

Quantitative Effects of Synthesis Conditions on Oil Absorptive Properties of Oil Gels Based on EPDM/4-*tert*-Butylstyrene

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ABSTRACT: The oil absorption properties of porous polymeric gels are dependent on their synthesis conditions. In this work, we have investigated whether it is feasible to find a quantitative relationship between the synthesis conditions of porous poly(EPDM/4-*tert*-Butylstyrene) gels and their behavior in the kerosene absorption through a factorial design of experiments. For this purpose, a series of such oil gels have been synthesized in toluene with various divinylbenzene (DVB) and EPDM contents. The kerosene absorbency and kerosene-absorption kinetics of oil gels were determined. Finally, empirical models correlating the synthe-

sis conditions with the kerosene absorbency (Q_{eq}) and kerosene-absorption kinetic constant (K) were calculated; it was observed that lower the DVB concentration and higher the EPDM fraction in the monomeric mixtures, the higher the kerosene absorbency. With regard to the kerosene-absorption kinetics, the largest K value was achieved with the lowest DVB concentration and the highest EPDM fraction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2213–2220, 2009

Key words: oil gel; factorial design of experiment; oil absorption; absorption kinetics; response surface

INTRODUCTION

The oil pollution of marine becomes more and more serious because of the development of petroleum industry and the marine oil transportation. One of the methods to solve this problem is using oil sorbents, such as silica gel,¹ zeolites,² active carbon,³ and natural and synthetic polymers.^{4–10} Some of them have proved to be highly efficient.

A critical step in the sorption processes is the choice of the most suitable absorbent for a specific separation problem. It is desirable that the absorbent should have a high absorption capacity, fast oil-absorption rate, good absorption selectivity of oil over water, convenient shipping and storage, lower density compared with water to float with or without oil absorbed, chemical stability.⁵ In this respect, polymeric absorbents have proved to be useful in the absorption of oil or oil-like solvents and, in particular, porous oil gels based on rubber have been intensively researched to investigate the influence of

the synthesis conditions on the structural characteristics and oil absorbency, previously.^{6,7} However, to the best of our knowledge, there are no works that have reported the quantitative relationships between the oil absorbency of oil gels and their synthesis conditions, nor have we found any information about research focused on the quantitative influence of the synthesis conditions of oil gels on the absorption kinetics, which would provide very valuable information for the design of oil gels.

Taking this into account, in this work, a series of porous oil gels based on EPDM/4-*tert*-butylstyrene were synthesized with several divinylbenzene (DVB) and EPDM concentrations through a factorial design of experiments with the goal of finding quantitative relationships between the oil absorptive properties of oil gels and DVB and EPDM concentration, which facilitates the synthesis of oil gels with predetermined absorption properties, and these quantitative relationships should be considered as a reasonable starting point in the choice of the most appropriate absorbent for a specific absorption process.

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EXPERIMENTAL

Materials

4-*tert*-Butylstyrene (*t*BS; Aldrich Chem, USA) and DVB (Fluka, USA) were each extracted with a 5%

aqueous sodium hydroxide solution and water, dried over anhydrous sodium sulfate, and distilled under reduced pressure before use. Benzoyl peroxide (BPO; Aldrich Chem) was recrystallized from a methanol solution. EPDM, having ethylidene norbornene as a termonomer (Aldrich, ethylene/propylene = 50/50, $M_n = 50500$, $M_w = 102000$, Mooney Viscosity = 85), and all other chemicals were used as received.

Polymerization

The EPDM/*t*BS copolymers were prepared in aqueous suspension polymerization using toluene as dilution, mixing together with BPO initiator 1 wt %. The weight percentage of DVB concentration in monomeric mixture and the monomeric fraction of EPDM (F_m) in EPDM/*t*BS mixture were varied. To hinder coalescence and break-up of droplets in the course of polymerization; gelatine, tricalcium phosphate, and sodium dodecylsulfate (SDS) were used as suspending agent at a certain ratio. The ratio of organic phase to water phase was 1 : 5.

