

Study of the behavior of an Epoxy coating food contact

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Abstract

Epoxyes have been used in the internal coating of cans to endure a long shelf life for canned goods; several types of interactions exist between this kind of packaging (container) and the packed product (contained). This container/contained contact can influence the properties of the packed product, we are interested in this study to contribute to the development of a new formulation in order to prepare an Epoxy coating able to come in contact with foodstuffs, thus our studies based on a selective choice of raw materials that respect the international regulation of food contact, while taking into account the stoichiometric parameters to have a well-cross-linked and resistant polymer.

However, the aim of this work is to study the behavior of this developed epoxy coating in contact with different simulant, which represent three categories of food. Within this study, we have characterized the epoxy paint by infra-red, and we have follow the mass variation and the sorption's kinetics of water, acid acetic, and ethanol in contact with epoxy film by the gravimetric technique, the results allowed us to calculate the diffusion coefficient of each simulant, and then compute the activation energy and thermodynamic parameters.

Moreover, the results of the gravimetric method show that the temperature impact the kinetics of diffusion more than the contact time do, the mass transfer depends on the nature of the simulant in contact and on its physic-chemical properties, it concluded also the mass stability of the epoxy coating from 25°C to 40°C.

Keywords: Epoxy, Absorption, food simulant, kinetics sorption, gravimetric method.

1. Introduction

Food and beverage cans usually have an internal thin coating layer in order to avoid direct contact between food and metal. Such coating can be based on vinylic, phenolic lacquers or epoxy resins [1]. Epoxy resins are currently used as matrices in advanced polymer materials because of their superior thermal, mechanical, and corrosion resistance properties [2]. Epoxies are thermoset polymers obtained by reaction within epichlorohydrin and bisphenol A (BPA) [3], they form particularly strong bonds with many materials, and some monomers can remain into the coating and later migrate to food, with a speed and extent depending on food characteristics [4]. The global demand of epoxy resin was estimated at roughly 18.6 billion \$ US in 2013 and was forecasted to reach 25.8 billion \$ US by 2018[5]. This increase in value reflects the increasing demand of epoxy resins in the global market over the coming years. Since the 1950s, epoxies have been used in the internal coating of cans to endure a long shelf life for canned goods, preserving them for many years [6]. According to recent data, the EU food and drink packaging industry, food and water industries (which include water delivery applications) use 17,600 tonnes of epoxy resins sold by ERC members every year [7]. This kind of materials should be sufficiently inert so that their constituents neither adversely affect consumer health nor affect the quality of the food [8], however the hydrophilic groups of epoxy resins absorb liquid molecules that consequently alter the physical and mechanical properties of the epoxy film [9]. Recca had reported in his study about epoxy resins for aerospace market that water absorption decreases the thermo-mechanical properties of composite materials [2]. Apicella, proposed three different modes for water sorption in an epoxy resin: (a) bulk dissociation of water in the polymer network; (b) moisture sorption onto the surface of holes that define the excess free volume of the glassy structure; and (c) hydrogen bonding between hydrophilic groups of the polymer and water. He also reported that the chemical structure of the polymer matrix constituents, as well as the processing conditions, influence the resulting polymer networks and hence the properties of the cross-linked polymer in wet environment [9]. In addition, the cross-linked network structure of epoxy resin expected to have water uptake, which is strongly bonded to polar nature of the specific functional groups [10]. The absorbed moisture can cause permanent chemical and physical changes by including crazes or micro cavities, and therefore accelerate the moisture diffusion, further [11]. The reaction with food components probably occurred during post packaging high temperature treatments of cans, in order to sterilize the content and thus obtain a prolonged shelf life [12]. Those kind of reactions between coating and food, and their toxicological profile importance, reveal a very little research that has been done in this aim (4118 articles on packaging, 1285 articles on food contact packaging versus only 120 articles on the migration of food contact materials) [13]. The water absorption effects in epoxies have been investigated using various techniques [14], so the originality of this study is that we had report the kinetics absorption of epoxy coating in contact with water, acid and ethanol. In order to predict the behavior towards foodstuffs of an epoxy coating that we had prepared in our laboratory using a selective raw material, a gravimetric method is used. The overall objective of the present work is to understand the performance and the characteristics of our epoxy film in contact with different simulant (water, acid, and ethanol), also studying the impact of temperature and time contact in his chemicals stability, and his degradations kinetics. The simulants used in this work represent three food families, whose adsorption, solubilization and absorption behaviors differ, (water for aqueous food, acid acetic for acidic food, and ethanol for alcoholic foods) [15].

2. Materials and methods

2.1. Synthesis of food contact epoxy paint:

Epoxy FC, is a solvent free epoxy paint based on Bisphenol A (Epichlorohydrin) epoxy resin (78%), and Alkyl Phenol polyamine as curing agent. Other products such as quartz and TiO₂ pigment have been added to improve the stability of our paint and to cover the substrate. The stoichiometric coefficient between the epoxy paint and the curing agent

(hardener), was a culmination of much previous work on the stability and the inertia of these food contact materials, to improve the cross linking of our developed paint. The formulation of epoxy and polyamine agent mixture applied in a scraper coating device with a thickness of 0.06 cm, and was left to dry for 24 hours before characterizing it and using it in the gravimetric technique.

2.2. FTIR-RA:

Fourier Transform Infrared Spectroscopy is based on the absorption of infrared radiation by the film of epoxy analyzed. It allows, via the detection of the characteristic vibrations of chemical bonds, perform the analysis of the chemical functions present in our coating. The infrared spectra recorded on a Nicolet Is10 FTIR-ATR spectrophotometer.

2.3. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA):

Differential thermal analysis and thermo gravimetric analysis (TGA 60 H SHIMADZU) scans carried out using about 20 mg of powder in platinum crucible and heating in 20- 120°C temperature range at the rate of 2.5°C/min.

2.4. Kinetics of evolution of the epoxy mass:

Gravimetric method is one of the methods used for studying the sorption of a liquid in solid material. In order to follow the evolution of the mass of the formulated epoxy. 54 samples of drayed Epoxy film with an area of 1dm² and 1.4g each, prepared for each temperature test (324 samples for global tests), and then immersed in 100ml of three solutions (distilled water, acetic acid 3%, ethanol 15%), under the effect of different temperatures from 25 °C to 80 °C and time contact from 5 min to 300 min. The protocol consists to prepare the samples beforehand, then putting them into contact with the chosen solution. Over time, the sample removed, wiped, dried and weighed to calculate the difference in mass before and after contact. Weightings carried out on a **PRECISA scale (250)**.

2.5. Calculation of the percentage of mass variation:

Equation (1) used to calculate the percentage change in mass of the epoxy sample after contact with simulants as a function of the residence time of the sample in the solution and at a temperature considered.

$$\Delta m = \frac{m_t - m_0}{m_0} \times 100 \quad (1) \quad [16]$$

With: **m₀**: designates the initial mass of the sample and **m_t**: the mass of the sample after an exposure time t.

The mass is raised when it is stable, or after a fixed duration (of the order of 10 minutes). We repeated the same procedure for each simulant. This study is devoted to the kinetic study of a film of epoxy paint in three simulants (acetic acid, distilled water, Ethanol ...), in this context, the temperature varied and then the mass variation in each simulant followed.

