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Combining vegetable oils and bioactive compounds via inverse vulcanization for antioxidant and antimicrobial materials

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ABSTRACT

The current great concern about plastic pollution opens up opportunities for the production of more sustainable polymers. Inverse vulcanization has emerged as a novel procedure to obtain inorganic-organic hybrid polymeric materials. Sulfur is attained as a by-product of oil refining production and makes inverse vulcanization a sustainable process due to a large amount of sulfur without a useful life. In previous studies, vegetable oils were used as a comonomer with sulfur to form copolymers based on sustainable raw material. Nevertheless, compounds from agro-wastes, could be a third comonomer that improves new copolymers bio-applications. In this study, a new series of copolymers with castor oil as vegetable oil and sulfur was formulated by adding a third compound bearing double bonds or heteroatoms. A study was conducted to assess the antimicrobial capacity and antioxidant activity of the copolymers obtained to demonstrate the benefits of adding a new comonomer to improve their bioactivity.

1. Introduction

Currently, there is a significant concern about the effect of plastics on the pollution of our planet due to the exponential increase in its world production, which has gone from 1.5 Mt in 1950 to 335 Mt in 2016 [1,2]. Plastics play an essential role in the packaging, agriculture, consumer electronics, and automotive sectors, and only 1% of the total annual production of plastics are bioplastics [3]. Nowadays, a significant social movement is committed to the production of bioplastics. This cause is because of the adverse effects of traditional plastics, which include their massive accumulation, contribution to global warming, and other environmental pollution problems that conventional plastics cause in their life cycle [4–7]. The preparation of more sustainable polymeric materials with novel structures and exciting properties is highly prioritized in modern polymer chemistry [8].

Chung et al. [9], developed the revolutionary inverse vulcanization concept. The concept efficiently used elemental sulfur (S_8) as a reaction medium and as a comonomer with other compounds that have double

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bonds. This process was established for the synthesis of new hybrid polymeric materials. Through inverse vulcanization, stable polymers with a very high sulfur content (50–90% sulfur by mass) can be obtained. Currently, sulfur is the tenth most abundant element on Earth, and it is valuable as a chemical reagent with important uses in industry, agriculture, or material science [10]. Around 70 million tons of sulfur are obtained as a by-product each year. Therefore, refined crude oil is currently the largest source of sulfur production [11]. Although several uses for sulfur have been previously described, there is still a net excess of sulfur that offers few economic services. Thus, finding a new large-scale use would be an important development and advance. Sulfur has a certain chemical inertness, exhibiting limited solubility in many organic solvents, except for poor solubility in some aromatics such as toluene, carbon disulfide, and pyridine [12]. All of this makes it challenging to synthesize polymers directly from sulfur under slight reaction conditions. The main limitations are overtaken by inverse vulcanization through ring-opening polymerization reaction [12]. The use of this new type of copolymers has opened a promising field for studying new materials with beneficial chemical and optical properties since they have been used in such vital fields as materials science, polymer technology, adhesives, electrochemistry, or water treatment. The specific properties of the copolymers depend on the nature of the bonds formed between sulfur and another compound with a double bond [13–16].

The properties of the copolymers could be controlled by the selection of the polymerization reaction conditions and the use of an appropriate comonomer. Vegetable oils can be considered a practical option for their use as green comonomers. Taking advantage of their properties, they can be used to produce copolymers from highly cross-linked thermosets to linear thermoplastics, making them applicable in a wide range of materials for various uses [17,18]. Based on these precedents, other copolymers could also be formed from a natural origin, such as agro-wastes, a source of a great variety of bioactive compounds [19]. A recent example of using an agro-waste, such as limonene, as a source of a comonomer compound in the inverse vulcanization process has been reported in the literature [20]. The use of copolymers of natural origin that come from residues of the agro-food industry would lead to obtaining polymeric material that offers a high degree of biodegradability, antioxidant power, and antimicrobial properties, as can be found in the other examples recently described in the literature [12,21,22].

