Study of Esterification Between the Used Tire and Citric Acid Molecules

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Abstract: The recovery and recycling of all used tires is a constant challenge in a century where respect for the environment is becoming increasingly important and a key success factor. The Environmental Protection Agency (EPA) has classified citric acid as "Generally Recognized as Safe – GRAS", in consequence its use as raw material is beneficial for all and allowed to the study of its esterification with used tread tires. The tread tire samples utilized during all experimentations have 1.062wt.% of sulfur and they were characterized by titrations based on Boëhm titration such as its acid sites densities determined with NaOH-0.05N was 2.0421E-03 moles×g^{-1} and its basic sites densities determined by HCl-0.1N was 2.5984E-03 moles×g^{-1}. Thus, the esterification with citric acid at 141°C under atmospheric pressure using a closed reflux assembly of the tire's tread part was carried out such as the quantities of citric acid were in excess in comparison to the tire's total sites quantities. A model molecule representative of the connections of the most important atoms in the tire was proposed and permitted to show the possible reactions-mechanisms occurring between the tire's acid and basic sites and the citric acid molecules during their esterification together catalyzed by the protonic acid-H$^+$ of the citric acid. It was demonstrated that the esterification between citric acid and tire's acid/basic sites occurred efficiency whether on surface, whether in tire's porous with a very important initial conversion of the sites until 90% only after 20mn. The calculated global observed speed constant of the esterification between citric acid and tire's acid/basic sites is equal to 2.33L^3×mol^{-3}×h^{-1}. It was noticed that during this esterification the citric acid esterified with the tire's acid/basic sites was dehydrated and explained the formation of alkenes organic function which quantities increased even after 2 hours. Thereafter, these tire's citric acid alkenes will form the first new sites and their addition reactions with citric acid molecules or dehydrated citric acid molecules gave citric acid polymers and/or poly-aromatics molecules which constituted the second new sites; their densities after 2 hours reactions were respectively 9.18E-04 moles×g^{-1} and 7.65E-04 moles×g^{-1}. After 2 hours of reaction, a soft dark materials with precipitates dark grains were recovered.

Keywords: Used Tire, Citric Acid, Esterification, Acid Sites, Basic Sites

1. Introduction

First, the used tire sample was characterized and its densities, acid sites, basic sites and sulfur weight rate were determined. Second, the esterification between citric acid and the used tire was done using a reflux assembly at 141°C under atmospheric pressure. Third, the evolutions of the total sites conversions and the total sites concentrations were followed with time and permitted to calculate the initial global speed constants. Finally, the alkene-organic functions of the esterified tire was titrated with HF-0.0026N and followed with time. The materials and chemicals used during these experimentations were KERN precision scale, magnetic stirrer, magnetic bar, beaker-250ml, graduated burette, test tube, pipette, mortar, oven, filter paper, citric acid, used tread tire, distilled water, HF-0.0026N, NaOH-

0.05N, HCl-0.1N, bromophenol blue.

2. The Citric Acid

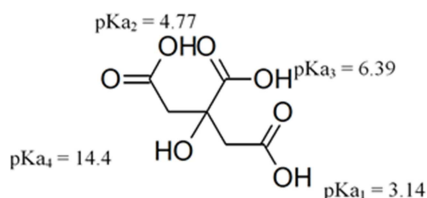### 2.1. Generalities and Applications of the Citric Acid

Figure 1. 3-hydroxybutane-1, 2, 4-tricarboxylic acid (Citric Acid).

Citric acid $C_6H_8O_7$ is a weak tricarboxylic acid α-hydrolyzed. It contains three acids with pKa such as pKa1 = 3.14, pKa2 = 4.77 and pKa3 = 6.39 and an α-alcohol function with pKa = 14.4 [1-3] (figure 1 – Table 1). By its reactivity, the citric acid was the object of several studies and was used in several fields such as the synthesis of citric acid polymers [4-6], the leaving creatures' molecules extraction by esterification with citric acid [7, 8], the trans-esterification between citric acid and oil to synthesize bio carburant [9, 10]. the alimentary manufacturing [11-14] and the citric acid derivatives was used in water treatment [15, 16] and oil-hydrocarbon additives [17, 18].