Calculation of the diffusion coefficient:

Diffusion is the process of transferring material from one part of the system to another. It is the result of random movements of molecules in the system. Consider two areas of the same system with different concentrations, where the molecules move randomly. A large number of molecules will move from the high concentration zone to the low concentration zone. This explained by the fact that in the high concentration zone, there are more migrating molecules. Therefore, a higher probability of these molecules will move towards the low concentration zone [17]. For the study of molecule diffusion in a polymer, we take the following simplifying assumptions:

- The distribution is done in accordance to Fick's laws,
- The diffusion coefficient is independent of the concentration,
- Diffusion in the plate is assumed to be unidirectional,
- The plate is considered to be symmetrical,
- The change in size of the plate during sorption is considered negligible.

For the Diffusion by the two sides of the film, the mathematical model given by the law of Fick is the following:

$$\frac{C(t,x)}{C_{\infty}} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left(-\frac{D(2n+1)^2 \pi^2}{L^2} t\right) \times \sin\left(\frac{(2n+1)\pi}{L} x\right) \quad (2) [18]$$

The quantity of liquid absorbed M_t by the polymer during a time t obtained by integrating the concentration $C(t, x)$ over the entire thickness L of the sample:

$$M_t = \int_0^L C(t, x) dx \quad (3) [18]$$

Which gives from equation (2):

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left[-\frac{D(2n+1)^2 \pi^2}{L^2} t\right] \quad (4) [18]$$

Where M_{∞} is the mass absorbed by the sample at thermodynamic equilibrium. This type of kinetics has a linear part for short diffusion times, $(M_t / M_{\infty}) \leq 0.55$, equation (2) simplified as follow:

$$\frac{M_t}{M_{\infty}} = \frac{4}{L} \sqrt{\frac{Dt}{\pi}} \quad (5) [18]$$

The latter equation is widely used to determine the diffusion coefficient of a solvent entering a polymer until a thermodynamic equilibrium established between the polymer and the solvent. Indeed, by plotting $M_t / M_{\infty} = f(t^{1/2})$, the slope α (linear part of the kinetics for short times on the curve $M_t / M_{\infty} = f(t^{1/2})$) gives direct access to the diffusion coefficient by the following relationship [13]:

$$D = \pi \left(\frac{\alpha L}{4} \right)^2 \quad (6) [18]$$

2.6. Calculation of activation energy for the different simulant at two different temperatures:

The dependence of the diffusion coefficient on temperature given by the following equation:

$$\ln D_1 = \ln(A) - E_a / RT_1 \quad (14) [19]$$

$$\ln D_2 = \ln(A) - E_a / RT_2 \quad (15) [19]$$

where A , E_a , R , and T are a pre-exponential factor, the activation energy of diffusion, the gas constant and the absolute temperature respectively.

If we subtract the two equations (14) and (15), we can easily deduce the activation energy.

2.7. Number of moles sorbed by the epoxy film:

The number of moles sorbed calculated by the following equation:

$$\frac{\Delta m}{W_p} = \frac{m_s}{W_p} \quad (16) [20]$$

Where, Δm is the mass variation calculated by equation (1), and m_s is the mass molar of each stimulant and W_p is the weight of polymer.

2.10. Volume fraction of the epoxy polymer:

The volume fraction of polymer in the swollen sample calculated using the following equation:

$$\phi = W_1 \rho / (W_1 \rho_p + W_2 \rho_s) \quad (17) [21]$$

Where, W_1 is weight of polymer, p_p is the density of polymer, W_2 is the weight of sorbed stimulant, and p_s is the density of stimulant.

2.11. Thermodynamic parameters:

The thermodynamic parameters of the adsorption reaction at equilibrium: standard free enthalpy ΔG° , standard enthalpy ΔH° and standard entropy ΔS° calculated in order to study the characteristics of the adsorption process of Epoxy in contact with different stimulant. The diffusion coefficient D makes it possible to determine all these thermodynamic quantities based on the following equations [22]:

$$\ln(D) = -\frac{\Delta H^\circ}{R.T} + \frac{\Delta S^\circ}{R} \quad (18) [22]$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (19) [23]$$

3. Results and discussions:

3.1. FTIR spectra:

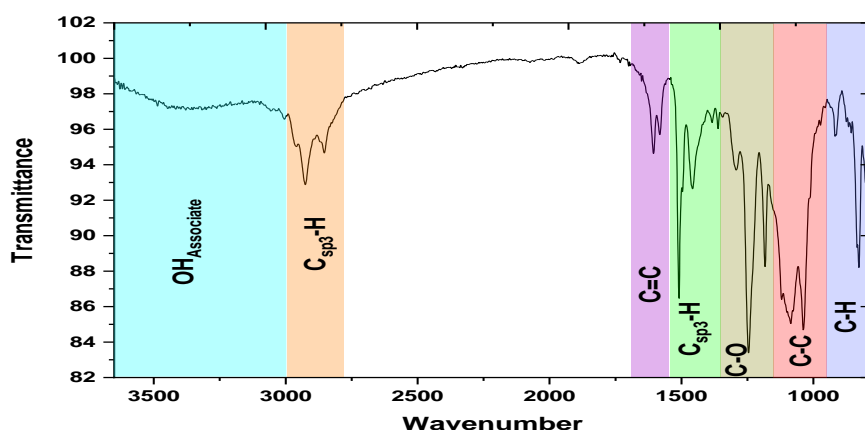


Fig.1: FT-IR spectrum of the epoxy film.

The infrared spectrum of the epoxy film shown in the figure 1; we have established the allocation of the different absorption bands, and we deduced the following points:

- 2900-2830 cm^{-1} "medium intensity" double peak band indicates C-H sp^3 elongation vibrations.
- 1650, 1600 cm^{-1} "Medium intensity" corresponds to several modes of elongation of the bonds C = C (sp^2).
- 1400-1480 cm^{-1} double-peak band moderately intense corresponds to elongations in the plane of C-Hybrid Sp^3 [C-H] bonds due to alkyl functions.
- 1200-1280 cm^{-1} high intensity band checks the presence of the C-O bond.
- 1050 and 1100 cm^{-1} high intensity band corresponds to the presence of C-C bonds in the molecule the order of 800 cm^{-1} .

The presence of a high intensity band between 1200 and 1280 verifies the presence of the C-O bond in the analyzed product, and the absence of a broad band indicates the presence of an OH bond in the order of 3400 cm^{-1} , also the absence of a band on the spectrum indicates the presence of a group C=O, these readings gives a strong chance that the analyzed product is either an Epoxy;

Several authors have characterized epoxy-amine systems, using Fourier transform infrared spectroscopy [24].

This technique has allowed several researchers [24] to study hydrogen bonds in epoxy-amine networks. These studies suggest the existence of many of these links in the networks, which persist over the glass transition (T_g) to the point of thermal decomposition. Bellenger et al. [25] and Williams et al. [25] shows that the unbound hydroxyl absorption band at about 3600 cm^{-1} hindered by the presence of a broad band of bound hydroxyls at $3600\text{--}3200\text{ cm}^{-1}$, attributed to hydrogen bond formation.

3.2. Thermo gravimetric analysis (TGA)/ Differential thermal analysis (DTA):

Thermo gravimetric analysis (TGA) consists of measuring the mass variation of the Epoxy film during a thermal cycle. [26]. The values obtained derived from the evolution of the parameters of the sample compared to that of a reference used as an inert standard.