One sustainable and green option to obtain copolymers with sulfur by inverse vulcanization has been carried out with vegetable oils due to the easy interaction of sulfur with triglyceride unsaturation. Previous studies have shown that sunflower, linseed, and olive oils have been applied to develop of lithium-sulfur battery cathodes [15,23]. In the same way, some systems have been described elaborating new polymeric materials with natural origin, from vegetable oils as raw material, that take advantage of some properties of them, thus, obtaining products for many applications [17,17,17]. In another study, soybean oil was chosen to react with elemental sulfur to be investigated as a source of sulfur for plants, as a fertilizer with improved oxidation capacity [24]. Even in water remediation, sulfur-based polymers obtained by inverse vulcanization of elemental sulfur with canola oil and other recycled cooking oils were able to produce an efficient adsorbent for mercury capture [25]. Thus, these kinds of copolymers previously formed by the inversed vulcanization methodology that present good properties could be interesting base compounds to improve by adding new chemical compounds with specific properties for the industry. A new generation of polymers is desirable to have antioxidant and antimicrobial properties to form new plastic materials. Therefore, phenol compounds have been reported as bioactive compounds with antioxidant and antimicrobial properties [19,26]. Compounds derived from polyphenols, such as cinnamic acid or bisphenol A, could be used for this purpose, being used as raw material for the formation of copolymers with bioactive properties from agro-waste. In addition, the use of bisphenol A for this methodology is interesting to give a clean utility to this compound that, although it is found in fruit packaging, is well known that it can cause damage to human health [27,28].

Furthermore, incorporating of heteroatoms (oxygen and nitrogen) in the main chain of the copolymer with these new chemical compounds can favour different properties such as antimicrobial and antioxidant properties [29,30]. Based on this premise, other compounds that can provide exciting characteristics to the final polymer material could be imidazole, one of the most used catalysts in chemical synthesis, which was also proposed to increase the reaction rate in this kind of copolymerization [31]. Likewise, another candidate which could also favour the kinetics of the reaction and bear a heteroatom would be the triallylamine [32,33]. In the same way, other compounds that carry double bonds and are suitable to have biological applications should be styrene, which has previously been used as a comonomer in other studies to obtain electric devices [8,34,35].

The aim of this work was the generation of new kinds of copolymers by inverse vulcanization, using elemental sulfur (S_8) and natural products to formulate new antioxidant and antimicrobial polymeric materials.

2. Experimental section

2.1. Raw materials

Castor Oil (CO) was supplied by Ginama (Valencia, Spain), and elemental sulfur (S_8) 99% was provided by the refining petroleum company CEPSA (Huelva, Spain). The third group of compounds for the production of copolymers was composed of Styrene (STY), Bisphenol A (BPH), Triallylamine (TAA), Imidazole (IMI) (Sigma-Aldrich, Steinheim, Germany), and Cinnamic acid (CIN) (Acros Organics, Geel, Belgium) (Fig. 1).

2.2. Synthesis of new materials by inverse vulcanization

Inverse vulcanization of elemental Sulfur, Castor Oil (CO), and a third compound were prepared following a slight modification of Chalker's preparation [16]. S_8 and CO were heated and melted under vigorous stirring until 170 °C within an oil bath in a round bottom flask, covered with cooling reflux to minimize the evaporation of reactants, for 60 min with a S/CO:80/20 weight ratio (Fig. 2A). For ternary copolymers, when blends S_8 and CO were heated at 170 °C, the third compound was slowly added. Blends were stirred for 60 min keeping the temperature to finish the comonomers conversion. The previous procedure was continued to synthesize 20 g of new copolymers with the following weight ratios: S/CO/STY:80/14/6, S/CO/BPA:80/14/6, S/CO/TAA:80/14/6, S/CO/CIN:80/14/6, and S/CO/IMI:80/14/6 (Fig. 2B).

