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INFLUENCE OF REACTION TIME AND CARBON DISULFIDE AMOUNT ON SULFOPHOSPHORYLATION REACTION OF PHOSPHORYLATED RESINS

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RESUMO

Neste trabalho, estudamos a reação de sulfofosforilação de resinas fosforiladas variando o tempo de reação e a quantidade de CS2 e caracterizando estes materiais por termogravimetria (TG) e espectroscopia no infravermelho (FTIR). A estabilidade térmica e os espectros de FTIR dos copolímeros de Sty-DVB foram significativamente alterados após as reações de fosforilação e sulfofosforilação. Os copolímeros não modificados apresentaram um estágio de degradação enquanto os copolímeros sulfofosforilados apresentaram dois estágios de degradação, devido à presença de fósforo e enxofre na matriz polimérica. Houve uma tendência ao aumento do teor de grupos sulfofosforilo incorporados nos copolímeros de Sty-DVB com o aumento da quantidade de CS2 e do tempo de reação. No entanto, para quantidades elevadas de CS2, não foi necessário um longo tempo de reação para transformar os grupos fosforilo em grupos sulfofosforilo. O melhor grau de conversão dos grupos fosforil em sulfofosforilo foi obtido pelo tempo de reação de 144 he 0,25 mol de CS2.

Palavras-chave: Sulfofosforilação, Sty-DVB, FTIR.

ABSTRACT

In this work, we studied the sulfophosphorylation reaction of phosphorylated resins by varying the reaction time and CS2 amount and characterized these materials thoroughly by thermogravimetry (TG) and infrared spectroscopy (FTIR). The thermal stability and the FTIR spectra of the Sty-DVB copolymers were significantly changed after the phosphorylation and sulfophosphorylation reactions. The unmodified copolymers presented one degradation stage while the sulfophosphorylated copolymers showed two degradation stages, due to the presence of phosphorous and sulfur in the polymeric matrix. There was a tendency for increasing content of sulfophosphoryl groups incorporated into the Sty-DVB copolymers with increasing CS2 amount and reaction time. However, for high CS2 amounts, a long reaction time was not necessary to transform the phosphoryl groups into sulfophosphoryl groups. The best conversion degree of phosphoryl into sulfophosphoryl groups was obtained by using reaction time of 144 h and 0.25 mol of CS2.

keywords: Sulfophosphorylation, Sty-DVB, FTIR.

1) INTRODUCTION

Organophosphorus and complex sulfur compounds have been reported to possess biocidal action [1,2]. The sulfur and phosphorus atoms of these compounds interact with positivity charged sites of the lipoproteins present in the bacterial cell wall, probably leading to protein denaturation [3].

Biocidal functional groups can be immobilized in polymer matrices. The immobilization of functional groups in polymer matrices is widely used, since chemical modification can be made in various types of polymer supports, through several synthetic routes [4].

Association of sulfur and phosphorous atoms in sulfophosphoryl groups confers biocidal properties to these innovative materials [3]. The phosphorylation reaction of styrene-divinylbenzene (Sty-DVB) copolymers has been studied in our previous work and the synthesized materials have been characterized [5].

In another our previous work has been reported the introduction of sulfophosphoryl groups into Sty-DVB copolymers [3]. Reaction of phosphoryl groups with CS_2 in order to introduce sulfophosphoryl groups into Sty-DVB copolymers was difficult to achieve, with low conversion degree [3]. This reaction was based on reaction of conversion of amino acid into dithiocarbamate groups [6], although they are different reactions. The sulfophosphorylated copolymers presented excellent biocidal activity, but the reaction proved to be extremely slow. In addition, the literature does not report the detailed study of the conversion reaction of phosphoryl into sulfophosphoryl groups and the broad characterization of the synthesized materials. The reaction time and the amount of carbon disulfide used in the sulfophosphorylation reaction are important reaction parameters. These parameters influence the sulfophosphorylation degree. Apart from being a chemical modification reaction in heterogenous phase, not described in the literature, since the reaction occurs in a crosslinked polymeric structure, therefore insoluble, the study has unpublished results regarding sulfophosphorylation reaction by varying and optimizing these parameters, which makes the work be inovative and relevant. Thus, the aim of this work was study widely the influence of these parameters in the sulfophosphorylation reaction and determine the optimum parameters for this reaction.

