

MODELING AND OPTIMIZATION BY THE EXPERIMENTAL DESIGN OF THE SYNTHESIS: TERPENE PHENOL RESIN CHARACTERIZATION AND THERMOGRAVIMETRIC STUDY

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Abstract:

The objective of this study is to determine the optimal conditions of the resin synthesis of stoichiometric terpene phenol by pure development of a methodological strategy using the experimental design technique. Thus a mathematical model can be established to represent the best synthesis of "descriptive model" to explain "explanatory model" and predict the response at a point where no experience has been made in "provisional model". By following the theoretical results obtained through modeling, we synthesized a new terpene phenolic resin, prepared by oligomerization of terpene and phenol. The resin synthesis was characterized by Fourier transform (FTIR), ^1H , ^{13}C analyzes. The behavior and thermal stability of hardening was followed by the thermogravimetric analysis (TGA).

Keywords: synthesis; Epoxy resin; Thermal properties; terpene phenol resin.

1. Intro-duction:

The method of experimental design is both new and old [1]. It is new for electronic and mechanical engineering. Initially developed and implemented by the British mathematician Sir Ronald Fischer [2], after 1945, the experiments' design aroused numerous publications and research in the Anglo-Saxon world. Statisticians as Yates, Cochran, Plackett and Burmann, enriched and disclosed the method [3] [4]. Natural terpenes are very soft materials that can be designed to provide molecular resin structures having a broad utility. A carbocationic conventional polymerization [5] of terpenic stream provides polyterpene resins having high solubility parameters (δ) which make them ideal for agents of adhesiveness of natural rubber, synthetic polyisoprene, and styrene-isoprene-styrene (SIS) copolymers blocks. The incorporation of an aromatic component in the currents of terpenic resin alimentation makes it somewhat more polar thus allowing the compatibilization with polybutadiene-styrene-butadiene-styrene (SB S) or (SB) n copolymers' blocks. The highest polarity resins can be prepared by the reaction of Friedel Craft based on oligomerization of currents of alimentation of terpene phenol [6].

2. Theoretical Approach

2.1 Choice of factors

The optimization of the terpene phenol resin synthesis involves many parameters involved in the synthetic resin. These parameters are summarized in Table 1.

Table 1: the parameters involved in the experience matrix of the resin synthesis of terpene phenol

Parameters	Notation	Quantity		Unit
Temperature	X ₁	50°C	120°C	°C
Duration of reaction	X ₂	3h	6h	h
[Terpene]	X ₃	0.5	3.5	mol/l
[Phenol]	X ₄	0.5	3.5	mol/l

2.2 Equation of the Model:

For a thorough synthesis optimization study, we should not be satisfied with a polynomial model of degree 2 and the response surface map. So it is necessary to use a polynomial model of degree of at least 2.

Among the plans for the use of a polynomial model of degree 2, we chose a matrix of the Doehlert experience that allows to find optimal qualities predicting the response calculated at all points in the field.

Table 2: Estimation of model coefficients associated with the performance and the determination of their significance in relation to the experimental dispersion.

Name	Coefficient	F.Inflation	Standard Deviation	t.exp.	Sig. %
b0	59.0000		7.2376	8.15	***
b1	-8.9000	1.00	3.2368	-2.75	*
b2	1.0970	1.00	3.2367	0.34	*
b3	4.4499	1.00	3.2368	1.37	**
b4	0.1582	1.00	3.2366	0.05	***
b11	-4.5000	2.34	8.8642	-0.51	63.3%
b22	-11.8340	2.34	8.8648	-1.33	22.9%
b33	-6.6659	2.50	8.6141	-0.77	47.3%
b44	17.5990	2.61	8.4085	2.09	8.0%
b12	-11.5473	1.22	8.3575	-1.38	21.5%
b13	2.8582	1.18	9.3438	0.31	76.6%
b23	-8.2498	1.18	9.3430	-0.88	41.5%
b14	-7.2725	1.13	9.7099	-0.75	48.7%
b24	-5.2950	1.13	9.7091	-0.55	60.9%
b34	-1.0321	1.13	9.7100	-0.11	91.5%

The set of operating conditions, carried out at random, and the analytical results of the yields of the corresponding reaction are summarized in Table 2. The principle of operating the results is based on the analysis of variance of regression, on calculating estimates of the model coefficients and on their

significance with respect to the experimental errors as well as calculation of the residue. All statistical calculations were carried out by the use of NEMRODW software.

