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Elucidating the graft copolymerization of methyl methacrylate onto wood-fiber

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Abstract

Graft copolymerization of methyl methacrylate onto wood-fiber, in dispersed media, was studied as function of temperature, concentration of redox initiator and surfactant. Results showed that grafting and emulsion polymerization processes were strongly related to those variables. In order to elucidate the actual grafting of poly(methyl methacrylate) (PMMA) onto wood-fiber, series of analysis were carefully performed. Scanning electron microscopy showed the presence of small agglomerates regularly distributed on the surface of the modified fiber, such agglomerates remained on the fiber surface after 24 h of chloroform extraction and were presumably grafted PMMA. Infrared analysis of the acid hydrolysis products of the modified fiber showed a clear characteristic signal of carbonyl groups at 1734 cm^{-1}. Such signal indicated the presence of fiber-PMMA chemical links, since simple physical interactions would not remain after the cellulose hydrolysis.

Keywords: Graft copolymerization; Emulsion polymerization; Wood-fiber; Methyl methacrylate; Redox-initiator

1. Introduction

Lignocellulosics represent one of the most important renewable sources of raw materials in the world. Wood is one of those derivatives and is probably the most important, since it is widely used in industrial applications. Unfortunately, during its industrialization considerable amount of this resource is wasted as sawdust (wood-fiber). The formulation of composite materials from wood-fiber and synthetic polymers is currently applied for reusing both kinds of materials. However, polar nature of lignocellulosics makes difficult their interaction with low polar polymers. Grafting of synthetic polymeric chains, is one of the most recurrent used methods to increase the compatibility between cellulose and a variety of synthetic polymers (Bledzki & Gassan, 1999). The first report related to cellulose surface modification goes back to 1950 (Stannett, 1982). Since then a wide variety of monomers have been grafted onto cellulose, either hydrophilic (Bardhan, Mukhopaddhyay, & Satya, 1977; Gürdağ, Yaşar, & Gürkaynak, 1997) or hydrophobic (Fernández, Casinos, & Guzmán 1990; Ghosh & Ganguly, 1994; Ghosh, Mitra, & Banerjee, 1973; Huang, Zhao, & Zheng, 1992) but in general acrylic monomers are the most commonly used. It is important to mention that not only pure cellulose have been modified but also several cellulose derivatives, either in pure (Bardhan et al., 1977; Gürdağ et al., 1997; Fernández et al., 1990; Huang et al., 1992) or raw form (Ghosh & Ganguly, 1994; Huang et al., 1992; Toda, 1962; Habibuddowla, 1982). Redox-initiators have been the most widely used for this task, where systems based on the ceric ion are commonly reported (Stannett, 1982; Bardhan et al., 1977; Gupta & Sahoo, 2001a).

In this research the grafting process of methyl methacrylate (MMA) onto wood-fiber was studied using a sodium bisulfite/potassium persulfate (SB/KPS) pair as the initiator. For their nature, the dispersed systems used for the grafting were considered as emulsion polymerizations and discussions were focused on this mechanism theory. Taking this into account the effects of (a) redox-pair molar ratio and overall initiator concentration at constant molar ratio, (b) surfactant concentration and (c) temperature, on the emulsion polymerization process are here

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reported. The evaluation of these effects will determine the range of concentration and temperature, where grafting is favored over MMA homopolymerization. Surfactant (dodecylbenzene sulfonate sodium salt, SDBS) concentrations were varied above and below its critical micellar concentration (cmc), 1.2 mmol l^{-1} (Myers, 1992), to evaluate the wood-fiber chemical modification at both absence and presence of micelles. Poly(methyl methacrylate) (PMMA) was selected for fibers surface modification because its compatibility with other common polymers and because its monomer high water solubility, 1.59% vol. (Min & Ray, 1974). It is worthy to mention that even though the chemical modification of cellulose or lignocellulosics with acrylic polymers have been widely reported (Canché-Escamilla, Rodríguez-Trujillo, Herrera-Franco, Mendizábal, & Puig, 1997; Gupta & Sahoo, 2001b; Flaké & Montserrat, 1991; Loría-Bastarrachea, Carrillo-Escalante, & Aguilar-Vega, 2002; Mohanty, Khan, & Hinrichsen, 2000; Tripathy, Jena, Misra, Padhi, & Singh, 1985), the interaction between these macromolecular compounds has not been clearly enough elucidated. Infrared spectrometry is generally one of the most recurrent employed techniques for characterizing such copolymers; however, because of the complex structure of lignocellulosics and their similarity in functional groups with acrylic polymers (presence of C=O in both) the characterization of these copolymers has been somehow speculative. In this paper we elucidate the actual formation of graft copolymers wood-fiber-*g*-PMMA.

Wood-fiber was modified and subsequently hydrolyzed to separate the lignin and cellulose components. It was considered that fiber hydrolysis would produce enough conditions to separate the physically anchored PMMA on the fiber; therefore, only the chemically bonded polymer would remain on the cellulose fractions. Thus, the presence of carbonyl groups in the cellulose hydrolysis products would presumably indicate the presence of grafting on the fiber.

2. Experimental section

2.1. Materials

For the grafting process the following reagents were employed: MMA from Aldrich Co.; dodecylbenzene sulfonate sodium salt (SDBS), potassium persulfate (KPS) and sodium metabisulfite (SMB) from Productos Químicos Monterrey, SA; acetone, chloroform, hexane and sulfuric acid were supplied by Fisher Scientific. All reagents and solvents were used without further purification. The wood-fiber of ponderosa pine was milled to a +80–100 mesh and dried in a convection oven at 100 °C for 24 h.

2.2. Surface modification

The graft copolymerization reaction was carried out in a three neck round-bottom flask of 250 ml, arranged with magnetic stirring. A typical grafting experiment was accomplished as follows: First, a mixture of wood-fiber/water/SDBS/SMB was loaded in the reactor and stirred for 30 min. Afterwards, MMA was added in order to form the emulsion and nitrogen was bubbled for 30 min to evacuate the dissolved oxygen. Next, the system was heated to the polymerization temperature and finally, an aqueous solution of KPS was injected to start the polymerization. Reaction time for the experiments was 4 h each. After the polymerization finished, the reaction products were transferred to a petri dish and dried in a convection oven at 100 °C for 12 h. Finally, the dried products were chloroform-extracted for 24 h and the weight gained by the fiber was assumed to be grafted PMMA. Table 1 shows the composition of each evaluated system. Throughout this paper the initiator is refereed to as a SB/KPS system; however, originally SB was not added into the reactor but SMB, which is hydrolyzed in the aqueous phase to form SB.

