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# Graft polymerization of wood sawdust and peat with ethylene carbonate. A novel method for the preparation of supports with enhanced mechanical properties to be used in biofiltration of organic vapors

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## ABSTRACT

The graft polymerization reaction between ethylene carbonate (EC) and scots pine sawdust (SPS) or peat moss (PM) offers a solvent-free approach to the simple and inexpensive aliphatic derivatization of these lignocellulosic fibers. This reaction was studied with liquid or vapor EC phases in three different reactor configurations: batch stirred (BSR), semi-continuous stirred (SSR) and continuous tubular in the gas phase (CVTR). The use of a vapor phase allowed a satisfactory grafting yield and minimal production of non-grafted polyol by-products. The crosslinking agent 4,4'-methylenebis(phenylisocyanate) (MDI) achieved superior characteristics to form shaped tablets resistant to water disaggregation, a high water retention capacity and high compression strength, characteristics that conventional organic supports like PM or PM-polyurethane foam mixtures used in biofiltration of waste gases do not completely possess.

## 1. Introduction

One of the most important components in the biofiltration of waste gases and vapors is the filter-bed composed by packed layers of a variety of solid materials serving both as a support carrier for the active microbial biomass and as a source of nutrients. Most of the papers published in the early 1980s dealt with carrier materials composed of organic matter (peat, compost, sawdust, etc.) (Dalouche et al., 1981; Ottengraf et al., 1986; Van Langenhove et al., 1986), while the use of inorganic matrices such as perlite, glass beads, vermiculite or polyurethane foam has gradually increased during the last decade (Shareefdeen et al., 1993; Devanny and Hodge, 1995; Kennes et al., 1996). Carriers comprising physical mixtures of organic and inorganic matter are also being used and may present advantages. The objective of incorporating particles of inorganic material into the filter-bed is to avoid its compaction and flow channeling aiming for an enhancement in biofilter hydrodynamic performance during long term operation (Baltzis and Shareefdeen 1994; Zilli et al., 1996; Veir et al., 1996; Lee et al., 1996). Also it has been mentioned that a mechanically strong non-biodegradable media should be used to prevent an excessive pressure

drop in biofilters resulting from biomass growth and support compaction, as compared to commonly used biodegradable particles such as peat (Kennes and Thalasso, 1998; Kibazohi et al., 2004).

The main objective of the proposed graft polymerization reaction on PM or SPS is to develop novel synthetic methods for the preparation of durable hydrophilic/hydrophobic supports that can be easily moulded into specific shapes to be used in the long term biofiltration of waste gases. This should represent a significant improvement to current methods in terms of mechanical resistance and hydraulic performance. Clearly, such approach should be economically and ecologically sound (free of solvent use) to justify further studies at a larger scale of biofiltration.

A possibility for a solvent-free graft polymerization on lignocellulosic waste resources is the treatment with cyclic carbonates. Among these, ethylene carbonate (EC) is innocuous to public health and the environment and widely used in industrial processes. Hereby a simple, clean and rapid process is proposed.

A polycarbonate ( $x$ ) or polyether ( $y$ ) is formed when treating EC with an alkoxide or hydroxide ion (initiator) which is able to open the strained epoxide ring in a direct  $S_N1$  or  $S_N2$  reaction as can be described in Fig. 1. The molar ratio of the carbonate to ether moieties in the product ( $x/y$ ) depends essentially on the reaction temperature (Harris, 1989, 1990). High temperatures favor ether function formation with evolution of carbon dioxide ( $CO_2$ ).

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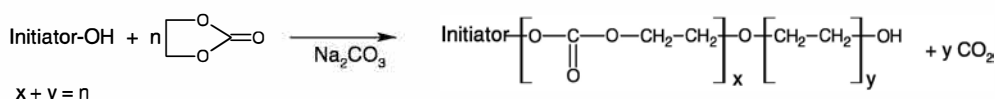


Fig. 1. Poly(ethylene ether carbonate) polyol polymerization over an initiator.