Table 2 brings together the various factors and their meanings. We notice that :

- ✓ To a significance level of 0.1%, i.e. to a confidence level of 99.9%, the two factors: The quantity of reagent adds a positive effect to the value of the response (reaction yield)
- ✓ For a significance level of 1%, i.e. for a confidence level of 99%, the flow factor of the reaction time is positive,
- ✓ For a significance level of 5%, i.e. for a confidence level of 95%, the interaction between the reaction time and the temperature have a positive effect on the value of the response which is the output.

2.3 Analysis of variance:

The analysis of variance allows us to see if the variables used for modeling as a whole have a significant effect on the response. The results of the analysis of the variance are summarized in Table 3. For the overall significance, the experimental value of $F_{\alpha}(n_1, n_2)$ in Table 3 ($F_{exp}(14,6) = 9.66$) is higher than the theoretical one ($F_{0.01}(14,6) = 7.60$). The regression is significant at a confidence level of approximately 99%.

Table 3: Analysis of variance: answer (response) / Yield Source

Source of variation	Sum of squares	Degrees of freedom	mean square	report	Signif %
Regression	1.95310^3	14	1.39510^2	9.6644	11.7%
residues	3.14310^2	6	5.23810^1		
Total	2.26810^3	20			
Standard Error of the response		7.2376			
R^2		0.861			
R^2A		0.538			
Number of degrees of freedom		6			

2.4 The Validation of the model:

The model validation is to ensure that the responses calculated for experimental points are roughly the same as the measured responses. Table 4 gathers the experimental results and the results calculated using the NEMRODW(90) software .

$$Y = b_0 + b_1 * X_1 + b_2 * X_2 + b_3 * X_3 + b_{11} * (X_1 * X_1) + b_{22} * (X_2 * X_2) + b_{33} * (X_3 * X_3) + b_{12} * (X_1 * X_2) + b_{13} * (X_1 * X_3) + b_{23} * (X_2 * X_3)$$

Table 4: Comparison between experimental results and values calculated from the model.

No exp	Y exp.	Y calc.	Difference
1	44.0000	45.6000	-1.6000
2	65.0000	63.4000	1.6000
3	34.0000	40.5000	-6.5000
4	54.0000	47.5000	6.5000
5	43.0000	48.6000	-5.6000
6	65.0000	59.4000	5.6000
7	55.0000	49.5000	5.5000
8	45.0000	50.5000	-5.5000
9	49.0000	42.6000	6.4000
10	52.0000	51.5001	0.4999
11	53.0000	59.4000	-6.4000
12	57.0000	57.4999	-0.4999
13	61.0000	58.4000	2.6000
14	62.0000	64.6000	-2.6000
15	65.0000	64.2000	0.8000
16	69.0000	68.6001	0.3999
17	72.0000	70.6000	1.4000
18	75.0000	75.8000	-0.8000
19	69.0000	69.3999	-0.3999
20	64.0000	65.4000	-1.4000
21	59.0000	59.0000	-0.0000

3. OPTIMIZATION:

The goal of this optimization is to meet a specific objective in our case: the synthesis of a terpene phenol resin is stoichiometric from phenol and monomer terpene. It is to find all the values of the operating variables (factors) causing the desired response by relying on economic constraints.

After analysing the system and the modeling response based on various factors, the optimum can be shown by the method of iso-response curves.