Table 1. Dominant Forms of "Citric Acid" According to the pH.

pH	Acid/base couple	pKa	Acid/Base reactions	Dominant forms	Dominant molecule/Ions
pH ≤ 3.14	AH_3/AH_2^-	3.14	$AH_3 \rightleftharpoons AH_2^- + H^+$	AH_3	Citric Acid
3.14 ≤ pH ≤ 4.77	AH_2^-/AH^{2-}	4.77	$AH_2^- \rightleftharpoons AH^{2-} + H^+$	AH_2^-	Di-Hydrogenocitrate
4.77 ≤ pH ≤ 6.39	AH^{2-}/A^{3-}	6.39	$AH^{2-} \rightleftharpoons A^{3-} + H^+$	AH^{2-}	Mono-Hydrogenocitrate
6.39 ≤ pH	AH^{2-}/A^{3-}	6.39	$AH^{2-} \rightleftharpoons A^{3-} + H^+$	A^{3-}	Citrate

2.2. Characteristics of the Citric Acid

Citric acid is solid with monoclinic as crystal structure, white, odorless and excessively sour flavor [3]. Citric acid exists in hydrates forms, the monohydrate melts towards 343.15°K and the anhydrous state melting point is 426.15°K. Citric acid is soluble in alcohol, ether, ethyl acetate and DMSO (Table 2) and insoluble in C_6H_6, $CHCl_3$, CS_2, and toluene. Its solubility in ethanol at 298.15°K is 62g/100g. Citric acid is very soluble in water and its solubility increases with the temperature as shown the following table (Table 3) [19].

Table 2. Citric acid physicochemical properties.

Physicochemical Properties	CITRIC ACID - $C_6H_8O_7$
Appearance	Crystalline white solid
Crystal structure	Monoclinic
Molar mass	192.12 [g.mol^{-1}]
Density	1.665 [g.cm^{-3}] anhydrous
	1.542 [g.cm^{-3}] monohydrate at 291.15°K
Melting point	426.15°K anhydrous
	343.15°K monohydrate
Boiling point	448.15°K
Solubility in ethanol	62g/100g
Solubility in water	59.20% at 293.15°K (Table 3)

Table 3. Evolution of the citric acid solubility in water (w/w) following to the temperature (°K).

T°K	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
Solubility (% g/100mg)	54.0	59.2	64.3	68.6	70.9	73.5	76.2	78.8	81.4	84.0

3. The Tire

3.1. Generalities - Characteristics and Valorizations of the Tires

The tire is a vulcanized rubber material [20]. It was synthesized by brut elastomer like polyisoprene with different reinforcing, plasticizer, additives and sulfur or over vulcanizing agents that transforms rubber from a plastic to an elastic state by a chemistry and thermic process that create macromolecules linked to form a tridimensional lattice [20, 21]. Once the tires are used, they can be, either recapped to be reused, either devulcanized and transformed into powder to recover depolymerized rubber whose content in ferromagnetic, textile or polluting materials should not exceed respectively 0.01% - 0.5% - 0.25% by weight for the European directive 21/2007 [22, 23] even if the tires' metals content was between 16% and 25% [24, 25]. Nevertheless, the demand for rubber powder and granulates in both the industrial and consumer markets has increased dramatically in recent years. They are used in a wide and growing range of applications: synthetic turf, playgrounds, sports fields, modified asphalt and asphalt, safety flooring, transport packaging interiors, conveyor belts, car mats, shoes, carpets, footwear, carpet pad, tiles, flooring, activated carbon, livestock bedding and elastomers and thermoplastic elastomers [25]. In short, the tire is a complex material composed not only of ferromagnetic compounds but also of inorganic and organic chemical compounds [26] with reactive sites that can be classified into acidic and basic sites. These sites could be quantified by the Boëhm titration [27-29].