2) EXPERIMENTAL

2.1 Introduction of sulfophosphoryl groups into Sty-DVB copolymer

The Sty-DVB copolymer of high porosity prepared by suspension polymerization by free radical was submitted to phosphorylation reaction with PCl_3 by varying the molar ratio PCl_3:$AlCl_3$ and the reaction temperature (Table 1) according to the method previously published [5]. The sulfophosphorylation reaction was carried out in a 100 mL reactor equipped with mechanical stirring by employing 0.25 g of phosphorylated Sty-DVB copolymer, a solution of 15 mL NaOH 1 M in ethanol and different amounts of CS_2 (Table 2). The reaction was maintained at 25 ºC for varied time periods (Table 2). After the reaction, the beads were washed several times with hot water until neutral pH, extracted with 100 mL acetone under reflux for 24 h in a Soxhlet apparatus and dried in an oven at 60 ºC for 24 h [3].

2.2 Characterizations

Thermal analyses of the copolymers were conducted with a TA Instruments (TGA Q50 V6.4 Build 193) employing 10 mg of powdered sample packed into the platinum pan. The temperature range was 30-700 ºC at a constant heating rate of 20 ºC min^{-1} under nitrogen atmosphere and a flow rate of 100 mL min^{-1} [7,8]. The determination of the total phosphorus of the phosphorylated copolymers was carried out by spectrophotometry using the molybdenum blue method [9]. Elemental analysis of the sulfophosphorylated copolymers was performed in a Vario Macro CHNS elemental analyzer and dynamic flash combustion was applied for sample analysis. FTIR spectra of the copolymers were obtained from KBr solid solution pellets by using a Perkin-Elmer (Spectrum One) spectrometer (4 scans and 4 cm^{-1}resolution).

3) RESULTS AND DISCUSSION

Sty-DVB copolymer with a macroporous structure was submitted to phosphorylation reaction by using PCl_3/ $AlCl_3$ according to the method previously published [5]. Subsequently this copolymer was reacted with CS_2 in order to introduce sulfophosphoryl groups onto polymeric matrix. A scheme for the phosphoryation and sulfophosphorylation reactions is proposed in Scheme 1.

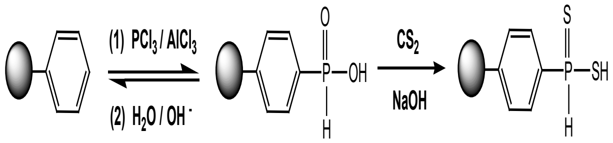


Figure 1: Phosphorylation reaction of Sty-DVB copolymer and reaction of phosphoryl groups with CS_2 to generate sulfophosphoryl groups [10].

The phosphorylation reaction was confirmed by bands at 2350 cm^{-1} due to P–H stretching vibration, 1170 cm^{-1} due to P=O stretching vibration, 991 cm^{-1} related to P–OH stretching vibration and 1440 cm^{-1} due to bond P-C_6H_5, as well as by spectrophotometry using the molybdenum blue method (Table 1).

Table 1: Phosphorous content incorporated into Sty-DVB copolymers for reaction with PCl_3/$AlCl_3$

Copolymer	Temperature (° C)	PCl_3:$AlCl_3$	P ᵃ (mmol. g^{-1})	Phosphorylation degree (%)
PC1	85	1:1	3.29	55.68
PC2	70	1:1	3.40	57.55
PC3	60	1:1	3.75	63.47
PC4	50	1:1	4.53	76.67
PC5	25	1:1	4.51	76.33
PC6	50	1:1.2	4.76	80.56
PC7	50	1:1.5	5.08	85.97
PC8	50	1:2.0	5.09	86.15
PC9	50	1:2.5	5.10	86.32

[a]Determined by spectrophotometry by using the molybdenum blue method [9]

Error = 0.01 mmol.g^1 resin; reaction time: 15 h [5]

The sulfophosphorylation reaction was confirmed by the presence of three bands at 2540, 2349 and 649 cm^{-1}, attributed to the S–H stretching vibration, P–H stretching vibration and P=S vibration, respectively [3], and by elemental analysis (Figure 2, Table 2).