3.1 Iso-response curves analysis:

By putting the values predicted by the model in the form of curves iso-response, we can analyze the effect of the factor on our response. The iso-response curves of the yield of the reaction depending on the temperature and the reaction time are shown in Figure 1.a. They confirm what we have already found previously in Table 2, i.e. a positive effect of the reaction time on the response which generally results by an increase in the yield when the temperature of the mixture is reduced.

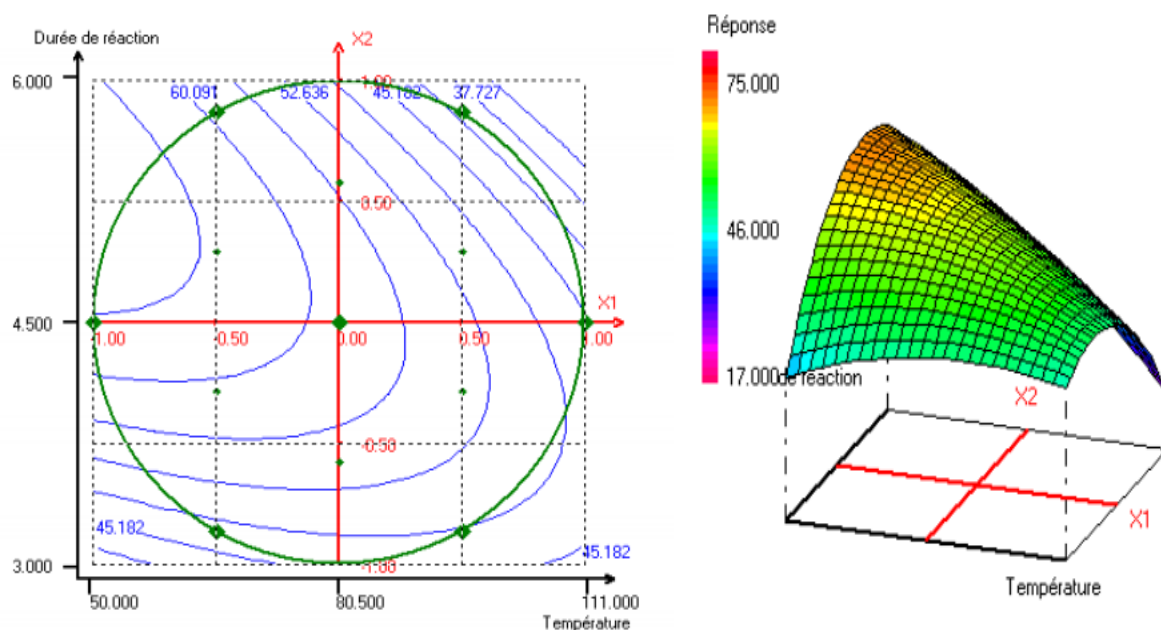
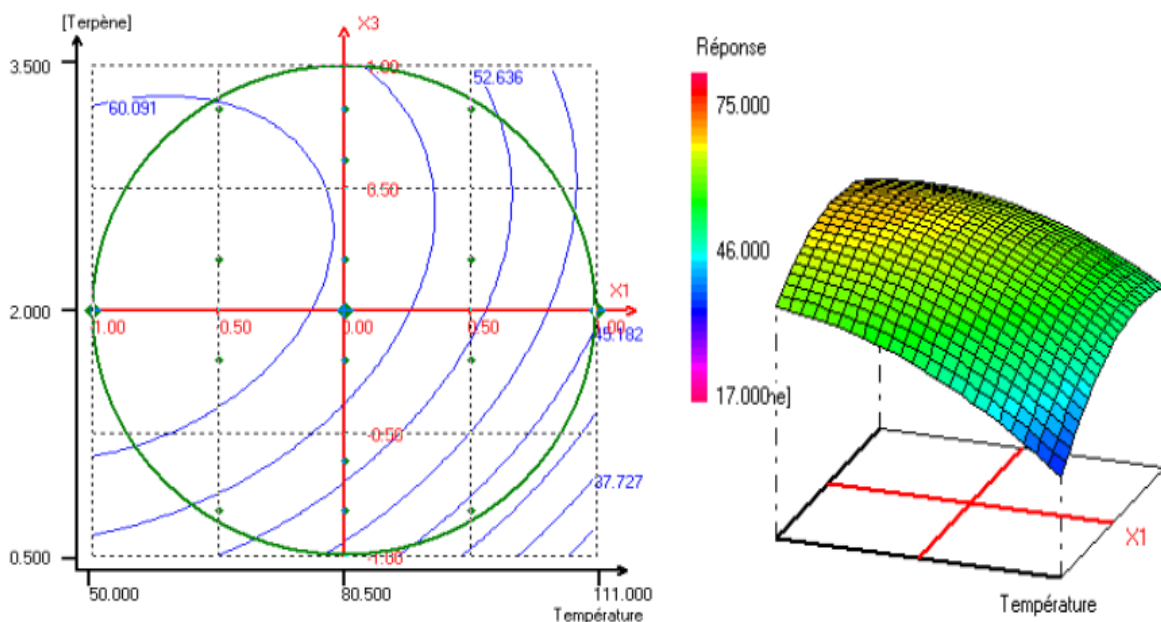