In addition, a new strategy to obtain copolymers to improve their future biological capacities is based on the elimination of vegetable oil

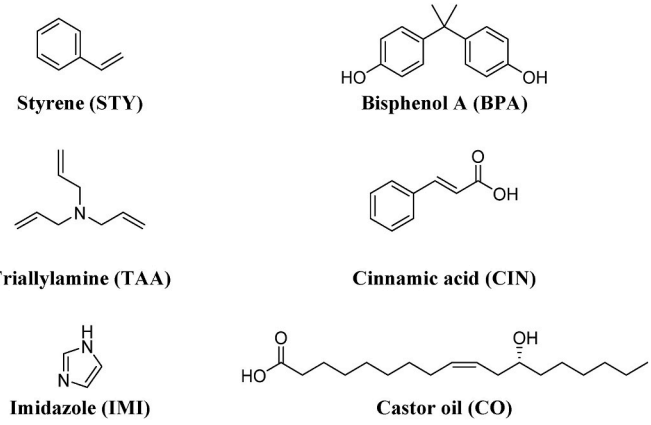

Fig. 1. Different comonomers are used for the generation of copolymers.

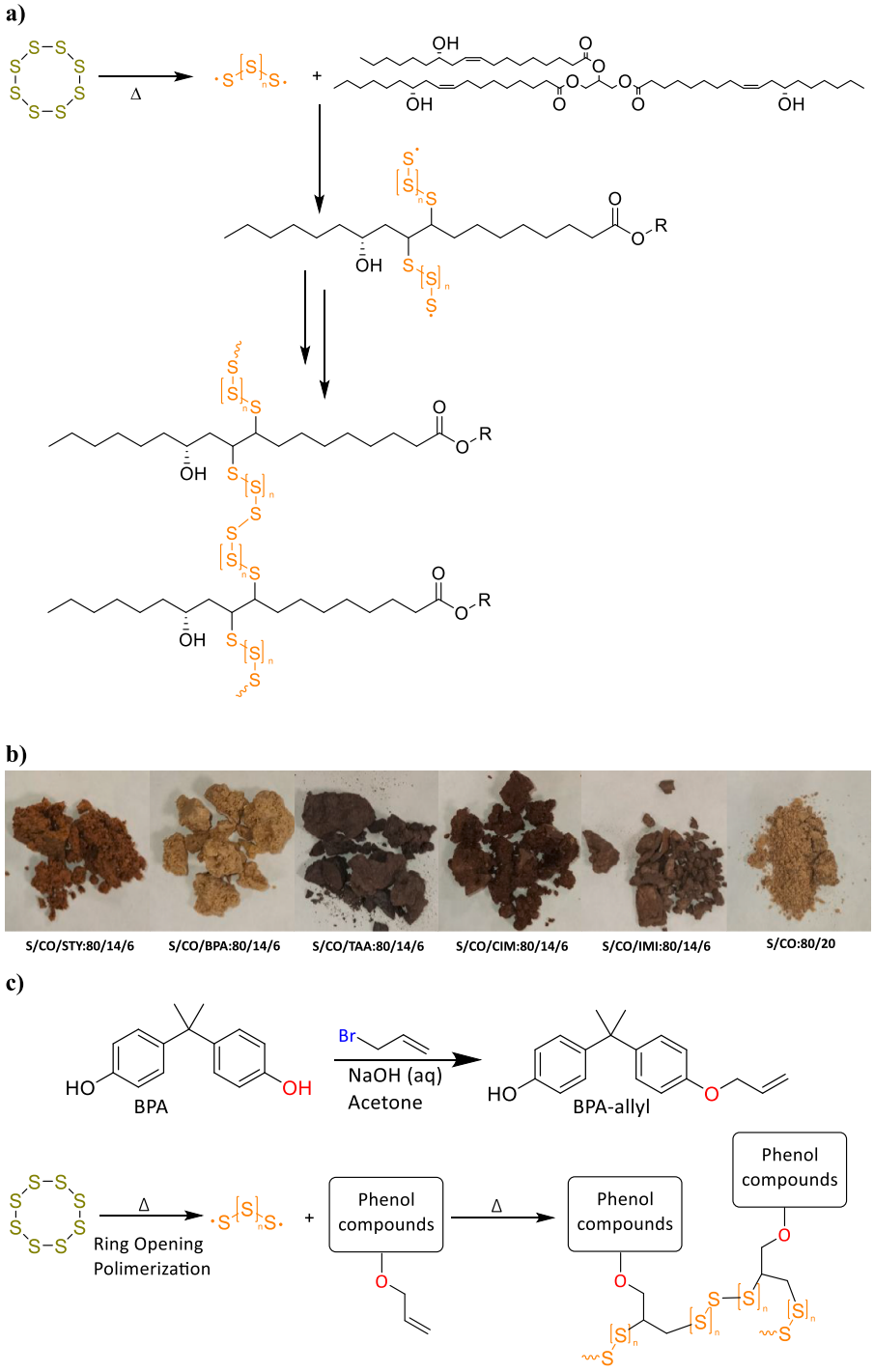

Fig. 2. a) Synthesis process of copolymer based on sulfur and castor oil by inverse vulcanization. b) (S/CO/X) copolymers generated with different chemical compounds. c) Allylation reaction of bisphenol A with allyl bromide, and methodology to obtain the desired copolymer by inverse vulcanization.

as a comonomer and the use of the best possible activity compounds as the second comonomer. For this, the introduction of double bonds in its structure is necessary, being bisphenol A, in the present study, was tested as a comonomer, which previously had suffered an allylation. This procedure is based on precedent research published [36]. In the flask, 20 g of BPA was added with a dissolution of 800 mL of 0.5 M NaOH (aq)/acetone (1:4). Then, 20 mL of allyl bromide was also added, and the mixture was allowed to heat for 5 h at 40 °C with continuous stirring. After that time, the solution was concentrated on leaving it in the extractor hood overnight. The remaining solution was acidified to pH 2 by adding concentrated HCl (aq). The resulting fraction was introduced in a separating funnel and washed four times with distilled water and hexane. Finally, it was left to dry in a hood for 48 h, and the polymer was formed by inverse vulcanization with a S/BPA-allyl:80/20 ratio as previously described (Fig. 2C).

2.3. Antioxidant activity assay

The dissolution of the copolymers in different organic solvents was tested with pyridine, dichloromethane, acetone, dimethyl sulfoxide, carbon disulfide, and tetrahydrofuran, obtaining it only in carbon disulfide and pyridine. 0.1 g of each material was dissolved in 25 mL of