3.2. The Boëhm Titration Application to Characterize the Tires

The surface characteristics of active carbons (ACs) depend on the content of heteroatoms, such as oxygen or nitrogen which determine the charge, hydrophobicity, and electronic density of the graphene layers. Other important factors are

the properties of adsorbate molecules: molecular size, solubility, pKa, character of functional group attached to an aromatic ring [28]. The hydrophobicity of adsorbed organic molecules is the main driving force in adsorption from aqueous phase on a hydrophobic surface of active carbon (Derylo-Marczewska et al. 2001). Surface chemistry significantly influences the wettability, adsorptive, electrical, electrochemical, catalytic, acid–base, redox, hydrophilic–hydrophobic, and other properties. In this case of study, the

aim was to evaluate the tires' acid sites and basic sites quantities that could react by esterification with the citric acid's organic functions (alcohol and the tricarboxylic acid) [7, 8]. Thus, titrations procedures (Table 4) and described below, based on the Boehm's titration method [15, 16, 27-29], was carried out to evaluate not only these acid sites composed mainly of Brönsted and Lewis acids but also these basic sites composed mainly of Brönsted and Lewis bases on the tires [30-33].

Table 4. *Concept of Brönsted/Lewis acid and basic sites characterized respectively by NaOH-0.05 and HCl-0.1N.*

Concept	Acid sites (S_A)	Base sites (S_B)
Brönsted	$S_A\text{-H} + NaOH \rightarrow S_A\text{-Na} + H_2O$	$S_B\text{-OH} + HCl \rightarrow S_B\text{-Cl} + H_2O$
Lewis	$S_A + NaOH \rightarrow Na\text{-}S_A\text{-OH}$	$\overline{S_B} + HCl \rightarrow H - S_B - Cl$

Firstly, before all analysis, the tires to be analyzed were cleaned-up such as they were putted in a beacher-250ml, then add sufficient hot water and mixed on a magnetic stirrer during few minutes to eliminate not only their dirties but also the remains of citric acid molecules on its surface after their esterification with citric acid's organic functions (alcohol and the tricarboxylic acids) [7, 8].

Secondly, to evaluate the tires' acid sites, take approximately 0.0306g of tire's sample in a beacher-250ml, add 6.04ml to 6.2ml of NaOH-0.05N and mixed with a magnetic stirrer during one hour. Then, the excess of NaOH

was titrated by HCl 0,1N (using helianthine as color indicator). The equivalent point was reached when in the mixed solution appears red vivid color.

Thirdly, to evaluate the tires' basic sites, take approximately 0.0306g of tire's sample in a beacher-250ml, add 6.04ml to 6.2ml of HCl-0.1N and mixed with a magnetic stirrer during one hour. Then, the excess of HCl was titrated by NaOH-0,05N (using helianthine as color indicator). The equivalent point was reached when in the mixed solution appears red vivid orange yellow.

Table 5. *Results of these titrations applied to the tires' acid/basic sites rate evaluation.*

Tire's basic sites density [moles×g^{-1}]	Density [g×ml^{-1}]	Tire's acid sites density [moles×g^{-1}]	Tire's sulfur rate [wt%]
2.5984E-03	0.587	2.0421E-03	1.062

3.3. The Global Reactions Mechanism Between Citric Acid's Organic Functions and the Tires Sites Catalyzed by the Citric Acid Protonic Acid-H$^+$

