Synthesis and Characterization of Menthol-Modified Poly (Methyl Acrylate) Composites: Application in Corrosion Protection

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Abstract**—**This study aims to valorize natural resources through the synthesis and characterization of innovative composites derived from mint leaves. The primary objective was to explore the potential of **menthol**, extracted from mint, as a functional agent incorporated into a **poly(methyl acrylate) (PMA)** matrix. PMA was synthesized via emulsion polymerization, a method known for its simplicity and low environmental impact. The possibility of grafting menthol onto the polymer chain was investigated to enhance the final material's properties. Spectroscopic analyses (**FTIR** and **UV-Vis**) confirmed the presence of characteristic functional groups, suggesting partial interaction or grafting between menthol and PMA. At a **17% menthol concentration**, a significant increase in both direct and indirect optical band gaps was observed, indicating improved structural organization of the polymer. The PMA chains likely adopt a more ordered arrangement, reducing electronic defects and promoting sharper optical transitions. This organization is probably stabilized by specific interactions, such as hydrogen bonding, between menthol and the polymer matrix. Gravimetric corrosion tests demonstrated the effectiveness of menthol in enhancing surface protection. The corrosion inhibition efficiency increased proportionally with the composite concentration, reaching a maximum of approximately 93.45%. Notably, this protective effect remained significant even at lower concentrations, confirming the material's potency as a corrosion inhibitor. The adsorption behavior followed the Langmuir isotherm model, indicating the formation of a monolayer on the metal surface. The calculated standard free energy of adsorption ($\Delta G° = –23$ kJ/mol) suggests a spontaneous physisorption process.

Keywords**—** Corrosion, Gravimetric, Menthol**,** PMA

1. INTRODUCTION

In modern industry, the durability of materials is a major concern, especially for metallic structures exposed to aggressive environments. Corrosion, a natural phenomenon of material degradation particularly in metals poses a significant economic and safety threat. Each year, economic losses caused by corrosion amount to billions of euros worldwide. Beyond financial costs, corrosion compromises the safety, reliability, and performance of equipment [1].

In response, various mitigation strategies have been developed, among which the use of corrosion inhibitors stands out as one of the most effective and economically viable methods [2]. Traditionally, corrosion inhibitors are organic or inorganic compounds that are often toxic and non-biodegradable. However, current environmental regulations and health standards demand a shift toward more eco-friendly materials. In this context, natural bioactive molecules are gaining increasing attention as sustainable alternatives.

Menthol, the major compound in essential oil extracted from mint leaves, has emerged as a promising candidate. It exhibits well-documented antibacterial properties [3] and contains chemically active functional groups (hydroxyls) that enable interactions with various surfaces, including polymers and metals. Moreover, polymers play a vital role in corrosion protection, biomedical devices, and packaging technologies [4]–[6]. These materials are widely used in the formulation of protective coatings, drug delivery systems, and active biodegradable films. Their versatility arises from their adjustable chemical properties, processability, and compatibility with functional additives. Poly(methyl acrylate) (PMA), a synthetic polymer from the polyacrylate family, is distinguished by its transparency, thermal and chemical stability, flexibility (due to its low glass transition temperature, approx. 9–12 °C), and ease of processing [7]–[9]. It also demonstrates good solubility in common organic solvents (e.g., THF, DMSO, ethyl acetate), which facilitates its use in both laboratory and industrial formulations [10]. To further enhance its functionality, chemical modification via grafting of bioactive molecules is a viable approach. Grafting allows the introduction of specific functional groups onto the polymer backbone without altering its fundamental properties, enabling the design of hybrid biomaterials with improved performance [11]. In this framework, the present study aims to develop a bifunctional composite material based on PMA grafted with menthol. This work involves the extraction of menthol from mint leaves by hydrodistillation, the synthesis of PMA via solution radical polymerization, followed by the chemical grafting of menthol onto the polymer in appropriate solvents. Grafting was carried out using varying amounts of menthol (0.1 g, 0.2 g, 0.4 g) to evaluate the influence of this parameter on the structure and properties of the final biocomposite. To characterize the resulting materials, two essential spectroscopic techniques were employed: Fourier Transform Infrared Spectroscopy (FTIR) to confirm the presence of menthol-

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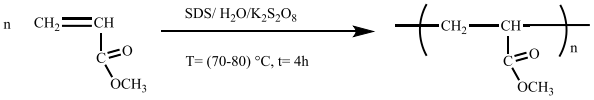
specific functional groups, and UV-Visible spectroscopy to study optical changes induced by menthol incorporation.