disulfide carbon to measure the antioxidant power. The antioxidant activity of the new material obtained was determined using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) spectrophotometric method [37] and was expressed as milligrams of Trolox equivalents per g polymer (g TEAC/g polymer).

2.4. Antimicrobial activity assay

The antimicrobial activity of the polymers was tested against two bacterial strains pathogenic to humans, *Escherichia coli* (Gram −) and *Bacillus cereus* (Gram +), and the yeast *Saccharomyces cerevisiae*. These microorganisms were grown in test tubes in an orbital shaker at 100 rpm until the cultures reached the stationary phase. Bacteria were cultured in LB medium at 37 °C, while yeasts were grown in YPD medium at 30 °C. An inoculum of 100 μL was added to 4 mL of culture medium containing 100 mg mL^{-1} of each copolymer. A culture without any polymer was used as a control of the microbial growth and, Castor Oil and S_8 were used as controls of the specific activity of the copolymers. The microorganisms were cultured overnight in the presence of the different copolymers. The inhibition of growth was measured through the optical density of the cultures at 600 nm in a spectrophotometer (Ultrospec 3100 pro, LabWrench) in comparison with the control culture without copolymers.

2.5. Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy (^{1}H NMR) was used to determine the chemical structures of the copolymers. ^{1}H NMR of copolymers samples was recorded at 500 MHz using a Varian Mercury 500 spectrometer. Deuterated pyridine-d5 was used as a solvent ($\delta = 7.18$, 7.55, 7.70 ppm). ^{1}H NMR shifts are reported relative to tetramethylsilane.