As described previously (§3) tires was a complex material composed mainly with carbon (C), sulfur (S), oxygen (O), nitrogen (N) and metals connected. These atoms and their derivatives in the tire contained in their electronic configuration Lewis/Brönsted acids and basics sites. Thus, the model molecule representative of the most important atoms connections in the tire and from which it's possible to explain their reactions/esterification with citric acid's organic functions (alcohol and the tricarboxylic acids) catalyzed by the citric acid's protonic acid-H$^+$ was on the figure 2.
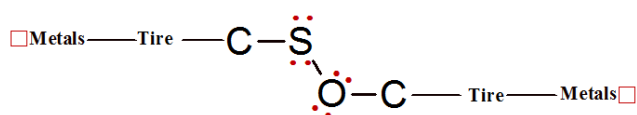

Figure 2. *Model molecule representative of the most important atoms connections in the tire.*

The following figure 3 showed these reactions between the tires' sites and citric acid's organic functions catalyzed by the citric acid's protonic acid-H$^+$ and their products. In general, the tires' basic sites $-\ddot{O}-$ or $-\ddot{S}-$ or eventually $-\ddot{N}-$ and eventually alkenes of tires' aromatics molecules were

activated by the citric acid's protonic acid H$^+$ catalyst, according to the mechanisms in figure 3, to give instables oxonium or sulfonium or ammonium ions and eventually carbocation ions which could react thereafter with citric acid molecules by esterifications or additions reactions to give these products (figure 3). On the other hand, the tires' acid sites like metals with free cell could be activated by the citric acids' oxygen electron pair, according to the mechanisms in figure 3, to give an instable complexes-coordination which could react by rearrangement under organometallic-coordination catalyst mechanisms into these metallic-products seen on the figure 3. These previous ascertainments conducted to the study of the esterification between the global tire sites and the citric acid's organic functions catalyzed by their protonic acid-H$^+$ in the following paragraph §.4.

4. The Esterification Between the Tire Sites and the Citric Acid Catalyzed by Protonic Acid-H$^+$

4.1. Experimental Conditions

As seen previously, the esterification and the addition reactions between citric acid's organic function and the tire's sites could be studied and followed simply by putting the

initial concentration of citric acid in excess in comparison to the initial tire's sites concentration as described the order degeneration method [1].