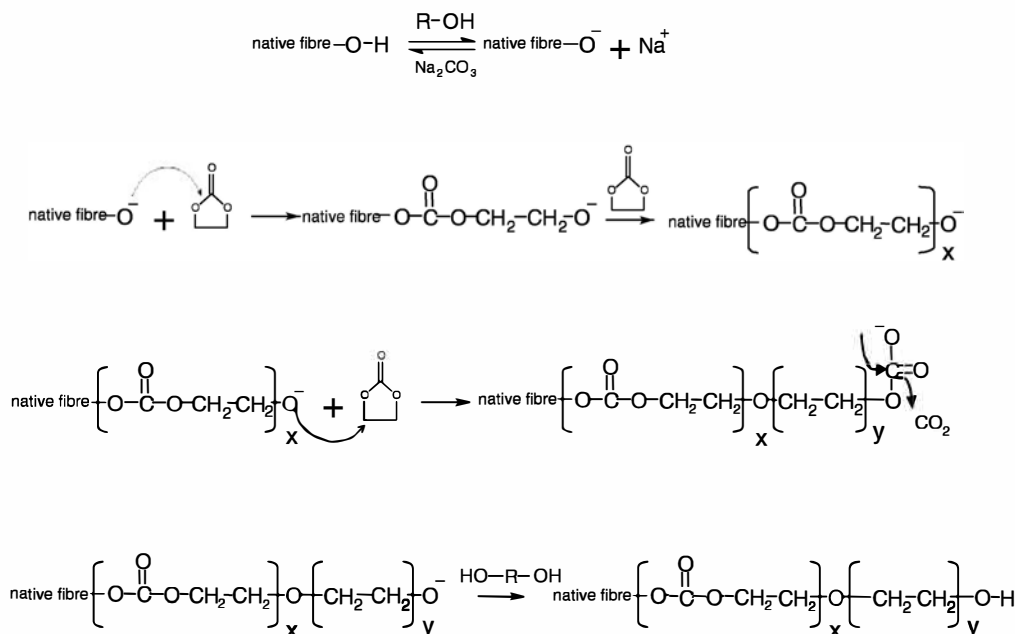


Fig. 2. Proposed reaction mechanism for the polymerization of Poly(ethylene ether carbonate) polyol over wood sawdust or peat moss acting as OH initiators.

Conversely, at relatively low temperatures a preferential carbonate function occurs. In addition, previous reports for EC reaction with monomer or diols have depended on the use of metals, metal alkoxides and organometallic compounds as catalysts (Fagerburg, 1984; Harris, 1989; Acemoglu et al., 1997; Gunatillake et al., 1998), whereas our approach employs sodium carbonate as a catalyst with a low ecological impact.

In principle, lignocellulosic matter present in SPS or PM should act as strong nucleophile able to open the EC leading to a grafted polymer. This reaction is an example of anionic polymerization. It has been reported that SPS possesses 4.5 mmol lignocellulosic material/g solids on average (Thiebaud, 1995) that should provide sufficient OH groups (see Fig. 2) for the preparation of graft polymerized tablets. Once theoretical availability of reacting groups was guaranteed and with the objective to minimize the consumption of EC, the polymerization reaction was studied in reactor systems where this reagent was fed in liquid or vapor phase. Such comparison was performed in three different modes of operation: batch stirred, semi-continuous stirred and continuous tubular.

## 2. Methods

### 2.1. Materials

SPS or PM (Peat Moss Company) with 0.5–1.25 mm particle size, were dried overnight at 110 °C before use. Sodium carbonate (0.25 mm, dried at 110 °C) and 4,4'-methylenebis(phenylisocyanate) (MDI) reagent grade chemicals were obtained from the Al-

drich, France. Ethylene carbonate (bp 243–244 °C/740 mmHg) reagent grade (98%) was obtained from Acros Organics, France. All reagents were used without further purification.

### 2.2. Synthesis of grafted SPS or PM polymers

#### 2.2.1. Batch stirred reactor (BSR)

Twenty grams of EC were introduced into a 1 L capacity glass reactor. The reactor was stirred (750 rpm) and attached to a reflux condenser. When the desired temperature was reached, 1 g of SPS (EC/SPS mass ratio of 20) and 0.05 g of sodium carbonate were added. The first series of experiments were performed in the range of 150–200 °C and 1–2 h of reaction time to establish the feasibility of the reaction.

#### 2.2.2. Semi-continuous stirred reactor (SSR)

The BSR reactor was modified to a SSR by controlling the addition of monomer. An initial load of 50 g of EC was introduced into the reactor to allow convenient stirring and mixing. When the programmed reaction temperature was reached, 5 g of SPS (EC/SPS mass ratio of 10) and 0.25 g of sodium carbonate were added. Thirty minutes after the start of the reaction the rest of the monomer was added dropwise in a 4 h period to reach a final EC/SPS mass ratio of 20.