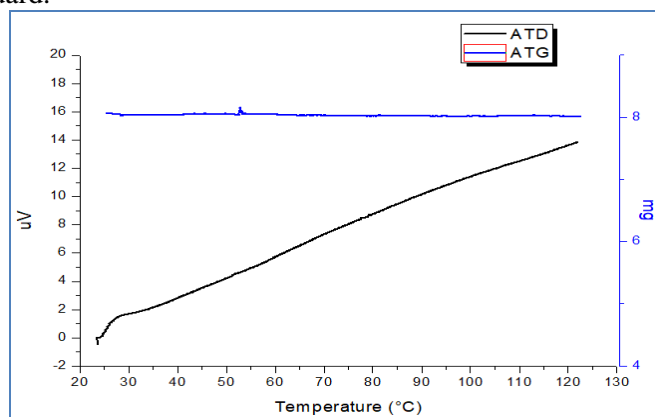


Fig.2: Thermo gravimetric curve of epoxy film.

As described the Figure 2, the curve of Thermo gravimetric analysis shows that there is no loss of mass during the temperature range of $25\text{ }^{\circ}\text{C}$ to $130\text{ }^{\circ}\text{C}$; Over the same temperature range (ThiHai Yen Qhach 2010) [27], performed thermal-gravimetric analyzes on a normal epoxy film and recorded a mass loss of 0.72% between $45\text{ }^{\circ}\text{C}$ and $130\text{ }^{\circ}\text{C}$ which is attributable to the evaporation of volatil organic compounds.

3.3. Kinetics of evolution of the epoxy mass:

As can be seen in the figures 3, 4, 5, 6, 7 and 8, the results of the variation in the mass of the epoxy paint film in contact with the different simulants for 300 minutes at sex different temperatures, shows that there is a stability of the mass up to $40\text{ }^{\circ}\text{C}$.

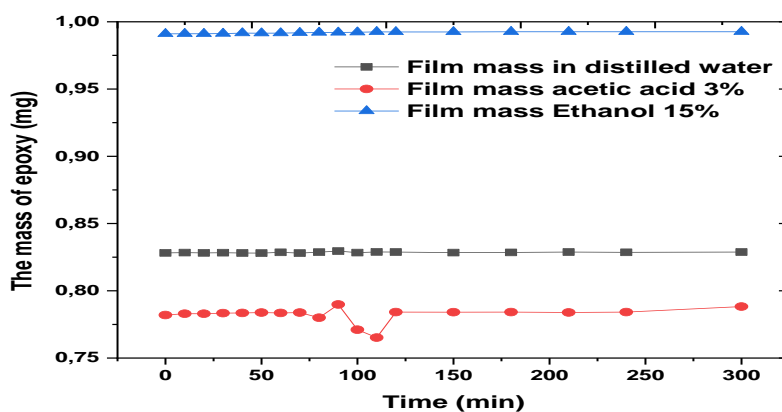


Fig.3: Evolution of the mass of epoxy film in contact with the simulants at 25°C .

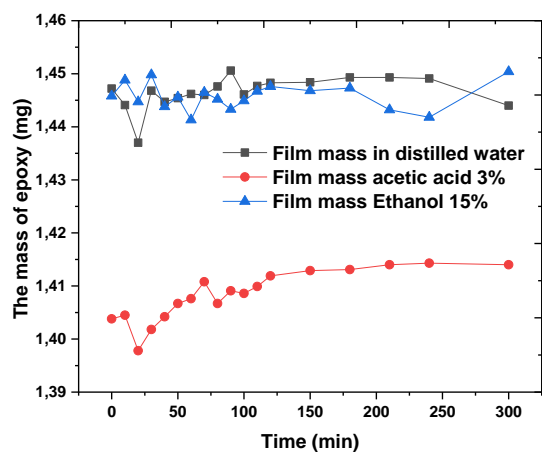


Fig.4: Evolution of the mass of epoxy film in contact with the simulants at 30°C.

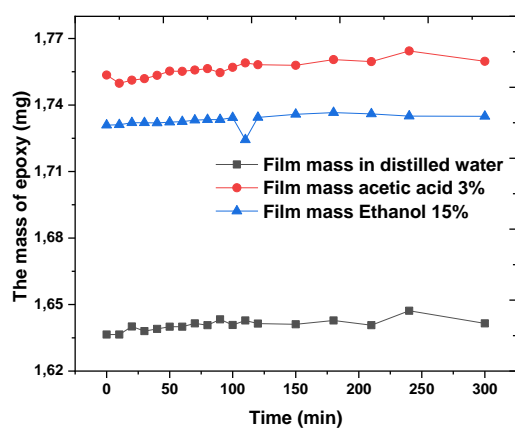


Fig.5: Evolution of the mass of epoxy film in contact with the simulants at 40°C.

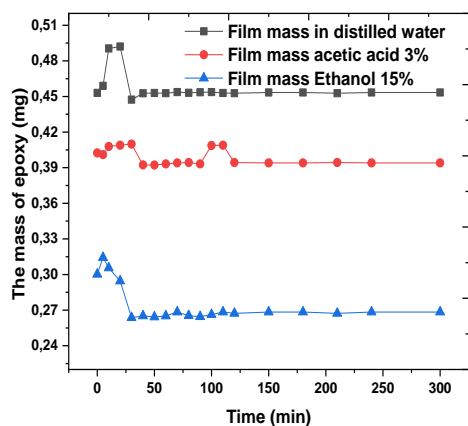


Fig.6: Evolution of the mass of epoxy film in contact with the simulants at 60°C.

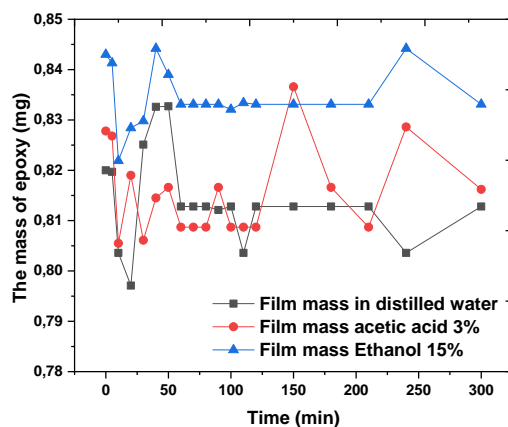


Fig.7: Evolution of the mass of epoxy film in contact with the simulants at 70°C.

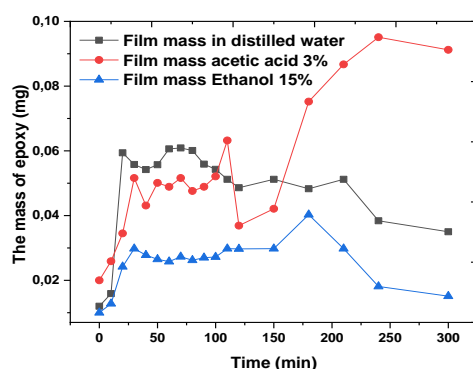


Fig.8: Evolution of the mass of epoxy film in contact with the simulants at 80°C.

The follow-up of the kinetics mass variation of epoxy in contact with different simulants, shows that the effect of the temperature is more important compared to that of the contact time, which remains insignificant. The results also show that, absorption is favored compared to the desorption which only takes place at 70 °C, explained by the fact that the epoxy resin does not resist beyond this temperature[28], and that our film begins to undergo degradation or cutting molecular bonds at this temperature. In addition, we see a significant absorption at 80 °C, explained by a cracking of the film at this temperature [29].