Indeed, the global speed is

$$v = k \times [citric\ acid]^{\alpha} \times [sites]^{\beta} \qquad (1)$$

If

$$[citric\ acid] \gg [sites] \qquad (2)$$

And, seeing that $0 \le \alpha$ and $\beta \le 1$.
So,

$$[citric\ acid]^{\alpha} \gg [sites]^{\beta} \qquad (3)$$

And the global speed became,

$$v = k_{see} \times [sites]^{\beta} \qquad (4)$$

Such as

$$k_{see} = k \times [citric\ acid]^{\alpha} \qquad (5)$$

Thus, to evaluate simply the value of the k_{see} and the sites' partial order α, the initial condition of all experimentations were in the vicinity of the value in table 6 such as the tire's sites densities was followed in different times of reaction by their titration according the Boëhm titration described previously on paragraph §3.2.
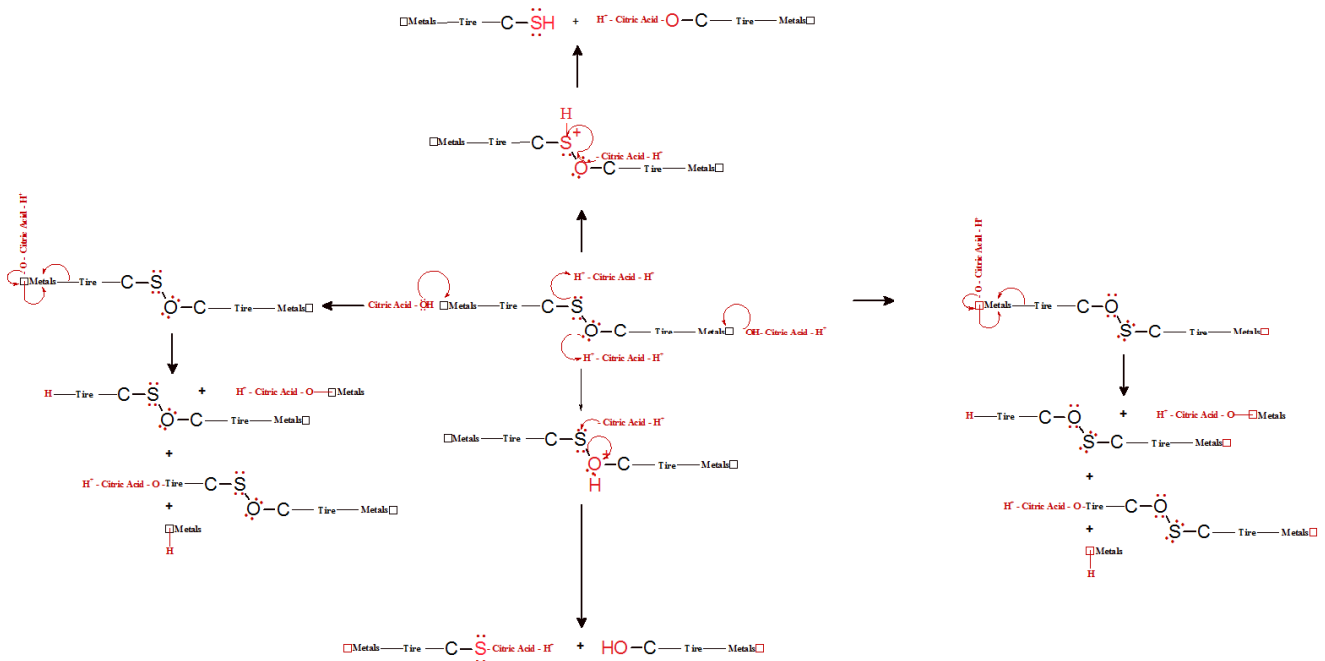

Figure 3. *Reactions between the tires' sites and citric acid's organic functions catalyzed by the citric acid's protonic acid-H+ and their products.*

4.2. Kinetics Results of the Esterification Between the Global Tire Sites and the Citric Acid Catalyzed by Their Protonic Acid-H$^+$

Table 6. *Experimental conditions of the esterification-addition between the global tire sites and the citric acid's organic functions catalyzed by their protonic acid-H$^+$.*

Characteristics	Values
Reactor	Reflux assembly [7, 8]
Temperature [°C]	141
Water volume [ml]	27.5
Tire weight [g]	1.00
Initial tire's acid sites [moles]	2.0421E-03
Initial tire's basic sites [moles]	2.5984E-03
Initial total sites concentration [moles×l^{-1}]	1.66E-1
Citric acid weight [g]	9.5
Citric acid moles [moles]	49.5450E-3
Ratio	
Initial - [citric acid]/[sites]	11

The following table 7 showed the evolutions of the sites conversion (figure 4) and the evolutions of the sites densities with the time reaction. First, the global tire's sites densities decreased from the initial time reaction to 1hour of reaction (Table 7) and confirmed the initial important tire's sites conversions (figure 4); these results confirmed not only that the esterification between the tire's basic and acid sites and the citric acid's organic functions occurred efficiency but also the citric acid's protonic acids-H$^+$ played efficiency their role as catalyst during these reactions as described on the figure 3 (§4.1.). Second, from 1hour to 2hour of time reaction the global tire's sites densities increased (Table 7). It announced that there was a formation of another sites on the tire and explained the diminution of the tire's sites conversion from 1hour to 2hour. These new sites came certainly from the transformation of the citric acid esterified with the tires' sites (figure 3). Indeed, it was demonstrated that the citric acid's hydroxyl-organic function could be initially dehydrated to form alkenes-

organic function [9, 10], also the citric acid's carboxylic acid-organic function could be decarboxylized to form another alkenes-organic function [34, 35] and these alkenes could reacted thereafter to obtain citric acid polymers [4-6]

and/or PNA-polynuclear aromatics molecules [17, 18] which increased not only the tire's acid sites but also the tire's basic sites at high time reaction in these conditions (figure 5).

