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Modeling and optimization using the experimental design methodology: Synthesis and characterization of a new homologous epoxy resin of DGEBA (diglycidyl 1,3-benzodiazole sulfide (DGBDS)

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Abstract

The purpose of this study is to determine the optimal conditions of synthesis of a new pure stoichiometric epoxy resin by developing a methodological strategy using the technique of experimental designs. Thus, we can establish a mathematical model in order to better represent the synthesis "descriptive model" to explain it "explanatory model" and to predict the answer of a point where no experiment has been made "provisional model". Following the theoretical obtained results by the modeling, we synthesized a new epoxy resin, prepared by the condensation of epichlorohydrin. The synthetic resin was characterized by Fourier Transform Infrared (FTI), ^{1}H, ^{13}C.

Keywords: Synthesis, Epoxy resin, Modeling, Experimental design, Characterization.

1.Introduction

The experimental design method is both new and old **[1]**, newfor mechanical and electronic engineering. Initially developed and put into practice by the British mathematician Sir Ronald Fischer **[2],** after 1945, the design of the experiment gives rise to numerous publications and research in the Anglo-Saxon world. Statisticians like Yates, Cochran, Plackett, and Burmann enrich and disclose the method **[3-4].** Among the thermosetting polymers are epoxy resins (ER) containing in their molecule two or more oxirane functions**[5]**. Their use affects several areas especially electronics, flame retardant, coatings (paints, varnishes, adhesives ...) and finally composites.The most widely used process for the preparation of epoxy prepolymers is by glycosylation, via the condensation of epichloridrine on structures containing at least two mobile hydrogens of the type: diacids**[6]**, diamines**[7]**, and polyphenols **[8, 9]** and sulfur **[10].**

1-1 Theoretical approach

The optimization of the DGDBS epoxy resin synthesis was based on two, KOH and NaOH bases which gave two F1 and F2 responses. To do this, several parameters are involved in resin synthesis. These parameters are grouped in Table **1**.

Table 1:*Experimental Domain*

	Factor	Unity	Center	No variation
U1	Temperature	°C	70.5000	20.5000
U2	Reaction time	h	6.0000	4.0000
U3	Concentration	g/l	1.5000	1.0000

1-2 Mathematical model

The responses are described by a polynomial model of the following form:

$$Y = b_0 + b_1 * X_1 + b_2 * X_2 + b_3 * X_3 + b_{11} * X_1^{\,2} + b_{22} * X^{\,2}_{\,2} + b_{33} * X^{\,2}_{\,3} + b_{12} * X_1 * X_2 + b_{13} * X_1 * X_3 + b_{23} * X_2 * X_3$$

1-3 Model

statistical analysis

The statistical analysis of these results, done using the NEMRODW software, is represented in Tables **2** and **3**. Table 2 shows that the variables selected for the modeling of the response have in general a significant effect at a confidence level, 99% (F_{exp} (9.7) = 63.37) is higher than the theoretical ($F_{0.01}$ (9.7) = 6.72).

Table 2: *Analysis of Variance: Y1 Response:Yield KOH*

Source of variation	Sum of squares	Degrees of freedom	Mean square	Report	Signif
Regression	0.5130	9	0.0570	61.3703	***
Residues	0.0065	7	0.0009		
Validity	0.0060	5	0.0012	5.1726	17.0%
Error	0.0005	2	0.0002		
Total	0.5195	16			

With: Fexp :experimental snedecor factor and *** : significant at99 % (F0.01(9,7) = 6.72)

Table 3: *Estimates and statistics of the coefficients: responseY1: Yield KOH*

Standard deviation of the response	0.030
R^2	0.987
R^2_a	0.971
R^2pred	0.910
PRESS	0.047
Number of degrees of freedom	7

From Table 3 we can say that all the factors have a satisfactory descriptive quality because the correlation coefficient R^2 = 0.987 is closer to 1. The estimated values of the model coefficients and the significance are given in Table 4 (Nemrodw software).

Table 4: *Analysis of coefficients*

Name	Coefficient	F.Inflation	Standard Deviation	t.exp.	Signif. %
b0	0.832		0.018	47.38	***
b1	0.172	1.00	0.008	20.83	***
b2	-0.025	1.00	0.008	-3.03	*
b3	-0.028	1.00	0.008	-3.41	*
b11	-0.053	1.16	0.009	-5.88	***
b22	-0.034	1.16	0.009	-3.74	**
b33	-0.064	1.16	0.009	-7.05	***
b12	-0.046	1.00	0.011	-4.29	**
b13	0.024	1.00	0.011	2.20	6.2%
b23	-0.031	1.00	0.011	-2.90	*

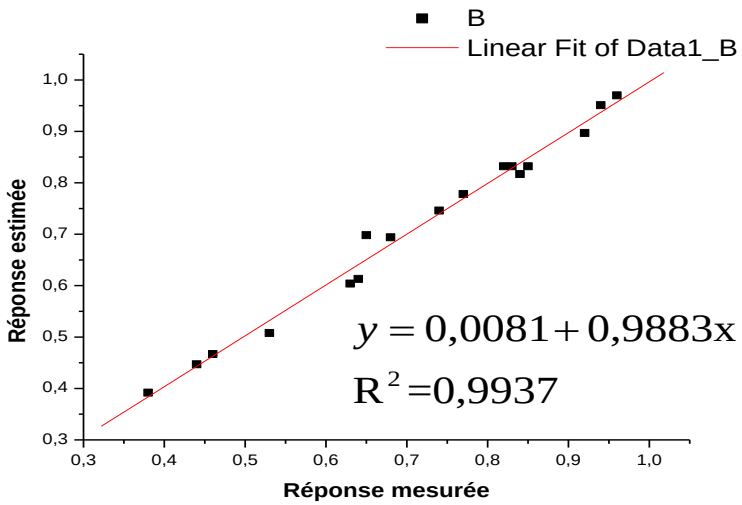

Figure 1: *Representation of the experimental yield according to of the theoretical*

From Figure **1**, we find that there is a correlation between the experimental and calculated values using the proposed model with a correlation coefficient R^2 = 0.9937, which shows that the regression equation obtained is interesting in this study.