2.3. Characterization

Monomer conversion (X, weight percent of monomer converted to polymer); grafting efficiency (Ge, weight percent of monomer converted to polymer grafted onto the fiber) and homopolymer (Hp, weight percent of MMA converted to PMMA in colloidal state) were determined by gravimetry according to Eqs. (1)–(3),

$$X = \frac{(S_2 + W_f) - (S_1 + W_f)}{M} \times 100 \quad (1)$$

$$\mathrm{Ge} = \frac{W_P - W_f}{M} \times 100 \quad (2)$$

Table 1
Composition of the evaluated systems to determine the effects of varying temperature, and concentration of initiator and surfactant on the grafting of MMA onto wood-fiber

Ex. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
KPS × 10^2 (mol l^{-1})	2	2	2	2	2	2	2	2	2	0.5	1	3	4	2	2	2
SB × 10^3 (mol l^{-1})	0	2	4	8	10	4	4	4	4	1	2	6	8	4	4	4
SDBS (mmol l^{-1})	2.0	2.0	2.0	2.0	2.0	0.5	1.0	3.0	4.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
T (°C)	60	60	60	60	60	60	60	60	60	60	60	60	60	40	50	70

All the systems contained 97.1 g of three-distillated-water, 5.0 g of wood-fiber (W_f) and 2.9 g of MMA (M).

$$Hp = X - Ge \quad (3)$$

where, M is the weight of MMA at the beginning of the experiment, S_1 (KPS + BS + SDBS) and S_2 (KPS + BS + SDBS + PMMA) are the weights of solids at the beginning and end of the test, respectively. W_f and W_p are the wood-fiber weights at the beginning and after chloroform extraction, respectively.

Fiber components were characterized according to ASTM procedures: (a) alcohol–benzene soluble mater (ASTM D11107-84), (b) water soluble mater (ASTM D1110), and (c) lignin content (ASTM D1106). Holocellulose (hemicelluloses plus cellulose) content was determined by weight difference after (a, b) and (c) treatments. Fiber characterization was performed as follows: first, a wood-fiber sample was dried in a convection oven at 100–105 °C for 2 h. In order to determine alcohol–benzene soluble mater the samples were put under alcohol–benzene (20/80, v/v) extraction for 8 h. After the extraction the fiber was dried at 80 °C for 6 h and the weight was registered. Next, the extracted dried fiber was transferred to a round-bottom flask together with 400 ml of deionized water, the system was refluxed with continuous stirring for 3 h. Afterwards, the solids were filtered, washed, dried and weighted to determine water soluble mater by weight difference. The non-water soluble solids were transferred into a 50 ml flask, followed by the addition of 15 ml of an aqueous solution (72% w/w) of sulfuric acid. The mixture was kept under continuous stirring at 12 °C for 2 h and then transferred to a 1 l round-bottom flask with 560 ml of water to dilute the acid solution to 3% w/w. Next, the mixture was refluxed for 4 h and the solids were allowed to precipitate and carefully filtered. The solids were dried, weighted and taken as the lignin contained in the fiber. Finally, the holocellulose content was calculated by subtracting lignin, alcohol–benzene and water soluble mater from the initial fiber weight.

Micrographies of modified and unmodified fiber were obtained by scanning electron microscopy on a SEM Jeol Mod. 5800 LV, the fiber samples were covered with gold before the analysis in order to avoid electrostatic charge. Infrared analyses were performed on a FTIR Nicolett, Series 2 Magna IR 750. For these determinations pellets of KBr with fiber were prepared by compression. Thermogravimetry was evaluated on a TGA, TA Instruments Hi-Res TGA 2920, under nitrogen atmosphere at a heating rate of 5 °C/min.

2.4. Blank preparation

In order to facilitate identification of the changes suffered by the wood-fiber, as a result of the chemical modification, a blank sample was prepared. Such blank was treated exactly under the same experimental conditions as experiment 11 described in Table 1, but in this case monomer was no used.

2.5. Fiber hydrolysis

Fiber hydrolysis was performed according to ASTM D1106 procedure as follows: 1 g of modified fiber (with 15% grafting) and 15 ml of an aqueous solution of sulfuric acid (72%, w/w) were loaded into a 50 ml flask. The mixture was softly stirred for 2 h at 20 °C. Next, the mixture was transferred to a 1 l flask and diluted with 560 ml of deionized water. The new mixture was allowed to reflux for 4 h. Afterwards, the solids of the mixture were recovered by filtration and the filtered solution was neutralized with a 1 M NaOH solution. The filtered solution contains water soluble cellulose fractions and sulfuric acid neutralization products. The presence of PMMA homopolymer in the filtered and neutralized solution was discarded due to PMMA water insolubility. On the other hand, it is assumed that entangled PMMA to cellulose fractions (glucosidic rings) could be stable in water solution because of their high hydrophilicity. Finally, the entire solution was dried and 10 g of solids were dispersed in 50 ml of acetone at room temperature for 30 min. Solids were allowed to precipitate and a sample of the clear solution was deposited on a KBr tablet for FTIR characterization. It was presumed that if the cellulose fractions solved in the acetone solution contained grafted PMMA then carbonyl signals should appear in the FTIR spectrum.

3. Results and discussion

Results for the wood-fiber characterization are reported in Table 2. This table shows contents of 25.1 and 74.4% wt, respectively, in agreement with literature reported (Brady et al., 1997) and similar to other lignocellulosics as jute, flax or sisal (Bledzki & Gassan, 1999).