#### 2.2.3. Continuous vapor phase tubular reactor (CVTR)

A jacketed glass column (length 0.8 m, diameter 0.05 m, total volume  $1.6 \times 10^{-3} \text{ m}^3$ ) was used as reactor. Heating was supplied by flowing hot oil through the jacket (maximum 180 °C). An initial load of 10 g of SPS or PM and 5 g of sodium carbonate were packed

into the reactor. To start the reaction, EC vapors were supplied by heating a vessel containing liquid EC and attached through glass fittings to the reactor. Reaction temperatures were 145, 160 or 180 °C.

### 2.3. Purification of the grafted SPS or PM polymers

At the end of the graft polymerization reaction, the remaining liquid phase was removed by filtration. The resulting solid fraction was Soxhlet extracted with acetone for 1 h. No specific removal of catalyst was performed since spontaneous powder sedimentation allowed for solid separation. In any event, small amounts of sodium carbonate on the fibers should have no significant adverse effect during the biofiltration of waste gases.

### 2.4. Grafting yield

The grafting yield was calculated on a gravimetric basis as a weight gain (%) by means of the following equation:

$$\text{Grafting yield(\%)} = \left[ \frac{\text{dry weight of treated and extracted} - \text{dry weight of initial extracted}}{\text{dry weight of initial extracted}} \right] \times 100\%$$

To quantify correctly the weight gain on the initial biomass, blank Soxhlet extractions with acetone were run for 1 h on SPS or PM because this solvent may dissolve extractives and some polyphenolic-lignin compounds present in the original material.

### 2.5. FTIR analysis of grafted products

After drying at 105 °C overnight, FTIR was used for the characterization of the raw and the grafted SPS or PM samples. A Jasco-460 Plus spectrophotometer was used with the KBr pellet method (3 mg of sample and 300 mg of KBr). The acquisition conditions were: spectral width of 4000–400  $\text{cm}^{-1}$ , 32 times accumulation, 4  $\text{cm}^{-1}$  resolution and signal processing by cosine apodization.

The absorbance values of the following bands:  $\text{CH}_2$  (2895  $\text{cm}^{-1}$ ), carbonate (1748  $\text{cm}^{-1}$ ) and ether (1120  $\text{cm}^{-1}$ ) were normalized to that of the OH band (3382  $\text{cm}^{-1}$ ); it was assumed that the latter remained constant (Gunatillake et al., 1998) in agreement with the schemes shown in Figs. 1 and 2.

### 2.6. Size exclusion chromatography (SEC) of the liquid medium

The liquid fraction obtained at the end of each reaction experiment contained mainly poly(ethylene ether carbonate) polyols (Harris, 1989), which were analyzed using a Precision Instruments System size exclusion chromatograph equipped with a refractive index detector IOTA 2, a Chromeleon-PA data acquisition system and a DIONEX (Sunnyvale, CA) auto sampling ASI-100. Tetrahydrofuran (THF) GPC reagent grade (Scharlau) was used as the mobile phase in conjunction with two mixed DPLgel 5  $\mu\text{m}$  gel columns plus one pre-column PLgel 5  $\mu\text{m}$  guard, 50  $\times$  7.5 mm. The temperature of the column was set at 25 °C and the mobile phase flow rate was 1 mL/min. All the samples were diluted (1/100 v/v) in THF and filtered using a 0.1  $\mu\text{m}$  pore size poly(tetrafluoroethylene) syringe filter (Chromatographic Specialties Inc., Brockville, Ontario). Poly(ethylene glycol) standards furnished by Polymer Laboratories with molecular weights of  $0.106 \times 10^3$ – $22.8 \times 10^3$  were used to generate a calibration curve.

### 2.7. Crosslinking of the grafted SPS or PM

During preliminary experiments, 5 g of SPS grafted to a comparable extent (according to FTIR analysis) was mixed with 5 g of glycerol or adipic acid to evaluate crosslinking efficiency. Other crosslinking agents were 2 g of 4,4'-methylenebis(phenylisocyanate) (MDI) or 2 g of residual poly(ethylene ether carbonate) polyol. Under an extraction hood each mixture was placed in a metallic mould to fabricate cylindrical tablets (3.8 cm diameter) at 200 °C, pressurized to 10 bar and left to react for 0.4 h to achieve crosslinking of the potentially exposed OH groups. The temperature for the MDI mixtures was limited to 160 °C because of possible polyurethane thermal degradation.