1-4 OPTIMIZATIONS: Analysis of isometric curves

The aim of this optimization is to meet a specific objective that is in our case: the synthesis of a pure and stoichiometric epoxy resin.

a) Determination of the optimal value of the duration of the addition

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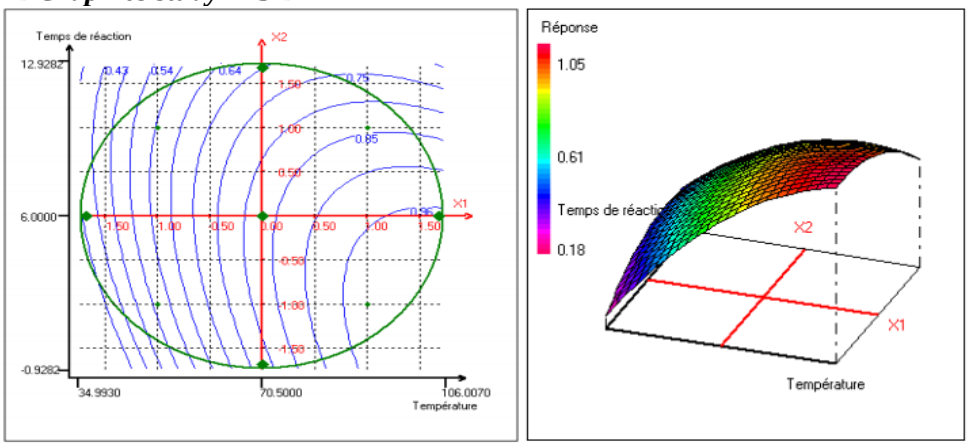

Figure 2: *Variation of the response - yield KOH: Temperature, reaction time*

It confirms with that we have already noted previously in Table 4, a positive effect of the temperature (106 °C) on the response, which generally results in an increase in yield when the reaction time is decreased (6 h) at a point of the fixed value of the concentration.

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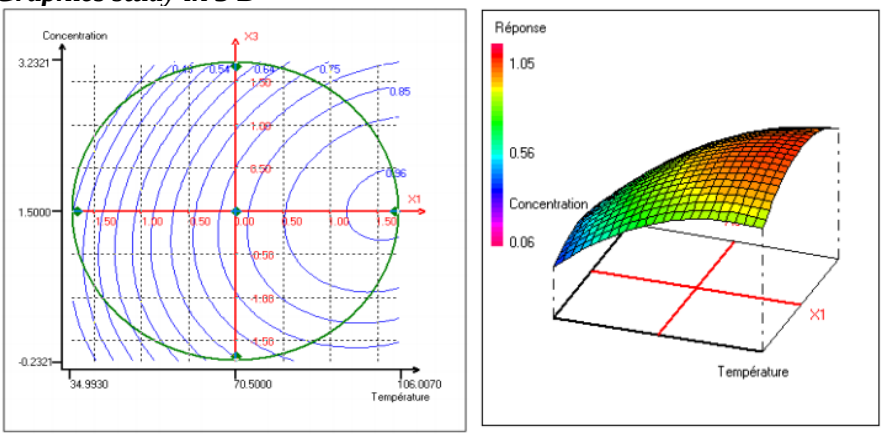

Figure 3: *Variation of the response - yield KOH: Temperature, Concentration*

It confirms with that we found previously in Table 4, a positive effect of temperature on the response which generally results in an increase in yield when the concentration of the base is minimized to1.5 g/l.

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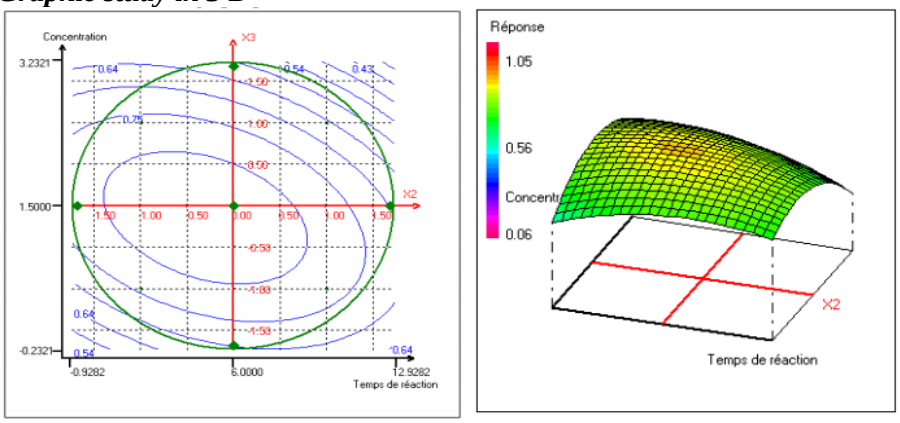

Figure 4: *Variation of the response - yield KOH: reaction time, Concentration*

From this figure, we notice that both factors have a slight effect on the response. These results confirm with that we have already seen previously in Table 4. So for a significance level of 99%, the equation of the model associated with the response is written:

$$\mathbf{Y = 0.832 + 0.172 * X_1 - 0.053 * X_1^2 - 0.064 * X_3^2}$$

1-5 Study of the effect of the base of NaOHon the reaction yield

The Table **5** shows that the variables retained for the modeling of the response that he has a significant effect at a confidence level of 99% (F_{exp} (9.7) = 64.53) is higher than the theoretical ($F_{0.01}$ (18.5) = 6.72).