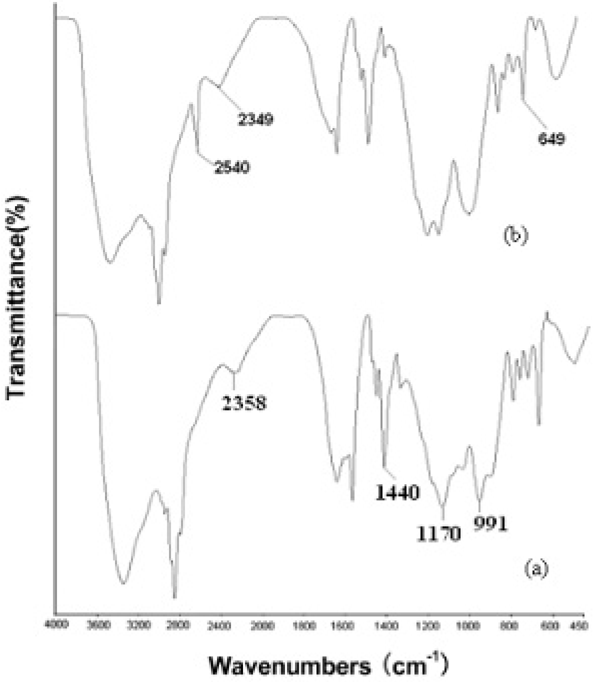


Figure 2: FTIR spectra of phosphorylated (a) and sulfophosphorylated (b) Sty-DVB copolymer

Table 2: Sulfur content incorporated into phosphorylated copolymers for reaction with CS_2

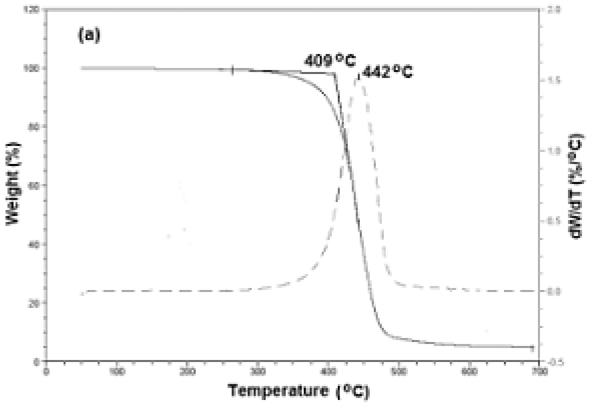
Copolymer	Time (h)	CS_2 (mol)	S (mmol.g^{-1})ᵃ	Sulfophosphorylation degree (%)
SC1	24	0.013	0.07	1.41
SC2	24	0.026	0.15	2.92
SC3	24	0.039	0.14	2.81
SC4	24	0.250	0.47	9.45
SC5	72	0.013	0.10	2.01
SC6	72	0.026	0.14	2.87
SC7	72	0.039	0.16	3.22
SC8	72	0.250	0.47	9.45
SC9	144	0.013	0.44	8.85
SC10	144	0.026	0.38	7.64
SC11	144	0.039	0.38	7.64
SC12	144	0.250	0.48	9.65

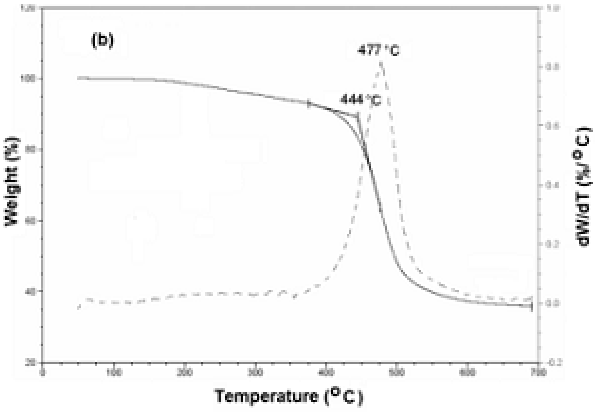
[a]Determined by elemental analysis, Error = 0.02 mmol.g^{-1}