Grafting of acrylic monomers onto cellulosic materials using KPS as the initiator has been reported in several occasions, as it has been found that sulfate radicals ($SO_4^{-\bullet}$) are able to form free radicals on compounds that contain hydroxyl groups (Ikada, Nishitaki, & Sakurada 1974;

Table 2
Characterization of the wood-fiber used in the present research and comparison with reported values

	Experimental (% wt)	Reported[a] (% wt)
Lignin	25.1	27
Holocellulose[b]	74.4	72
Hemicellulose		31
Alcohol–benzene	0.36	
Water	0.12	

[a] Brady et al. (1997).
[b] Cellulose plus hemicellulose.

Table 3
Conversion of monomer, X (%), Grafting efficiency, Ge (%) and homopolymer, Hp (%), obtained for every evaluated system

Ex. no.	S_1 (g)	S_2 (g)	W_p (g)	T (°C)	Ge (%)	Hp (%)	X (%)
1	0.5869	3.0825	5.2842	60	9.02	77.33	86.35
2	0.6057	3.1132	5.2709	60	9.37	77.39	86.76
3	0.6245	3.1460	5.8853	60	30.63	56.62	87.25
4	0.6613	3.3799	5.6191	60	21.42	72.65	94.07
5	0.6801	2.7888	5.5142	60	17.79	75.20	72.97
6	0.5738	3.0010	5.4476	60	13.07	70.92	83.99
7	0.5907	3.0880	5.3167	60	14.10	72.31	86.41
8	0.6583	2.8200	5.5514	60	19.08	65.40	74.80
9	0.6921	2.8786	5.4999	60	17.30	68.50	75.66
10	0.2025	2.5040	5.5567	60	19.26	60.37	79.64
11	0.3454	2.6340	5.9432	60	32.64	47.53	79.19
12	0.9030	3.2940	5.4708	60	16.29	66.44	82.73
13	0.1808	3.5855	5.0902	60	3.12	80.09	83.21
14	0.6245	2.5725	5.5694	40	15.20	52.20	67.40
15	0.6245	2.8071	5.4656	50	19.10	56.42	75.52
16	0.6245	3.0771	5.7109	70	24.60	60.27	84.87

Mukhopadhyay, Prasad, & Chatterjee, 1975). Eq. (4) describes the free radical generation mechanism of the SB/KPS system (Klásek, Kaszonyiová, & Pavelka, 1986).

$$H_2O + HSO_3^- + 2S_2O_8^{2-} \rightarrow 3HSO_4^- + 2SO_4^{-\bullet} \quad (4)$$

Table 3 shows X, Ge and Hp data for every performed experiment, as a function of initiator, surfactant and temperature. Fig. 1 shows the plot of Ge (%) versus molar ratio of initiator [SB/KPS]. Results indicate that variations in SB concentration, keeping KPS concentration constant, presented a very important effect on the grafting process. Ge (%) showed a maximum in grafting at a molar ratio of 0.2. It is believed that at lower ratios the concentration of SB is not enough to react with KPS to produce free radicals through the redox mechanism. Apparently, with this initiator mixture there is a threshold ratio (close to 0.2) where the system behaves as a redox initiator; however, under that ratio the system apparently produces only free radicals by the KPS thermal decomposition process. As a result at the initiator ratios of 0 (only KPS) and 0.1 the grafting was similar. On the other hand, ratios above 0.2 gradually produced higher amounts of free radicals while approaching to the stoichiometric ratio (0.5). It was expected that this increment in free radicals concentration would improve the grafting; however, that effect also favored the formation of more polymer particles, which consequently increased the formation of homopolymer. Klásek et al. (1986) and Klásek, Bačáková, Kaszonyiová and Pavelka (1985) reported the grafting of MMA onto gelatin and collagen fiber. They performed similar experiments with mixtures of SB/KPS, where 0.2 was the molar ratio that produced the highest grafting, as reported in this paper. Eromosele (Eromosele, 1994) studied the grafting of acrylonitrile onto cellulose (extracted from cotton) using potassium permanganate ($KMnO_4$)/thioacetamide (TAS) as the redox-initiator. He reported a maximum in Ge (%) when varied the concentration of either $KMnO_4$ or TAS, in the initiator ratio. In general in the mentioned papers decrements in grafting were attributed to increments in the initiator concentration, but also to deactivation of free radicals due to side-reactions as shown in Eqs. (5)–(7) (Klásek et al., 1986). In the present work it is believed that deactivation of sulfate radicals was not significant, since the used molar ratios were not higher than 0.5.

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^- + HO^\bullet \quad (5)$$

$$2SO_4^{-\bullet} + HSO_3^- \rightarrow 2HSO_4^- + SO_4^{2-} + H^+ \quad (6)$$

$$2HO^\bullet + HSO_3^- \rightarrow SO_4^{2-} + H_2O + H^+ \quad (7)$$

An initiator molar ratio of SB/KPS = 0.2 was selected to study the effect of the overall initiator concentration (I = SB + KPS) on the grafting. Fig. 2 shows the plot of Ge (%)

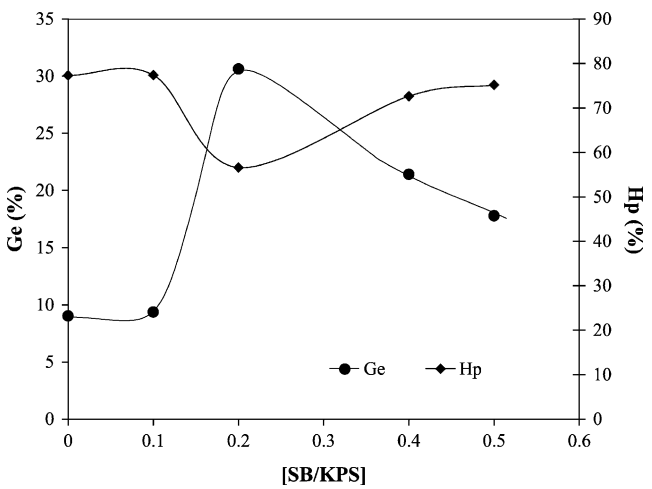

Fig. 1. Effect of varying initiator molar ratio on the grafting of PMMA onto wood-fiber. KPS and SDBS concentration was kept constant at 0.02 and 2.0 mmol l^{-1}, respectively. All the experiments were accomplished at 60 °C.