3.4. Sorption kinetics of the different simulants at sex different temperatures:

The calculation of the quantity sorbed, as a function of temperature, can be seen in the table1.

Table 1: Sorption kinetics of the different simulants at different temperature.

Temperature	25°C	30°C	40°C	60°C	70°C	80°C
Q sorbed water (mg)	0.00975	-0.0118	0.06776	0.24988	-0.2126	82.1459
Q sorbed acid acetic (mg)	0.00898	0.0833	0.04035	0.10082	-0.426	42.4439
Q sorbed ethanol (mg)	0.02466	-0.0009	0.03157	-2.3262	-0.3471	39.9041

The results shows that, the quantity absorbed by the various simulants by the epoxy film at 25°C is very negligible compared to 60°C and 80°C, and that that of the water is more important compared to that of ethanol followed by acetic acid, explained by its low molar mass. This can show that the epoxy film produced contains more meso-sites and microsites than macro-sites, which proves a high density of polymer cross-linking [30]. We also note from the study of the sorbed quantity, that the saturation of the sites with ethanol is faster in comparison with water and acid, the nature and the length of its molecular chain can explain this phenomenon.

3.5. Calculation of Diffusion Coefficient:

In our case, and in order to calculate the diffusion coefficient of the different simulants in contact with the epoxy film at room temperature, the absorption curve as a function of $t^{1/2}$, plotted, which is supposed that is of the Fickian type [31]. To identify the type of sorption, we adopt a more adequate representation and which consists in plotting the evolution of the ratio between the mass M_t of the different simulants in the polymer at the time t of aging and that at equilibrium M_∞ , as a function of the square root of time of contact.

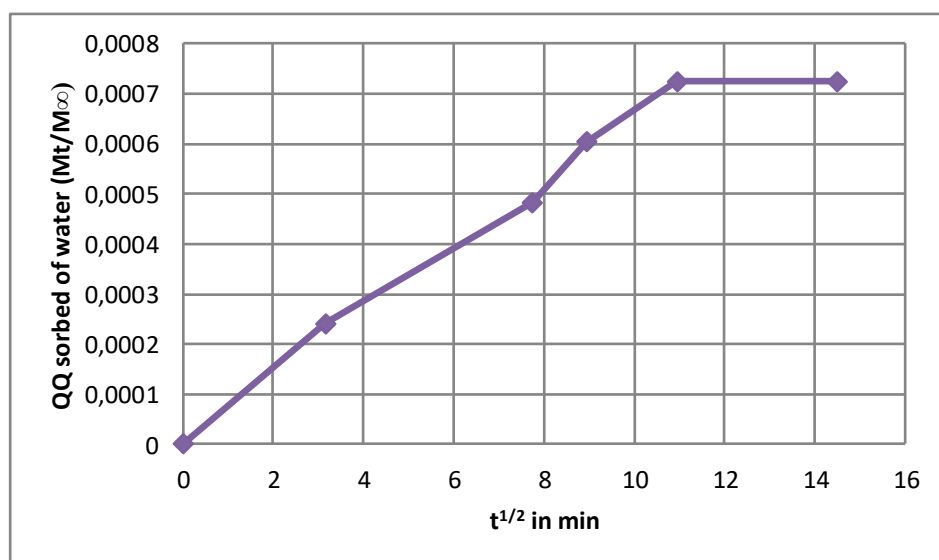


Fig. 9: Sorption kinetics of epoxy in contact with water at 25°C.

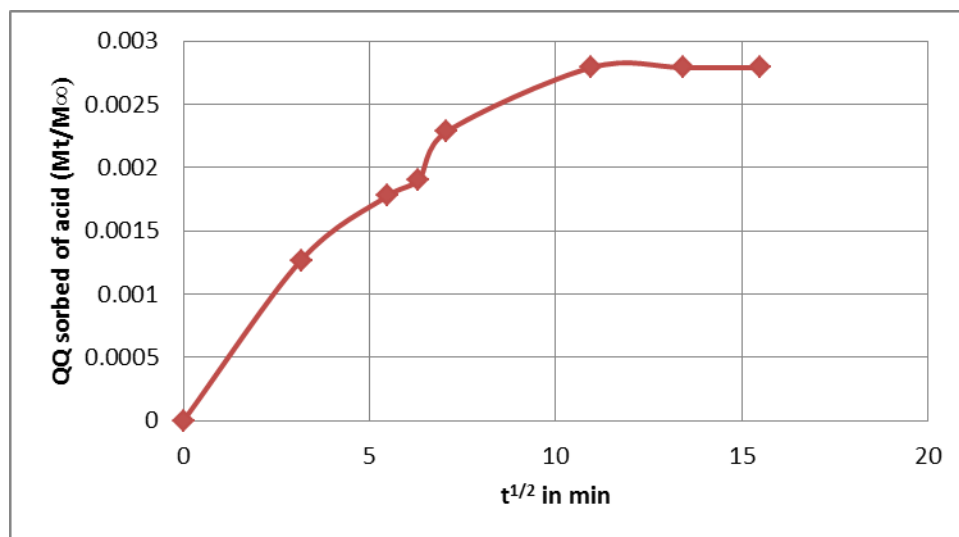


Fig.10: Sorption kinetics of epoxy in contact with Acid at 25°C.

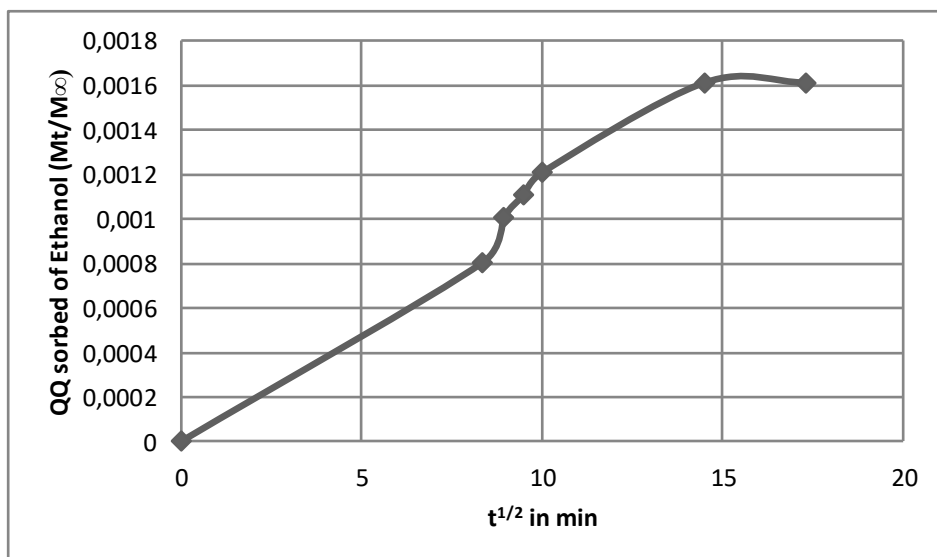


Fig.11: Sorption kinetics of epoxy in contact with Ethanol at 25°C.