Fig 1a: yield of iso-response curve according to X1-X2

According to Fig 1.a, we observe a change in the shape of the iso-response curve which turns into an ellipse which features an optimum when the reaction time increases from 3 hours to 6 hours. the decreased



temperature is 70 ° C. We can get a good reaction yield of terpene phenol by 60.09%.

Fig 1b: yield of iso-response curve according to X1-X3

According to Fig 1b, we see a change in the shape of the iso-response curve which is transformed into an ellipse that characterizes an optimum. We notice a recovery in the iso-response curves in the experimental field. We also notice from the iso-r ponse curve that the reaction yield increases significantly with the amount of the added reagent (excess). When the amount of the added reagent (terpene) is 1.25 mol / l, the output value would be around 37% with the maximum temperature.

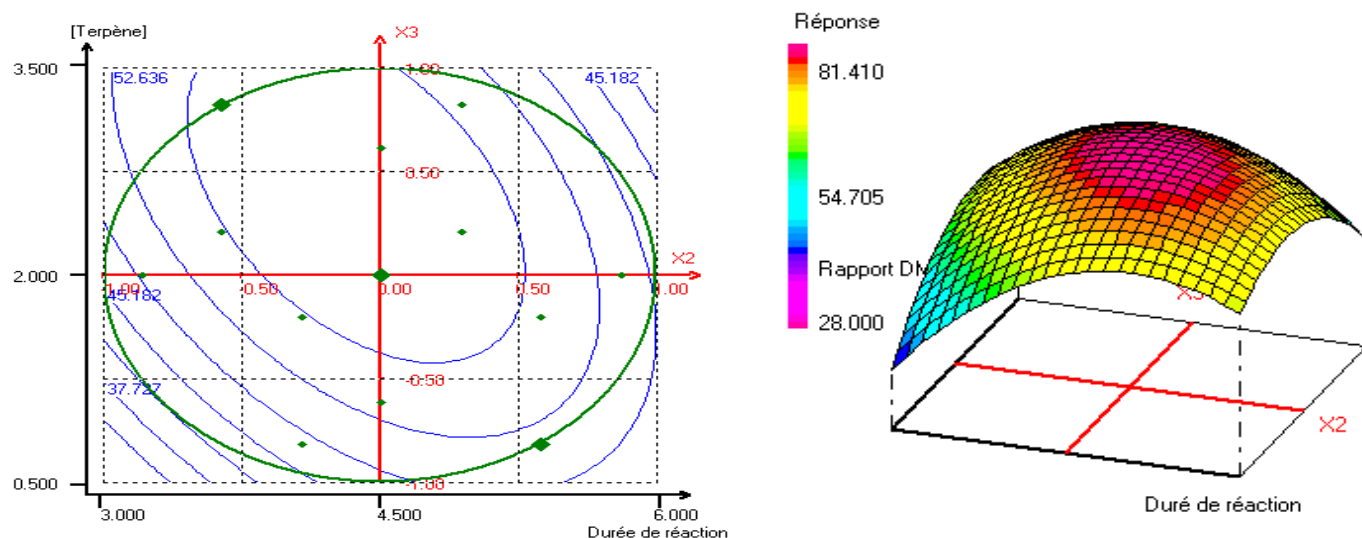


Fig 1c: iso-response curve of the performance according to X2-X3

In figure 1c, we see a collapse of the iso-response curves when the Yield of the reaction increases from 37.72% to 52.63%, and the amount of the added reagent is important. Thus the increase of this factor tends to promote the effect of the length of the reaction on the response.

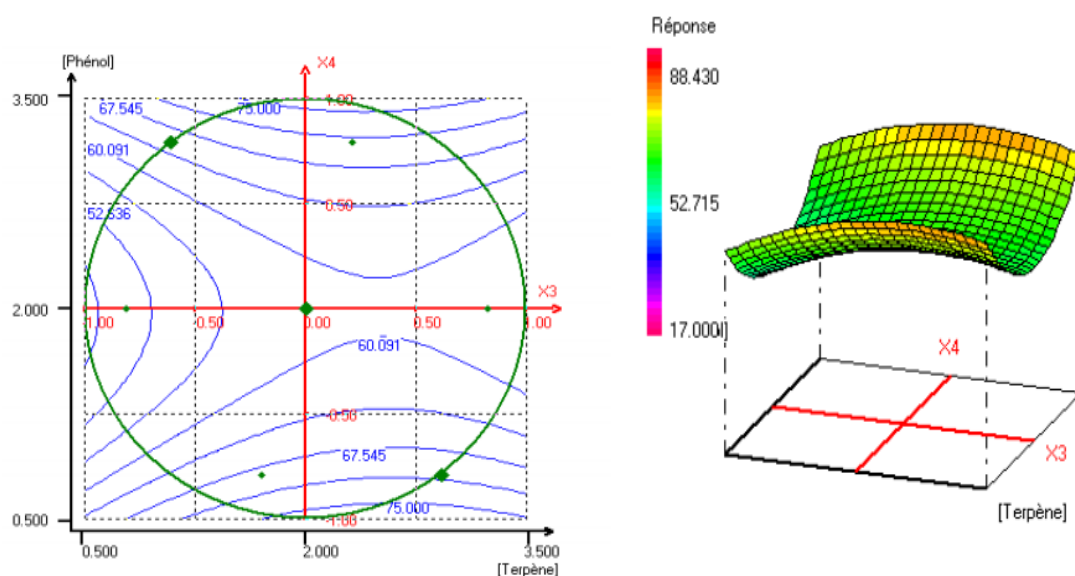


Figure 1d: iso-response curve of the performance according to X3-X4

From the iso-response curve (Fig: 1d), we are shown that the quantities of the stoichiometric reagents are added to achieve a good return.