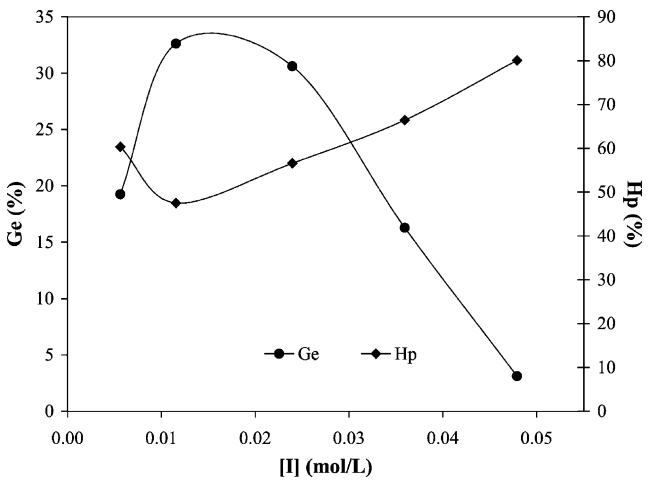

Fig. 2. Effect of increasing initiator overall concentration on the grafting of PMMA onto wood-fiber. Experiments were carried out at a molar ratio of SB/KPS = 0.2, the overall initiator concentration was taken as I = SB + KPS. The grafting temperature was 60 °C.

versus (I). As it can be seen a maximum in the grafting occurred around 30% at a concentration of 0.024 mol l^{-1}. This is in agreement with the Smith-Ewart theory (Smith & Ewart, 1948) which predicts that the rate of polymerization depends only on two variables, the concentrations of surfactant and initiator. Increments in the rate of polymerization are related to faster monomer diffusion rates from the emulsified droplets into the aqueous phase and into the polymer particles. So the diffusion process determines the polymerization period where the monomer is in the aqueous phase and therefore, its availability to react with macroradicals (radicals formed on the cellulose) to form grafted PMMA chains. The increment effect on the overall concentration and initiator molar ratio can be explained under the context of the emulsion polymerization theory. That is, when the concentration of free radicals increases (in the aqueous phase) the rate of polymer particle formation also increases and as a consequence, the monomer is consumed at higher rates. This former behavior reduces the interaction time between the monomer and the fiber, and as a result the grafting drops. Similar studies have been reported previously using different initiation systems, in general, it was also found initial increments on the grafting up to a maximum followed by a progressive reduction on the grafting (Bardhan et al., 1977; Toda, 1962; Mukhopadhyay et al., 1975; Athawale & Lele, 2000). This means that independently of the used initiation system, the competition between the grafting and the homopolymerization reactions is an important issue to be considered.

It was believed that the wood-fiber could have presented some effect over the surfactant micellation process since, as mentioned previously, lignocellulosics are highly polar compounds. Hence, it could be possible to exist some interaction between OH groups on the fiber and the polar head group of the surfactant, which may affect the emulsion polymerization process. In Fig. 3, plots of specific conductivity (k) versus [SDBS], for the systems water/SDBD and water/SDBS/wood-fiber are shown. By this technique critical micellar concentration (cmc) is determined as function of the increment of k with respect to [SDBS]. Under cmc the relationship $\Delta k/\Delta$[SDBS] is constant and surfactant molecules behave as conductive species. When cmc is reached the formation of micellar aggregates starts and a change in slope is observed. Above cmc micellar aggregates behave now as conductive species, since they are heavier than the single surfactant molecules, their mobility is lower and the relationship $\Delta k/\Delta$[SDBS] decreases. As it is observed slope changes appeared at very close concentrations, around 1.37 mmol l^{-1}, which is in agreement with previous reported value for SDBS of 1.2 mmol l^{-1} (Myers, 1992). Therefore, any important effect, on the polymerization system, is expected as a consequence of the fiber presence.

The effect of varying the surfactant concentration (on the grafting process) was one of the main objectives in this study, since in several reports a surfactant is used but its effect on the grafting has not been studied in detail. For that, overall initiator concentration (0.024 mol l^{-1}) and initiator molar ratio (0.2) were kept constant and the surfactant concentration was varied in a range of 0.5–4.0 mmol l^{-1}. Fig. 4 shows the plot of Ge (%) versus [SDBS]. As it is observed, the plot presented a maximum in grafting at a surfactant concentration of 2.0 mmol l^{-1}, followed by a progressive decrement in the grafting. This behavior indicated, as expected, that the surfactant concentration played a decisive role in the grafting process. It is believed that at the two first surfactant concentrations (0.5 and 1.0 mmol l^{-1}) the low grafting could be related to the polymer particle formation mechanism. Since there are no micelles, the homogeneous-coagulative nucleation mechanism (Feeney, Napper, & Gilbert, 1984) controls the particle formation process. In this kind of system the particle formation rates are slow and the concentration of oligomeric radicals in the aqueous phase is higher than in the micellar systems. It is thought that this high concentration of oligomeric radicals would increase the probability

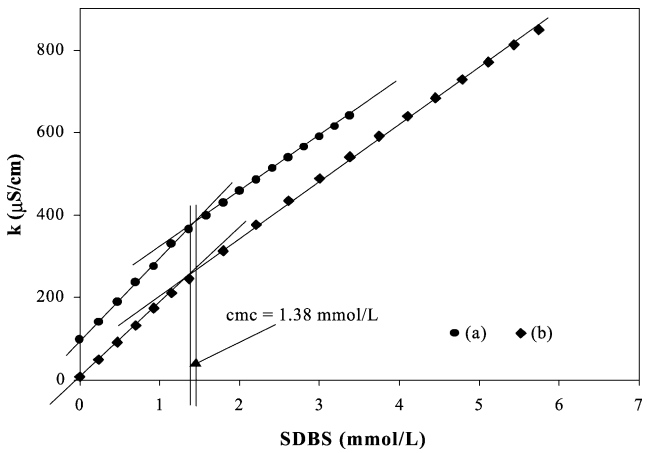

Fig. 3. Plots of specific conductivity versus surfactant concentration for (a) water/wood-fiber/SDBS and (b) water/SDBS systems. Cmc determinations were run at 30 °C.