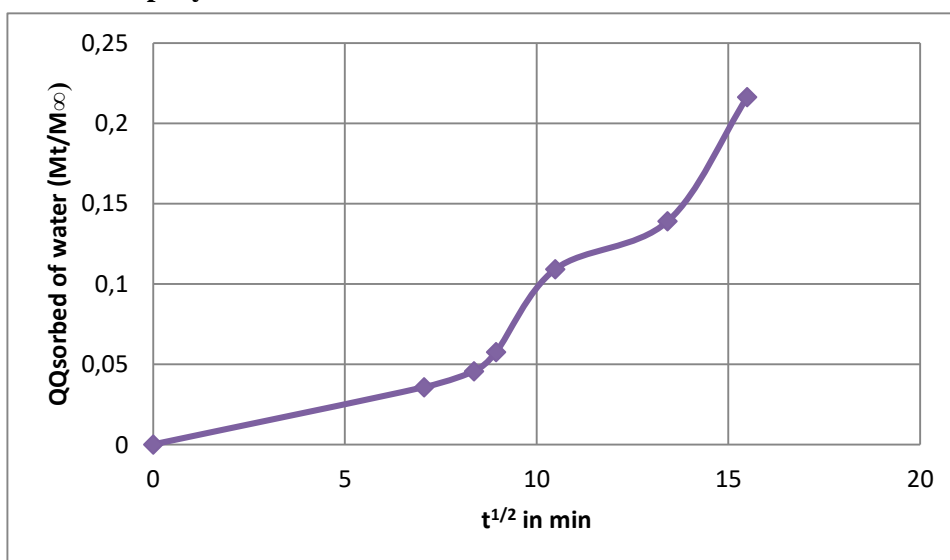


Fig.12: Sorption kinetics of epoxy in contact with water at 40°C.

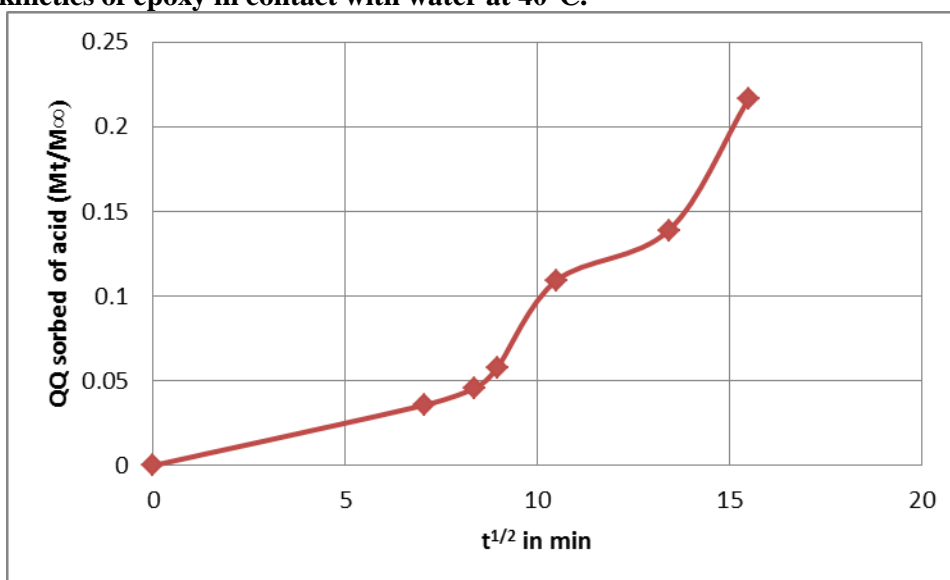


Fig.13: Sorption kinetics of epoxy in contact with acid acetic at 40°C.

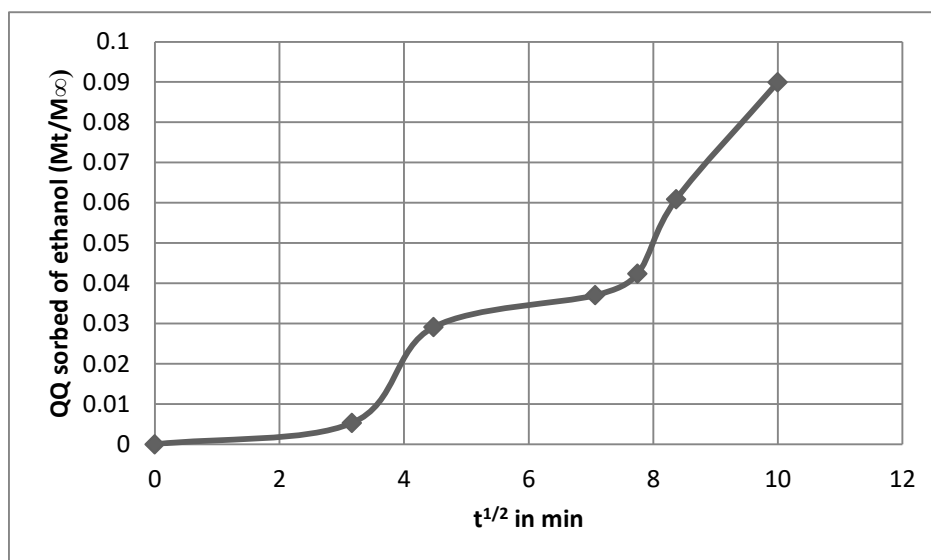


Fig.14: Sorption kinetics of epoxy in contact with Ethanol at 40°C.

Us shows the figures 9, 10, 11, 12, 13 and 14, the diffusion coefficient D , calculated from equation 6 by knowing the thickness L of the Epoxy film, which is of the order of 0.06 cm, the table 2 and 3 represents the diffusion coefficients of each stimulant at 25°C and 40°C.

Table 2: Diffusion coefficient of different stimulant in contact with epoxy at 25°C.

WATER DIFFUSION COEFFICIENT AT T=25°C	1.143E-15
ACID DIFFUSION COEFFICIENT AT T=25°C	31.583E-15
ETHANOL DIFFUSION COEFFICIENT AT T=25°C	1.821E-15

Table 3: Diffusion coefficient of different stimulant in contact with epoxy at 40°C.

WATER DIFFUSION COEFFICIENT AT T=40°C	2.489E-12
ACID DIFFUSION COEFFICIENT AT T=40°C	5.006E-12
ETHANOL DIFFUSION COEFFICIENT AT T=40°C	5.494E-12

Diffusion coefficient of the three simulants in contact with the epoxy film at 25°C, over 300 minutes, shows that of the acid is greater followed by ethanol and that water has the lowest coefficient of diffusion. These results have been confirmed by calculating the number of moles entering for each simulant at this temperature, of which we find that the number of moles absorbed by the acid is the largest followed by ethanol and that the number of moles absorbed of water is the weakest. Table 3 shows that the diffusion is quietly rise from as the temperature increases from room temperature to 40°C. Mousa Ghaemy, Anita Hassanpour Shahriari, and Seyed Mojtaba Amini Nasab, worked on Cure Kinetics and Water Absorption of epoxy, they found that the diffusion coefficient rises from $1.6 \times 10^{-12} \text{ m}^2/\text{s}$ to $7.1 \times 10^{-12} \text{ m}^2/\text{s}$ as the water temperature increases from room temperature to 65°C [32]. While our results as can be seen in tables 2 and 3, the coefficients diffusion rise from $1 \times 10^{-15} \text{ m}^2/\text{s}$ to $2 \times 10^{-12} \text{ m}^2/\text{s}$ for water, in general we can resume that those results represent a micro diffusion.

3.6. Calculation of activation energy for the different simulant at two different temperatures:

Table 4: Activation energy of the different simulants sorbed by the epoxy film at different temperatures.