In a 250 mL four-necked reaction flask fitted with a variable mechanical stirrer, thermometer, nitrogen gas inlet, and reflux condenser, the suspension copolymerization reaction was started at 40°C, and 5°C was elevated every hour up to 80°C. The copolymerization and crosslinking reactions taking place in the monomer-diluent droplets result in the formation of beads having a glassy, opaque, or milky appearance, the resulting copolymer beads were then filtered and washed with hydrochloric acid and hot water orderly, and then dried under a vacuum at 60°C until to a constant weight. The diluent, the residual monomers, and the uncrosslinked copolymers were removed by extracted with tetrahydrofuran and *n*-hexane in a Soxhlet apparatus, finally they were dried under vacuum at 60°C until the weight was constant.

Oil-absorption test

Oil-absorptivities of oil gels were determined by ASTM (F726–81)¹¹: 0.1 g gel was put in a stainless steel mesh ($4 \times 4 \times 2 \text{ cm}^3$), and immersed in kerosene. The swollen gels were taken out at regular time intervals, wiped superficially with tissue paper gently, weighed on a balance and replaced into the same bath. This procedure of swelling and weighing was continued until the sample achieved a constant final weight. The equilibrium oil absorbency of crosslinked polymer gel Q_{eq} can be calculated

$$Q_{\text{eq}} = \frac{W_e - W_0}{W_0} \quad (1)$$

where W_0 is the initial weight of the sample and W_e is the weight at equilibrium.

Design and analysis of experiments

To perform the research reported here, the design of experiments methodology was followed.^{12–15} This procedure allows one to determine if interactions between the factors occur and to obtain quantitative cause-effect relationships. Use of this methodology requires the following steps:

Problem identification

The aim of this work was to study the quantitative effect of the synthesis conditions (factors) on the oil absorptive properties of the product obtained (responses). The advantage of knowing these relationships is that it facilitates the synthesis of oil gels with predetermined absorptive properties.

Factor identification

Previous experimental findings have revealed that the DVB concentration, the EPDM fraction, and the solvating power of the porogen have a critical effect on the oil absorptive properties of gels. The effects of the concentration and type of initiator and the polymerization temperature are less pronounced. This work focused on the study of the effects of the DVB concentration and EPDM fraction. Accordingly, the other reaction conditions remained the same in all experimental runs carried out.

Level identification

In this stage, the range of values of the factors (levels) must be selected. In an earlier work, we identified in a general manner the range of values of the DVB concentration and EPDM fraction that leads to the production of porous oil gels. The values investigated by us were chosen within this range. The highest level for the DVB concentration was 15%.

The research was initially planned as a two-factorial design, with only four experiments, designated *Design I*. These first four experiments were then replicated (experiments 5–8) to obtain an estimate of the experimental error and a more precise estimate of the effects of the factors on the response. The real values of the levels investigated in *Design I* are those corresponding to the points depicted with a triangle in Figure 1. The design matrix of *Design I* is given in Table I, which also shows the order in which the experiments were performed. This run order was determined in a randomized way because the statistical study of the results requires that the observations be independently distributed random

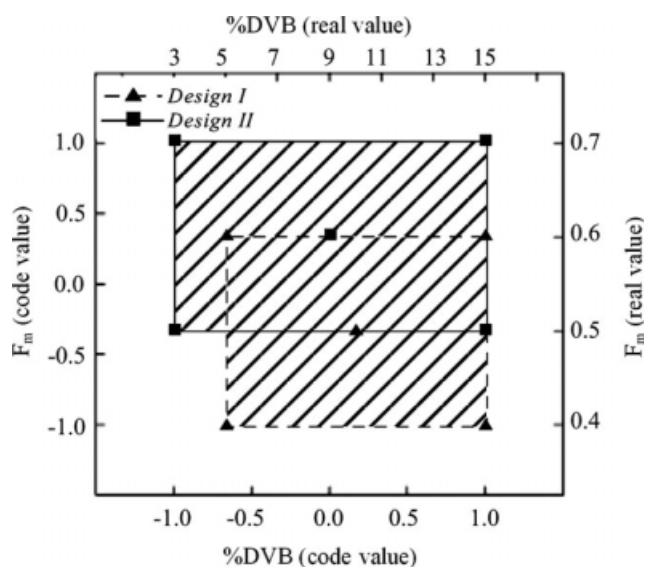


Figure 1 Factor levels used in the experiments carried out in Design I and Design II. The coded values in this figure correspond to those used in the multiple linear regression analysis, which are designated as the Global coded scheme. The shaded region indicates the application range for the correlations obtained.

variables. To facilitate the interpretation of the results, the real values of the levels were coded by assigning a value of -1 to the low level and a value of $+1$ to the high level of the range studied. Additionally, since a potential concern in the use of two-level factorial designs is the assumption of linearity in the factor effects, two center points were also included in the design with a view to checking whether there was curvature. These center points, corresponding to experiments 9 and 10 of Design I, are also shown in Figure 1.

