Acta Scientiae et Technicae, Vol 9, number 1, 2021. ISSN 2317-8957

Preliminary evaluation of the antimicrobial activity of dithiocarbamate resins based on GMA-EDGMA copolymers

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ABSTRACT

In this work we report the development of a new strategy for the preparation of dithiocarbamate resins based on glycidyl methacrylate-ethylene glycol dimethacrylate (GMA-EDGMA) copolymers. The methodology for introduction of the dithiocarbamate moieties on these copolymers was based on reaction with ethylenediamine, triethylenetetramine, tetraethylenepentamine and then reaction with carbon disulfide under alkaline medium. The antimicrobial activity of these products was evaluated employing inhibition halo tests against *Escherichia coli* (Gram-negative bacteria) and *Staphylococcus aureus* (Gram-positive bacteria). Data of N_2 adsorption indicated that GMA-EDGMA copolymer containg a mesoporous structure. Data of FT-IR indicated that reaction of copolymers with diamines occurred in a reazoable proportion however the reaction of the aminated derived with CS_2 occurred in lower proportion. Only the copolymer containing dithiocarbamate groups prepared by reaction with diethyltriamine and carbon disulfide showed halo of inhibition against *E. Coli* and *S. Aureus* bacteria.

Keywords: Biocidal polymers, dithiocarbamate resins, glycidyl methacrylate copolymers, porous polymers

RESUMO

Neste trabalho relatamos o desenvolvimento de uma nova estratégia para a preparação de resinas ditiocarbamato à base de copolímeros de glicidil metacrilato-etilenoglicol dimetacrilato (GMA-EDGMA). A metodologia para introdução das porções ditiocarbamato nestes copolímeros foi baseada na reação com etilenodiamina, trietilenotetramina, tetraetilenopentamina e a seguir na reação com dissulfeto de carbono em meio alcalino. A atividade antimicrobiana desses produtos foi avaliada por meio de testes de halo de inibição contra Escherichia coli (bactéria Gram-negativa) e Staphylococcus aureus (bactéria Gram-positiva). Os dados de adsorção de N2 indicaram que o copolímero GMA-

EDGMA contém uma estrutura mesoporosa. Dados de FT-IR indicaram que a reação de copolímeros com diaminas ocorreu em proporção reazoável, porém a reação do derivado aminado com CS2 ocorreu em proporção menor. Apenas o copolímero contendo grupos ditiocarbamato preparados por reação com dietiltriamina e dissulfeto de carbono apresentou halo de inibição contra as bactérias E. Coli e S. Aureus.

Keywords: Polimeros biocidas, resinas de ditiocarbamato, copolímeros de glicidil metacrilato, polímeros porosos

INTRODUCTION

Materials containing dithiocarbamate groups have been shown to be efficient in removing heavy metals (Shaaban et al., 2013; Bai et al., 2011; Costa & Teixeira, 2010), precious metals recovery (PMs) (Ag, Au, Pd, and Pt) (Biswas et al., 2021a, Biswas et al., 2021b), adsorption and speciation of As^{3+} (Nakakubo et al., 2020), separation of ethylenediaminetetraacetic acid-copper complexes of liquid solutions (Yan et al., 2019), speciation of cationic dyes (Liu et al., 2020), among other applications. These dithiocarbamate groups have been introduced onto different supports such as cellulose (Nakakubo et al., 2020; Biswas et al., 2021a, Biswas et al., 2021b), silica (Bai et al., 2011) and crosslinked copolymers based on styrene-divinylbenzene (Sty-DVB) (Shaaban et al., 2013; Costa & Teixeira et al., 2010;). Sty-DVB copolymers have been highlighted as supports due to the simplicity of preparation these particles, low cost of the monomers, possibility of preparing particles with different properties (size, size distribution, surface area, pore volume, pore diameter, etc), easy modification of these structures through functionalization with different groups (Maksin et al., 2012).

The introduction of dithiocarbamate groups on Sty-DVB copolymers can be achieved through several strategies. Cunha and colleagues (2007) describe that the introduction of dithiocarbamate groups on copolymers is commonly preceded by a step of activation of benzene rings through chloromethylation, chlorosulfonation or Friedel Crafts acylation followed by reaction with different amines and finally reaction with carbon disulfide (CS_2) in basic medium. Costa & Teixeira (2010), Costa and colleagues (2012) relate a pathway to preparation of dithiocarbamate resins based on nitration of supports, reduction of the nitro groups to amine groups and reaction of CS_2.