The thermal stability of the Sty-DVB copolymer was significantly changed by the modification reactions (Figure 3). The unmodified copolymer by contain only thermally degradable organic material presented mass loss of 95.0%, leaving 5.0% residue, and presented only one significant weight loss step at 409 ºC and a single DTG peak, related to the decomposition of the main chain of this copolymer at 442 ºC (Figure 3-a). Although the phosphorylated copolymer has presented only a single DTG peak at 477 ºC, the TG curve profile was different, indicating two weight loss stages. In addition, the degradation of this material left 35.7% residue (Figure 3-b). The displacement of the single DTG peak and the increase of the residue content confirm the presence of incorporated phosphorous (not thermally degradable). Phosphorous compounds are normally resistant to oxidation reactions [2]. Sulfophosphorylated copolymer presented a change in the DTG curve profile, attributed to the unfolding at 510 ºC (Figure 3-c). This behavior was observed for all samples that presented high incorporated sulfur content. The incorporation of sulfur in phosphoryl groups caused a change in the degradation stage where the decomposition velocity of the polymeric chains is fastest.

Table 1 shows the results of phosphorous content and phosphorylation degree of the copolymers after phosphorylation reaction. This reaction was conducted by varying the molar ratio PCl_3:$AlCl_3$ and the reaction temperature.

It is possible to observe that the increase of the reaction temperature disfavors the phosphorylation reaction. The copolymer reacted at 85 ºC presented phosphorylation degree of 55.68%. This can be explained by the volatilization or hydrolysis of reactant PCl_3.





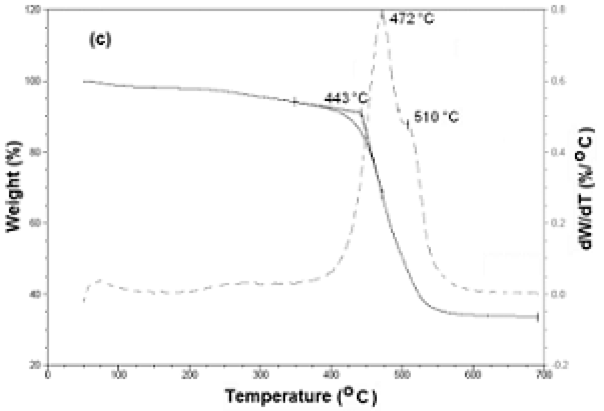


Figure 3: TG and DTG curves of the (a) Sty-DVB copolymer support (b) phosphorylated copolymer and (c) sulfophosphorylated copolymer

We also verified that the excessive increase of the amount of $AlCl_3$ (PCl_3:$AlCl_3$ < 1/1.5) does not contribute to reaction, because electrophile formation (PCl_2^+) is limited by PCl_3 concentration (Scheme 1). We can say that the best conditions for phosphorylation reaction are: temperature 50 ºC and molar ratio PCl_3:$AlCl_3$ = 1:1.5 (copolymer PC7), once the copolymers PC8 and PC9 presented phosphorylation degree practically constant when compared to PC7.

Table 2 shows the sulfur content incorporated into phosphorylated copolymers after sulfophosphorylation reaction. This reaction was conducted by varying the reaction time and the amount of CS_2 in relation to the phosphoryl group content.