These analyses confirm successful grafting and provide insight into the molecular organization of the materials. Finally, the anticorrosion and antibacterial properties of the synthesized materials were evaluated to assess their potential for applications in metal surface protection and medical environments. The incorporation of natural compounds such as menthol into a polymeric matrix offers a sustainable alternative to traditional synthetic and often polluting additives [12].

II. EXPERIMENTAL

*A. Synthesis of **Poly(methyl acrylate)***

0.4 g of sodium dodecyl sulfate (SDS), used as an emulsifying agent, is added to distilled water contained in a sealed three-neck flask. The system is subjected to constant magnetic stirring. Then, methyl acrylate (MA) is gradually added to the solution. Next, 0.2 g of potassium persulfate, used as a radical initiator, is introduced to initiate the polymerization reaction. The reaction continues for 2 hours at a constant temperature of 80 °C.



At the end of the reaction, the polymer is recovered by initially drying the mixture. The solid is then dissolved in acetonitrile and precipitated in ethanol. Finally, the purified polymer is thoroughly dried at room temperature.

B. Grafting of Menthol onto Poly(methyl acrylate)

We evaluated the influence of menthol concentration on its chemical grafting onto poly(methyl acrylate) (PMA) chains by dissolving 1.00 g of PMA in 10 mL of dichloromethane, preparing menthol solutions of 0.10 g, 0.20 g, and 0.40 g in 10 mL of ethanol, and then mixing these solutions under magnetic stirring at room temperature for 4 hours.

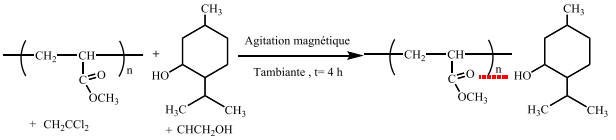


TABLE 1: QUANTITY AND PERCENTAGE OF MENTHOL ADDED TO THE COMPOSITES.

Composites	Menthol Quantity (g)	Menthol Weight (%)
0,1-MPMA,	0.1	9
0,2-MPMA	0.2	17
0,4-MPMA	0.4	29

III. CHARACTERIZATION

A. IR Spectroscopy (FTIR)

FTIR analysis of PMA samples containing increasing concentrations of menthol (9%, 17%, 29%) reveals significant changes in the characteristic bands around 3300 cm^{-1} (O–H stretch) and 1730 cm^{-1} (C=O stretch). The sample with 9% menthol shows the most pronounced spectral changes, notably a strong attenuation of the O–H band and a subtle broadening or shift of the C=O band**,** indicating strong hydrogen bonding interactions between menthol and PMA. At low concentration, menthol is more homogeneously dispersed in the polymer matrix, promoting effective interactions. At higher concentrations (17% and 29%), menthol tends to self-associate (via O–H groups), reducing its availability to interact with the polymer.

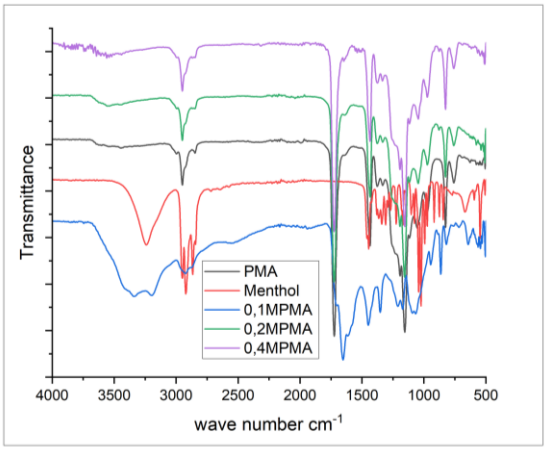


Fig. 1 – FTIR spectra of PMA, menthol, and the composites 0.1-MPMA, 0.2-MPMA, and 0.4-MPMA.