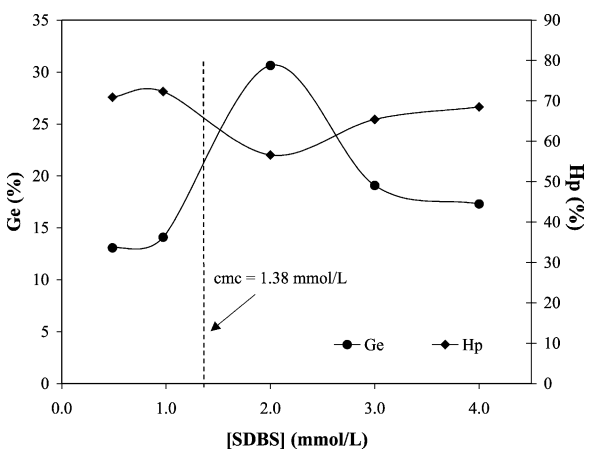

Fig. 4. Effect of varying the surfactant concentration on the grafting of PMMA onto wood-fiber. The overall concentration of initiator was 0.024 mol l^{-1} at a molar ratio of 0.2. Experiments were carried out at 60 °C.

of recombination reactions between macroradicals and the oligomeric radicals in growth. This condition would decrease the propagation reactions producing grafted chains with low polymerization degree, which could explain the low values of grafting. Therefore, this response variable was evaluated as a function of the gained weight and not with respect to the number of grafted chains.

As seen in Fig. 4, the maximum in grafting was found slightly above the cmc. Under these conditions micellar nucleation is the predominant mechanism to form polymer particles. The observed decrease in the grafting content, at higher surfactant concentrations, could be explained again in terms of the emulsion polymerization mechanism. Since the rate of polymerization rises with the increment in the surfactant concentration, the monomer is polymerized progressively faster and its chance to react with macroradicals is reduced and as a consequence, restricting the grafting and favoring the homopolymerization. If it is considered that above cmc there is a great micellar surface area, then the probability for coupling reactions, between oligomeric radicals and chains in propagation grafted onto the cellulose surface, should be low. Therefore, the degree of polymerization above cmc could reach higher values than in the absence of micelles, being this dependent on the residence time of the monomer in the aqueous phase.

Temperature was the last variable studied in the grafting of MMA onto the wood-fiber, for this evaluation the overall concentration (0.024 mol l^{-1}s) and the molar ratio (0.2) of initiator were kept constant, as well as the surfactant concentration (2.0 mmol l^{-1}). Fig. 5 shows the plot of Ge (%) versus temperature (°C). Here, it is observed that the grafting increased in a temperature range from 40 to 60 °C, but at 70 °C the grafting decreased. Gürdağ et al. (1997) and Bardhan et al. (1977) reported a similar behavior for the grafting of acrylic monomers onto cellulose using KPS and ceric ammonium nitrate as redox initiators, respectively. Both groups attributed the decrement in grafting to the effect

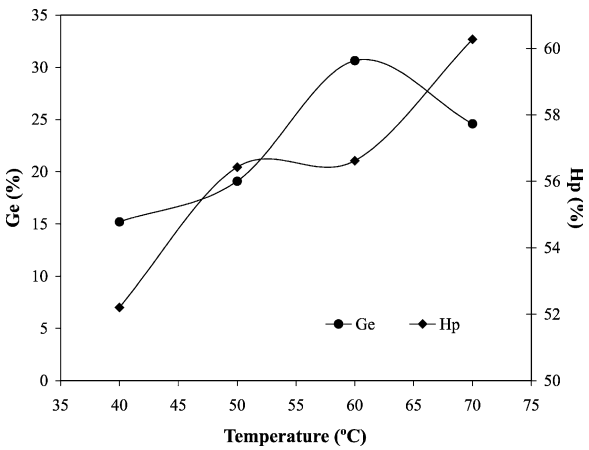

Fig. 5. Effect of varying the temperature on the grafting of PMMA onto wood-fiber. Experiments were carried out using an overall concentration of 0.024 mol l^{-1} at a molar ratio of 0.2. The surfactant concentration was 2.0 mmol l^{-1} in all cases.

of temperature over the reactive species that generate the grafting reactions. In free radical polymerization reactions temperature is a reaction promoter, since the rate of free radicals generation increases with temperature. As mentioned above, in the present investigation the grafting was progressively favored with a temperature increment from 40 to 60 °C; however, at the highest temperature (70 °C) homopolymerization was favored. This last behavior implies a progressive increment in the polymerization rate with respect to temperature, in other words, the monomer was polymerized faster as temperature increased and eventually the homopolymerization mechanism will take over the grafting.

During the evaluation of the different variables it was evident that two polymerization mechanisms were taking place simultaneously: (a) the grafting of MMA onto the wood-fiber and (b) the homopolymerization of MMA through a conventional emulsion polymerization mechanism. It is believed that in the first mechanism the sulfate radicals create free radicals either on the lignin or on the cellulose (macroradicals). However, it is known that phenols (on the lignin) are excellent free radical scavengers. Ghosh and Ganguly (1994) reported that phenols inhibit the grafting reactions onto lignocellulosic fibers. Therefore, it is presumed that the grafting reactions of MMA onto the fiber were mainly achieved over the cellulosic fraction. It is important to note that the macroradicals could have reacted either with the monomer present in the aqueous phase (in order to propagate polymeric chains) or with small water-soluble oligomeric radicals, with length close to its critical chain length, which is 5 monomer units for PMMA. Above this degree of polymerization the oligomeric radicals will not be more water-soluble, which reduces their possibility of recombination with macroradicals. In the present work it was not determined which mechanism had the highest contribution on the grafting content or whether or not both of them happened. However, both of them are chemically possible.