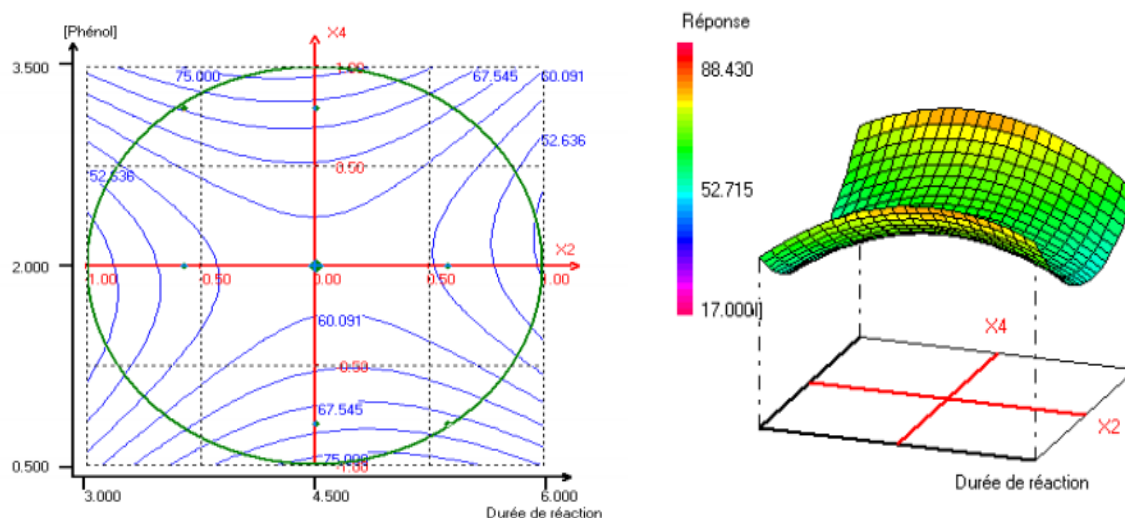


Figure 1e: the iso-response curve of the performance based on X2-X4

Figure 1.e shows the iso-response curve of a response Y (blue) according to two input factors X2 and X4. We are also shown in this figure that the response Y is maximal to a maximum value of X4 factor, and the factor X2 has an influence on this response.

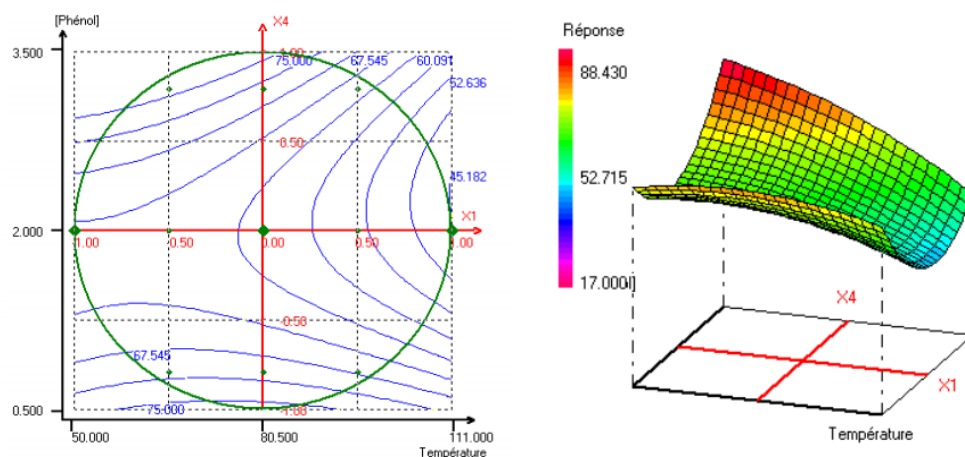


Fig 1.f: the iso-response curve of the performance according to X1-X4

Figure 1.f shows the iso-response curve of a response Y (blue) according to two input factors X1 and X4. We are also shown in this figure that the response Y is maximal to a maximum value of X4 factor, and the factor X1 has a slight influence on this response.

3.2 Determining optimal conditions:

We see from this figure, if the amounts of the reagents added in excess and the reaction time is simultaneously increasing or when the reaction time increases and the temperature remains unchanged or vis

versa, the product yield increases until the theoretical stoichiometric value of the resin is equal to 75 remaining unchanged. Some detect the optimal conditions for the synthesis of terpene phenol resin from monomers terpenes and phenol.

Reaction time: 6 hours, Temperature: 80 ° C, concentration of terpene and phenol in excess

4. Materials and methods:

4.1 Preparation of resin:

Terpene phenolic resins have low molecular weight (MW) of the order of oligomers which are prepared using the reaction of Friedel Crafts through steps.

