grafted fibers remain higher than that of the original fibers and than that of the PMMA polymer.

The mechanism of this fiber modification is based on the introduction of a number of xanthate groups into the cellulose molecules and on the contact of the derived activated cellulose macroradicals with polymerizable monomers in the presence of a peroxide catalyst[30]. The surface of samples C, D and E shown in Figures 1.c, 1.d and 1.e indicates the deposition of matter, that is assumed to be the grafted polymer, in the voids, capillaries and cavities of the wood fiber substrate. When the amount of this grafted polymer formed increases, it eventually fills the total volume of the voids in the wood fibers. Figure 1.e shows that the grafted polymer chains extend into the microscopic pores and wraps the fiber. This is the reason of the decrease of the external surface area of sample E. The pores, the cavities and lumen of the wood fibers are all blocked by the polymer, limiting the diffusion of Krypton atom into the graft PMMA chains.

Samples C and D have the highest surface area. At 30-50 PL*, empty cavities and pores are still present and detectable by the SEM (Figures 1.c and 1.d). The spacings between graft polymer chains on wood fiber surface are probably sufficiently large to permit the adsorption of Kr atoms into the grafted PMMA chains and uncovered wood fiber cavities. The surface area of samples C and D thus represents the combined surface area of wood fiber and graft polymer chains.

Thermodynamics Of Adsorption

Table III shows the difference in thermodynamic properties of various samples and follows the surface state variation with the substrate modification. IGC allows to calculate q_d, $\Delta G^o{}_A$, $\Delta S^o{}_A$ and $\gamma^L{}_S$ of the non-mobile phase.

Differential Heat Of Adsorption, q_d

The differential heat of adsorption, q_d, for samples B, C, D, E are higher than that of sample A and F (Table III). These are a result of a high energy interaction between the vapor probe and the non-mobile phase. The values of q_d of the n-alkanes vary lineary with the number of carbon atoms, n, suggesting a flat orientation of the probe vapor on the non-mobile phase during adsorption[11-14] (Figure 6). The slope of this linear variation represents the incremental contribution by each methylene group[10-11]. This behavior is observed for all samples and the slope is specific for each sample (Table IV). Figure 6

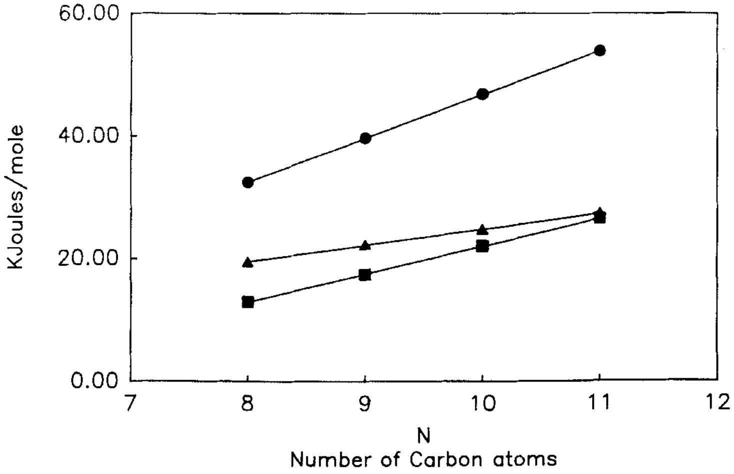

Fig. 6 Thermodynamic functions of adsorption at zero surface coverage on CTMP fibers as a function of the number of carbon atoms of the n-alkanes at 298.15°K (sample A), $-\Delta H^{o}_{A}$ (●), $-\Delta G^{o}_{A}$ (▲) and $-T.\Delta S^{o}_{A}$ (■).

illustrates the linear variation of q_d with the number of carbon atoms for sample A.

The corresponding heats of liquefaction, ΔH_L, for the n-octane, n-nonane, n-decane and n-undecane are 41.8, 46.8, 51.8 and 56.8 kJ/mole, respectively[34]. The isosteric heat of adsorption is the heat developed when 1 mol of adsorbate is adsorbed by an infinite amount of solid without change in the fraction of surface covered by the adsorbate[9]. The isosteric heat of adsorption, q_{st} (Table V), is equal to q_d + RT and it compares well with ΔH_L. CTMP fiber and PMMA sample have their q_{st} close to ΔH_L for the n-decane probe. Similar phenomenon have been reported for TMP fiber[10], cellulose fibers[11-13], cellophane[31], and PET[32].