Some works describes the preparation of copolymers based on glycidyl methacrylate (GMA) by aqueous suspension polymerization, functionalization of these copolymers with different diamines and evaluation of the final products as chelating to metal ions (Nastasovic et al., 2016; Sadeek et al., 2014, Maksin et al., 2012; Nastasovic et al., 2009). However, the preparation of dithiocarbamate resins from GMA copolymers containing diamines has not been explored in literature.

Antimicrobial polymers have several advantages over low molecular weight biocidal compounds, related to the greater stability of these materials. These polymers have potential applications for the inhibition of biofilm formation (Mandu et al., 2020). The antimicrobial capacity of dithiocarbamate resins was evaluated in a unique work previously published (Costa et al., 2012). The development of materials with antimicrobial capacity and ability to remove other contaminants (such as metals) is interesting from both economic and ecological points of view.

This work describes a new strategy for the preparation of dithiocarbamate resins based on synthesis of glycidyl methacrylate-ethylene glycol dimethacrylate (GMA-EDGMA) copolymers, reacting these copolymers with ethylenediamine, triethylenetetramine, tetraethylenepentamine and finally a reaction with carbon disulfide (CS_2). The antimicrobial activity of these materials was previously evaluated employing inhibition halo tests against *Escherichia coli* (Gram-negative bacteria) and *Staphylococcus aureus* (Gram-positive bacteria).

MATERIALS AND METHODS

The experimental part was divided into five steps: Preparation of GMA-EDGMA copolymers, reaction of the copolymers with different diamines, reaction of the copolymers with CS_2 aiming to prepare dithiocarbamate resins, characterization of the copolymers before and after modifications reactions, preliminary evaluation of the antimicrobial activity these polymers.

Chemicals

Glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDMA), ethylenediamine, triethylenetetramine and tetraethylenepentamine were acquired by Sigma-Aldrich Brasil Ltda and used as received. 2,2-azo-bis-(isobutyronitrile) (AIBN) was purchased from Mig Química Ltda (São Paulo, Brazil) and used after recrystallization with methanol. The microorganisms used in this work were *Escherichia coli* (ATCC 11229), purchased from Newprov and *Staphylococcus aureus* (ATCC 25923), acquired from Kwik Stik. The culture media used were Nutrient Broth and Nutrient Agar (both acquired from Neogen), Tryptical broth and Tryptic Agar (CASO + Power Agar) (both acquired from Sigma-Aldrich). Other reagents and solvents were purchased from Isofar Indústria e Comércio de Produtos Químicos Ltda and used as received.

Synthesis of glycidyl methacrylate-ethylene glycol dimethacrylate (GMA-EDGMA) copolymers

Preparation of GMA-EGDMA copolymers by aqueous suspension polymerization was previously published (Costa et al., 2020). These materials were synthesized in a 1 L three-necked round-bottom reactor flask equipped with a mechanical stirrer (IKA, model RW20 DS32), reflux condenser, oil bath, heating plate (IKA C-Mag H57 S32) and a thermostat (IKA, model ETS D5) (Figure 1). The aqueous phase (composed by 198 mL of water, PVA and NaCl (both at 1.0% w/v in relation to water content)) was prepared and transferred to the reactor. The organic phase constituted by GMA (0.24 mol), EDGMA (0.06

mol), AIBN (0.003 mol), cyclohexane (22 mL) was prepared and transferred to the same reactor already containing an aqueous phase. The reactional mixture was stirred continuously at 350 rpm at 85 °C for 24 hours. The beads were washed several times with hot water, ethanol and methanol, and finally dried at atmospheric pressure for 48 h at 60 °C. The experimental part was divided into five steps: Preparation of GMA-EDGMA copolymers, reaction of the copolymers with different diamines, reaction of the copolymers with CS_2 aiming to prepare dithiocarbamate resins, characterization of the copolymers before and after modifications reactions, preliminary evaluation of the antimicrobial activity these polymers.