Since it was found that the oil gels obtained at the low level of EPDM content were rigid, a new central two-factorial design, designated *Design II*, was planned using higher levels for this factor. More-

over, a broader range of the DVB concentration was considered in this new set of experiments to enlarge the studied region. Again, 10 experiments were performed in this design, corresponding to four experiments of the two-factorial design (experiments 11–14), another four experiments to replicate them (experiments 15–18), and two center points (experiments 19 and 20). The values of the levels investigated in Design II correspond to the points depicted as squares in Figure 1, and the design matrix is shown in Table II.

Response identification

Because the most important items used for evaluating a absorbent are absorptive properties. Therefore, the oil absorbency and oil absorptive rate were chosen as responses. Both responses were correlated with the synthesis conditions through multiple linear regression analysis.

RESULTS AND DISCUSSION

Oil absorbency

Taking one gel sample from each pair of replicates for oil absorption test, the kerosene absorbency is shown in Figure 2. It is observed that the oil absorbency of the gel increases with the larger fraction of EPDM, which can be explained that EPDM is macromolecular and oleophilic soft monomer, whereas *t*BS is rigid monomer, and thereby addition of EPDM content in polymerization can reduce the oil gel's rigidity caused by phenyl group in *t*BS structure. The more EPDM content, the looser structure of polymeric gel, and more solvent can be held. Additionally, the oil absorbency decreases with increasing DVB concentration. This is because an increase in the amount of a chemical crosslinking agent causes the formation of a denser network of the copolymer

TABLE I
Design Matrix and Values of Responses for Design I

Experiments		Factors and interaction					Responses		
No.	Run order	%DVB		F_m		%DVB F_m	Q_{eq} (g g ⁻¹)	K (min ⁻¹)	R^2
		Real values	Code values	Real values	Code values				
1	3	5.0	-1	0.4	-1	+1	18.56	0.043	0.973
2	4	15.0	+1	0.4	-1	-1	7.37	0.030	0.966
3	1	5.0	-1	0.6	+1	-1	22.62		
4	2	15.0	+1	0.6	+1	+1	11.14	0.042	0.983
5	6	5.0	-1	0.4	-1	+1	18.10		
6	7	15.0	+1	0.4	-1	-1	7.70		
7	5	5.0	-1	0.6	+1	+1	21.75	0.044	0.975
8	8	15.0	+1	0.6	+1	+1	10.48		
9	9	10.0	0	0.5	0	0	15.36	0.042	0.983
10	10	10.0	0	0.5	0	0	14.92		
Effects on Q_{eq}			-11.08		3.56	-0.29			

TABLE II
Design Matrix and Values of the Responses for Design II

Experiments		Factors and interaction					Responses		
No.	Run order	%DVB		F_m		%DVB F_m	Q_{eq} (g g ⁻¹)	K (min ⁻¹)	R^2
		Real values	Code values	Real values	Code values	Code values			
11	11	3.0	-1	0.5	-1	+1	18.76	0.048	0.972
12	12	15.0	+1	0.5	-1	-1	9.32		
13	15	3.0	-1	0.7	+1	-1	19.63	0.051	0.968
14	12	15.0	+1	0.7	+1	+1	6.83	0.040	0.983
15	17	3.0	-1	0.5	-1	+1	17.50		
16	18	15.0	+1	0.5	-1	-1	11.87	0.033	0.968
17	13	3.0	-1	0.7	+1	+1	20.25		
18	14	15.0	+1	0.7	+1	+1	6.10		
19	19	9.0	0	0.6	0	0	13.62		
20	20	9.0	0	0.6	0	0	12.77	0.043	0.978
Effects on Q_{eq}			-10.51		-1.16	-2.97			

and reduces the chain length between crosslinks, which reduces oil absorbency.

Absorption kinetics

The oil-absorption kinetics of oil gels is shown in Figure 2, where Q_t plotted versus time. Because all the gels have different structural characteristics as a result of their different synthesis conditions, the curves of the absorption kinetics differ from some gels to others. More careful scrutiny of the curves reveals that the rate of approach to equilibrium is smaller for the gels synthesized with the highest DVB concentrations. However, before attempting to establish a quantitative inter-relationship between the absorption kinetics and the synthesis conditions for all the gels, it is necessary to collect further information about the mass-transfer processes that participate in the global absorption process.