In the protonation of terpene (typically alpha-pinene), the results of the cationic species are then reacted with phenol. For steric reasons, the initial alkylation (terpenylation) is

produced at the para position of the phenol which is followed by a subsequent and limited alkylation with both ortho-positions. The chain extension beyond "dimer" occurs when the terpene pendant groups (para and some ortho) are again cationized. These

protonated species may then react with another phenolic monomer in a type of chain extension. Once alkylated, the phenol fraction becomes more sensitive to the reaction at the phenolic hydroxyl group, which gives rise to O-alkylation by Terpinyl fractions.

4.2 Characterizations:

The ^1H spectra, ^{13}C and ^{31}P NMR spectra were obtained on a spectrometer of BRUKER AVANCE 300 NMR using CDCl_3 as a solvent. The thermal degradation was carried out by TGA dynamically and the pyrolysis of the samples was conducted in an atmosphere of inert nitrogen. The viscosimetric behavior was measured using a viscometer of "RHEOTEST" in the temperature range of 30 to 80 ° C and at a rate of 1 s⁻¹ of shear.

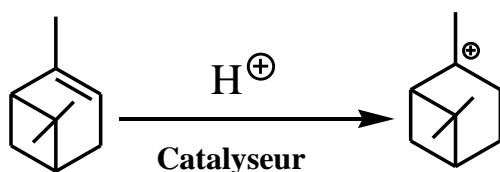
5. Results and discussion:

5.1 Terpene phenol resin synthesis:

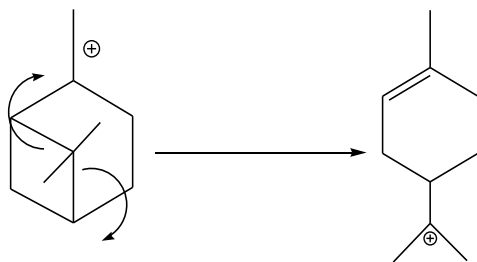
The synthesis of the terpene phenolic resin (TP) requires two steps. In the first step, carbocationic formation of terpene according to a Friedel Crafts. The protonation of terpene, usually isoprene, results in a cationic species which reacts with the phenol, in the second stage.

In the first step:

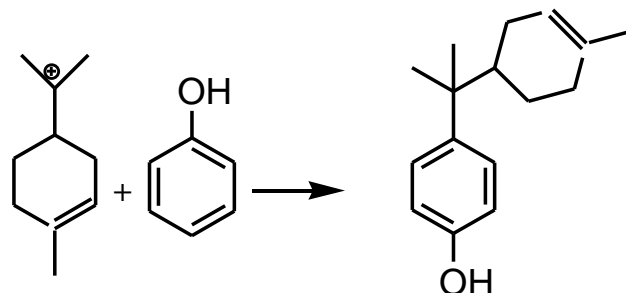
The protonation of terpene monomer by the Friedel Crafts reaction



α -pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene)



+In the second step:



The cationic species which react with the phenol for steric reasons, the alkylation initial (terpenylation) occurs at the para position of the phenol followed by alkylation limited to the higher one of the two ortho positions. The extension of the plus chain beyond "dimer" occurs when the terpene pendant groups (some para and ortho) are cationized again. These protonated species may then react with another phenolic monomer in a type of chain extension.

5.2 Terpene phenolic resin

5.2.1 Spectral characterization by NMR of ^1H :

7.059; 7.048 (s, 4H aromatic), 6.65 (1-benzene) 2.1 (cyclohexane CH), 1.39 (CH₃ methyl 1- beta (CR) 5 ppm (aromatic-OH), 2.01, 1.91, 2.04 (cyclohexene) ^{13}C NMR (ppm): 142 (s, C-1 benzene), 126.5 (s, CH, Benzene) 123.4 (CH, 1-ethylene), 27.8 (s, CH₂ aliphatic ethylene).

5.3 The thermal behavior of the terpene phenol resin

The study of the thermal stability of the product was conducted using thermogravimetric analysis. The results obtained for this resin are illustrated by the curve in figure2.