In parallel experiments, 50 ml of formic acid was introduced into a 1 L capacity glass reactor. When the temperature of 50 °C was reached, 5 g of grafted SPS and 5 g of glutaraldehyde were added under agitation. The reaction time was 0.5 h. The resulting mixture was placed in the metallic mould for tablet production under the conditions described previously.

In addition, two blank tablets of raw SPS and PM (blended SPS–MDI and PM–MDI) were prepared with MDI as described previously and used as controls.

### 2.8. Compression strength measurement

Tablets from 5 g each of SPS or PM with different grafting yields and 2 g of MDI were obtained. Thermopressure conditions were 160 °C and 3 bar during 0.4 h.

The water content of the previously synthesized tablets was defined as water fraction (*W*) accordingly to Gottlieb (1988) and corresponded to the equilibrium value reached after 21 days of soaking in de-ionized water. The original water fraction (*W*<sub>0</sub>) in the support was measured by drying the tablets at 105 °C for 10 h, after which weight remained constant.

Compression strength measurements were made to the tablets by the stress–strain test (Billmeyer, 1984). The SPS or PM tablets were placed on a metal base into the opening of a TA-XT2 texture analyser, exactly below the test needle (5 mm diameter) attached to the pneumatic arm. A constant displacement velocity of 0.1 mm/s was applied. Compression strength, needle displacement and test time data were recorded in a computer connected on-line. The compression strength values of the hydrated tablets are of the utmost importance since it can be related to the volume compression of the filter-bed packing (compaction).

## 3. Results and discussion

### 3.1. Batch stirred reactor

A preliminary study made on SPS, as given in Table 1, shows that the  $\text{CH}_2$  band to OH ratio (absorbance 2895  $\text{cm}^{-1}$ /absorbance 3382  $\text{cm}^{-1}$ ) presented a progressive rise from 0.25 to 0.66 while increasing the reaction temperature from 150 to 180 °C during 2 h of reaction time with respect to SPS control (0.21). The carbonate band to ether ratio (absorbance 1748  $\text{cm}^{-1}$ /absorbance 1120  $\text{cm}^{-1}$ ) reached its highest value at 175 °C. Higher temperatures to this threshold value tended to increase the ether function

**Table 1**  
Operation conditions for SPS graft polymerization in BSR reaction system

	Temperature (°C)	Reaction time (h)	Ratio CH <sub>2</sub> /OH	Ratio carbonate/ether	Residual homopolymer average Mw <sup>a</sup> (g/mol)
SPS	–	–	0.21	–	–
E11	150	2	0.25	–	<b>180</b> , 320
E12	160	2	0.31	0.15	<b>180</b> , 320
E13	175	1.5	0.42	0.16	<b>88,180</b> , 284
E14	175	2	0.66	3.51	<b>180</b> , 320
E15	180	1	0.63	0.19	<b>88, 180</b> , 320
E16	180	1.5	0.68	0.36	<b>180</b> , 320
E17	180	2	0.66	0.09	180
E18	200	1.33	0.69	0.40	<b>88, 180</b> , 320
E19	200	1.33	0.65	0.43	<b>88, 180</b> , 320

<sup>a</sup> The predominant Mw-values are in bold figures.

with acceptable CH<sub>2</sub>/OH ratio (grafting). In the experiments at 200 °C, the reaction time was halted after 1.33 h of reaction time due to darkening of the liquid media promoted by excessive heating.

As discussed, the graft polymerization of EC over an initiator bearing a hydroxyl group may lead either to a grafted carbonate or an oxyethylene group with CO<sub>2</sub> production. The proportion between these two moieties depended especially on the reaction temperature.