Table 5: *Analysis of the variance: Y2 response: NaOH yield*

Source of variation	Sum of squares	Degrees of freedom	Mean square	Report	Signif
Regression	0.5520	9	0.0613	64.5346	***
Residues	0.0067	7	0.0010		
Validity	0.0062	5	0.0012	5.3021	16.6%
Error	0.0005	2	0.0002		
Total	0.5586	16			

Avec: Fexp :Snedecor experimental factor and *** : significant at 99 % (F0.01(9,7) = 6.72)

Table 6: *Estimates and statistics of the coefficients: responseY2: Yield NaOH*

Standard deviation of the response	0.030
R^2	0.987
R^2_a	0.971
R^2pred	0.910
PRESS	0.047
Number of degrees of freedom	7

The global analysis consists in determining the values of the coefficients of determination R^2, $R^2_{adjusted}$ and R^2 predictive. According to this table, we can say that the model presents a satisfactory descriptive quality since the values of R^2 (0.988) and $R^2_{adjusted}$ (0.973) are close to 1.

1-5-1 Statistical analysis of model coefficients

The purpose of this statistical test is to know if there are coefficients that are not influential, that is to say, that have no effect on each of the responses.

Table 7:*Analysis of coefficients*

Name	Coefficient	F.Inflation	Standard Deviation	t.exp.	Signif. %
b0	0.813		0.018	45.78	***
b1	0.174	1.00	0.008	20.91	***
b2	-0.024	1.00	0.008	-2.91	*
b3	-0.029	1.00	0.008	-3.46	*
b11	-0.057	1.16	0.009	-6.23	***
b22	-0.048	1.16	0.009	-5.27	**
b33	-0.078	1.16	0.009	-8.54	***
b12	-0.053	1.00	0.011	-4.82	**
b13	0.025	1.00	0.011	2.29	5.4%
b23	-0.018	1.00	0.011	-1.61	15.0%

It can be seen from this table that the coefficients b_{13}, b_{23} are not influential on the response since the value of the significance of these coefficients is greater than 5%. We will now confirm these results by studying the adequacy graph of the model.

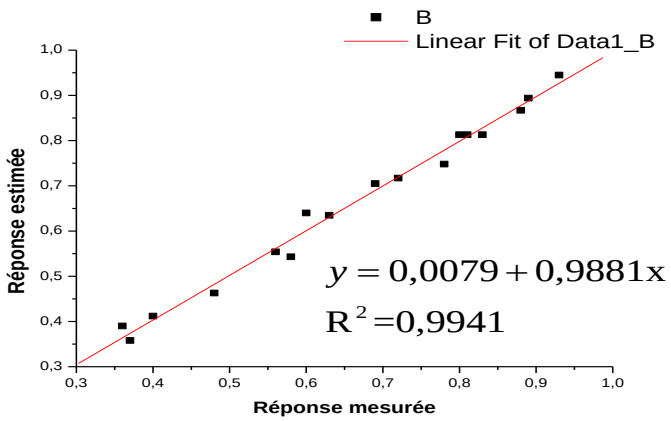

Figure 5: *Representation of experimental yield according to the theoretical*

From the figure**5**, we find that there is a correlation between the experimental and calculated values using the proposed model with a correlation coefficient R^2 = 0, 9941, which shows that the regression equation obtained is interesting in this study.

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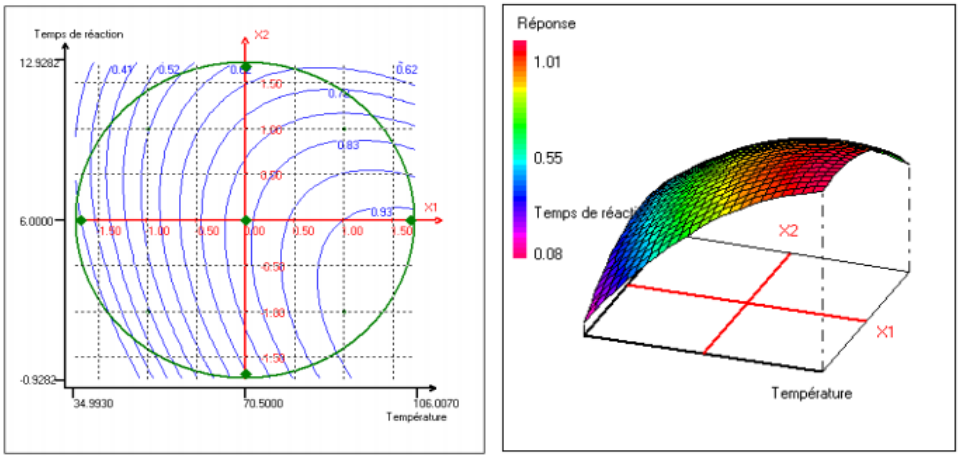