ACTIVATION ENERGY of water (KJ/mol)	3.98E+02
ACTIVATION ENERGY of acid (KJ/mol)	2.62E+02
ACTIVATION ENERGY of ethanol (KJ/mol)	4.15E+02

As can be seen in the table 4, the activation energy of ethanol and water is greater than Ea acid, but in general, those results represent a high value, which shows a very weak interaction between epoxy and simulants, many researchers recorded different values of 41.8 kJ/mole and 26.8 kJ/mol for their research on different materials system [33]. Overall the diffusion of the three stimulants is extremely low in the order of 10^{-15} very lower parts per trillion. It is a phenomenon, which is favored by the temperature between 25°C to 40°C, but it remains all the same very weak. Which confirm that we need too much activation energy to promote this phenomenon.

3.7. Number of moles of the different simulants sorbed by the epoxy film at different temperatures:

The positive values for the numbers of moles absorbed by the epoxy film in contact with different simulant present in table 5, represent an absorption phenomenon which has taken place, while the negative values explain that there is a desorption. By analyzing this data, the effect of the temperature is more important on the kinetics of water absorption. Moreover at 60°C the desorption of ethanol is favored, justified perhaps by the fact that this temperature is close to its boiling point (78°C), those results are in accordance with the test of global migration prepared on our last paper, showing that the migrate quantity of the ethanol is the largest compared with acid and water[34].

Table 5: Number of moles of the different simulants sorbed by the epoxy film at different temperatures

Temperature	25°C	30°C	40°C	60°C	70°C	80°C
Nbr of mole sorbed water	0.00296	-0.0451	0.22984	3.08145	-1.4392	379.982
Nbr of mole sorbed acid	0.01873	0.09881	0.03832	0.1152	-0.8569	35.3393
Nbr of mole sorbed ethanol	0.0037	-0.0014	0.03959	-15.782	-0.8938	86.6162

3.8. Volume fraction of the epoxy polymer in contact with different stimulants at different temperatures:

Table 6, illustrates the results of calculating the fraction of the volume of our polymer for each simulant of contact as a function of temperature. The free volume is practically stable for the three simulants from 25°C to 40°C. At 60°C, this volume experienced a fall explained by the absorption phenomenon, which took place.

Table 6: The volume fraction of the epoxy polymer in contact with different stimulants at different temperatures.

Temperature	25°C	30°C	40°C	60°C	70°C	80°C
Volume fraction epoxy in Water	0.99	1.01234	0.93438	0.79428	1.28265	0.01161
Volume fraction epoxy in acid	0.99365	0.94398	0.97206	0.93299	1.43566	0.03202
Volume fraction epoxy in ethanol	0.96864	1.00118	0.96019	-0.4866	1.83782	0.01872

The occupation of the free sites by the different simulants increases at 70°C as explained previously by the results of the sorbed quantity. These findings justified by the phenomenon of desorption and which was important in the case of ethanol followed by acid and water, at 80°C. This volume is very small although the quantity absorbed is large; this reduction is justified by the fact that at this temperature there was cracking of the film. Many studies by other workers [35] of water sorption in epoxy resins demonstrates a variation from about 10^{-7} and 10^{-9} for the diffusion coefficient, using gravimetric method, but just a few researchers are studying the effect of the nature or chemical and physical properties of different stimulants on the behavior of epoxy film [13]. The conclusion of the impact of the effect of temperature on diffusion, shown in a study by Oussama Zaki to calculate the sorbed amount of amyl acetate in polypropylene at 23°C and 40°C [36].

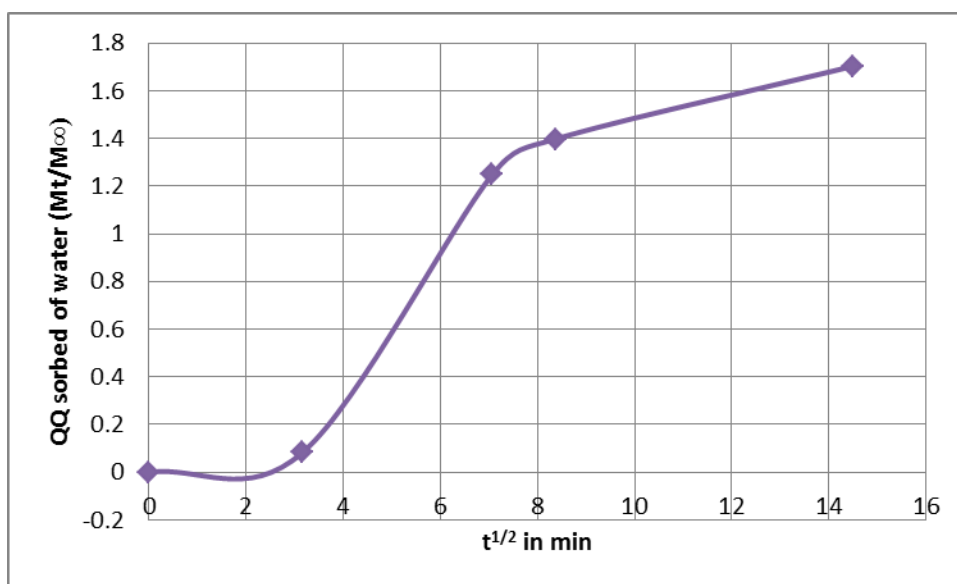


Fig.15: Sorption kinetics of epoxy in contact with water at 80°C.

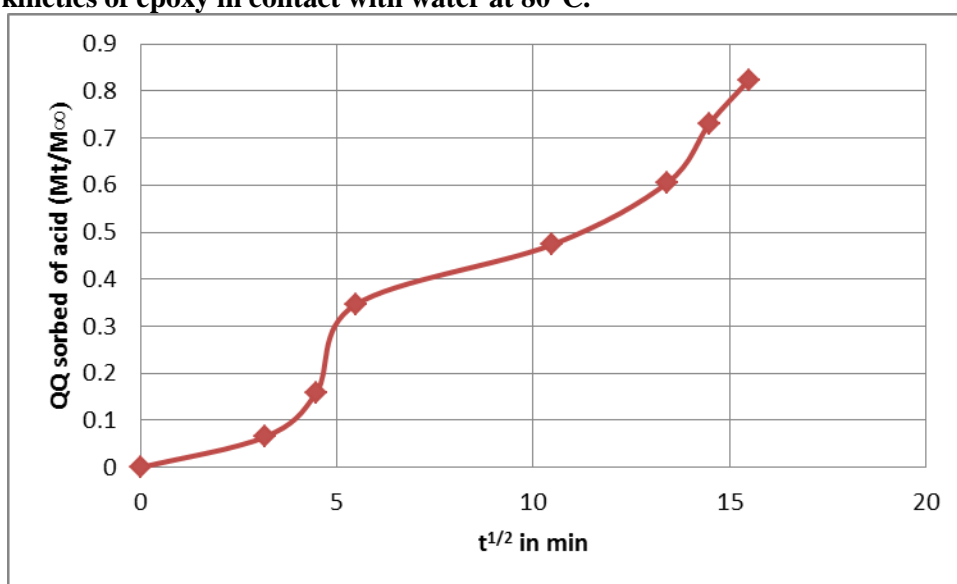


Fig.16: Sorption kinetics of epoxy in contact with acid at 80°C.