3. Results and discussion

3.1. Structural analysis of the new copolymers via solution NMR spectroscopy

Nuclear magnetic resonance spectroscopy was used to determine the chemical structures of castor oil and the other copolymers synthesized. The representative ^{1}H NMR spectra, taken by dissolving the samples in deuterated pyridine-d5 of castor oil and new copolymers, are shown in Fig. 3. As can be clearly observed in Fig. 3, the alkene = CH proton peaks at $\delta = 5.60$ and $\delta = 5.80$ ppm present in castor oil are completely absent or overhead by peaks for other copolymers. Similar behavior was obtained in the inverse vulcanization process with castor oil, and sulfur recently carried out by Tikoalu et al., [16]. The new C–S bonds should appear at $\delta = 1.30$ ppm in the ^{1}H NMR spectra but were masked. According to previous studies, sulfur-based copolymers should present signals of the thiol group around 1.5 ppm [38]. The HOD peak appears around $\delta = 5$ ppm belonging to the impurities of deuterated solvent [39].

Different peaks appear that belong to the aromatic region from new copolymers against castor oil and S/CO:80/20 copolymer (Fig. 3). Imidazole peaks appear in $\delta = 7.03$, 7.55, and 8.16 ppm from the S/CO/IMI copolymer, similar to that described by Butt et al., [40]. Cinnamic acid double peaks appear in $\delta = 6.91$, 7.33, 7.60, and 8.03 ppm from the S/CO/CIM copolymer. A similar chemical shift of cinnamic acid was described in the study by Bezerra França et al., [41]. The S/CO/TAA copolymer does not appear any peak representative from triallylamine, it is masked with castor oil. Peaks from bisphenol A appear in $\delta = 7.12$ and 7.27 ppm in the S/CO/BPA copolymer similar to that described in another reaction by van den Hoek and Fossum [42]. Finally, multiple peaks appear around $\delta = 7.29$ ppm from S/CO/STY in the aromatic region from styrene. Wręczycki et al. [8], described similar aromatic peaks suggesting that the phenyl groups were located randomly along with the macromolecules since the two peaks of the aromatic region observed in other copolymers not appear.

3.2. Study of antioxidant activity from the new copolymers

The antioxidant capacity of the new copolymers was calculated employing DPPH radical scavenging methods and compared with the antioxidant activity of castor oil and sulfur. As can be seen in Fig. 4, the S_8 has an insufficient radical scavenging capacity concerning to the other substances measured. In a recent study with inorganic sulfur salts, Na_2S and Na_2S_2 were used to observe if they had antioxidant activity, and reduction of DPPH was observed similar to what was observed with S_8 [43]. On the contrary, castor oil has been observed to have antioxidant activity that does not increase over time. This antioxidant activity of castor oil is attributed to the phenol compounds of the oil itself [44]. In the copolymer S/CO a minor increase of antioxidant activity was observed concerning to castor oil. Therefore, the addition of another compound that has antioxidant capacity in the copolymer could increase this property.

Copolymers with STY, IMI, and CIM have increased their antioxidant activity against the copolymer with only CO. However, the antioxidant activity of the copolymers with BPA and TAA has decreased this activity with respect to copolymer S/CO. Higher antioxidant activity was observed when the copolymers had hydrophobic compounds such as styrene or imidazole [45]. The hydroxyl groups of S/CO/BPA responsible for scavenging DPPH radicals could be connected to the network during polymerization, as a result of which their ability to scavenge DPPH radicals decreased [45]. Furthermore, the hydroxyl groups of bisphenol A were not detected at the ^{1}H NMR of the S/CO/BPA copolymer, as shown in Fig. 4. New polymeric materials from agro-wastes with high antioxidant capacity and moderate mechanical properties are an alternative to replace traditional plastic containers [46]. Therefore, this new generation of copolymers synthesized with sulfur and compounds derived from agro-wastes could be very promising.

3.3. Study of antimicrobial properties from the new copolymers

Due to the increase of multi-factor resistant microbes, it is necessary to find new compounds with antibacterial and antifungal properties. In the present study, the antimicrobial activity of the new copolymers generated was assessed against two bacterial species, one Gram - (*E. coli*) and one Gram + (*B. cereus*), and one yeast (*S. cerevisiae*).