Figure 1: Apparatus used in the preparation of the copolymers

Reaction of copolymers with diamines

The reactions with diamines were conducted in the apparatus used on preparation of copolymers, however the 1 L three-necked round-bottom reactor was replaced by a 250 mL flask. All reactions were conducted at 80 ºC, for 24 h and by employing an agitation of 100 rpm. Reaction with ethylene diamine: In this reaction 11 g of GMA-EDGMA copolymer, 38.9 mL of ethylene diamine solubilized on 19.4 mL of dimethylformamide were employed (Nastasovics et al., 2009, Donia et al., 2006).

Reaction of triethylenetetramine: This reaction was conducted by employing 11 g of GMA-EDGMA copolymer, 63.8 mL of triethylenetetramine and 39.5 mL of toluene (Nastasovics et al., 2009).

After reaction with diamines the copolymers were reacted with carbon disulfide (CS_2). A solution of NaOH in ethanol (100 mL, 1 mol/L) was prepared and transferred to the reactor containing the copolymer aiming to maintain the pH of the medium at around 10.0. Then 51,2 mL of CS2 were also transferred to the reactor. The reaction remained for 7 days with low stirring of the magnetic stirrer and without heating. At the end of this period, the copolymer was washed with distilled water, ethanol and acetone and dried in an oven at 60°C for 24 hours. (COSTA et al., 2012).

Characterization of the copolymers

The materials were characterized by determining:

(i) apparent density by using the graduated cylinder technique, according to ASMT 19985;

(ii) scanning electron microscopy (JEOL, Model JSM 6490 LV). Before analysis, the samples were covered with gold. Magnifications of 250x and 20000x were employed.

(iii) surface area (BET equation), pore volume and pore diameter (BJH equation). These parameters were determined through construction of N_2 adsorption isotherms by varying the relative pressure (P/P_0) (ASAP – Model ASAP 2020);

(iv) FT-IR spectrometry performed on an Infrared Spectrometer with Fourier transform (PERKIN ELMER, Model 1720X), in the frequency range of 4000 to 400 cm^{-1} and after pasting of the samples with KBr;

(v) titration of epoxide rings was realized after reaction of the GMA-EDGMA copolymer with tetramethylammonium chloride in presence of glacial acetic acid followed of titration with perchloric acid (0.1 N) acid in glacial acetic acid and acetic anhydride (in the presence of crystal violet indicator) (Costa et al., 2020; Jay, 1964).

(vi) Thermogravimetric analysis was conducted with a TA Q50 instrument, by employing a temperature range of 50-650 ºC, heating rate of 20 ºC/min under N_2 atmosphere (flow rate of 60 mL/min).

Evaluation of the antimicrobial activity

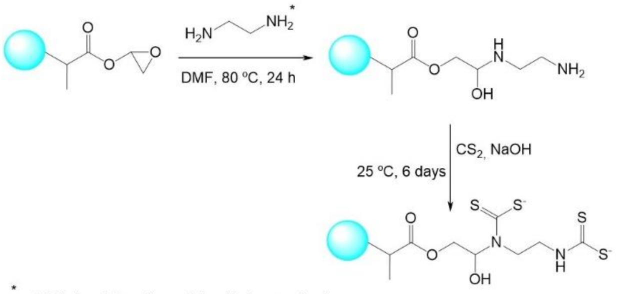
Preliminary procedures: (ii) all glassware and plates were previously submitted to autoclave aiming to ensure the sterility of the medium, (ii) sterility of the culture medium was analyzed through incubation of 5% of the solutions at 37 ºC for 48 h, (iii) Saline solution 0.9 % m/v was prepared by employing Milli Q water, (iv) Tryptic Soy Broth (CASO), Nutrient Broth, Nutrient Agar and Tryptic Agar (CASO + Power Agar) were prepared in a 250 mL Erlenmeyer flasks, (v) Agar plates were prepared in a laminar flow hood previously sterilized. Each plate was prepared by using 20 mL of nutrient agar or tryptic agar.

Inoculation: On a laminar flow hood, three colonies were isolated (with the aid of a disposable loop) from plate containing *E-coli* colony, which had already been prepared a week before. These colonies were placed in an Erlenmeyer flask containing the nutrient broth. Three colonies of *S. aureus* were also isolated from plates previously prepared and placed in an Erlenmeyer flask containing the CASO broth. These Erlenmeyer flasks containing the bacteria in their respective broths were placed in the shake apparatus with stirring at 200 rpm at 37 °C for 24 hours.