Figure 6: *Variation of response - Yield NaOH: Temperature, reaction time*

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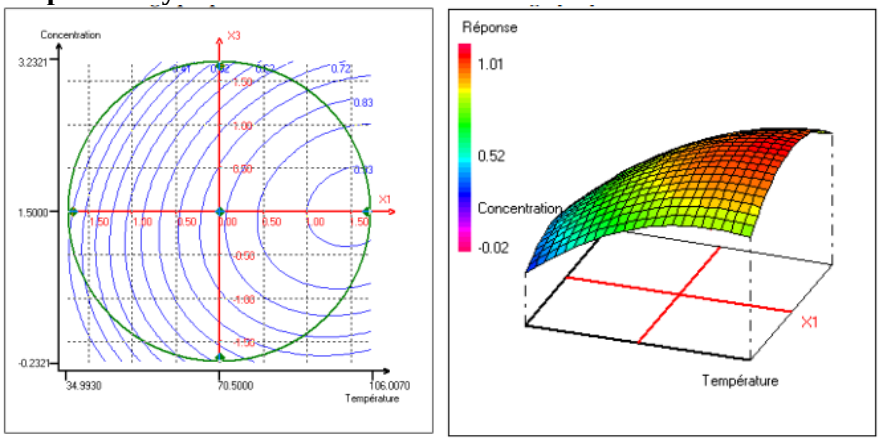

Figure 7: *Variation of response - yield NaOH: Temperature, Concentration*

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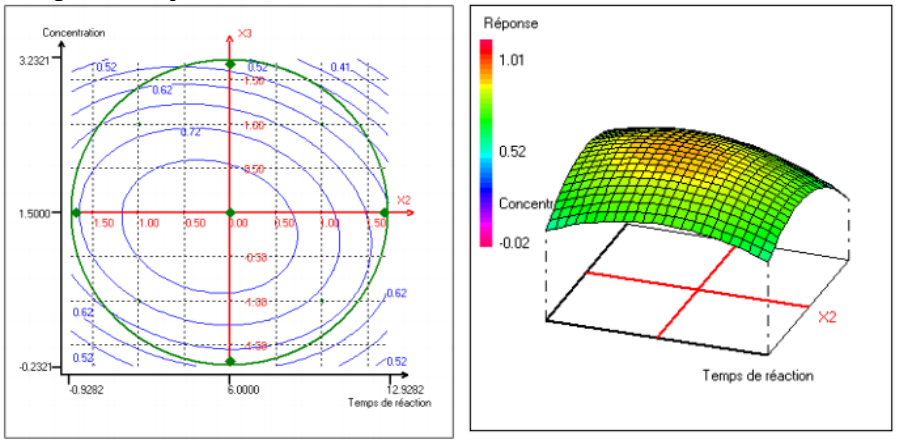

Figure 8: *Variation of response - Yield NaOH: Reaction time, Concentration*

So for a significance level of 99% the equation of the model associated with the response is written: $\mathbf{Y = 0.813 + 0.174 * X_1 - 0.057 * X_1^2 - 0.078 * X_3^2}$

1-5-2 Internal test points

To validate the model at any point in the experimental domain of interest, there is a technique called the validation of the model at the test points.

Table 8: *Estimates and statistics of the coefficients: response (KOH)*

	After Test Point	Before Test Point
Standard deviation of the response	0.009	0.030
R^2	0.999	0.987
R^2_a	0.997	0.971
R^2pred	0.997	0.910
PRESS	0.002	0.047
Number of degrees of freedom	6	7

The multiple linear correlation coefficients now clearly quantifies the very good quality of the adjustment (since R^2 = 0.999≈1).

Table 9: *Table of residues: Response Y1: Yield KOH*

After Test Point				Before Test Point		
N° Exp	Yexp.	Ycalc.	Difference	Yexp.	Ycalc.	Difference
1	0.530	0.532	-0.002	0.530	0.508	0.022
2	0.920	0.921	-0.001	0.920	0.897	0.023
3	0.640	0.637	0.003	0.640	0.613	0.027
4	0.840	0.841	-0.001	0.840	0.817	0.023
5	0.460	0.461	-0.001	0.460	0.467	-0.007
6	0.940	0.944	-0.004	0.940	0.951	-0.011
7	0.440	0.441	-0.001	0.440	0.447	-0.007
8	0.740	0.739	0.001	0.740	0.746	-0.006
9	0.380	0.380	-0.000	0.380	0.392	-0.012
10	0.960	0.958	0.002	0.960	0.970	-0.010
11	0.770	0.766	0.004	0.770	0.778	-0.008
12	0.680	0.682	-0.002	0.680	0.694	-0.014
14	0.630	0.628	0.002	0.650	0.698	-0.048
15	0.820	0.833	-0.013	0.630	0.604	0.026
16	0.830	0.833	-0.003	0.820	0.832	-0.012
17	0.850	0.833	0.017	0.830	0.832	-0.002
-----	-----	-----	-----	0.850	0.832	0.018
13	0.650	0.773	-0.123			

The comparison between the 'Yexp' (measured responses) and 'Ycalc' (predicted by the model) columns confirms that the fit is of very good quality. The other columns proposed by this software evaluate the difference between measured and predicted responses.

1-5-3 Internal test points

Table 10: *Estimates and statistics of the coefficients: Response Y2: Yield NaOH*

	Après point test	Before Test Point test
Standard deviation of the response	0.021	0.031
R^2	0.995	0.988
R^2_a	0.988	0.973
R^2pred	0.957	0.913
PRESS	0.024	0.049
Number of degrees of freedom	6	7

The multiple linear correlation coefficients now clearly quantifies the very good quality of the adjustment (since R^2 = 0.999≈1).