A temperature of 175 °C was therefore used for the rest of this study, since it resulted mainly in a carbonate structure grafted to native fibers with the lowest possible reaction temperature to avoid possible structural substrate damage. Values of average molecular weight (Mw) from analysis of the liquid phase obtained at the end of the reaction ranged from 180 to 320 g/mol. This result indicates the occurrence of undesirable homopolymerization (possibly initiated over bound water molecules accompanying the dried vegetal substrate or any other initiators present in the monomer) that corresponded to the dimer, trimer, and tetramer of EC monomer. The results observed in Table 1 indicate that only small poly(ethylene ether carbonate) chains were grafted to SPS, attributed mainly to the absence of EC reagent (Mw of 88 g/mol) after reaction times greater than 1.5 h. Additionally, EC ring opening in liquid media, monomer dimerization or even EC affinity towards generated polyols may occur (Gunatillake et al., 1998).

With the objective of increasing the polymer chain size grafted to SPS, a SSR configuration was mounted. A lower initial EC/SPS mass ratio of 10 was chosen to prevent high initial generation of undesirable non-grafted homopolymer by-products.

### 3.2. Semi-continuous stirred reactor

To control the homopolymerization reaction, EC was added dropwise semi-continuously. Results are shown in Table 2. A large increase in both the carbonate band to ether (absorbance 1748 cm<sup>-1</sup>/absorbance 1120 cm<sup>-1</sup>) and the CH<sub>2</sub> to OH ratios (absorbance 2895 cm<sup>-1</sup>/absorbance 3382 cm<sup>-1</sup>) was obtained with respect to BSR experiments, indicating a sustained improvement in grafting (from CH<sub>2</sub>/OH of 0.21 for the control to 2.47 for the treated sample). Such values reflect that grafting is composed mainly of carbonate units whose values stayed constant practically throughout all the semi-continuous reaction, that is, a carbonate/ether ratio ≈ 17. Both parameters are in accordance to the weight gain observed on raw SPS. Also final liquid phase analysis revealed that non-grafted homopolymers covered an approximate range of 10–40 EC units.

A maximum value in CH<sub>2</sub> band to OH ratio and grafting yield were obtained after 14 h (run E25). After this time, monomer traces or even dimers and tetramers were not found in the liquid

**Table 2**  
Operation conditions at 175 °C for SPS graft polymerization in SSR reaction system

	Reaction time (h)	Grafting yield (%)	Ratio CH <sub>2</sub> /OH	Ratio carbonate/ether	Residual homopolymer average Mw <sup>a</sup> (g/mol)
SPS	–	–	0.21	–	–
E21	6	128	0.80	17.14	180, 320, 1080
E22	8	140	1.60	14.27	180, <b>1800</b>
E23	10	150	1.65	15.58	180, <b>1050</b>
E24	12	170	1.98	17.24	180, <b>1800</b> , 4000
E25	14	230	2.47	19.21	180, 320, <b>4000</b>
E26	16	133	1.59	17.73	<b>4000</b>

<sup>a</sup> The predominant Mw-values are in bold figures.

phase. It is also possible that at longer reaction times a loss of groups grafted to SPS occurred since only large homopolymers are obtained, sustained also by a parallel reduction in grafting yield (E26 experiment).

Despite the semi-continuous system ability to attain a high grafting yield, the presence of non-grafted homopolymers was still an undesirable trade off. One potential solution would be to start the reaction under vacuum, where the active water bound molecules or monomer impurities could be eliminated initially at reduced temperature followed by monomer addition. Also, such arrangement should minimize the EC initial quantity necessary to start the reaction. However, for both BSR and SSR arrangements there is a minimum liquid to solid ratio necessary for an adequate mixing by stirring of the initial suspension (EC/SPS of 10). With this reasoning a CVTR reactor was proposed in which the EC reagent is fed through a vapor phase. In principle, this should lead to a significant reduction in undesirable non-grafted homopolymers formation.

### 3.3. Continuous vapor phase tubular reactor

In this arrangement, the solid organic material is in contact with a constant flow of EC present in vapor phase and avoiding the need of a stirring device. In addition, since the EC concentration is maintained at a low value, non-grafted homopolymers formation is limited. A final advantage is that the reduced pressure system (400 mbar) allowed EC volatilization at 120 °C instead of 244 °C. EC vapors were heated to reach reaction temperatures of 145, 160 or 180 °C and then contacted with the mixture of fibers and the catalyst packed into the reactor.