B. UV Spectroscopy Analysis

The UV-Visible spectra of PMA/menthol composites show a maximum absorbance between 200 and 300 nm, corresponding to π→π* or n→π* electronic transitions of the carbonyl groups in PMA. The sample containing 9% menthol exhibits the highest absorbance, indicating optimal interaction between menthol and the polymer matrix, likely through hydrogen bonding. At this concentration, menthol is well dispersed, promoting effective interaction with PMA.

In contrast, absorbance decreases in the 17% and 29% menthol samples, suggesting saturation of interaction sites or the formation of menthol micro-aggregates**,** which limit its effect. This behavior confirms that a low concentration of menthol allows for better incorporation and modification of the polymer's optical properties**.**

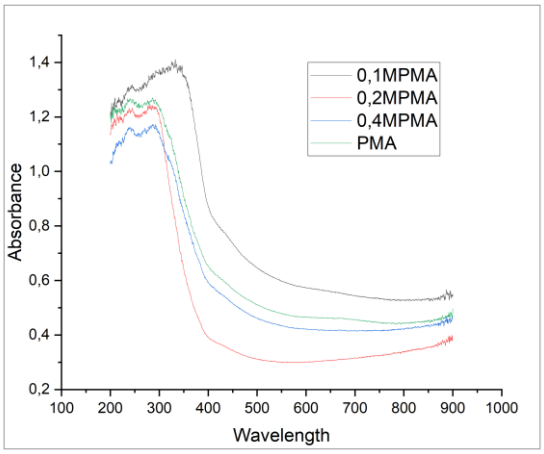


Fig. 2 – UV-Visible spectra of PMA and the composites 0.1-MPMA, 0.2-MPMA, and 0.4-MPMA.

III. GRAVIMETRY

The gravimetric method offers the advantage of simple implementation and does not require complex equipment. It is based on measuring the mass loss (Δm) of a sample with surface area **S**, after an immersion time **t** in a corrosive solution maintained at a constant temperature [13].

$$V = \frac{K}{t} \qquad K = \frac{(m0 - mt)}{s}$$

V: Corrosion rate.

$$E\,(\%) = \left(\frac{V - Vinh}{V}\right).100 \ (g/h.cm^2)$$

Where **V** and **Vinh** are the corrosion rates of the sample without and with the addition of the inhibitor, respectively.

Mass loss measurements provide an initial approach to study the corrosion inhibition of mild steel in an electrolytic solution**.** The dimensions of the mild steel samples used are 2.8 × 2.8 cm. These samples are immersed in 30 mL of 5% NaCl solution, with and without the addition of various PMA–Menthol composites (MPMA).

The inhibition efficiency is determined after 2 hours of immersion at 35 °C (see Fig. 3 and 4).

A B C D E F

Fig. 3 Visual appearance of mild steel before immersion at the same concentration of different composites: (A) in a 5% NaCl solution + 0.1 MPMA, (B) 5% NaCl + 0.2 MPMA, (C) 5% NaCl + 0.4 MPMA, (D) 5% NaCl + PMA, (E) 5% NaCl + Menthol, (F) 5% NaCl without composites.

A B C D E F

Fig. 4 Visual appearance of mild steel after 2 hours of immersion: (A) in a 5% NaCl solution + 0.1 MPMA, (B) 5% NaCl + 0.2 MPMA, (C) 5% NaCl + 0.4 MPMA, (D) 5% NaCl + PMA, (E) 5% NaCl + Menthol, (F) 5% NaCl without composites.