As can be seen in Table 2, there is a tendency for increasing sulfur incorporation into the copolymers with the increase of the CS_2 amount in the reaction mixture for the reaction times of 24 and 72 h. However, for reaction times of 144 h this effect is not pronounced. Several works have demonstrated that the reaction with carbon disulfide conduces to low conversion degrees and many of these works employ reaction times of 144 h (6 days) [6,11]. It is possible to suppose that this time is sufficient for that the reaction equilibrium is reached, in other words this reaction time is sufficient for that the saturation of the medium is perceived. Comparing the sulfophosphorylated copolymers pairs SC1/SC4 and SC5/SC8, it is possible to observe that an increase of about 19 times in the CS2 proportion caused an increase of about 580 and 370% in the sulfur content, respectively (Table 2). With a reaction time of 144 h, the amount of CS2 added did not significantly change the incorporated sulfur content. The FTIR spectra of these copolymers show that the bands at 2540, 2349 and 649 cm^{-1}, attributed to S-H, P-H and P=S, respectively, are more intense for the copolymers SC4 and SC8, reacted with high amounts of CS_2, confirming their higher content of sulfophosphoryl groups [3,12] (Figure 4 - A and B). Analyzing the thermal decomposition temperatures (T_{dm}) of the sulfophosphorylated copolymers (Table 3) it is possible to observe that the copolymers SC4 and SC8 presented a second degradation stage (T_{dm2}) when compared to copolymers SC5 and SC8, respectively. The unfolding (T_{dm2}) at 510.33 ºC in the copolymer SC4 and at 509.87 ºC in the copolymer SC8 (Figure 5) showed that these two materials incorporated more sulfur when compared to copolymers SC1 and SC5, respectively. In addition, the copolymers SC4, SC8 and SC12 (Figure 6), with addition of high amounts of CS2 (0.25 mol), showed two degradation stages due to high incorporation of sulfur into the polymeric matrix. It is also important to observe (Table 3) that the copolymers SC9, SC10, SC11 and SC12, with long reaction times (144 h), showed equally two degradation stages due to high incorporated sulfur contents. Sulfophosphorylated copolymer SC12 showed the highest temperature onset (436.89 0C). It is due to this polymeric resin has presented higher sulfophosphorylation degree inducing the increase of the initial degradation temperature.

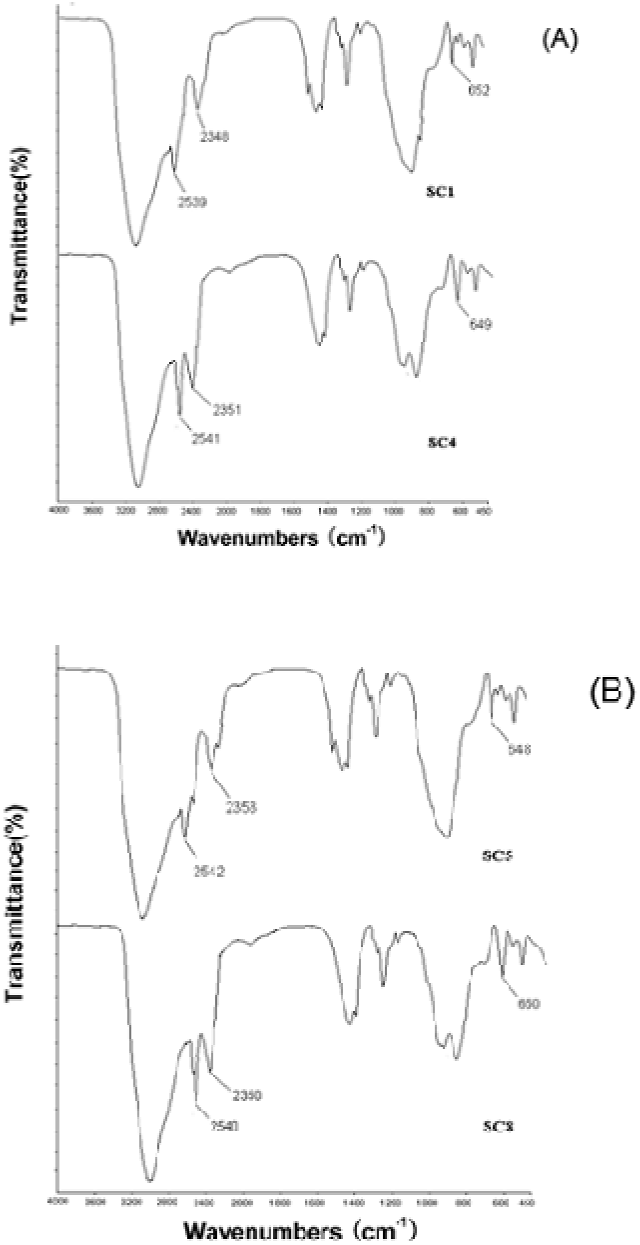


Figure 4: FTIR spectra of sulfophosphorylated copolymers SC1 and SC4 (A) and SC5 and SC8 (B)