It is well known that the absorption of kerosene can be described in terms of a three-step mechanism, which contains three steps¹⁶: (1) A short initial stage of a high absorption rate due to the solvation of the network chains; the main driving force of this process is the change in the free energies of mixing and elastic deformation during expansion of the network; (2) a longer stage of a constant, slow absorption rate due to the resistance of diffusion into the pores on account of the pore structure and dimensions; and (3) a third stage of a plateau value because of absorption saturation.

The first-order kinetics equation is commonly used to describe the experimental absorption rate, which is directly proportional to the oil absorbency at any given time before the maximum or equilibrium absorption (Q_{max}) has been reached. If Q_t is the oil absorbency at time t , ($Q_{max} - Q_t$) is the unrealized absorption of oil medium. If K is the absorption

kinetic constant which is dependent on the synthesis conditions of gels, then¹⁷:

$$\frac{dQ}{dt} = K(Q_{max} - Q_t) \quad (2)$$

which integrates to:

$$\ln \frac{Q_{max}}{Q_{max} - Q_t} = Kt \quad (3)$$

From eq. (2), the relationship between Q_{max} and Q_t can be obtained:

$$Q_t = Q_{max}(1 - e^{-Kt}) \quad (4)$$

The kinetic curves calculated from the eq. (4) are plotted in Figure 3, where they can be compared with the experimental kinetic data for each gel. It may be observed that most of the experimental kinetic data are situated on the theoretical curves, indicating that the first-order absorption kinetics is able to describe the mass-transfer process adequately through the gels.

A rapid look at the values of K for each gels allows us to corroborate in a quantitative way the preliminary qualitative findings achieved from inspection of the location of the experimental kinetic

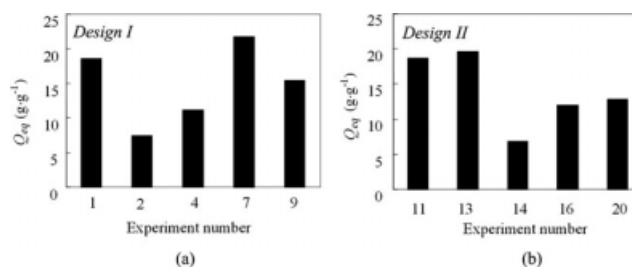


Figure 2 Kerosene absorbency of gels in Design I (a) and Design II (b).

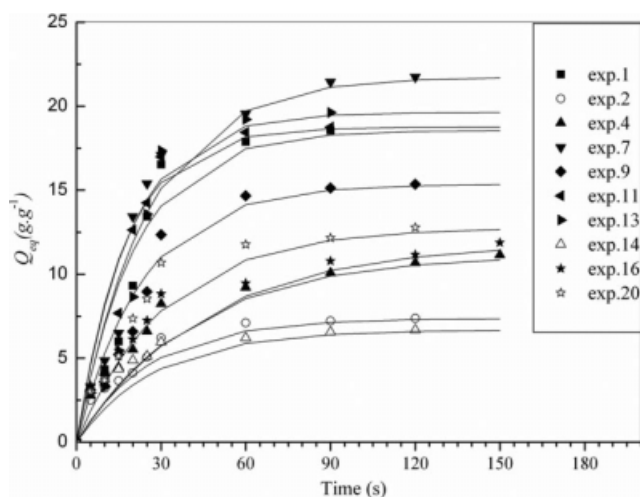


Figure 3 Curves of the kerosene-absorption kinetics of gels. The symbols represented experimental data, and solid lines were calculated with the first-order kinetics equation [eq. (4)].

data in Figure 3: the gels synthesized with the highest concentrations of DVB show the smallest rate of approach to equilibrium and, hence, have the lowest K values.

Factorial designs of experiments

After experiments 1–10 of Design I were performed, the oil absorption test was conducted. From the values of this response for each type of gels, listed in Table I, the effect of the factors and interaction Q_{eq} was calculated. The values of the effects of both factors and their interaction are reported in the last row of Table I.