The value of the inhibition efficiency given is the average of three tests carried out under the same conditions for each mass. It is calculated using the following equation:

$$E(\%) = \left(\frac{V - Vinh}{V}\right).100 \ \ (g/h.cm^2)$$

where **V** and **V_inh** represent the average corrosion rates of the steel after immersion in the absence and presence of the inhibitor, respectively.

TABLE 1 CORROSION RATES AND INHIBITION EFFICIENCIES MEASURED FOR DIFFERENT MPMA COMPOSITES IN 5% NACL MEDIUM AT 35 °C FOR 2 HOURS.

Menthol Concentration in MPMA Composite	**Vinh (g/cm².h)**	**E (%)**
Blank (No inhibitor)	3,5	-
Menthol only	0,9993	71,77
PMA only	1,275	63.98
9 %	1,2865	63,66
17 %	1,28	63,84
29 %	1,0169	71,40

According to Figure 5 , it can be observed that the inhibition efficiency increases with the menthol concentration in the composite, reaching approximately 71.40%. This protective efficiency is significant even at low concentrations.

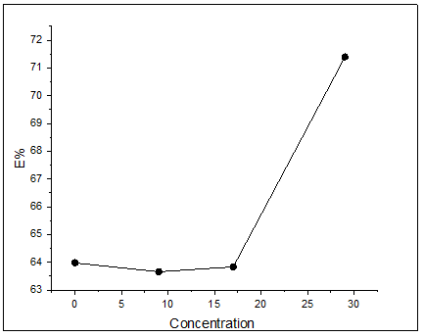


Fig. 5 – Evolution of the corrosion inhibition efficiency of mild steel immersed in 5% NaCl solution as a function of composite concentration.

Experimental procedure with a composite containing 29% menthol at different concentrations

The samples, of the same dimensions and under the same conditions, were immersed in 30 mL of a 5% NaCl solution, with or without the addition of various concentrations of the 29MPMA composite (containing 29% menthol). The corrosion

inhibition efficiency was determined after 2 hours of immersion at 35 °C.

TABLE II CORROSION RATES AND INHIBITION EFFICIENCIES FOR DIFFERENT CONCENTRATIONS OF 29MPMA IN THE CORROSION OF MILD STEEL IN 5% NACL AT 35°C FOR 2 HOURS.

Concentration of 29MPMA	**Vinh (g/cm2.h)**	**E (%)**
0,266	1,0169	71,40
0,66	0,9247	85,61
2	0,5165	91,96
2,66	0,409	93,45

The analysis of the results in Table 2 clearly shows that the composite exhibits excellent corrosion inhibiting properties for steel in a 5% NaCl environment. The variation in the inhibition efficiency (E) of the 29MPMA composite with its concentration is shown in Figure 6.

According to Figure 6, the inhibition efficiency increases with the composite concentration, reaching approximately 93.45%. This protective efficiency is significant even at low concentrations.

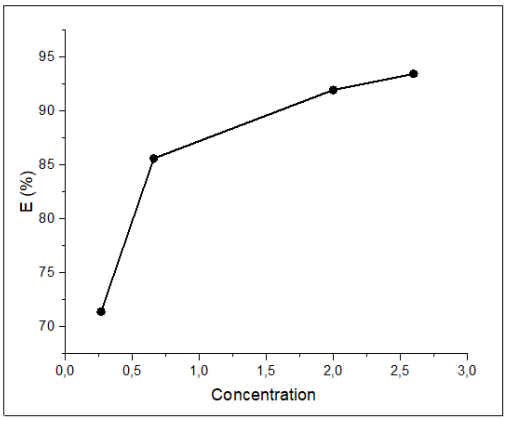


Fig. 6 – Evolution of the inhibition efficiency of mild steel immersed in 5% NaCl as a function of the 29MPMA composite concentration.

IV. ADSORPTION ISOTHERMS

The corrosion inhibition mechanism of the composite containing 29% menthol is explained by its adsorption onto the surface of the steel. This adsorption can occur in three forms: physisorption, chemisorption, or a mixed type.