Experiment: In the plates containing Nutrient Agar, four holes were made, these plates were divided into four quadrants. To these wells, 10μL of Agar were added. The process was repeated for another 5 plates. The cultures of *S. aureus* and *E-coli* were previously diluted in saline solutions. Suspensions were adjusted to 3 x 10^8 cells/mL. These concentrations were determined by turbidimetry (spectrophotometer Hach DR 5000, 600 nm) by employing the McFarland standard (Mandu et al., 2020). For sowing, the cultures were transferred with Swab to previously prepared plates. Cultures of *E. coli* were transferred to plates containing nutrient agar and cultures of *S. aureus* were transferred to plates containing tryptic agar. On each well, 10μL of agar were added, two of these wells were filled with resin (21 mg). The plates were incubated at 37 ºC for 48 hours in an oven. At the end of the period, the formation or not of a halo around the wells containing the resins were evaluated. This experiment was conducted in triplicate.

RESULTS AND DISCUSSION

The new strategy to preparation of dithiocarbamate resins development in this work is based on modification of GMA-EDGMA copolymers through reaction with different amines and finally reaction with CS2. The products generated in each step are shown in Figure 2. When GMA-EDGMA is reacted with diamines the epoxide ring present on the GMA monomer undergoes an opening which results in an ester group containing a portion of amino alcohol. In basic medium the amino groups undergo deprotonation resulting in dithiocarbamate groups attached to the polymeric structure.

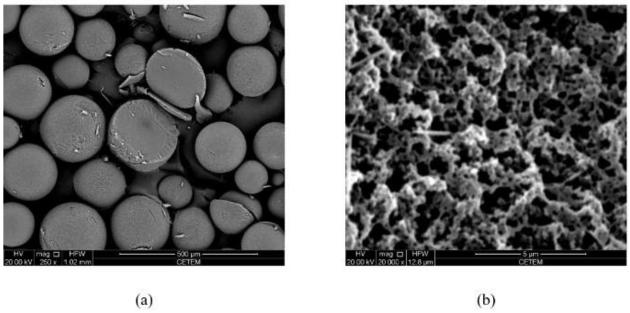


* or triethylenetetramine or tetraethylenepentamine

Figure 2: Functionalization of GMA-EDGMA copolymers with diamines and CS2 in order to prepare dithiocarbamate resins

Preparation of GMA-EDGMA copolymer

A study involving the better conditions for the synthesis of GMA-EDGMA copolymers was previously published (Costa et al., 2020). This copolymer was prepared by using 80% of GMA, cyclohexane as diluent, 50 % of dilution degree. Figure 3 shows Scanning Electron micrographs obtained after coating the samples with gold. Textural properties of these materials were summarized in Table 1. Figure 4 shows N2 adsorption-desorption isotherms for this material.

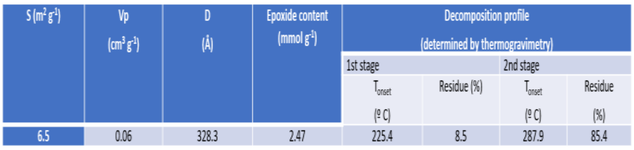


(a)

(b)

Figure 3: Scanning Electron micrographies (SEM) of the GMA-EDGMA copolymer, (a) magnification of 250x, (b) magnification of 20.000 x

Table 1: Morphological properties of the GMA-EDGMA copolymer (Costa et al., 2020)



S ($m^2 g^{-1}$)	Vp ($cm^3 g^{-1}$)	D (Å)	Epoxide content ($mmol\ g^{-1}$)	Decomposition profile (determined by thermogravimetry)			
				1st stage		2nd stage	
				T_{onset} (º C)	Residue (%)	T_{onset} (º C)	Residue (%)
6.5	0.06	328.3	2.47	225.4	8.5	287.9	85.4

S: specific surface area (determined by N2 adsorption employing BET equation), Vp: pore volume (determined by N2 adsorption by employing BJH equation), D: pore diameter (determined by N2 adsorption by employing BJH equation), epoxide ring content: determined by titration according to methodology previously published (Costa et al., 2020), T_{onset}: initial temperature of degradation determined by thermogravimetry