Within the range of values of the factors studied in Design I, it was observed that the %DVB factor is the key factor influencing the Q_{eq} response negatively: an increase in the DVB concentration results in a considerable decrease in the Q_{eq} response. The

effect of the F_m factor on the response is, by contrast, less important and is positive (i.e., the higher the EPDM fraction, the higher the Q_{eq}). Regarding the interaction of the factors, and considering its negative effect on response, we can state that the higher the %DVB, the lower the Q_{eq} and that this effect becomes more pronounced as the level of F_m declines.

After the effects were calculated, an analysis of variance (ANOVA) was applied to the experimental Q_{eq} results to establish the statistical significance of the influence of the factors, their interaction, and curvature. The results are shown in Table III.

ANOVA gives the values of the F statistics and their corresponding P values for each source of variation studied (factors, interaction, and curvature). From the values calculated for the F statistics, it may be concluded that both factors, except for their interaction, have a significant effect on the Q_{eq} response within the range investigated and that this influence is linear because the value of the F statistics for curvature is lower than the tabulated value, $F_{0.05,1,5} = 6.61$, where 0.05 is the level of significance, 1 is the degrees of freedom of these sources of variation, and 5 is the degrees of freedom of the error. Furthermore, the ANOVA indicates there is no evidence of interaction between the factors in the response over the region of exploration.

Likewise, in the second factorial design, Design II, experiments 11–20 were run, and the Q_{eq} response was calculated for the oil gels thus obtained. From the values of this response, the effects of the factors and interaction were determined; they are shown in the last row of Table II. When the values of the effects of the factors and interaction are scrutinized, it can be seen that the %DVB factor has the greatest effect on the Q_{eq} response within the range studied. This effect is negative and, therefore, the higher the DVB concentration, the lower the Q_{eq} . Interestingly, the effect of the F_m factor on the response is also

TABLE III
ANOVA Tables for Designs I and II

Design	Source of variation	Sum of squares	Degree of freedom	Mean square	F	P
I	%DVB	245.75	1	245.75	1445.58	<0.001
	F_m	25.42	1	25.42	149.53	<0.001
	%DVB F_m	0.17	1	0.17	1.00	0.366
	Curvature	0.29	1	0.48	2.82	0.250
	Residual error	0.85	5	0.17		
	Total	272.48	9			
	$F_{0.05,1,5} = 6.61$					
II	%DVB	220.71	1	220.71	227.54	<0.001
	F_m	2.69	1	2.69	2.77	0.157
	%DVB F_m	17.64	1	17.64	18.18	0.008
	Curvature	0.55	1	0.55	1.20	0.485
	Residual error	4.87	5	0.97		
	Total	246.46	9			
	$F_{0.05,1,5} = 6.61$					

negative. This means the optimized EPDM fraction is 0.6.

Also in this case, as in Design I, the statistical significance of the effects of the factors, their interaction and curvature, was calculated by applying ANOVA to the experimental data of Design II. The results are also shown in Table III and indicate that %DVB and interaction between %DVB and EPDM fraction have a significant influence in the response, and this influence is linear because the value of the F statistics for curvature is smaller than the tabulated value $F_{0.05,1,5} = 6.61$, where 0.05, 1, 5 have the same meaning as before.

The values of the effects of the factors and their interaction are not the same in both designs. This can be explained considering that these values depend on the amplitude of the range of the levels of the factors studied and that, in this work, this amplitude was different from one design to the other. It can be noted that in Design I, both factors except for their interaction have a significant effect on the response, whereas in Design II, EPDM fraction has no significant influence on the response. This is consistent with the previous conclusion that the maximum EPDM content is 0.6.

Fitting a response surface to Q_{eq}

To enable the prediction of the Q_{eq} at any combination of levels of the factors, a multiple linear regression analysis was applied to fit a response surface model to the 20 experimental results. Initially, a model including quadratic terms was fitted to the data despite the results in Design I, II indicated both factors, their interaction, and the curvature were not all significant. The regression coefficients of a second-order response surface model were estimated by the least-squares method,¹⁵ affording the equation

$$\widehat{Q}_{eq} = 16.0 - 5.60x_{\%DVB} + 0.05x_{F_m} - 0.76x_{\%DVB}x_{F_m} - 0.52x_{\%DVB}^2 - 2.10x_{F_m}^2 \quad (5)$$

where \widehat{Q}_{eq} denotes the predicted value of the Q_{eq} response and the terms $x_{\%DVB}$, x_{F_m} and $x_{\%DVB}x_{F_m}$ represent the coded values of %DVB, F_m , and their interaction, respectively. Likewise, $x_{\%DVB}^2$ and $x_{F_m}^2$ are the coded quadratic terms responsible for the curvature of the model. In this case, the coded scheme followed is designated *Global*, as indicated in Figure 1.