Fig. 6 shows a series of electron micrographs of wood-fiber, which were taken before and after the grafting process, as it is observed there are evident differences in their appearance depending on the experimental stage. First, Fig. 6a shows the wood-fiber before the modification and Fig. 6b shows the same fiber after the emulsion polymerization process. It can be seen on Fig. 6b that the fiber surface is almost completely covered by a thick layer of PMMA, which is mainly physically deposited. On the other hand, Fig. 6c, which was taken after 24 h of chloroform extraction, shows the presence of well-defined agglomerates whose texture is different from that of the unmodified fiber surface. Such agglomerations were found regularly on the surface of the modified fibers and, of course, not on the unmodified ones. It was presumed that those agglomerates were grafted PMMA; however, this assumption is not evident since some possible interconnected network (microfibers-PMMA) could have been

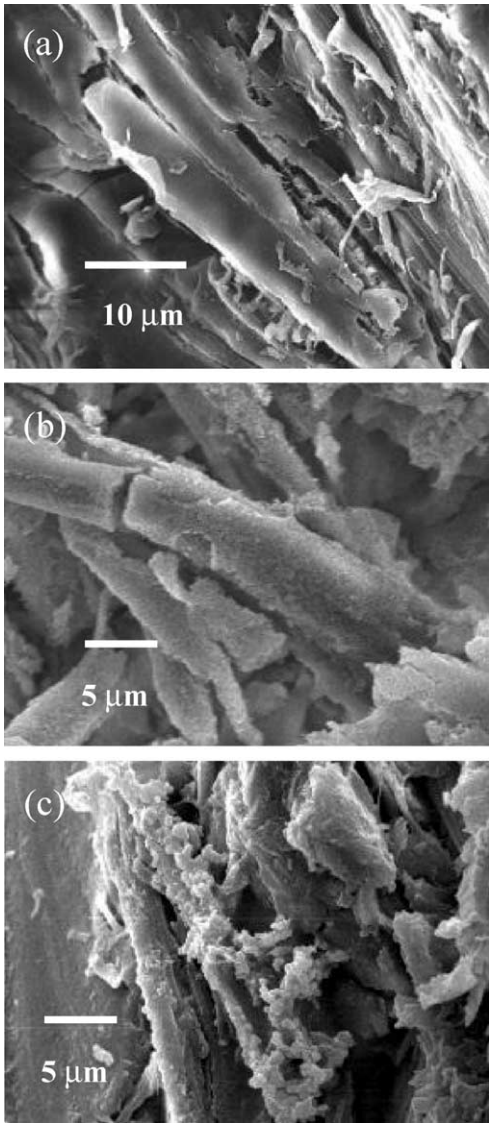

Fig. 6. Scanning electron micrographies of a modified wood-fiber sample during different stages of the modification process: (a) before modification, (b) modified (30% grafting) before chloroform extraction, (c) modified (30% grafting) after chloroform extraction.

formed. According to literature solvent extraction of residual monomer and homopolymer have been considered to assume the occurrence of chemical bonds between lignocellulosics and synthetic polymers (Ghosh et al., 1973; Tripathy et al., 1985). Hence, in order to present a clearer characterization of the copolymer formation, a deep evaluation of the modified fibers was performed. It is expected that with the evaluation of the products of the fiber hydrolysis, it could be elucidated whether or not the PMMA is actually forming a graft copolymer with the wood-fiber.

Fig. 7 shows the infrared spectra (FTIR) for unmodified wood-fiber (a) and for three modified and chloroform extracted (for 24 h to eliminate PMMA homopolymer) fiber with different grafting content (b,c,d). As it can be seen, all the spectra presented basically the same pattern of signals, including one peak at 1734 cm^{-1} typical of carbonyl groups

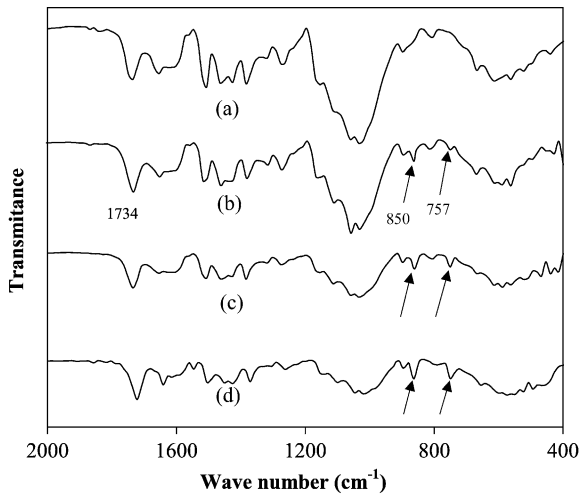

Fig. 7. Infrared spectra for wood-fiber samples with different PMMA grafting contents: (a) unmodified, (b) 10, (c) 20 and (d) 30% of grafting.

(C=O). According to this, it is not possible to attribute completely those signals to carbonyl groups of PMMA, since lignin presents a high content of this kind of functional groups too. However, there were two characteristic peaks of PMMA at 757 and 850 cm^{-1}, which appeared in the modified fiber spectra but not on the unmodified fiber one. Canché-Escamilla et al. (1997) reported the grafting of MMA onto cellulose extracted from henequen, the FTIR spectra of the modified cellulose showed the same set of peaks mentioned above including the one close to 1734 cm^{-1}, which were attributed to PMMA grafted onto cellulose. In the present case, it can be pointed out that the signal at 1734 cm^{-1} presented progressive increments with respect to the signals between 900 and 1200 cm^{-1}, as the grafting efficiency increased from 10 to 30%. This effect could be related to the amount of PMMA on the modified fiber but it does not imply an actual chemical interaction between both macromolecular compounds.