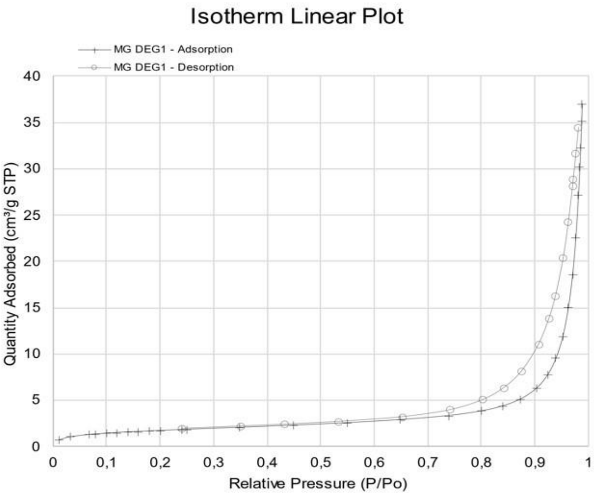


Figure 4: N2 adsorption-desorption isotherms of GMA-EDGMA copolymer

SEM micrographs (Figure 3-a) reveal that this material contains a spherical morphology. It is possible to observe the presence of smaller and larger particles in the analyzed sample indicating a wide particle size distribution. The magnification of 20000x of the external surface of the beads (Figure 3-b) showed the presence of larger pores on polymeric structure. However, data obtained from N_2 adsorption shows that this copolymer containing low specific surface and pore volume (Table 1). Data of pore diameter (Table 1) and analysis of the N2 adsorption/desorption isotherm (Figure 4) indicate that this material contains a mesoporous structure. It is possible to observe a hysteresis between adsorption and desorption processes and the profile of this isotherm is similar to type IV (characteristic of mesoporous materials). Considering that the specific area is directly proportional to the pore volume and inversely proportional to diameters of these pores its value will depend on the compromise between these two variables (Cunha et al., 2004). The data of surface area and pore diameters obtained for this copolymer can also be explained considering that the polymerization reaction was conducted in the presence of cyclohexane, a diluent that shows a value of Hildebrand solubility parameter quite different from GMA monomers. Probably the phase separation process occurred before gel point via χ-induced syneresis contributing to formation of lower surface area and larger pore volume (Gokmen & Du Prez).

Content of GMA introduced on copolymer (theorical value) was 5.21 mmol/g. Thus, the content of epoxide ring is also 5.21 mmol/g of copolymer. Content of epoxide determined by titration was 2.47 mmol/g. This difference between content of epoxide, ring theorical and experimental, can be related to two factors: (1) loss of monomer during polymerization reaction, GMA is a polar monomer. NACl was employed on aqueous phase, aiming to reduce the solubility of the mononomers in water (salting-out effect), however it is possible to suppose that part of this monomer was solubilized in water during the reaction and was not introduced into polymeric matrix. (2) During titration only accessible epoxide rings were determined. Thus, it is possible that epoxide rings present in the internal structure of the polymeric matrix were not accessible to reactant tetramethylammonium bromide and have not been determined by titration.

GMA-EDGMA copolymer presented two stages of degradation. The first stage of decomposition (T_{onset} 225.4 ºC) can be attributed to degradation of the epoxide ring. Residue content obtained after this first degradation can be related with content of these rings (more reacted groups present on this copolymer). The second stage of decomposition (Tonset 287.9 ºC) can be related with degradation of all polymeric matrix (Costa et al., 2020).

Reaction with GMA-EDGMA with different diamines

GMA-EDGMA copolymer was reacted with diamines of different chain lengths: ethylenediamine, triethylenetetramine, tetraethylenepentamine (Figure 2). These reactions were conducted aiming to observe how the chain length of these diamines influences on antimicrobial activity of the dithiocarbamate resins. As commented before, biocidal polymers can be insoluble polymeric contact disinfectants or demand-release disinfectants (Valle et al., 2013). It is possible to suppose that the increase in content of antimicrobial groups and alterations in chain length of these groups cause alterations in the action mechanism of these two types of disinfectants. The increase in content and chain length of the antimicrobial groups can favor the contact between the bacteria and the antimicrobial group or contribute to release of the active compound in the medium, increasing the biocidal activity these groups. Reaction between GMA-EDGMA copolymer and diamines were accompanied by FT-IR spectrometry (Figure 5).