The usefulness of the model was checked by applying ANOVA to the regression equation. It was determined that at least one of the five regressor variables contributed significantly to the model. However, the test for the lack of fit of the model indicated that this quadratic model was not adequate to explain the experimental data. Hence, a

higher-order model incorporating cubic terms was calculated

$$\widehat{Q}_{eq} = 15.9 - 15.0x_{\%DVB} - 6.35x_{F_m} - 2.85x_{\%DVB}x_{F_m} + 0.07x_{\%DVB}^2 - 5.10x_{F_m}^2 + 9.62x_{\%DVB}x_{F_m}^2 + 0.93x_{\%DVB}x_{F_m}^2 + 10.1x_{\%DVB}^3 - 0.96x_{F_m}^3 \quad (6)$$

Again, in this case, the ANOVA for the significance of the regression was performed to check the adequacy of the cubic model, and it was observed that at least one of the nine regressor variables had a nonzero regression coefficient. The test for the lack of fit of the model indicated that this quadratic model was adequate to explain the experimental data. Therefore, the next step, to determine which regressor variables contributed significantly to the model, was to test the significance of the individual regression coefficients. Their t statistics and their corresponding P values are reported in Table IV.

The regression coefficients were statistically significant, with a level of significance of 0.05 if the absolute values of their t statistics were higher than $t_{0.025,10} = 2.228$, where 0.025 is the half-value of the level of significance and 10 represents the degrees of freedom of the residual error. Therefore, since the t statistics for the regression coefficients of %DVB%DVB, %DVB F_mF_m , and $F_mF_mF_m$ were smaller than 2.228, the regressor variables $x_{\%DVB}^2$, $x_{\%DVB}x_{F_m}^2$, and $x_{F_m}^3$ could be eliminated from eq. (6), then the experimental data were subjected again to multiple linear regression analysis, the following reduced cubic model was obtained

$$\widehat{Q}_{eq} = 15.8 - 14.8x_{\%DVB} - 5.69x_{F_m} - 2.52x_{\%DVB}x_{F_m} - 4.62x_{F_m}^2 + 10.4x_{\%DVB}x_{F_m}^2 + 7.75x_{\%DVB}^3 \quad (7)$$

Since eq. (7) is a different model from eq. (6), another new ANOVA was performed to determine the significance of the regression. The ANOVA results are summarized in Table V.

TABLE IV
Statistical Significance of the Regression Coefficients of the Cubic Model for Q_{eq} Given by Equation 2

Term	t	P
Constant	43.35	<0.001
%DVB	-9.36	<0.001
F_m	-5.00	0.001
%DVB F_m	-6.88	<0.001
%DVB%DVB	0.13	0.897
F_mF_m	-8.10	<0.001
%DVB%DVB F_m	5.42	<0.001
%DVB F_mF_m	1.40	0.191
%DVB%DVB%DVB	5.89	<0.001
$F_mF_mF_m$	-0.72	0.490
$t_{0.025,10} = 2.228$		

TABLE V
ANOVA for the Significance of Regression of the Reduced Cubic Model of Q_{eq} Given by Equation 3

Source of variation	Sum of squares	Degrees of freedom	Mean square	F	Tabulated F	P
Regression	518.45	6	86.04	161.88	$F_{0.05,3,16} = 2.92$	<0.001
Residual error	6.94	13	0.53			
Lack of fit	1.22	3	0.41	0.72	$F_{0.025,3,16} = 3.71$	
Pure error	5.72	10	0.57			
Total	525.39	19				
$R^2 = 0.987$			0.987			
$R^2_{adj} = 0.981$			0.981			

In this case, the P value for the F statistic of the regression is smaller than 0.001, indicating that at least one of the six regressor variables contributes significantly to the reduced cubic model, as mentioned before. Furthermore, the coefficient of multiple determination, R^2 , is close to 1, meaning that the model fits the experimental data well. In addition, the adjusted R^2 statistic, R^2_{adj} , is close to R^2 , which confirms that nonsignificant terms have not been included in the model. With regard to the test for the lack of fit, since the F statistic calculated does not exceed $F_{0.05,3,10} = 3.71$, it can be said that the reduced cubic model given by eq. (7) fits the experimental data well and that this model can be used to predict Q_{eq} at any value of the %DVB and F_m factors within the region studied. The significance of the individual regression coefficients was also tested, again showing that all of these coefficients were statistically significant.