Table 3 shows the results obtained for SPS in the CVTR system. Clearly, results were poor with no grafting at 145 or 180 °C. Furthermore, some material decomposition was observed for the later temperature. At 160 °C modest yields were obtained up to 76%, however the carbonate band to ether ratio was also low. We observed similar results with E36 compared to that of E13 in BSR experiments. Such behavior suggests a deficient contact between EC vapors, the catalyst and the exposed OH groups available for the reaction. In any event, the exposed OH groups should play a very important role in the selectivity to the graft reaction. A different organic substrate was then evaluated.

Because of its long-lasting stability to microbial attack, PM is a well-known packing material for the biofiltration of waste gases. However, PM presents severe compaction and hydrodynamic limitations (Dalouche et al., 1981; Hirai et al., 1990; Cho et al., 1992; Acuña et al., 1998; Jang et al., 2004). Therefore, it was desired to test the graft polymerization in continuous vapor mode for PM, taking advantage that such arrangement should avoid mineral salts leaching and other nutrients essential for microbial consortia consolidation in biofilters. The results for PM on a CVTR reactor and the conditions used are presented in Table 4. It is observed that



**Table 3**

SPS graft polymerization in continuous CVTR vapor phase reaction system at 400 mbar vacuum

	Temperature (°C)	Reaction time (h)	Grafting yield (%)	Ratio CH <sub>2</sub> /OH	Ratio carbonate/ether
SPS	–	–	–	0.21	–
E31	145	4	0	0.21	–
E32	180	4	0	n. a.	n. a.
E33	160	2.5	42	0.28	3.0
E34	160	4.75	60	0.28	3.43
E35	160	6.5	70	0.49	3.55
E36	160	8.0	76	0.76	3.14

n. a. = not available.

the total carbonate band to ether and CH<sub>2</sub> to OH ratios increased rapidly after 4.75 h, indicating that a high grafting yield composed mainly by poly(ethylene carbonate) units occurred.

A comparison in the grafting yield progress for SPS and PM at 160 °C for the CVTR reactors is presented in Fig. 3. Results show a shift in profile after 4.75 h suggesting a significant difference in the availability of OH initiators that relates to compositional and structural variations. Specifically, we refer to the hemicellulose (Hc), lignin (L) and cellulose (C) structures present in the SPS and PM, which was determined by the ADF–NDF method (Van Soest and Wine, 1968) and reported in Table 5. Accordingly, a slower graft polymerization start-up on PM as compared to SPS could be related to the lower proportion of C and Hc structures on PM (31%) compared to SPS (70%). The fact that after 4.75 h a sustained grafting occurs only for PM can only be related to the larger amount of extractible material. This group could include important quantities of other components like humic acids, waxes, resins, etc., that may act as extra OH groups that become accessible to EC.

### 3.4. Crosslinking of the grafted SPS or PM

Explorative experiments with SPS 150% grafting yield (obtained from reproducible SSR reactions) were realized to test aggregation of the grafted SPS particles. Such particles were subjected to high pressures and temperatures to obtain films and tablets; nevertheless the final structures presented poor thermoset properties and heterogeneous particle distribution that resulted in low integrity during manipulation in aqueous solutions. For this reason external crosslinking agents like glycerol, adipic acid or even residual poly(ethylene ether carbonate) polyol with average Mw of 4000 g/mol were added to improve cohesion and resistance. However, no improvement in tablet aggregation under aqueous solutions was achieved.

In contrast, when MDI was added as crosslinking agent to both grafted SPS and PM, a significant improvement in mechanical resistance was obtained as compared to controls obtained with raw (i.e., not grafted) samples. Also, hard and mechanically resistant tablets were obtained when, in addition to MDI, 2 g of residual homopolymer obtained as reaction by-product at the end of the polymerization reaction was added before tablet formation. This

**Table 4**

PM graft polymerization in continuous CVTR vapor phase reaction system at 400 mbar vacuum

	Reaction time (h)	Grafting yield (%)	Ratio CH <sub>2</sub> /OH	Ratio carbonate/ether
PM	–	–	0.06	–
E41	2.5	15	0.30	2.55
E42	4.75	52	0.48	9.06
E43	8.0	138	0.98	10.88
E44	10.0	150	1.29	12.18