Chemical structure of the GMA-EDGMA copolymer is presented on Figure 2.

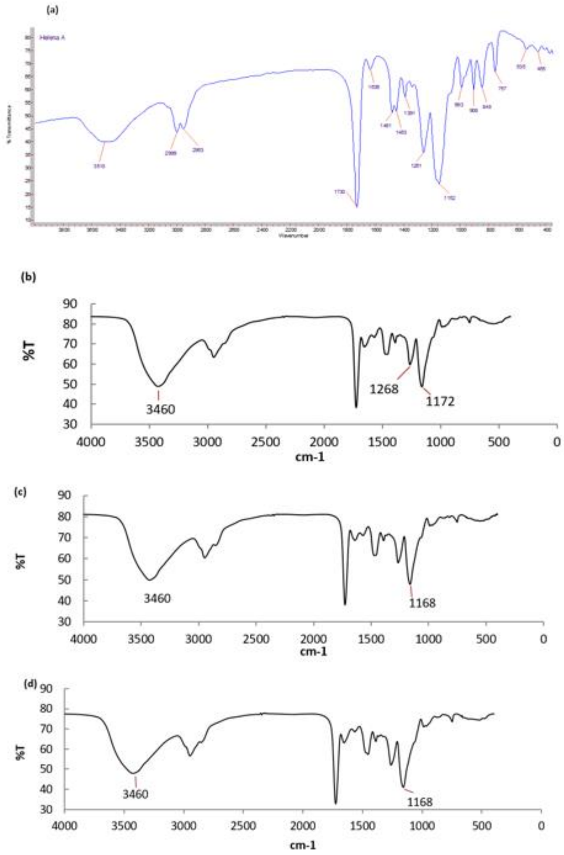


Figure 5: FT-IR spectra of the: (a) unmodified GMA-EDGMA copolymer, (b) GMA-EDGMA copolymer after reaction with ethylenediamine, (c) GMA-EDGMA copolymer after reaction with triethylenetetramine, (d) GMA-EDGMA copolymer after reaction with tetraethylenepentamine.

The spectrum of the GMA-EDGMA copolymer (Figure 5-a) shows a band at 3510 cm-1 attributed to hydrogen bonds between carbonyl or epoxide groups (polar) and water and expressive band at 1732 cm-1 related with C=O stretching (due ester groups on monomers structures), bands at 1261 cm-1 and 993 cm-1 due to symmetrical and asymmetrical stretching of epoxide rings (present on GMA monomer) (Costa et al., 2020; Silvertein et al. 2005). The FT-IR spectra of the products after reaction with diamines (Figure 4-b, 4-c, 4-d) shows an increase in intensity of the band at 3460 cm-1 attributed to symmetrical and asymmetrical stretching of N-H bond, new bands at 1172 cm-1 and 1168 cm-1 due C-N stretching and a significative reduction of the bands at 1261 and 993 cm-1 (attributed to epoxide ring). These results indicate that during reaction the epoxide ring was opened and amine groups were successfully introduced onto the polymeric structure. A variation in intensity of these bands related with N-H and C-N groups was expected, due to reactions with diamines containing more groups C-N (triethylenetetramine and tetraethylenepentamine), however these variations were not observed on these spectra.

Preparation of dithiocarbamate resins

Products generated after reaction of GMA-EDGMA copolymer with different amines were reacted with carbon dissulfide on basic medium in order to introduce dithiocarbamate groups on the polymeric structure (Figure 2). These reactions also were accompanied by FT-IR spectroscopy (Figure 6). The presence of bands attributed to C=S bond at 2100 cm^{-1} were not observed on these spectra, indicating a lower degree of conversion of amine groups to dithiocarbamate groups. Bands at 1131 cm^{-1} are absent, probably covered up by band due C-N stretching. However, the presence of the small band at 672 cm^{-1} attributed to C-S stretching indicates the occurrence of reaction between amine groups and CS_2 in basic medium (that generated dithiocarbamate groups on copolymer matrix) (Costa & Teixeira, 2010).