Scrutiny of the regression coefficients of eq. (7) reveals that high Q_{eq} can be obtained by decreasing the DVB concentration and that this influence becomes more marked as the EPDM fraction increases. The presence of quadratic and cubic terms implies that there are stationary points in this relationship. In the contour plot of eq. (7), as illustrated

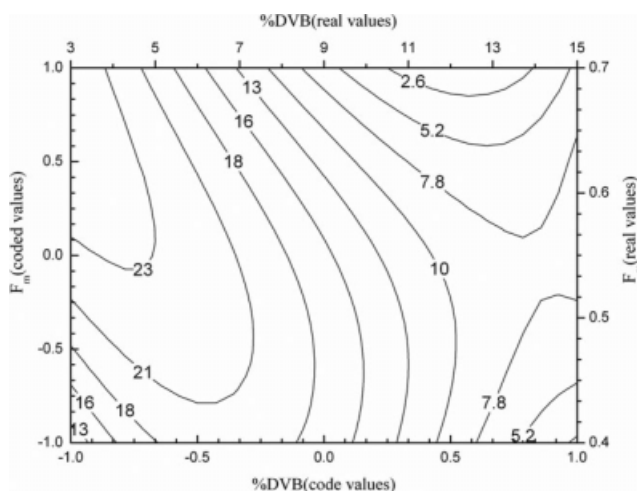


Figure 4 Contour plot of Q_{eq} ($g\ g^{-1}$) according to the reduced cubic model given by eq. (8).

in Figure 4, it may be observed that a maximum Q_{eq} of $24.26\ g\ g^{-1}$ should be obtained when operating with a DVB concentration of 4.14% and a EPDM fraction of 0.60.

Correlation between the absorption kinetics of the gels and their synthesis conditions

After it had been observed that there were differences in the absorption kinetics of the gels because of their different synthesis conditions, it seemed appropriate to investigate whether there was a quantitative relationship between the characteristics of the absorption kinetics and the operating conditions (values of % DVB and F_m).

Accordingly, to search for a correlation suitable for predicting the amount of kerosene absorbed at different times on several different oil gels, as a function of their synthesis conditions, the model given by eq. (4) was chosen as a starting point because of its good fit to the experimental kinetic data.

Taking into account that, in eq. (4), K has been shown to be dependent on the synthesis conditions, this term was substituted by a second-order polynomial in the following manner:

$$Q_t = Q_{max} \{1 - \exp[-(a_0 + a_1x_{\%DVB} + a_2x_{F_m} + a_3x_{\%DVB}x_{F_m} + a_4x_{\%DVB}^2 + a_5x_{F_m}^2)t]\} \quad (8)$$

where $x_{\%DVB}$ and x_{F_m} represent the coded values of %DVB and F_m , respectively (see Table I). To fit eq. (4) to the kinetic data, multiple nonlinear regression techniques were used. The regression

TABLE VI
Regression Coefficients of Equation 8

Regression coefficient	Value	95% confidence
a_0	0.04114	0.00142
a_1	-0.00668	0.00086
a_2	0.00382	0.00101
a_3	0.00175	0.00111
a_4	-0.00102	0.00190
a_5	-0.00006	0.00166

$R^2 = 0.957$

TABLE VII
Regression Coefficients of Equation 9

Regression coefficient	Value	95% confidence
a_0	0.04114	0.00058
a_1	-0.00682	0.00070
a_2	0.00373	0.00085
a_3	0.00185	0.00094
$R^2 = 0.953$		

coefficients (a_0, a_1, \dots, a_5) were estimated with the Levenberg-Marquardt algorithm, and the values obtained are shown in Table VI, together with their 95% confidence intervals.