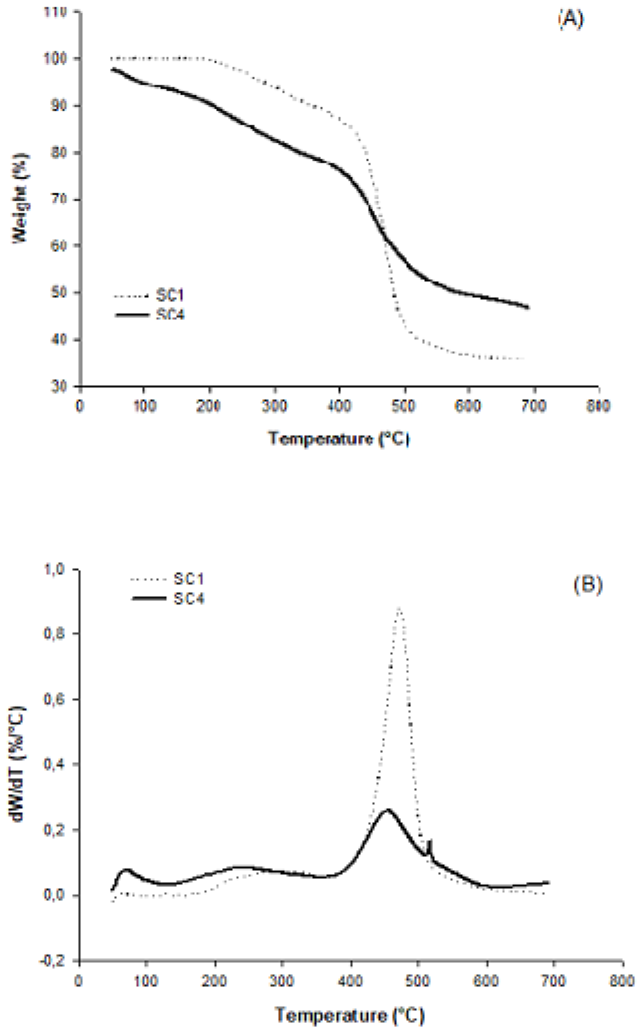
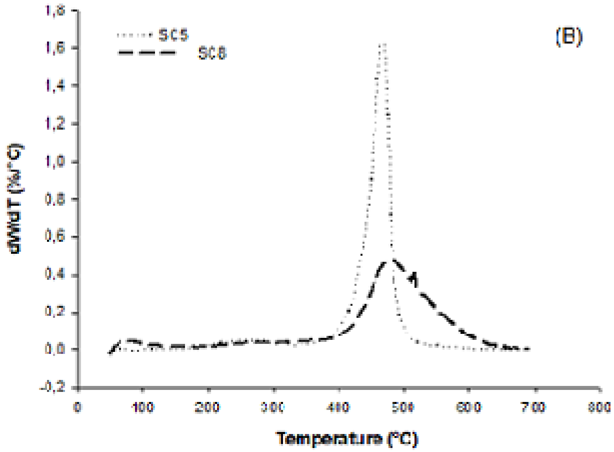


Figure 5: TG (A) and DTG (B) curves of sulfophosphorylated copolymers SC1 and SC4



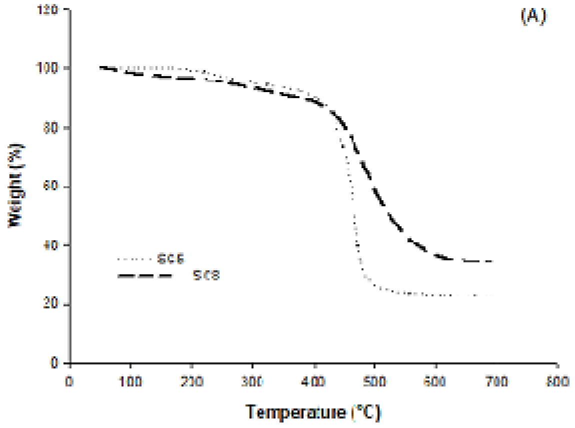


Figure 6: TG (A) and DTG (B) curves of sulfophosphorylated copolymers SC5 and SC8