In order to clarify the presence of PMMA grafted onto the treated fiber, cellulosic and lignin fractions of the blank and modified fiber with 30% of PMMA, were separated. The technique employed was the hydrolysis of both fibers with a sulfuric acid aqueous solution following the ASTMD1106 procedure. Fig. 8 shows the FTIR spectra for (a) sugar of reference obtained from the hydrolysis of the blank fiber and (b) sugar extracted from the 30% modified fiber. As can be observed, the new spectra showed important changes in the signal pattern according to those observed in Fig. 7. The new pair of spectra were similar again; however, a signal in 1734 cm^{-1} on (b), corresponding to carbonyl groups, can be clearly observed. The spectrum for (a) showed a signal in the same wave number for carbonyl groups but in this case is very small. Some important aspects could be inferred from this figure, first, that proportional differences in the peaks at 1734 cm^{-1} indicate the presence of PMMA on the sugar even though cellulose hydrolysis; second, that there was a stronger interaction between

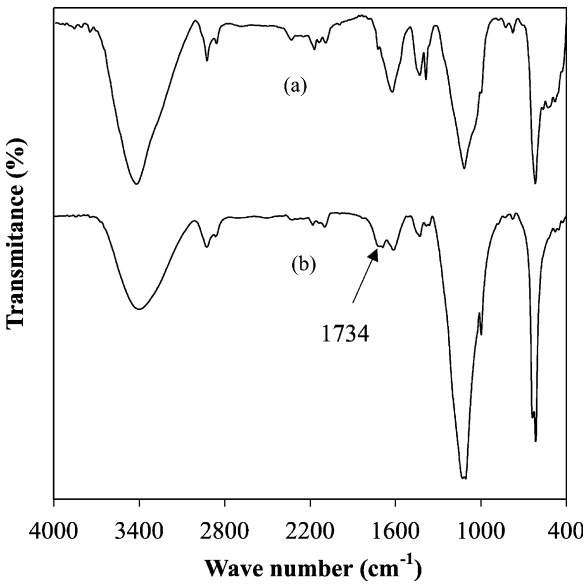

Fig. 8. Infrared spectra for hydrolyzed wood-fiber samples: (a) unmodified and (b) with 30% of grafting.

the fiber and PMMA than a mere physical interaction, since PMMA signals were determined from an aqueous phase where this polymer is insoluble even though cellulose hydrolysis and third, apparently carbonyl groups were formed on the sugar structure due to acid solution influence. Athawale and Lele (2000) reported the hydrochloric acid hydrolysis of graft copolymers starch-methacrylonitrile (MAN) using ceric ion as the initiator. In this report it was considered that polymetacrylonitrile (PMAN) was separated from the starch because of acid action but starch hydrolysis was not considered.

Thermogravimetric analyses (TGA) were carried out in order to evaluate the effect of the chemical modification on the thermal stability of fiber with different PMMA contents.

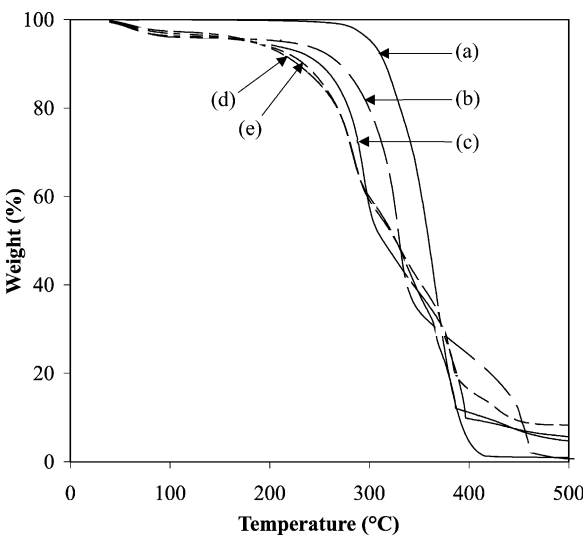

Fig. 9. Thermograms for (a) PMMA, (b) unmodified fiber, (c) fiber with 10% of grafting, (d) fiber with 20% of grafting and (e) fiber with 30% of grafting.

Fig. 9 shows thermograms for (a) PMMA, (b) unmodified fiber, (c), (d) and (e) correspond to fiber samples with 10, 20 and 30% wt of PMMA content, respectively. It can be observed that PMMA is more thermally stable than all fiber samples and that unmodified fiber is slightly more stable than the grafted ones (c–e). It can also be observed that degradation temperature of grafted fiber samples decreased as PMMA content increased and that fiber samples with grafting of 20 and 30% have similar behavior. Fig. 10 shows derivothermograms for all fiber samples, in this figure it is clear that the modified fiber (b–d) presented lower thermal stabilities than the unmodified sample (a). It was found later that grafted fiber degradation was related to the strong oxidative activity of KPS, and as a consequence, a loss in thermal stability was determined. The occurrence of degradation on cellulosic compounds, by effect of the grafting process, has been commonly reported (Athawale & Lele 2000; Ghosh & Gangopadhyay, 2000); however, some others have reported increments in thermal stability (Canché-Escamilla et al., 1997). Derivothermograms for the grafted fiber samples (b–d) presented a pair of transitions at 320 and 360 °C. These peaks are related to the presence of the PMMA on the fiber, since those increased with the raise of polymer content on the fiber and in addition, the derivothermogram for the PMMA (e) presented two peaks at the mentioned temperatures (320 and 360 °C). The presence of these peaks is a clear indication that PMMA is present on the fiber; however, the way as they interact is still not evident.

The previous evaluation of the thermal stability of the modified fiber indicated clearly the presence of PMMA on the fiber. However, it is not evident whether or not there was a chemical interaction between them. Taking this into

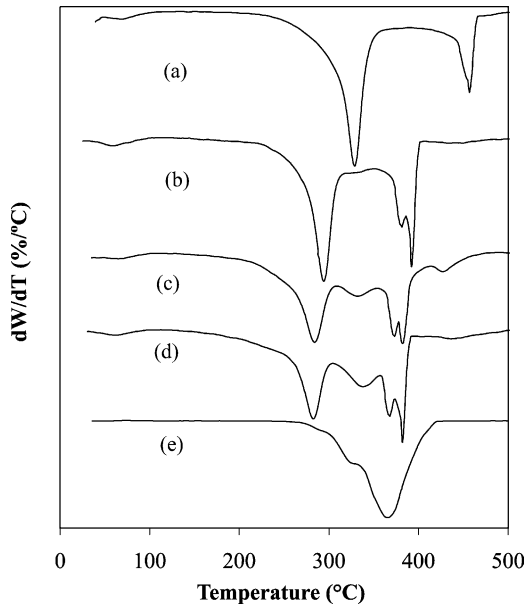

Fig. 10. Derivothermograms for (a) unmodified fiber, (b) fiber with 10% of grafting, (c) fiber with 20% of grafting and (d) fiber with 30% of grafting and (e) PMMA.