According to the growth inhibition data, the results reflect that the extracts showed relatively good inhibitors activity against the tested microorganisms (Fig. 5). The best results were obtained for *B. cereus*, against which the majority of the new copolymers presented a relevant growth inhibition. At the same time, sulfur and castor oil had practically no effect on their growth. Among the new copolymers, phenolic compounds, such as BPA and CIM, showed a strong inhibitory effect (90%) on the growth of *B. cereus*. Furthermore, it was observed that IMI inhibited its growth by 93% and TAA by 61%. Finally, STY only presented 34% growth inhibition on *B.cereus,* and the S/CO polymer had no significant effects on its growth. In the case of *E. Coli*, no inhibition of growth was observed in the presence of sulfur. The new copolymers showed an inhibition ability similar to that of castor oil (44%), the most significant being for BPA with 49% (Fig. 5).

In a recent study, it was shown that the hydrophobic ricinoleic acid chains of CO could pierce the bacteria attached to the copolymers, forming holes that cause leakage, lysis, and consequently, the death of the microorganism [47]. The hydrophobic chains of the copolymers might have less affected the growth of Gram over Gram + bacteria due to the different composition of their cell walls. Gram – bacteria contain an additional outer membrane with phospholipids and lipopolysaccharides, while Gram + bacteria lack this outer membrane and possess a thicker peptidoglycan layer instead [47–49]. Concerning *S. cerevisiae*, the new copolymers showed considerable inhibition activity, as it was