Tetraethylenepentamine contain more amino groups than triethylenetetramine and ethylenediamine. Thus, it was expected that the dithiocarbamate resin derived from aminated resin containing tetraethylenepentamine had a higher content of dithiocarbamate groups than the resin derived from aminated resins containing triethylenetetramine and ethylenediamine groups. Variations in band intensity related to dithiocarbamate groups were expected, due to variations in the chain lengths of the diamines. However, analyzing these spectra, it was possible to observe that no significative alterations of intensity of these bands were observed. This could have happened for two reasons: (i) low conversion rate of amino groups to dithiocarbamate groups; (ii) difficulty in observing these bands in the spectra of cross-linked polymers. These spectra were obtained after pasting of the samples with KBr. This process can be more difficult depending on the sample composition.

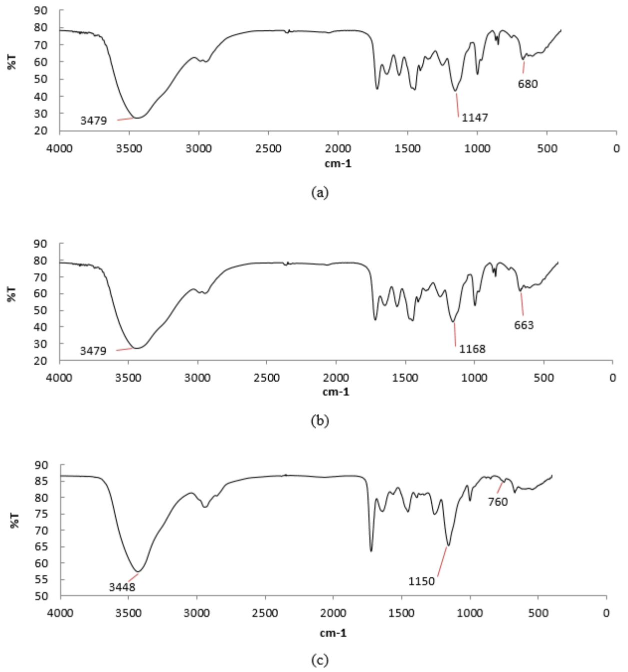


Figure 6: FT-IR spectra of the: (a) GMA-EDGMA copolymer reacted with ethylenediamine and CS_2, (b) GMA-EDGMA copolymer reacted with triethylenetetramine and CS_2, (c) GMA-EDGMA copolymer reacted with tetraethylenepentamine and CS_2

Preliminary evaluation of antimicrobial activity of the materials

Preliminary evaluation of the antimicrobial activity for all materials was evaluated through measurements of the halo of inhibition against two bacterial cultures: *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria) (Table 2).

Table 2: Data of inhibition halo for different materials against *E. coli* and *S. aureus*

Materials	E. coli	S. aureus
GMA-EDGMA copolymer	Absent	Absent
GMA-EDGMA copolymer reacted with ethylenediamine	Absent	Absent
GMA-EDGMA copolymer reacted with triethylenetetramine	Absent	Absent
GMA-EDGMA copolymer reacted with tetraethylenepentamine	Absent	Absent
GMA-EDGMA copolymer reacted with ethylenediamine and CS_2	Absent	Absent
GMA-EDGMA copolymer reacted with triethylenetetramine and CS_2	1.5 cm	1.5 cm
GMA-EDGMA copolymer reacted with tetraethylenepentamine and CS_2	Absent	Absent

Only dithiocarbamate resin prepared from copolymer modified with diethylenetriamine and reacted with CS_2 showed a halo of inhibition against two bacteria. It is possible to suppose that polymers with epoxide groups and amino groups did not show antimicrobial activity. As commented before, preparation of aminated copolymers was realized by employing diamines with different chain lengths (ethylenediamine, triethylenetetramine, tetraethylenepentamine). This was done aiming to prepare dithiocarbamate resins with varied structures, containing more content of these groups and more distant groups of the polymeric matrix. It was expected that the increasing in content of antimicrobial groups and the increasing in chain length of these groups would favor the contact between the bacteria and the antimicrobial group or contribute to release of the active compound in the medium, increasing the biocidal activity these groups.