Table 11: *Table of residues: Response Y2: Yield NaOH*

Avant point test				Before Test Point		
N° Exp	Yexp.	Ycalc.	Difference	Yexp.	Ycalc.	Difference
1	0.480	0.463	0.017	0.480	0.482	-0.002
2	0.880	0.867	0.013	0.880	0.886	-0.006
3	0.560	0.554	0.006	0.560	0.574	-0.014
4	0.780	0.748	0.032	0.780	0.768	0.012
5	0.360	0.390	-0.030	0.360	0.385	-0.025
6	0.890	0.894	-0.004	0.890	0.889	0.001
7	0.400	0.412	-0.012	0.400	0.406	-0.006
8	0.690	0.705	-0.015	0.690	0.700	-0.010
9	0.370	0.358	0.012	0.370	0.348	0.022
10	0.930	0.945	-0.015	0.930	0.935	-0.005
11	0.720	0.717	0.003	0.720	0.707	0.013
12	0.630	0.635	-0.005	0.630	0.625	0.005
13	0.600	0.640	-0.040	0.580	0.562	0.018
14	0.580	0.543	0.037	0.800	0.814	-0.014
15	0.800	0.813	-0.013	0.810	0.814	-0.004
16	0.810	0.813	-0.003	0.830	0.814	0.016
17	0.830	0.813	0.017	-----	-----	-----

The comparison between the Yexp (measured responses) and Ycal (model predicted responses) columns confirms that the fit is of very good quality.

1-6 Search for the optimum KOH

From the previous results, the best least squares model is used to write the mean predicted response in the form:

$Y = 0.833 + 0.172 * X_1 – 0.025 * X_2 – 0.043 * X_3 – 0.058 * (X_1*X_1) - 0.039 * (X_2*X_2) – 0.047 * (X_3*X_3) – 0.046 * (X_1*X_2) + 0.024 * (X_1*X_3) – 0.031 * (X_2*X_3)$

This model has been simplified and summarizes only the factors, the interaction effects and the coefficients of the models of the 2nd square having judged their meanings in a confidence interval of 99%.

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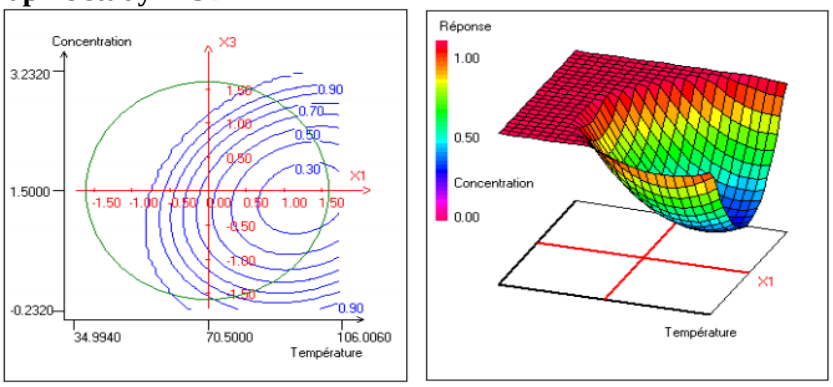


Figure 9: *Variation of desirability in the plane: Temperature, Concentration*

Graphic study in 2DGraphic study in 3D

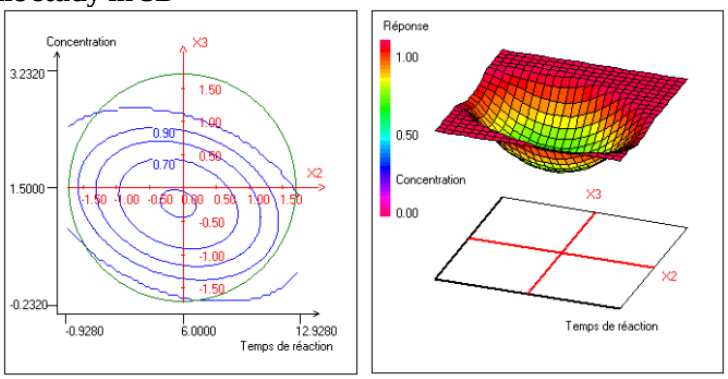


Figure 10: *Variation of desirability in the plane: reaction time, concentration*

❖ **Search for the optimum NaOH**

From the previous results, the best least squares model is used to write the mean predicted response in the form:

$Y = 0.814 + 0.174 * X_1 – 0.061 * (X_1*X_1) - 0.052 * (X_2*X_2) – 0.065 * (X_3*X_3) – 0.053 * (X_1*X_2)$

This model has been simplified and summarizes only the factors, interaction effects, and coefficients of the 2nd square models that have judged their meanings within a 99% confidence interval.