The surface coverage (θ) for different concentrations of the inhibitor in a saline medium is defined using the following equation:

$$\Theta = \frac{V - Vinh}{V}$$

Where **V** and **Vinh** are the corrosion rates after 2 hours of immersion in the saline medium without and with the addition of the inhibitor, respectively. The adsorption of the composite was studied according to the Langmuir adsorption isotherm.

The metal surface coverage rate is given by the following relation:

$$\Theta = \frac{KC}{KC+1}$$

Where **K** denotes the adsorption coefficient or the equilibrium constant of the adsorption process, and **C** is the concentration of the inhibitor. Rearranging this equation gives:

$$\frac{C}{\theta} = \frac{1}{K} + C$$

Table– Concentration of 29MPMA composite and the ratio C/θ

C g/L	C/θ
0,266	0,3725
0,66	0,7709
2	2,1748
2,66	2,8464

Figure 7 shows the variation of the ratio C/θ as a function of the composite concentration, which is linear. This indicates that the adsorption of the composite on the steel surface in a 5% NaCl medium follows the Langmuir adsorption isotherm, with a slope value of 0.99.

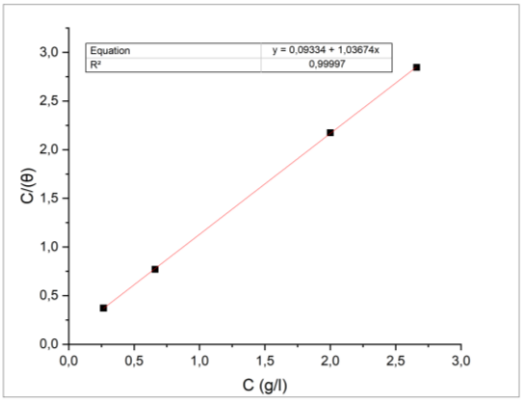


Fig.7 – Langmuir adsorption isotherm of 29MPMA composite at different concentrations on mild steel in 5% NaCl at T = 35°C.

This clearly shows the formation of a monolayer and the absence of interactions between the adsorbed molecules. It is observed that the linear correlation coefficient is close to 1, and the slope value is nearly equal to unity. This confirms that the adsorption of the molecules follows the Langmuir isotherm, and the equilibrium constant of the adsorption process is related to the standard free energy of adsorption (**ΔG°**) by the following relation:

$$\Delta G°ads = -(1000K)$$

With the water concentration taken as 1000 g·L^{-1} in the solution, the thermodynamic data obtained from the Langmuir isotherm for the studied 29MPMA composite are as follows:

$$\Delta G°ads = -23750{,}08 \text{ kJ mol}^{-1}, (K = 10{,}7135 \text{ g.l}^{-1})$$

The negative value of ΔG° indicates the spontaneity of the adsorption process and the stability of the adsorbed layer on the metal surface [14].

A value of ΔG° around -20 kJ·mol^{-1} or less negative is associated with electrostatic interactions between charged molecules and the charged metal surface (physical adsorption), whereas a value close to -40 kJ·mol^{-1} or more negative implies charge transfer between organic molecules and the metal surface (chemisorption) [15].

The measured ΔG° value is –23 kJ/mol, indicating spontaneous physical adsorption characterized by electrostatic interactions and van der Waals forces.

V. CONCLUSION

This work aimed to valorize mint leaves by incorporating menthol, a natural extract, into a poly(methyl acrylate) (PMA) polymer matrix synthesized via emulsion polymerization. The study demonstrated the possibility of partial grafting of menthol onto PMA, confirmed by spectroscopic analyses (FTIR, UV-Vis). Corrosion tests revealed an increasing protective effect with higher menthol concentration. The adsorption of the composite on mild steel follows a Langmuir isotherm, indicating spontaneous physical adsorption (ΔG° = –23 kJ/mol). These findings open promising perspectives for the development of bioactive composite materials based on plant extracts.

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