CTMP fiber and PMMA have weak interactions with the n-decane probe. The surface of CTMP fiber and PMMA non-mobile phase shows homogeneous and low energy sites based on their low q_d values. Gray[23] reported almost the same value of q_d for the PMMA and the TMP fiber[10-11]. The presence of extractives and lignin at the CTMP surface provide a smooth homogeneous surface coating which interacts weakly with the n-decane probe. This explains the high q_{ST} of H_2O_2 treated CTMP (Sample B) in comparison with the initial fiber (Sample A).

For samples C, D and E, q_{st} is about 5.0 ± 1 kJ/mole higher than $-\Delta H_L$ for n-decane (Table V). The heat of adsorption on these non-mobile phases, compared to the heat of liquefaction of the corresponding probe, is due to the great interaction between the vapour-probe and the surface of sample. These samples show a surface with high energy adsorption sites due to the presence of at least two types of sites: one from the CTMP and the other from the graft polymer chains. Therefore, surface of these samples (C, D and E), are heterogeneous. At 50% PL*, sample D exhibits the highest q_d, and this parameter decreases with the increase of PL*. At 50% PL* and less, vapor probes injected can interact both with sites of CTMP and sites of grafted polymer, whereas at PL* higher than 50%, the grafted polymer is so dense that it is difficult for a probe to be adsorbed on a CTMP site.

The differential heat of adsorption, q_d, varies with the surface coverage during adsorption and is dependent upon the concentration of vapor probe injected[23]. For a given sample, q_d varies linearly with the chain length of the alkanes. The incremental $-\Delta H^o{}_A$ per $-CH_2-$ is 7.00, 7.14, 7.37, 7.50, 7.10 and 4.90 at 298.15°K for samples A, B, C, D, E and F, respectively (Table IV). The incremental $-\Delta H^o{}_A$ per methylene group, $-\Delta H^o{}_A$ $(-CH_2-)$, can be compared with the differential heat of adsorption, q_d. Kiselev and Yashin[33] have noted a similar linear relationship and have pointed out the characteristics of a non-specific and a monolayer[10] adsorption. Then, the increment per methylene group for $\Delta H^o{}_A$ of a series of n-alkanes may be more informative on the fiber surface modifications in terms of adsorption processes. In conclusion, q_d, the differential heat of adsorption, is dependent upon the adsorption process involved and the nature of the probe. q_d also varies with the nature and the density of the sites of the non-mobile phase.

Standard Free Energy Of Adsorption $\Delta G^o{}_A$

The standard free energy of adsorption, $\Delta G^o{}_A$, is calculated from the retention volume by using Equation 8. $\Delta G^o{}_A$ is the energy necessary to transfer one mole of vapour probe from its gaseous state at 1 atm to a standard state of the adsorbent surface. The choice of the surface reference state[25] for the computation of $\Delta G^o{}_A$ is arbitrary. However, Figure 6 shows a linear variation of $\Delta G^o{}_A$ with the number of carbon atoms for a series of n-alkanes probes for a given non-mobile phase. The slope of $\Delta G^o{}_A$ versus the number of carbon atoms is the incremental variation of the free energy of the methylene group, $-\Delta G^o{}_A(-CH_2-)$. The slope of the curve Ln Vg versus the number of carbon atoms at a fixed temperature for a non-mobile phase, also permits the computation of $-\Delta G^o{}_A(-CH_2-)$. Values of $-\Delta G^o{}_A(-CH_2-)$ obtained from the two methods were similar. The incremental variation of the free energy of the methylene group $-\Delta G^o{}_A(-CH_2-)$ is a parameter independent of the choice of arbitrary constants and independent of the surface area of the stationnary phase. This parameter reflects only the interaction of vapour probe and surface molecules of the non-mobile phase as a function of the temperature.

Table IV shows the $-\Delta G^o{}_A(-CH_2-)$ of various non-mobile phase at 298.15°K. CTMP fibers exhibit a value of 2.58 ± 0.05 kJ/mol comparable to those reported in the literature, 2.90 kJ/mol for Kraft papers[35], 2.70 kJ/mol for TMP fibers[10], 2.99 kJ/mol for cotton cellulose[10-12] and 2.95 kJ/mol for cellulose paper[34]. Sample D shows the highest value resulting from a high interaction between the vapour probe and the sample surface. This interaction