Graphic study in 2DGraphic study in 3D

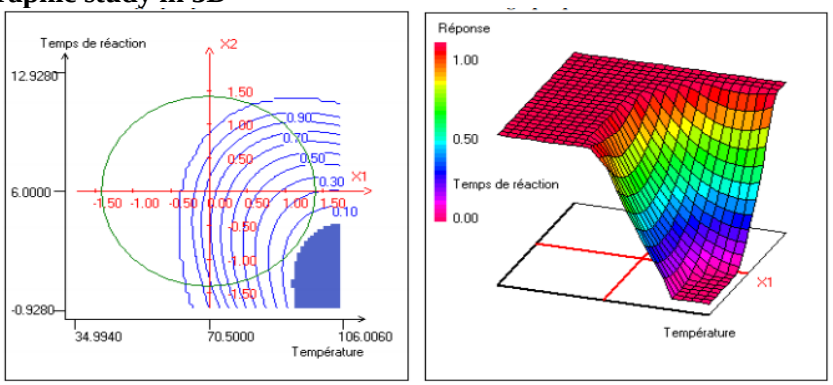


Figure 11: *Variation of desirability in the plane: Temperature, reaction time*

Graphic study in 2DGraphic study in 3D

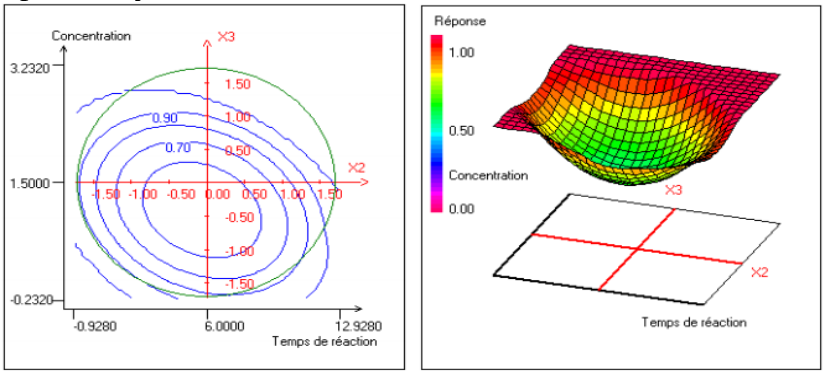


Figure 12: *Variation of desirability in the plane: reaction time, concentration*
FIXED FACTORS: Temperature = 66.8085 °C

In this study, a centered composite plan is used. This plane is used in a spherical domain, the location of the optimum on the boundary of the spherical domain. The search for an optimum is done using experience plan software; the solutions found the lead to major quality factors. The results are summarized in Table 12.

Table 12: *Result of the optimum search*

The optimum factors when using NaOH			
Variable	Value	Factor	Value
X1	-0.267375	Temperature	65.0188
X2	0.661770	Reaction time	8.6471
X3	0.869694	Concentration	2.3697
The optimum factors when using KOH			
X1	-0.180072	Temperature	66.8085
X2	0.780158	Reaction time	9.1206
X3	0.989102	Concentration	2.4891

2- Material and method

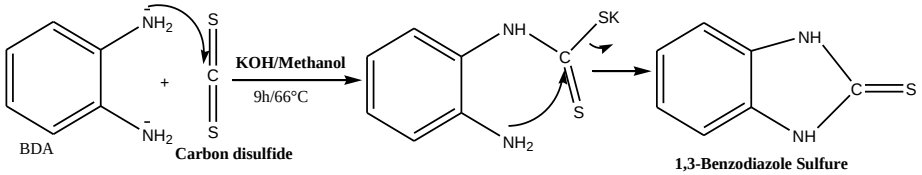
All of the basic chemicals were provided by Acros Chemical Co. and Aldrich Chemical Co. Our material formulated from matrix consisting of new resin DGBDS reticulated with methylene dianiline MDA.

2-1 Synthesis of the epoxy resin

2.1.1 Synthesis of the new epoxy resin based on (DGBDS)

The Diglycidyl resin of 1, 3-benzodiazole sulfide (DGBDS) is produced by the action of epichloridin on 1,3-benzodiazole sulfide, the synthesis is described by the following reaction scheme:

1st step: the synthesis of 1,3-benzodiazole sulfide from benzene dianiline (BDA) and carbon disulfide according to the reaction:



2nd step: the action of epichlorohydrin on 1,3-benzodiazole sulfide

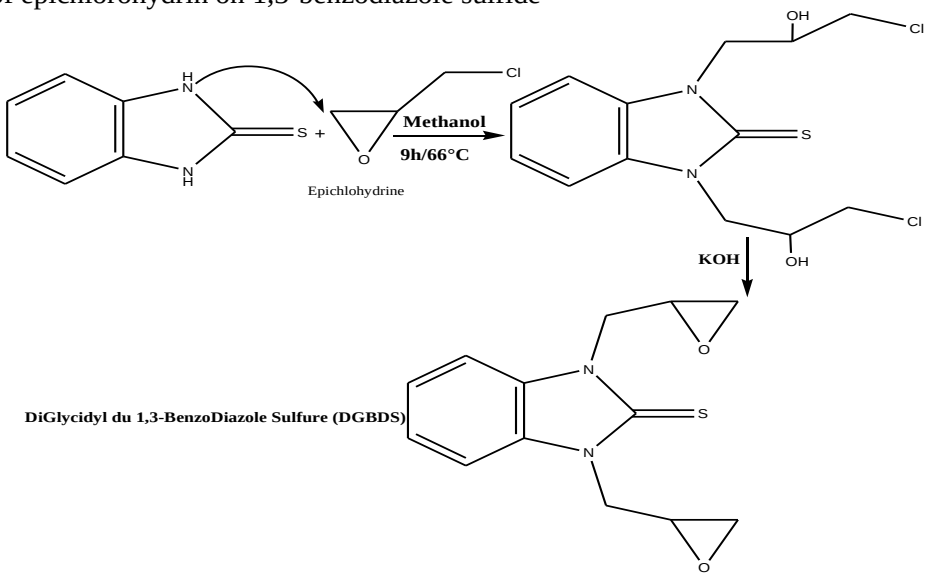


Figure 13: Synthetic scheme of diglycidyl of 1,3-benzodiazole sulfide (DGBDS)

2-2 Characterization methods

2-2-1 Fourier Transform Infrared (FTI)

The IR spectrometer used is a BRUKER Fourier Transform Spectrometer (FTIR). The light beam passes through the sample to a thickness of about 2 µm. The analysis is carried out between 4000 cm^{-1} and 600 cm^{-1}.

2-2-2 Nuclear Magnetic Resonance (NMR)

The analysis of RMN ^{1}H, ^{13}C were obtained using an AVANCE 300 Bruker type device, dissolving the product in the $CDCl_3$The chemical shifts are expressed in ppm.