Table 7. Tire's sites conversions and Tire's sites densities evolutions with the time reaction.

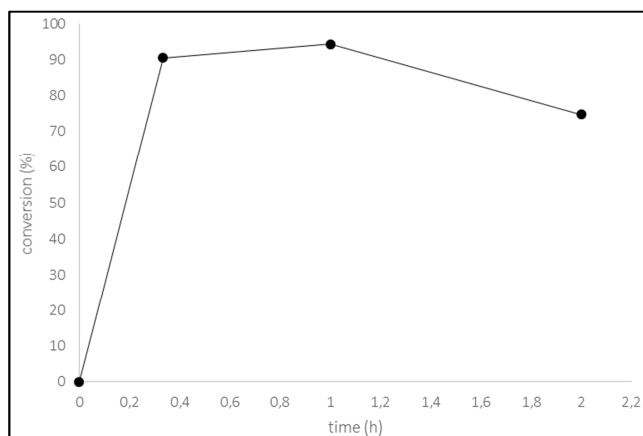| Time (h)	Conversion (%)	Total sites concentration [moles×l^{-1}]	Acid sites densities [moles×g^{-1}]	Basic sites densities [moles×g^{-1}]
0	0	1,66E-01	2.05E-03	2.49E-03
0.33	90.53	1,61E-02	2.65E-04	1.75E-04
1	94.36	9,92E-03	8.93E-05	1.72E-04
2	74.80	9,70E-02	8.10E-04	1.51E-03

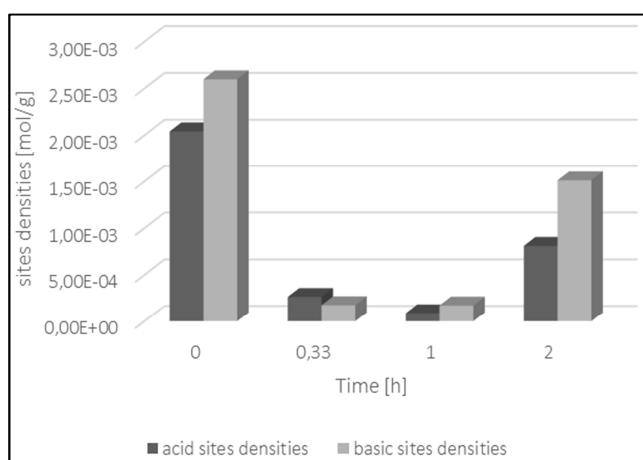*Figure 4. Tire's sites conversions evolutions with the time reaction.*

Figure 5. Tire's sites densities evolutions with the time reaction.

Third, according to these experimental conditions described previously (§4.1. – Table 6), the kinetic constants of this reaction were calculated by resolving the integral method [36] at the initial time. Thus, the calculated observed speed constant k_{see} equals to 77.0174E-2L^2×mol^{-2}×h^{-1} = 12.836×10^{-3}L^2×mol^{-2}×mn^{-1} and the sites partial order β is equal to 1. Indeed, assuming that in this previous experimental conditions the global basic speed constant is negligible, the deduced calculated initial global (acid) speed constant k≈k$_{acid}$ is equal to 57,200 [L^2×mol^{-2}×h^{-1}]=953 [L^2×mol^{-2}×mn^{-1}] seeing that the half reaction time is equal to 0.17 [h]. Thus, the global

order of this reaction is three seeing that according to the previous studies of esterification with citric acid which is in the same time reactant and source of the catalyst protonic acid-H$^+$, the partial order with the citric acid was all the time two [9, 10, 34, 35].