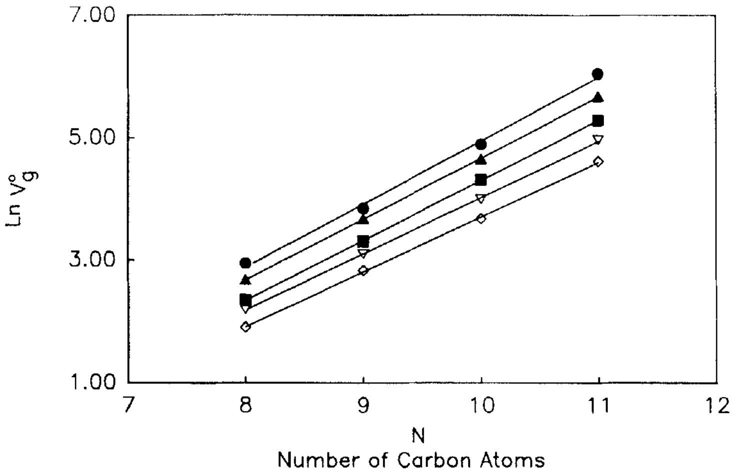

Fig. 7 Ln($V^o g$) versus the number of carbon atoms in n-alkanes for untreated CTMP fibers at various temperature: 293.15°K (●), 298.15°K (▲), 303.15°K (■), 308.15°K (▽) and 313.15°K (◇).

is due to the presence of 50% graft polymers chains onto CTMP fiber.

Standard Entropy Of Adsorption, ΔS^o_A

The entropy of adsorption, $-\Delta S^o_A$, of n-alkanes on various samples vary from 36 to 118 J/mole•K (Table III). The lowest values are obtained for sample F and A, whereas grafted samples B, C, D and E presented high values. These high value for B, C, D and E could probably be associated to the further lost of translational, or vibrational or rotational degrees of freedom due to the adsorption onto high energy sites. The lowest value of entropy is obtained for sample F, indicating that its surface is more homogeneous than sample A. The nature of the surface of the PMMA (sample F) is such that the adsorbed molecule is more mobile than that on the surface of the unmodified CTMP fibers (sample A). This may be due to the fact that the surface of the PMMA is

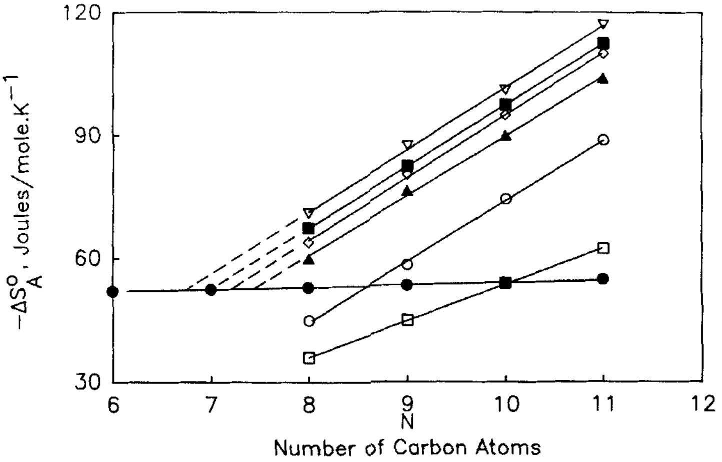

Fig. 8 ΔS^o_A versus the number of carbon atoms of alkanes for samples A (○), B (▲), C (◇), D (■), E (▽) and F (□) and the calculated theoretical value (●).

smoother and more homogeneous at the molecular level than that of the CTMP fiber. Figure 8 illustrates that for samples B, C, D and E, the experimental and theoretical values[25,34-35] of entropy of adsorption (if extrapolated) coincide at n = 7. On cellulose, Lee and Luner[34] report a coincidence at n = 6. Since CTMP fibers are a mixture of cellulose and lignin, and PMMA is different from cellulose, the coincidence occurs at n = 10 and n $\simeq$ 9 for sample F and A, respectively. These suggest that on grafted samples B, C, D and E, n-heptane behaves as a two dimensional gas with two degrees of unrestricted freedom while n-decane and n-nonane behave as a two dimensional gas on PMMA and CTMP fiber filled columns, respectively. Figure 8 also shows that the theoretical values of entropy of adsorption, $-\Delta S^o_T$, are smaller than all the experimental values for the samples B, C, D and E, and in particularly for the high molecular mass alkane, nC_{10} and nC_{11}, for all samples. The decrease of entropy values upon adsorption results from the loss of one degree of translational freedom for the n-alkane[25]. The decrease of entropy of about 15 to 30 J/mole•K is observed for the grafted samples (B, C, D and E) and this cannot be solely explained in terms of vibrational or rotational entropy changes upon adsorption, and suggests the loss of an additional degree of translation freedom due to the presence of new heterogeneous sites on fiber surface, which are graft polymer chains.