For the regression model to be stable and statistically valid, the confidence intervals must be smaller than the respective values of the regression coefficients (in absolute values). In this case, the 95% confidence intervals for the regression coefficients a_4 and a_5 are larger than the values of the regression coefficients themselves. This may indicate that these regression coefficients are not needed. Therefore, the regressor variables $x_{\%DVB}^2$ and $x_{F_m}^2$ were eliminated from eq. (8), resulting in the equation

$$Q_t = Q_{\max} \{1 - \exp[-(a_0 + a_1 x_{\%DVB} + a_2 x_{F_m} + a_3 x_{\%DVB} x_{F_m})t]\} \quad (9)$$

When the regression analysis was performed again, the values of the regression coefficients of eq. (9) were determined. These values are given in Table VII, where the 95% confidence intervals are also shown. It can be observed that the 95% confidence intervals are much smaller than the values of their corresponding regression coefficients after a_4 and a_5 are removed. Despite the correlation coefficient, R^2 , is not enhanced to close to 1, all this indicates that the model given by eq. (9), with the values shown in Table VII, is statistically valid and stable and, hence, suitable for reliably predicting the kerosene-absorption kinetics of these gels.

From the values of the regression coefficients obtained, it can be deduced that the fastest absorption is achieved when the gels are synthesized with the lowest DVB concentration and biggest EPDM fraction, at which the oil gels may exhibit the highest proportion of pores.

CONCLUSIONS

Porous oil gels based on EPDM/4-*tert*-butylstyrene using toluene as diluent have been synthesized. The DVB concentration and the EPDM fraction in the reactive mixture were varied to study their effects on the oil absorptive characteristics of the gels, namely the kerosene absorbency and kerosene-absorption

kinetic constant. The experiments were planned through a factorial design of experiments and using this procedure, together with multiple linear regression analysis, quantitative relationships (empirical models) between the synthesis conditions and these oil absorptive characteristics were obtained. These may be of use for determining suitable compositions of polymerization mixtures for obtaining poly (EPDM/*t*BS) gels with predetermined oil absorptive properties. The quantitative relationship found between the synthesis conditions and the kerosene absorbency indicates that the smaller the %DVB and the higher EPDM fraction, the higher the kerosene absorbency.

With regard to kerosene-absorption kinetics, the first-order kinetic model proved to be a reliable model to explain the experimental kinetic data, and it was therefore used to calculate the kerosene-absorption kinetic constant (K) through nonlinear multiple regression analysis. In this case, it was observed that the fastest absorption was achieved with the lowest DVB content and highest EPDM fraction. However, it is necessary to take into account that any change in the oil medium involves a change in the type of oil-gel interaction and changes in the viscosity. Therefore, since the models given in this work were obtained with kerosene, any significant change in the oil medium will introduce inaccuracies in the predictions.

References

- Hrubesh, L. W.; Coronado, P. R.; Satcher, J. H. *J Non-Cryst Solids* 2001, 285, 328.
- Meininghaus, C. K. W.; Prins, R. *Microporous Mesoporous Mater* 2000, 35, 349.
- Stenzel, M. H. *Chem Eng Prog* 1993, 89, 36.
- Choi, H. M. *J Environ Sci Health Part A* 1996, 31, 1441.
- Jang, J.; Kim, B. S. *J Appl Polym Sci* 2000, 77, 914.
- Zhou, M. H.; Cho, W. J. *Polym Int* 2001, 50, 1193.
- Zhou, M. H.; Cho, W. J. *J Appl Polym Sci* 2002, 85, 2119.
- Zhou, M. H.; Cho, W. J. *J Appl Polym Sci* 2003, 89, 1818.
- Atta, A. M.; Arndt, K. F. *J Appl Polym Sci* 2005, 97, 80.
- Atta, A. M.; El-Ghazawy, R. A. M.; Farag, R. K. *Polym Int* 2005, 54, 1088.
- ASTM. Standard Method of Testing Sorbent Performance of Adsorbents E1, F726; ASTM: West Conshohocken, Pennsylvania, 1993.
- Himmelblau, D. M. *Process Analysis by Statistical Methods*; Wiley: New York, 1970.
- Box, G. E. P.; Hunter, W. G.; Hunter, J. S. *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building*; Wiley: New York, 1978.
- Draper, N. R.; Smith, H. *Applied Regression Analysis*; Wiley: New York, 1981.
- Montgomery, D. C. *Design and Analysis of Experiments*; Wiley: New York, 2001.
- Kangwansupamonkon, W.; Damronglerd, S.; Kiatkamjornwong, S. *J Appl Polym Sci* 2001, 79, 504.
- Yao, K. J.; Zhou, W. J. *J Appl Polym Sci* 1994, 53, 1533.