2-2-3 Humidity setting

The Humidity setting of the samples of the reticulated resin is expressed by the following formula:

$$P = \frac{M_i - M_s}{M_s}$$

P: Humidity setting; **Ms**: The mass of the dry sample; **Mi**: The mass of the sample immersed

3- RESULTS AND DISCUSSIONS

3-1 Fourier Transform Infrared (FTI)

The IR absorption spectra of 1,3-benzodiazole sulfide and DGBDS are shown in Figures 14 and 15, respectively:

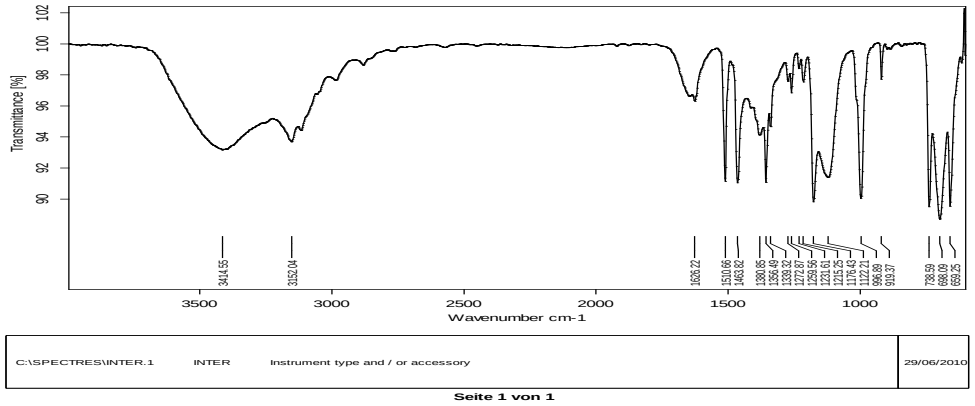


Figure 14: *Absorption spectra of 1,3-benzodiazole*

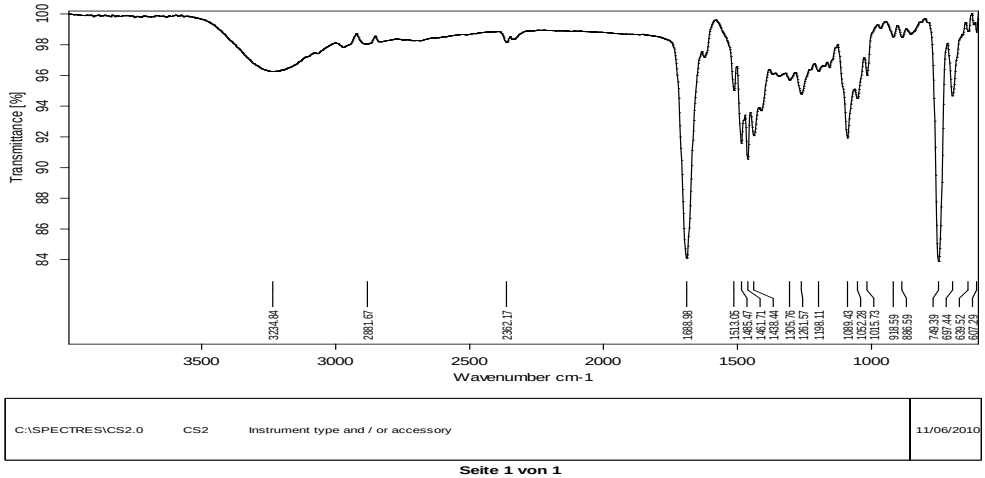


Figure 15: *Absorption spectra by IR of DGDBS*

Table 13: IR absorption bands of the two products.

Position of bands	**Interpretations**
3114(3500-3050)	-*v* NH amine and amide associate
3152	
1626(1650-1550)	-δ NH secondary amine
1510(1525-1470)	-*v C-C* aromatic nucleus
1122(1120)	-Thioamide
698 (700-570)	- Sulfide, thiol
659	

		Description
3234(3500-3050)	-*v*NHamine and amide associate	Decrease in intensity
1513(1525-1470)	-*vC-C* aromatic nucleus	
886(950-810)	-*v*C-O-C Epoxides	Appearance

The presence of the secondary amine, thioamide, and sulphide (or thiol) peaks confirms the structure of the 1,3-benzodiazole sulphide obtained during the first step of the synthesis, the second IR analysis shows the appearance of an epoxy peak and the disappearance of the secondary amine peak, by cons several peaks in the two spectra remain to be interpreted.

3-2 Nuclear magnetic resonance (NMR)

❖ ***The NMR 1H***

The NMR ^{1}H of the product obtained shows the presence of different types of protons, so that the protons CH of the oxirane ring give a split doublet centered at 2.77ppm, the proton CH_2 epoxide resonates like a multiplet centered at 2.63 and 2.38ppm, protonsCH2methylene 1-α-C (N) (= S) appear as a distribution doublet centered at 3.70 and 3.45 ppm, the proton CH carried by the benzene nucleus resonates like amultiplet centered at 7.26 ppm.

❖ ***NMR 13C:***

The NMR 13C of the product obtained shows the presence of different types of 13C, as well as the carbon (-CH2) aliphatic oxirane 1-α-C ring,resonates as a singlet centered at 45.9 ppm, the carbon -CH epoxide ring 2- α-C aliphatic gives a singlet centered at 48.8 ppm, NC carbon resonates as singlet centered at 56.7 ppm, carbon -CH benzene ring gives a doublet centered at 126.8 ppm, carbon (-C) (1-NC = S) resonates as a 139 ppm singlet and finally the carbon (-C) thioamide also resonates as singlet centered at 168.7 ppm.