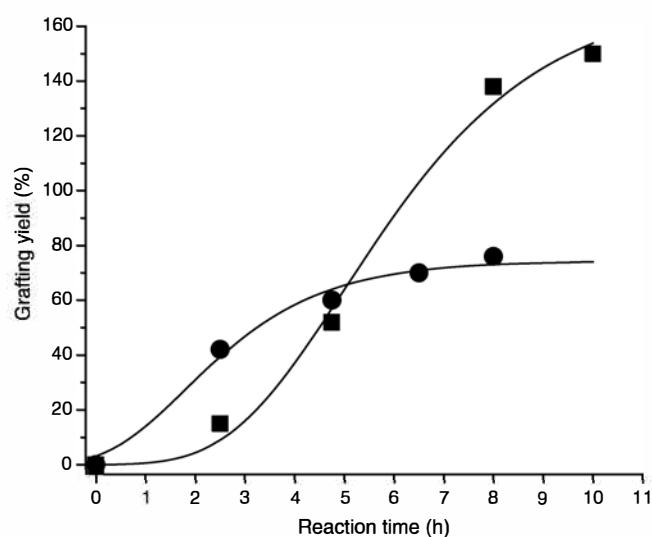


Fig. 3. Grafting yield (%) profiles for (●) SPS and (■) PM obtained in CVTR reactor at 160 °C.

**Table 5**

Composition of major compounds (dry basis, extractible free) of supports determined according to the ADF–NDF method

	Dry matter (%)	Extractibles (%)	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Ash (%)
SPS	92	13	41	29	29	0.7
PM	85	23	6	25	67	1.3

should allow for the recycling of poly(ethylene ether carbonate) that was not grafted into the biomass. The tablets were then characterized further in terms of resistance to compression as an important mechanical property.

### 3.5. Compression strength measurements

During fabrication of final tablets, a pressure of 3 bar was applied instead of 10 bar in order to generate a larger amount of empty space between the fibers (and possibly a higher available surface), without sacrificing integrity and the capacity to retain water as well.

Water content in untreated SPS or PM tablets was rather high in the order of 4 g water/g dry support in both cases. However, such control preparations lose its integrity easily after soaking in water for an extended amount of time. Hence, polymer grafting is an option to retain integrity as long as water content is maintained.

Figs. 4 and 5 show compression strength values (*N*) and water content (*W*) as a function of polymer grafting yield for SPS and PM tablets respectively, after soaking the tablets for 21 days in water. For SPS (Fig. 4) water remained fairly constant up to 60% grafting yield, followed by a small decrease. A similar pattern was observed for compression strength indicating that up to 60% grafting yield the particles retained a good resistance to compression value of 250 *N* with no loss of water content (around 60% on a wet basis). Such values are of interest since it has been reported that supports with water contents in the range of 40–60% are recommended to sustain an adequate microbial activity during biofiltration (Wang et al., 1996; Kennes and Thalasso, 1998; Janni et al., 2001). Also, compression values of 250 *N* are substantially larger than those reported for novel materials in the scarce literature dealing with composite materials adequate for biofiltration (Chan

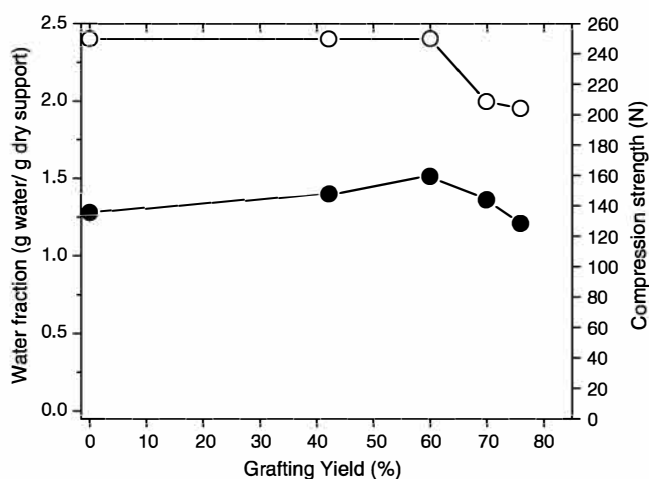


Fig. 4. Equilibrium water content (●) and compression strength (○) for synthesized SPS tablets.