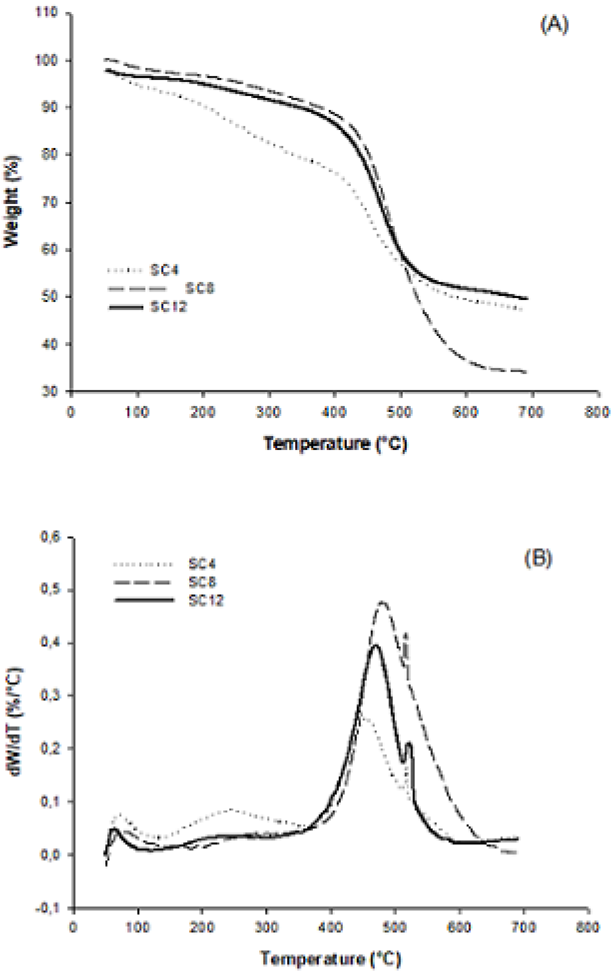


Figure 7: TG (A) and DTG (B) curves of sulfophosphorylated copolymers SC4, SC8 and SC12

Table 3: Thermal decomposition temperatures of the sulfophosphorylated copolymers

Copolymer	T_{onset}^{a} (°C)	T_{dm1}^{b} (°C)	T_{dm2}^{b} (°C)
SC1	421.67	464.13	-
SC2	426.44	465.76	-
SC3	427.39	467.24	-
SC4	432.52	468.01	510.33
SC5	428.29	455.89	-
SC6	429.92	463.89	-
SC7	430.67	469.99	-
SC8	433.22	481.91	509.87
SC9	430.93	477.23	510.95
SC10	431.78	475.39	508.23
SC11	432.11	476.19	509.56
SC12	436.89	478.87	511.01

[a] Initial temperature degradation; [b] Temperature where the degradation rate is maximal
Error = 0.05 ºC

Comparing the sulfophosphorylated copolymers SC1/SC5/SC9, SC2/SC6/SC10 and SC3/SC7/SC11 can be noted a tendency for increasing incorporation of sulfur with the increase of the reaction time (Table 2). This behavior is also confirmed by the FTIR spectra and TG/DTG curves of these materials, as can be seen in Figure 8 (FTIR spectra of SC1, SC5 and SC9 copolymers) and Figure 9 (TG/DTG curves of SC1, SC5 and SC9 copolymers). The bands at 2538, 2348 and 653 cm^{-1}, attributed to S-H, P-H and P=S, respectively, are more intense for the copolymer SC9 (Figure 8), reacted with longer reaction time (144 h), confirming higher content of sulfophosphoryl groups.

Sulfophosphorylated copolymer SC9 showed a change in the DTG curve profile attributed to the unfolding at 510.95 ºC (Figure 9). This behavior can be explained by the increase of the incorporation of sulfur when used long reaction times. When 0.25 mol of CS_2 was used in the reaction mixture, the sulfur content incorporated into SC4, SC8 and SC12 copolymers for the three reaction times (24, 72 and 144 h) remained practically constant (Table 2). This behavior is also confirmed by the TG/DTG curves of SC4, SC8 and SC12 copolymers (Figure 7). The DTG curves of these three copolymers present similar shifts, indicating the presence of the same amount of sulfophosphoryl groups in the copolymers. Thus, can be said that for high amounts of CS_2 the reaction equilibrium is soon reached and the effect of the increase of the reaction time about the sulfur content is not perceived.