3-3 Humidity setting

We measured the humidity setting of two samples (DGBDS) and a mixture of DGEBA / 20% (DGBDS) / MDA. The results are respectively represented by the following two figures 16 and 17.

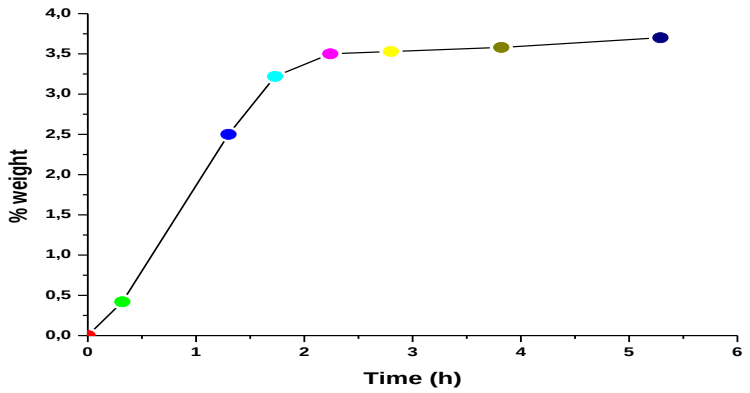


Figure 16: *Humidity setting test of DGDBS/MDA*

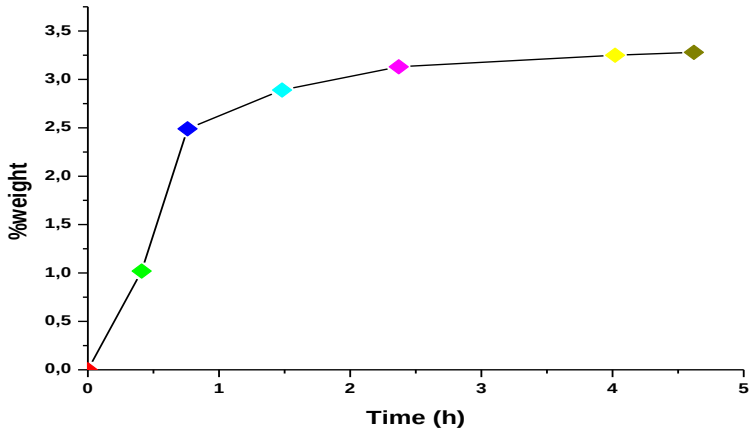


Figure 17:*Humidity setting test of DGEBA/DGDBS/MDA*

From Figures 16 and 17, we notice that the diffusion of the humidity obeys the fickien behavior and we observe a maximum of diffusion as a function of time. Thus, the maximum water absorption of the samples is respectively 4.58% and 4.22%.

3-4 Determination of the storage temperature

The curve represents the effect of temperature on the viscosity of new resin diluted in chloroform.

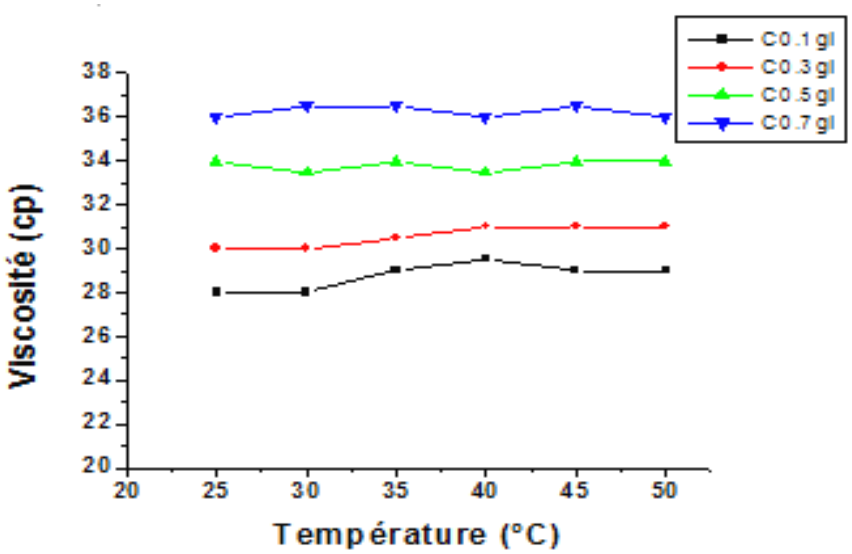


Figure 18: *Effect of temperature on the viscosity of synthesized epoxy resin*

The viscosity increases by increasing the percentage of resin, which can be explained by the progress of the homopolymerization reaction. Viscosity increases with increasing solute molecular weight. The viscosities of each ratio remain constant as a function of temperature. It emerges from this analysis that the sulfur-based resin has thermal stability to avoid self-crosslinking during storage. We can, therefore, confirm that our synthetic resins can be stored at temperatures above 45 °C without fear of damage.

4- CONCLUSION

During this study, we developed a new bifunctional epoxy resin. The new epoxide has been synthesized and characterized by 1H, 13C, NMR, and IR-TF. The results confirmed the structure of our resins. The epoxy resin was cured with methylene dianiline curing agents (MDA) to provide corresponding epoxy polymers on one hand. On the other hand, we measured the moisture intake of two samples (DGBDS) and a mixture of DGEBA / 20% DGBDS / MDA. As we measured the viscosity of the resin as a function of temperature. In this study, the centered composite plane has been used in a spherical domain, the location of the optimum at the center of the spherical domain, allows building a new plane by decreasing the experimental domains of the two input factors.

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