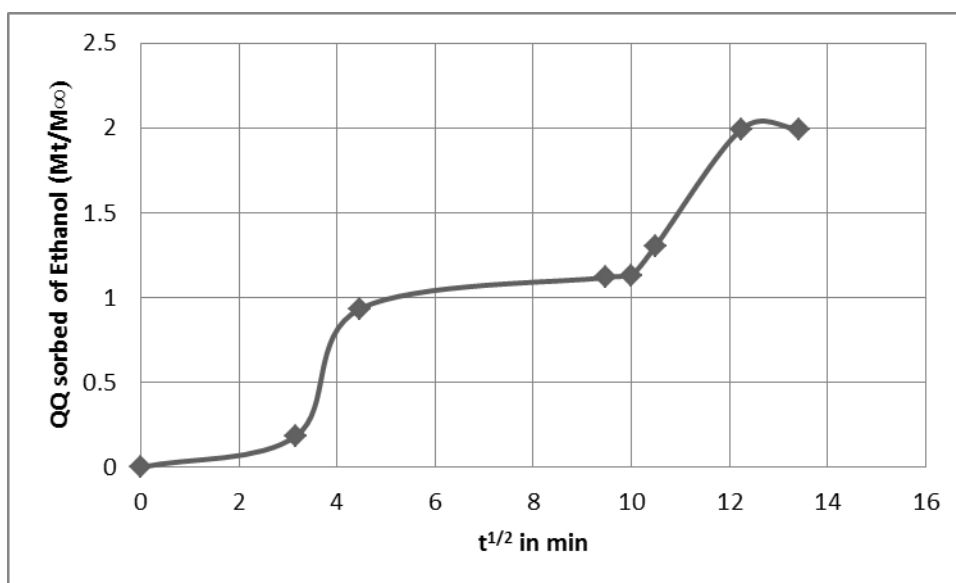


Fig.17: Sorption kinetics of epoxy in contact with Ethanol at 80°C.

The figures 15,16 and 17, shows that the sorption kinetics of different simulants in contact with Epoxy paint at 80°C, is of the sigmoidal type [36], in this case we are talking about a limitation of the sorption kinetics at the interface of the Epoxy polymer. That is to say that during the transfer of the molecules to the polymer, they braked at the interface before diffusing inside the polymer [36]. In our case study, this limitation of the kinetics is more durable in the case of the acid followed by water and ethanol. The results also shows that the diffusion at this temperature is more important in the case of acid and ethanol, this remark explains that the absence of strong interactions between water and the Epoxy polymer can suggest a weak sorption at the start followed by diffusion in the material then, under the effect of the temperature.

3.9. Thermodynamic parameters:

The calculated values of ΔH , ΔS and ΔG , listed in Tables 7, 8 and 9.

Table 7: Thermodynamic parameters of epoxy paint in contact with water.

ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol)	
		25°C	40°C
397.75	0.207	335.783	332.665

Table 8: Thermodynamic parameters of epoxy paint in contact with acid.

ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol)	
		25°C	40°C
262.151	-0.232	331.558	335.049

Table 9: Thermodynamic parameters of epoxy paint in contact with ethanol.

ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol)	
		25°C	40°C
414.618	-0.224	481.546	484.913

Changes of entropy (ΔS), enthalpy (ΔH), and Gibbs free energy (ΔG) of the studied curing reaction were determined using the data provided from the kinetic analysis and diffusion coefficient.

It is important to point out that there was good agreement between the kinetics and thermodynamic results.

Thermodynamic parameters confirm the stability of the epoxy paint in contact with the three solutions (water, acid and ethanol). The values of the transfer enthalpy being of a positive order for the three solutions, shows that the reaction is endothermic, and therefore the sorption is disadvantaged at low temperature. In addition, the positive values of the free Gibb's Energy show that the transfer phenomenon is not spontaneous. The results of the entropy being almost zero for water confirms, that our material undergoes no structural change in contact with water, and for ethanol and acid, being of negative order explain that the reactions at the interface of the epoxy not done in an orderly manner.

On their study of the kinetics and thermodynamic characteristics of a nickel-containing epoxy polymer prepared through curing of DGEBA with bis-Ni (II)-diethylenetriamine-iodide inorganic curing agent, Ghaemy, Rostami and Omrani and other works [37][38], show that the thermodynamic parameters, can be of great importance in epoxy reactions.

4. Conclusion:

In the present study, epoxy paint have been developed and put in contact over 300 min, with different simulants at different temperatures, which allowed us, to follow and analyze, its behavior by the gravimetric technique, used by several researchers [39]. In order to evaluate the impact of the temperature and the contact time on the properties of the polymers [40], but also we studied the impact of the nature of simulants, the results attests the stability of the films. In addition this work demonstrate that absorption phenomenon is favored compared to desorption, which justifies that contact with the epoxy film and under these said exposure conditions containing content, slightly influences the aging of the film but without diffusing substances to simulants[41]. This finding leads to conclude that crosslinking density of epoxy paint developed is high, and that the sites of its molecular matrix is quite small us discussed in many works of polymers resistance characteristics [42], moreover a good agreement between the kinetics and thermodynamic results was also found, indicating the stability of epoxy in contact with food stuffs.

References:

- 1- Robertson, Gordon. (2016). Food packaging: principles and practice. CRC press.
- 2- Blanco, I., Cicala, G., Costa, M., & Recca, A. (2006). Development of an epoxy system characterized by low water absorption and high thermo-mechanical performances. Journal of applied polymer science, 100(6), 4880-4887.
- 3- Vidil, T., Tournilhac, F., Musso, S., Robisson, A., & Leibler, L. (2016). Control of reactions and network structures of epoxy thermosets. Progress in Polymer Science, 62, 126-179.