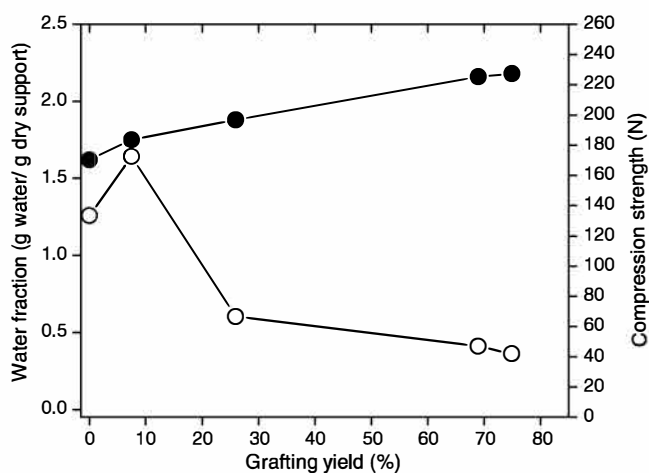


Fig. 5. Equilibrium water content (●) and compression strength (○) for synthesized PM tablets.

and Lu, 2003). For preparations above 60% in grafting yield, the loss in water retention and compression strength could be due to a thermally related fragmentation of cellulose and hemicellulose fibers present in wood that collapse the general structure of the composite matrix. This may result in the observed weakening of the linking forces between fibers that cause a drop in compression strength.

The observed values for PM tablets presented in Fig. 5 show significant differences compared to SPS. Clearly, water content increases steadily up to 150% grafting yield, whereas the strength increases up to 15% grafting yield followed by a rapid drop. In contrast to SPS, PM structure is based on complex associations of lignin and humic acid like molecules with globular shape, instead of fiber like geometries (see Table 5), explaining the different patterns observed. Clearly the results obtained for PM is of interest since strong tablets with up to 180 N compression strength and a water content above 60% (on a wet basis) can be obtained for a grafting yield of only 15%, a value associated with a low, and potentially economical, consumption of carbonate. As reported by Gottlieb (1988), the fact that a water content substantially above 0.9 g water/g dry support was obtained with significant swelling, suggests the formation of an interpenetrating network of poly (ethyl-

ene ether carbonate) grafted to the original SPS or PM, and with a large hydrophilic surface.

It has been recognized that the biofilter removal performance of VOCs can be improved by combining the biological action of microorganisms with the adsorption capacity of the filter-bed media (Janni et al., 2001; Devlinny et al., 1999). In general, ceramic and inorganic materials show a slow rate of VOC adsorption as compared to organic supports like PM (Jang et al., 2004). For future work, it is now possible to study hexane adsorption, as a representative and environmentally important VOC, for the obtained carbonate grafted tablets reported in this work. It is expected that the enhanced hydrophobic sites provided by the ethylene groups in the grafted materials should result in greater adsorption rates and hence in a larger availability of the carbon source for the microbial biofilm attached to the support. In addition, the demonstrated hydrophilic nature of the composite material should provide an appropriate hydration level for a sustained microbial activity. Finally, the resistance to compression obtained should guarantee a long term operation without a significant loss of structural properties during biofiltration operations.

#### 4. Conclusions

The graft polymerization of EC on wood sawdust or peat can be obtained by means of sodium carbonate instead of organometallic catalysts. It is assumed that grafting occurs in an analogous reaction pattern to EC polymerization as shown in Figs. 1 and 2. Grafting on both supports was established by FTIR, monitoring peak signals at 2895, 1748 and 1120  $\text{cm}^{-1}$ , and weight gain after polymerization. Appreciable formation of poly(ethylene ether carbonate) chains grafted to these fibers were observed. For SPS a grafting yield of 230% was obtained in a SSR reactor, although an undesirable large amount of residual homopolymer was also produced. For both supports, this limitation linked to a poor yield on monomer utilization was resolved noticeably when monomer was supplied in the gas phase in a CVTR reactor, a clear improvement over current methods. Fabricated tablets of grafted PM and SPS showed a general tendency to increase water retention in proportion to grafting yield. Grafted tablets were also stronger than non-grafted tablets as measured by compression strength. In particular, PM tablets with only 15% grafting yield (i.e., a low consumption of monomer) showed strong compression resistance with an appropriate water retention capacity (above 60% on a wet basis) to support the microbial activity needed in biofiltration operations. Such materials are excellent candidates as filter-bed packing for an efficient biofiltration of VOC. Experiments to establish the capacity of VOC adsorption by the grafted support and biofiltration tests in packed bed columns are currently under progress.

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