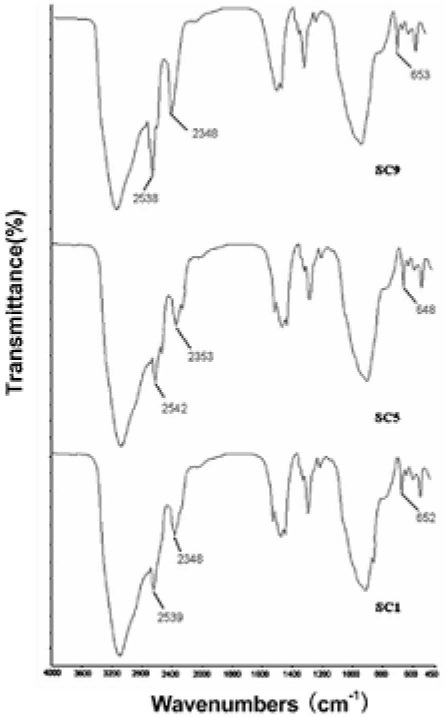
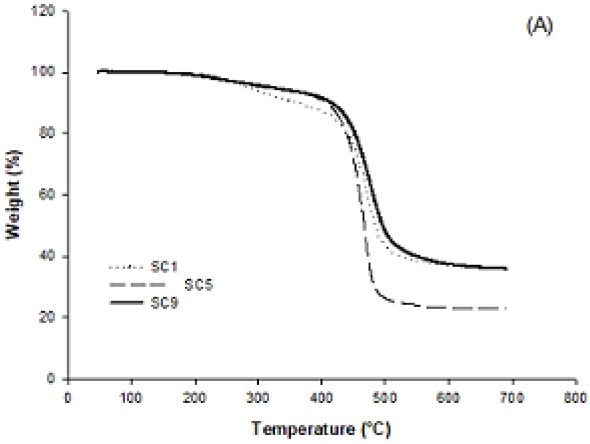


Figure 8: FTIR spectra of sulfophosphorylated copolymers SC1, SC5 and SC9



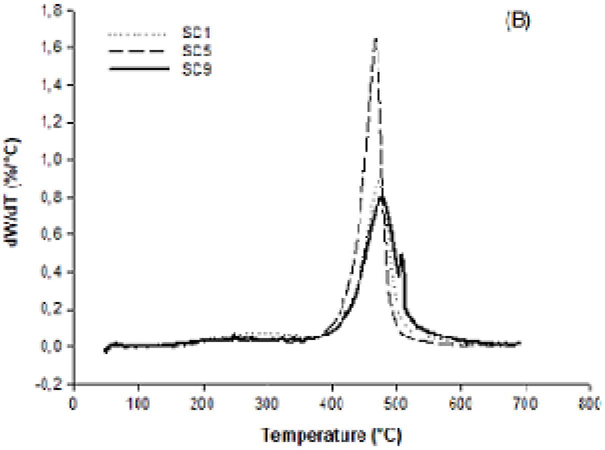


Figure 9: TG (A) and DTG (B) curves of sulfophosphorylated copolymers SC1, SC5 and SC9

CONCLUSION

The thermal stability and the FTIR spectra of the Sty-DVB copolymers were significantly changed after the phosphorylation and sulfophosphorylation reactions. There was a tendency for increasing content of sulfophosphoryl groups incorporated into Sty-DVB copolymers through the use higher amounts of CS2 and longer reaction times.

For high amounts of CS_2, a long reaction time is not necessary to transform phosphoryl into sulfophosphoryl groups. The best conversion degree of phosphoryl into sulfophosphoryl groups was obtained by using reaction time of 144 h and 0.25 mol of CS_2. The results of the optimization of the reaction parameters to transform phosphoryl into sulfophosphoryl groups will contribute to the achievement of efficient biocidal materials.

5) ACKNOWLEDGEMENTS

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