Dithiocarbamate resin derived from aminated resin containing tetraethylenepentamine did not show an inhibition halo against *E. coli* and *S. aureus*. It is possible to suppose that: (i) the reaction of the aminated resin containing triethylenetetramine with CS2 was more efficient, resulting in a higher content of dithiocarbamate groups that were released in the medium generating the inhibition halo observed (Figure 7); (ii) it is possible to assume that there must be a "limit", that is, neither a very small or a very large molecule could present the ideal interaction with the bacteria, dithiocarbamate resin prepared from aminated resin containing diethylenetriamine (intermediate size amine) showed a more favorable interaction with bacteria resulting in damage to the cell wall or changing the metabolism of these bacteria leading to its death or stopping its reproduction.

Gram-positive bacteria are different from Gram-negative bacteria. Gram-positive bacteria have a larger cell wall, as they have several layers of peptidoglycans, there is the presence of teichoic and lipoteichoic acids, but they do not have an outer membrane or lipopolysaccharides (LPS). The Gram-negative bacteria, on the other hand, have an outer membrane and LPS, but few peptidoglycan layers. As the inhibition halo was similar for the two types of bacteria it is possible to suppose that the action mechanism of the dithiocarbamate resin was also similar for these two bacteria. This data indicates that these dithiocarbamate groups were released into the medium resulting in the inhibition halos observed.

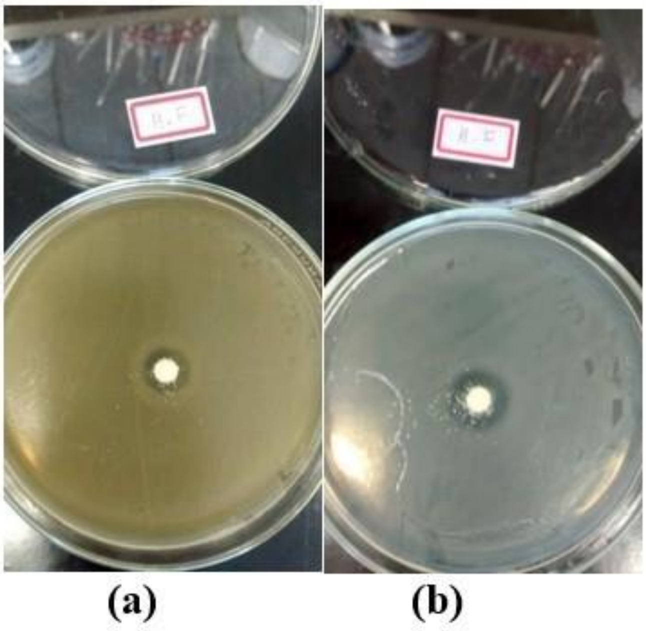


Figure 7: (a) inhibition halo against *S. aureus* (b) inhibition halo against *E. coli*

CONCLUSIONS

Data of SEM and N_2 isotherms revealed that GMA-EDGMA copolymer contained a mesoporous structure. This material shows surface area of 6.5 m2/g and pore diameters of 328 Å. Content of epoxide ring determined by titration was 2.47 mmol/g indicating loss of GMA monomer during polymerization, and also indicating that not all epoxide groups were accessible to reactant tetramethylammonium bromide and have not been determined by titration. This copolymer showed two decomposition stages related to the degradation of ring epoxide and degradation of the polymeric matrix. Reaction of GMA-EDGMA copolymers with different diamines was confirmed by FT-IR. It was possible to observe new bands attributed to presence of N-H and C-N on polymeric matrix, besides a significative reduction of the bands attributed to epoxide rings. However, no notable variations in intensity of these bands due to reaction of the copolymer with the different diamines were observed. Significant variations in the FT-IR spectra after reaction of the aminated resins with CS_2 to produce dithiocarbamate resins were not observed, indicating that this reaction probably occurred with lower conversion degree. Only dithiocarbamate resin prepared from copolymer modified with diethylenetriamine and reacted with CS_2 showed a halo of inhibition against *S. aureus* and *E. coli*. It was possible to suppose that the reaction of the aminated resin containing triethylenetetramine with CS_2 was more efficient. Probably this resin contained a higher content of dithiocarbamate groups in this polymeric matrix, that were released in the medium resulting in the halo of inhibition observed.

ACKNOWLEDGMENTS

This study was financed in part by Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ). We also express our thanks to Mirian A. Oliveira for assistance with figure 3.

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