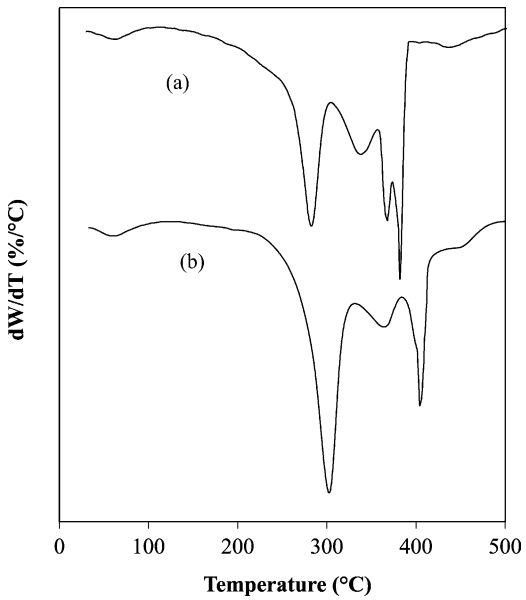

Fig. 11. Derivothermograms for (a) fiber with 30% of grafting and (b) physical mixture. The used fiber for (a) was pretreated with the SB/KPS mixture in the absence of MMA, before mixing with PMMA.

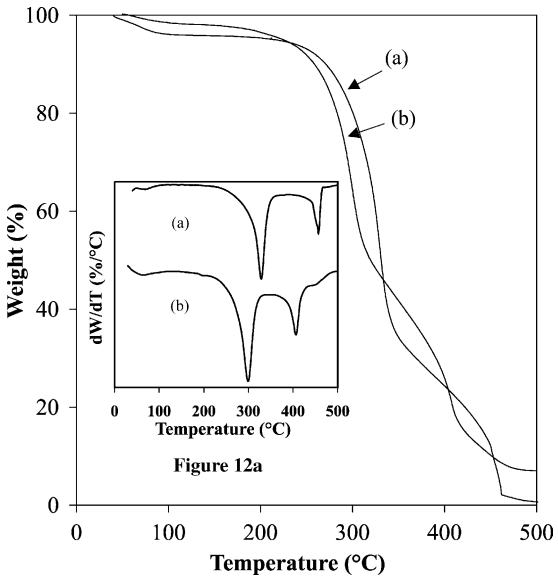

Fig. 12. Thermograms for (a) wood-fiber without any previous treatment and (b) fiber pretreated with the SB/KPS mixture in the absence of MMA and PMMA. Fig. 12a shows derivothermograms for those samples.

account two samples with equivalent amounts of PMMA, (a) modified fiber with 30% of grafting and (b) physical mixture fiber/PMMA, were analyzed by TGA. It is important to mention that the physical mixture was prepared using blank fiber. Fig. 11 shows derivothermograms for both fiber samples where some differences in the thermal patterns can be observed. First, the physical mixture (b) presented a slightly higher thermal stability than the grafted fiber (a) and second, in both samples PMMA degradation signals appeared at the same temperature; however, the form as these peaks appear in every derivothermogram is not exactly the same. It is believed that these differences are related to the way as the PMMA and the fiber are linked in each case. For example, in the grafted fiber one end of the PMMA chains is chemically bonded to the fiber, whereas in the physical mixture there is only a superficial interaction between the fiber and the PMMA. This is probably the reason for the similarity between the peaks for PMMA (Fig. 10e) and for the physical mixture. The last implies that PMMA on the grafted fiber have such an interaction that modifies the form of the peaks. It is worthy to mention that the fiber for the physical mixture presented a decrement in thermal stability even though those were pretreated only in the presence of the initiator, which discards any effect of the monomer on the fiber degradation.

The reduction in thermal stability of the fiber in the physical mixture suggests that the initiator was responsible for the degradation. In order to prove this, untreated and blank fiber samples were evaluated by TGA. Fig. 12 shows thermograms for both samples, it is observed that the blank fiber (b) was less thermally stable than the untreated (a). Derivothermograms (Fig. 12a) clearly showed that the blank fiber (b) was less thermally stable, since the cellulose and the lignin peaks appeared around 20 °C lower than in the untreated sample (a). This implies that both the cellulose and the lignin are susceptible to thermal degradation in the presence of this kind of initiation system. If derivothermograms for both the physical mixture (Fig. 11b) and the blank fiber, Fig. 12a(b), are compared, it can be observed that in both cases the degradation signals for the cellulose and the lignin appears almost at the same temperature. This let us to conclude that the decrement in thermal stability in the wood-fiber is clearly due to effects of the initiation system.

4. Conclusions

Under evaluated conditions it was found that PMMA grafting onto the wood-fiber was strongly dependent on variations in temperature and concentration of initiator and surfactant. It was clear that increments in the concentration of initiator or surfactant progressively favored the emulsion polymerization mechanism, while the grafting was reduced. The former implies an evident competition between grafting and homopolymerization reactions. It is quite important to consider the kinetics of the emulsion polymerization mechanism, since if the period where the grafting takes place (intervals I and II) could be determined so the prolongation of that period could be possible, for example, by adding more monomer before interval II finished. At the moment, the study of the kinetics of the grafting is under evaluation, results of this study will be reported later.

In general, characterization suggested a strong interaction between the wood-fiber and the PMMA. The infrared spectra of the hydrolysis products confirmed the existence of a chemical link between the cellulose and the PMMA. This was based on the consideration that

PMMA physically anchored on the wood-fiber would not remain after hydrolysis. Characterization through thermogravimetry indicated clear differences between grafted and ungrafted fiber samples (or physical mixtures). Grafted fiber decomposition temperatures shifted towards lower values, which imply the presence of degradation, as a consequence of the highly oxidative nature of the initiation redox-system. Finally, it could be concluded that the characterization results were considered as enough evidence to elucidate that the analyzed systems corresponds to true graft copolymers wood fiber-*g*-PMMA.

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