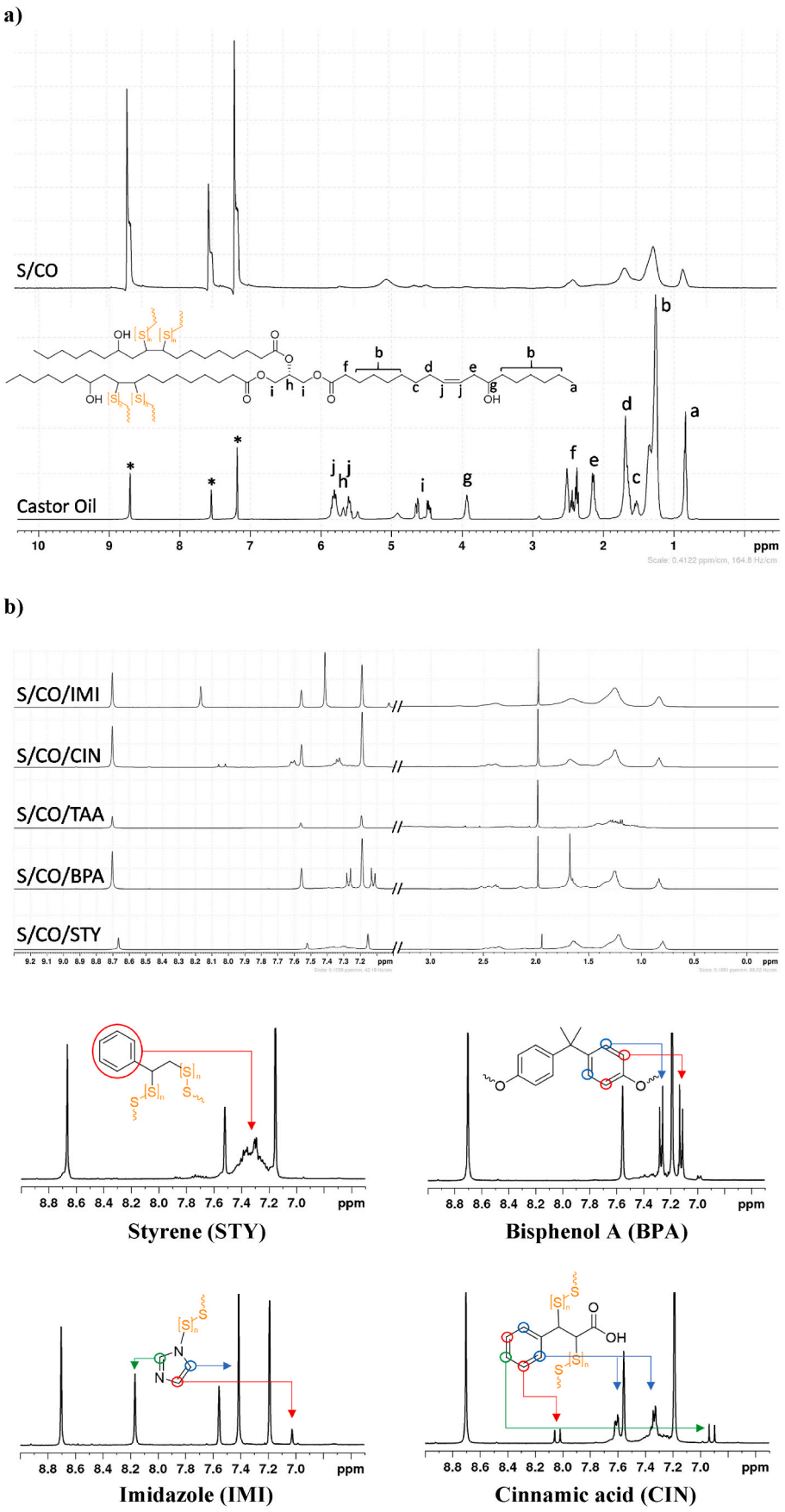

Fig. 3. a) ^{1}H NMR spectra of castor oil and hybrid copolymer structure. b) Comparative aromatic region of each copolymer and castor oil.

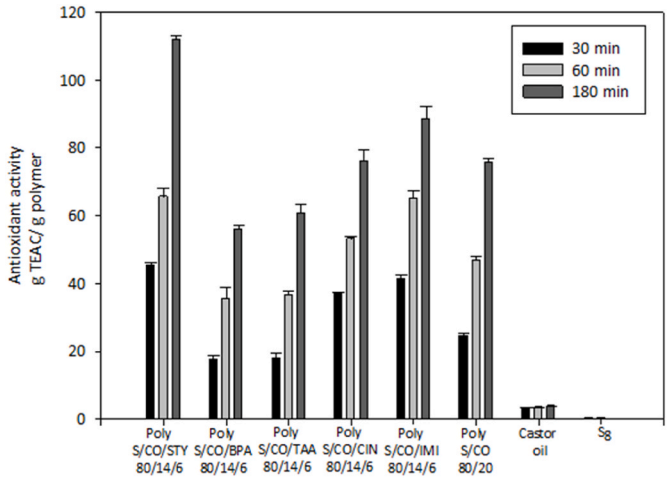

Fig. 4. Antioxidant activities from different new copolymers determined by DPPH.

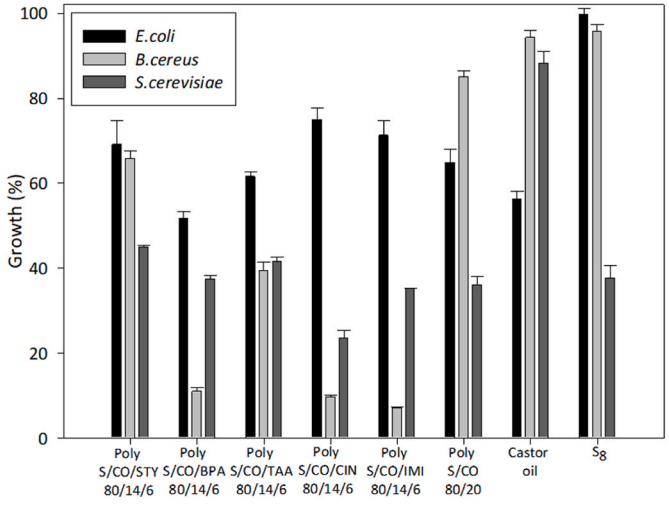

Fig. 5. Growth inhibition assay of the new copolymers against Gram - and Gram + bacteria and yeast.

also observed with S_8 (63%). It should be noted the action of CIM, which was the most active copolymer against *S. cerevisiae*, with growth inhibition of 76% (Fig. 5). This susceptibility to copolymer observed in *S. cerevisiae* could be due to the composition of its cell wall, which is mainly formed by a layered meshwork of β-glucans, chitin, and mannoproteins.