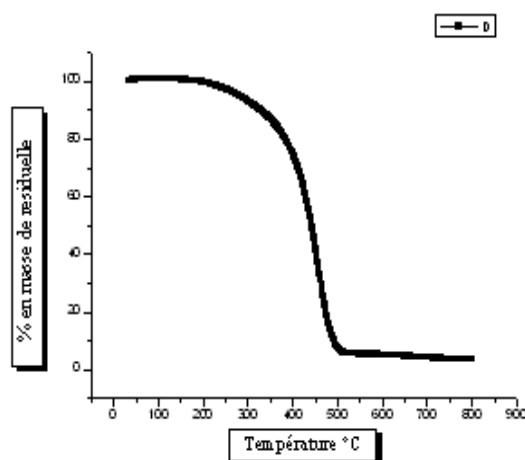


Figure 4: pyrolysis terpene phenol resin sample

The main thermal characteristics of the resin of TP, extracted from the curves In Figure (4), are summarized in Table 2. We notice that the decomposition of TP resin begins at a temperature of 320 ° C.

We then classified the main characteristic of Table 4 according to the conventional standards, with:

Td: starting temperature of decomposition (weight loss of 2%)

T10: temperature at 10% of mass loss

T50: temperature at 50% of mass loss

SDR: threshold of rapid decomposition

R500: fraction of the residue at 500%

Table 4: Major identified thermal characteristics

Resin	Td (°C)	T10 (°C)	T50 (°C)	Sdr	residue at 500 ° C (%)
TP	219	346	401	389	21,7

5.4 Study of the viscometric properties of the terpene phenol resin:

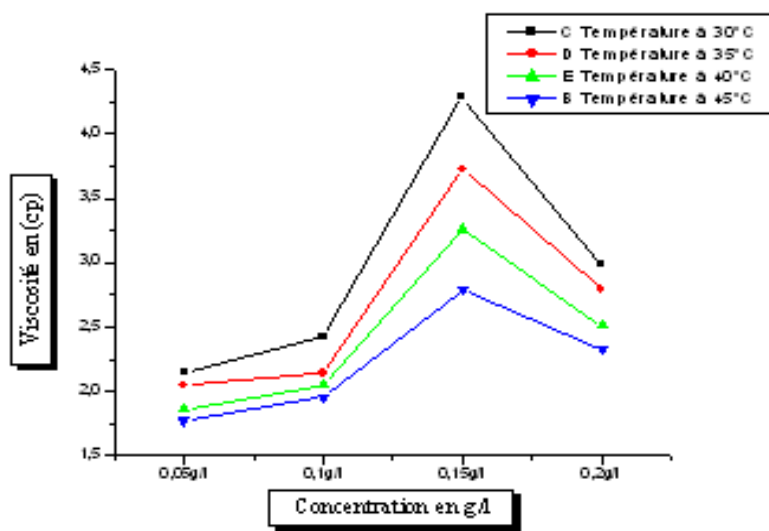


Figure 2: Effect of temperature on the viscosity of the terpene phenol

From Figure 2, the viscometric property can be directly related to the chemical structure or the degree of conversion of the reagent system. The viscosimetric behavior of the prepared resin was studied at different temperature ranges. The curve shows the effect of temperature on the viscosity of the new resin diluted in chloroform. The viscosity increases by increasing the percentage of resin, which can be explained by the increase of the reaction of homopolymerization.

6. CONCLUSION:

Terpene resins phenols are widely seen as having a stronger polarity than all adhesive agents. They provide a specific adhesion in EVA and SBC systems. Their polarity and high softening points are combined to provide an excellent grip in hot applications of binding and packaging. These versatile resins can likewise used in the binding adhesives that require resistance to the ink oil. They will improve the adhesion of hot

packaging and pressure-sensitive adhesives of substrates which are difficult to bond like the recycled coated paper, glass and metal foils.

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