5. Study of the Tire's Alkene Evolutions During the Esterification Reaction

As explained previously, the tire's alkene-organic function rate evolution was responsible of the formations of new basics and acid sites on the esterified tire and could influenced its quality (§4.2.). As a consequence, the alkene-organic function titration was carried-out using the HF-0.0026N procedure [37, 38] such as just after addition of the color indicator bromophenol blue, the titrated solution was blue. First, after adding some milliliters of HF-0.0026N, the titrated solution turn into uncolored-transparent and it was considered to corresponding to the tire's on surface citric acid alkene quantity. Second, after continuing the titration the titrated solution turned into transparent-yellow which was considered to corresponding to the tire's porosities alkene quantity. And finally after continuing the titration the titrated solution turned into yellow which corresponded to the tire's over sites attacked by the HF-0026N quantity. That's why the results of these tire's organic function rate evolutions were shown in the following table 8.
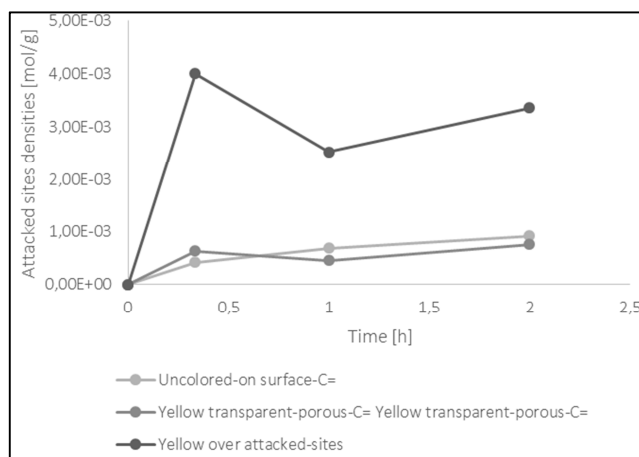

Figure 6. Tire's sites titrated and attacked with the HF-0026N solution evolution.

Table 8. *Tire's sites titrated and attacked with the HF-0026N solution.*

Time (h)	Uncolored-on surface-C$^=$ [mol/g]	Yellow transparent-porous-C$^=$ [mol/g]	Yellow over attacked-sites [mol/g]
0.33	4.22E-04	6.32E-04	4.01E-03
1	6.88E-04	4.59E-04	2.52E-03
2	9.18E-04	7.65E-04	3.36E-03

First, the tires' uncolored-transparent on surface-alkene organic function increased all the time and confirmed the formation of alkene by tire's citric acid dehydration and/or decarboxylation. It is also the same for the citric acid molecules located in the tire's porosity. But, for this second case a slight diminution was noticed between [0.33h; 1h] which indicated that they reacted and were certainly transformed into citric acid polymers like citric acid polymers [4-6] and/or PA-poly-aromatics molecules [17, 18]. Indeed it was observed that the esterified tires became soft and dark. Third, as seen on the figure 6, the uncolored-transparent on surface-alkene curve joined the tire's porosities alkene which indicated the addition reaction between these molecules to form the tires' citric acid polymers like citric acid polymers and/or PA-poly-aromatics molecules. Finally, the over attacked sites diminution recorded between [0.33h-1h] confirmed their reaction with citric acid molecules to form the esterified tires as shown on the figure 3 and explained on the paragraph-§4.2.

6. Conclusion

It was showed that the esterification with citric acid of used tires under atmospheric pressure allowed to their recycling to new materials which could be utilized as new filler for the synthesis of materials using polymerization reactions because of their non-negligible acid and basic sites like alkenes, electron pair and atoms with vacant cell. These materials were soft and indicated that they were regenerated not only on surface but also in their porosity to give more tire-citric acid-reticulated materials with potential acid and basic sites such as its sulfur content were less than 0.5%. Indeed, the solution with the soft dark materials with precipitates dark grains recovered after 2hours of reaction could be continued until total dehydration to give dark crispy materials.

Acknowledgements

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