- 4- Nerín, Cristina, Margarita Aznar, and Daniel Carrizo (2016). Food contamination during food process. *Trends in food science & technology* 48 (2016): 63-68.
- 5- Global Epoxy Resin Market (2017) 3rd Edition Latest Update. Acmite Market Intelligence.
- 6- Bopp, Alvin F. (2019). The Evolution of Food Preservation and Packaging. Chemistry's Role in Food Production and Sustainability: Past and Present. American Chemical Society, 211-228.
- 7- EU Food packaging Epoxy Resins updated Socio-economic Assessment', 2019
- 8- Brown, Helen, James Williams, and Mark Kirwan (2011). Packaged product quality and shelf life. *Food and beverage packaging technology* Ed2. 59-83.
- 9- Han, S. O., & Drzal, L. T. (2003). Water absorption effects on hydrophilic polymer matrix of carboxyl functionalized glucose resin and epoxy resin. *European Polymer Journal*, 39(9), 1791-1799.
- 10- Ivanova K.I., Pethrick R.A., Affrossman S., (2000) Investigation of hydrothermal ageing of a filled rubber toughened epoxy resin using dynamic mechanical thermal analysis and dielectric spectroscopy, *Polymer*, 41, 6787-6796.
- 11- Ahmad, Z., Ansell, M. P., & Smedley, D. (2010). Effect of nano-and micro-particle additions on moisture absorption in thixotropic room temperature cure epoxy-based adhesives for bonded-in timber connections. *International journal of adhesion and adhesives*, 30(6), 448-455.
- 12- Sevenich, R., Bark, F., Crews, C., Anderson, W., Pye, C., Riddellova, K., ... & Knorr, D. (2013). Effect of high-pressure thermal sterilization on the formation of food processing contaminants. *Innovative food science & emerging technologies*, 20, 42-50.
- 13- Scientific and technological cooperation between the EU and the United States, The Council approved successive extensions in 2004 (Decision 2004/756/EC).
- 14- Zhou, Jiming, and James P. Lucas. (1999) Hygrothermal effects of epoxy resin. Part I: the nature of water in epoxy. *Polymer* 40.20, 5505-5512.
- 15- Norme Code : NM 11.4.006 Emballages en matières plastiques Migration globale des constituants des matériaux et objets en matière plastique destinés à entrer en contact avec les denrées alimentaires Règles de base.
- 16- Kalyani, S., Smitha, B., Sridhar, S., & Krishnaiah, A. (2008). Pervaporation separation of ethanol–water mixtures through sodium alginate membranes. *Desalination*, 229(1-3), 68-81.
- 17- Cocaud, J., Céline, A., Fréour, S., & Jacquemin, F. (2017, June). Vers une méthodologie d'identification des paramètres de diffusion d'eau dans les polymères et composites. *Sciences de l'ingénieur/matériaux*.
- 18- Lao, L. L., Peppas, N. A., Boey, F. Y. C., & Venkatraman, S. S. (2011). Modeling of drug release from bulk-degrading polymers. *International journal of pharmaceutics*, 418(1), 28-41.
- 19- Fahmy, A. A., & Hurt, J. C. (1980). Stress dependence of water diffusion in epoxy resin. *Polymer Composites*, 1(2), 77-80.
- 20- Dada, A. O., Olalekan, A. P., Olatunya, A. M., & Dada, O. J. I. J. C. (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ unto phosphoric acid modified rice husk. *IOSR Journal of Applied Chemistry*, 3(1), 38-45.
- 21- MARZOCCA, A. J (2007). Evaluation of the polymer–solvent interaction parameter χ for the system cured styrene butadiene rubber and toluene. *European polymer journal*, vol. 43, no 6, p. 2682-2689.
- 22- Valero, A., & Vieillard, P. (2012). The thermodynamic properties of the upper continental crust: Exergy, Gibbs free energy and enthalpy. *Energy*, 41(1), 121-127.

- 23- Sugimoto, N., Nakano, S. I., Katoh, M., Matsumura, A., Nakamuta, H., Ohmichi, & Sasaki, M. (1995). Thermodynamic parameters to predict stability of RNA/DNA hybrid duplexes. *Biochemistry*, 34(35), 11211-11216.
- 24- Fast Fourier transform IR characterization of epoxy GY systems crosslinked with aliphatic and cycloaliphatic EH polyamine adducts, G Nikolic, S Zlatkovic, M Cakic, S Cakic, C Lacnjevac... - *Sensors*, 2010.
- 25- Impact modified epoxy/montmorillonite nanocomposites: synthesis and characterization Isil Isik, Ulku Yilmazer*, Goknur Bayram Department of Chemical Engineering, Middle East Technical University, ODTU Kimya Muhendisligi, 06531 Ankara, Turkey Received 5 March 2003; received in revised form 27 June 2003; accepted 15 July 2003.
- 26- A thermogravimetric analysis was also performed to quantify the kinetics of coal oxidation, such as the characteristic temperatures, the reaction activation energy, and the frequency factor. From: *Coal and Peat Fires: A Global Perspective*, 2019.
- 27- Thi Hai Yen Qhach. Etude de la durabilité d'un primaire epoxy anticorrosion : rôle de l'interphase polymère/métal et conséquence sur l'adhérence. *Polymères*. Université du Sud Toulon Var, 2010.
- 28- Deng, Shiqiang, Lin Ye, and Klaus Friedrich. (2007) Fracture behaviors of epoxy nanocomposites with nano-silica at low and elevated temperatures. *Journal of materials science* 42.8: 2766-2774.
- 29- Tian, Q., Yuan, Y. C., Rong, M. Z., & Zhang, M. Q. (2009). A thermally remendable epoxy resin. *Journal of Materials Chemistry*, 19(9), 1289-1296.
- 30- Bouvet, G., Dang, N., Cohendoz, S., Feaugas, X., Mallarino, S., & Touzain, S. (2016). Impact of polar groups concentration and free volume on water sorption in model epoxy free films and coatings. *Progress in Organic Coatings*, 96, 32-41.
- 31- GRACE, Landon R. et ALTAN, M. C. (2013). Non-fickian three-dimensional hindered moisture absorption in polymeric composites: Model development and validation. *Polymer composites*, vol. 34, no 7, p. 1144-1157.
- 32- Ghaemy M., Barghamadi M., Behmadi H (2006), Studies of cure kinetics and chemical resistance of the cured products of DGEBA with aromatic diamines, *Iranian Polymer Journal*, 15, 375-383.
- 33- Núñez, L., Villanueva, M., Fraga, F., & Nunez, M. R. (1999). Influence of water absorption on the mechanical properties of a DGEBA (n= 0)/1, 2 DCH epoxy system. *Journal of Applied Polymer Science*, 74(2), 353-358.
- 34- KADRI. Zineb, RAJI. Yousra, and Souad ZYADE. (2019). Characterization and migration from an Epoxy coating to food stuffs. *REVUE DE L'ENTREPRENEURIAT ET DE L'INNOVATION* 2.8.
- 35- Philippe, L. V. S., Lyon, S. B., Sammon, C., & Yarwood, J. (2008). Validation of electrochemical impedance measurements for water sorption into epoxy coatings using gravimetry and infra-red spectroscopy. *Corrosion Science*, 50(3), 887-896.
- 36- Zaki, Oussama. (2008). Contribution à l'étude et la modélisation de l'influence des phénomènes de transferts de masse sur le comportement mécanique de flacons en polypropylène. Diss.
- 37- Ghaemy, M., Rostami, A. A., & Omrani, A. (2006). Isothermal cure kinetics and thermodynamics of an epoxy–nickel–diamine system. *Polymer international*, 55(3), 279-284.
- 38- Ahlafi, H., Moussout, H., Boukhelifi, F., Echetna, M., Bennani, M. N., & Slimane, S. M. (2013). Kinetics of N-deacetylation of chitin extracted from shrimp shells collected from coastal area of Morocco. *Mediterranean Journal of Chemistry*, 2(3), 503-513.
- 39- Chetouani, A., Elmsellem, H., Bendaha, H., Aouniti, A., Mimouni, M., & Bouyanzer, A. (2014). Comparative study of the inhibition of extracts from the peel and seeds of Citrus Aurantium against the corrosion of steel in molar HCl solution. *Moroccan Journal of Chemistry*, 2(1), 2-1.

- 40- Akodad, M., Baghour, M., Moumen, A., Skalli, A., Azizi, G., Anjjar, A., ... & Daoudi, I. (2021). Adsorption of a basic dye, Methylene Blue, in aqueous solution on bentonite. *Moroccan Journal of Chemistry*, 9(3), 9-3.
- 41- Heman, Marie-Barbar. (2008). Contribution à l'étude des interphases et de leur comportement au vieillissement hygrothermique dans les systèmes à matrice thermdurcissable renforcés de fibres de verre. Diss.
- 42- RANE, A. V., ABITHA, V. K., & JADHAV, S. (2020). Non-Isocyanate Polyurethane Systems: A Review. *Moroccan Journal of Chemistry*, 8(4), 8-4.