London Component Of The Surface Free Energy, $\gamma^L{}_S$

The London component of free energy of surface obtained according to equation 11 are 36.4, 40.1, 42.3, 46.0, 34.2 and 29.0 ± 0.1 mN.m^{-1} for samples A, B, C, D, E and F respectively, at 298.15°K (Table V). Dorris and Gray[10-13] reported $\gamma^L{}_S$ values from 34 to 52 mN.m^{-1} for cellulose at various water content, with $\gamma^L{}_S$ decreasing with the amount of water absorbed. For comparison, Schultz[36-38] also reported $\gamma^L{}_S$ of carbon fibers treated with epoxy varying from 34 to 50 mN.m^{-1}, and Gray[39] obtained values of 38.8 to 54.4 mN.m^{-1} for treated and untreated carbon fibers. Dorris and Gray[10] also found $\gamma^L{}_S$ values of 36 to 43 mN.m^{-1} for TMP fiber surfaces rich in lignin which are more similar to the CTMP fiber used in this study. The $\gamma^L{}_S$ decrease with the presence of lignin or hemicellulose on wood fibers is attributed to the low porosity and energetically uniform sites as reported by Luner[40].

The values of $\gamma^L{}_S$, 50 mN.m^{-1} for cotton cellulose fibers reported by Dorris and Gray[11] compares well with the experimental values of 47 mN.m^{-1} based on contact angle and equilibrum spreading pressure measurements at 40°C. Similar results were obtained with polyethylene terephtalate, with $\gamma^L{}_S$ based on IGC measurements and on contact angle data[31]. However, there are no wettability data for cellulosics fibers to compare our data with since wood fibers have a rough and heteregenous surface rather unsuitable for contact angle measurements.

H_2O_2 treated sample B shows a high $\gamma^L{}_S$ in comparison of sample A (Table V), since H_2O_2 dissolved some lignin and hemicellulose on the surface and this increased the external concentration of high energy sites. The grafted samples C and D have a higher $\gamma^L{}_S$ than sample B. The difference between sample C, D and B, is the amount of grafted polymer chains on the external surface, which also increases their surface area. In a first approximation, the presence of a new type of site created by grafting explains the difference in adsorption process. At high PL*, i.e. 60%, $\gamma^L{}_S$ decreases and indicates that the density of sites is also an important factor in adsorption. The behavior of $\gamma^L{}_S$ gives an indication on the adsorption process and suggests that this phenomenon is dependent on the nature or type of sites and the density of sites at the external surface of the solid. It could be expected that, at low coverage, adsorption will yield information about the higher energy adsorption sites.

The surface of the fiber is enriched in PMMA, due to its difficulty in reaching the bulk of the fiber. The actual surface PL* may be higher than the bulk PL*. However, the value of $\gamma^L{}_S$ still reaches a maximum between 50-60% PL* (samples D and E, Table V). At 60% PL* the value of $\gamma^L{}_S$ decreases, since that of the pure polymer PMMA is lower. This non-linear variation of $\gamma^L{}_S$ with respect to PL* is due to the non-homogenous composition of the surface and its enrichment in PMMA.

The behaviour of $\gamma^L{}_S$ correlates well with others thermodynamic parameters such as $\Delta H^o{}_A$, $\Delta G^o{}_A(-CH_2-)$, and $\Delta S^o{}_A$, indicating that adsorption on a solid surface is dependent on the nature and density of the sites. Spectroscopic studies (FTIR, ESCA) by Riedl et al.[30,41], show that grafted samples, at a PL* level higher than 50%, have their external chemical surface nearer to that of the pure polymer. The concern of this study is the adhesion phenomenon of wood fibers and polymer matrix: adsorption gives important information about their interface in terms of interaction, and these results show that adhesion may not be a simple function of % polymer grafted at the surface.

CONCLUSIONS

Inverse gas chromatography is a powerful, versatile and convenient method to study and characterize solid surfaces. It provides an alternate route to measure the surface free energies which avoids some problems of contact angle measurement on wood fibers. The adsorption of n-alkanes at infinite dilution as a function of temperature allows to calculate $\Delta H^o{}_A$, $\Delta G^o{}_A$, $\Delta S^o{}_A$ and $\gamma^L{}_S$.

The adsorption on modified CTMP fibers appears to be dependent both of the nature and density of the sites of external surface as revealed by the behaviour of thermodynamics functions and the specific surface area.

$\gamma^L{}_S$ appears to be a substantial and reproducible function for following the chemical and physical changes that occur before and after grafting of polymer onto wood fibers surface. The values obtained, indicated that, at 60% PL*, grafted fibers surface have their fundamental thermodynamic parameters nearer to that of the polymer than to the wood fiber, indicating that the polymer shields the initial fiber as confirmed, by FTIR[41] and ESCA[30] studies.

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