3.4. Promising strategy for a new generation of polymers with sulfur and phenol compounds

A new study utilizing waste products such as lignin has also used the inverse vulcanization process to form new copolymers [36]. Starting from substituting the hydroxyl groups of the lignins with allyl bromide, it can be favored the reaction of allyl lignin with S_8, whereby part of the sulfur forms cross-links polysulfide with lignin to produce a three-dimensional network. This research gives new avenues of studies of compounds with hydroxyl groups to form of new copolymers from the formation of allylic compounds and S_8 by inverse vulcanization that could have a higher antioxidant and antimicrobial capacity from the contribution of phytochemicals [19].

A previous study with BPA was carried out to form the allylation of the hydroxyl of BPA (BPA-Allyl), and subsequently, the inverse vulcanization reaction was performed. The formation of the two synthesized compounds (S/BPA-allyl:80/20) has been characterized by ^{1}H NMR. The reaction of BPA with allyl bromide (BPA-allyl) is observed to have been carried out almost entirely since no signal is observed in $\delta =$ 11.30 ppm of the hydroxyl group concerning the unreacted BPA (Fig. 6). In addition, it is observed that the signs of the double bond of the allyl group appear in $\delta = 5.20$, 5.44, and 6.06 ppm. Finally, when BPA-allyl reacts by inverse vulcanization with sulfur (S/BPA-allyl), the peaks of the double bond belonging to the allyl group disappear due to the union with sulfur (Fig. 6). These facts imply that this new strategy is valid for continuing the research with phenol compounds obtained from agro-wastes, offering new properties and applications to future polymers.

4. Conclusions

Different copolymers were prepared by inverse vulcanization with sulfur, castor oil, and a third chemical compound. These copolymers have been shown to have antioxidant power due to the heteroatoms of the third chemical compound. Furthermore, these copolymers have been antimicrobial activity, especially against Gram + bacteria such as *Bacillus cereus* and yeasts such as *Saccharomyces cerevisiae*. It is concluded that inverse vulcanization is an excellent method to obtain new copolymers using agro-wastes and a good option for synthesizing of new bioactive compounds with antioxidant and antimicrobial properties.

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Author contributions

Conceptualization, J.C.-C., P.G.V, R.L., and J.U.; methodology, J.C.-C., P.G.V, M.S.-M., and J.U.; resources, A.S., A.F.-R., R.F.D.V., R.B., F.G.F., and J.U.; writing—original draft preparation, J.C.-C..; writing—review and editing, A.S., A.F.-R., F.G.F., and J.U.; supervision, R.L., and J.U.; funding acquisition, A.A.C, J.E.M.A., R.B., F.G.F., and J.U.

All authors have read and agreed to the published version of the manuscript.

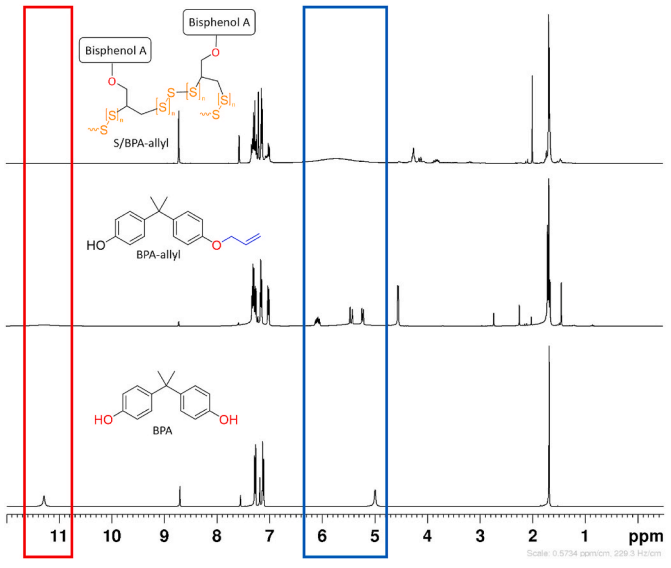

Fig. 6. ^{1}H NMR of BPA and BPA-allyl from the reaction with allyl bromide, and ^{1}H NMR spectra of BPA-allyl obtained by inverse vulcanization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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