Optimized Formulation of an Oxidative Curing System for Liquid Polysulfide Sealants Used in Fuel Tanks by D-Optimal Design Method

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ABSTRACT: In this work, the effective parameters in liquid polysulfide curing system were optimized by D-optimal design method. Five main components in the formulation, carbon black, vulcanizing agents (MnO_2, $Na_2Cr_2O_7$, and PbO_2), $CaCO_3$, fumed silica, and chlorinated paraffin, were selected. Mechanical and chemical properties of the samples were investigated. The results showed that tensile strength, hardness, viscosity, and optimum cure time (t_{90}) presented a suitable coordination with reduced quadratic model. For elongation at break and swelling tests, reduced two-factor interaction (2FI), and for peel strength, a linear model showed the best correlation. To achieve the desirable properties for liquid polysulfide sealants used in fuel tanks, an optimized amount of the above components in the formulation were used. Finally, MnO_2 curing system, compared with $Na_2Cr_2O_7$ and PbO_2, was selected as the best choice. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2550–2562, 2011

Key words: polysulfides; response surface methodology; sealants; carbon black; vulcanization

INTRODUCTION

The commercial vulcanization process of liquid polysulfide (LPS) or polysulfide oligomers are based on the oxidation of —SH groups with dioxides of a transition metal like MnO_2, PbO_2, or $Na_2Cr_2O_7$. In this process, the oxidation of mercaptan end groups and branches leads to the formation of disulfide crosslinks. Scheme 1 represents the basis of a commercial vulcanization process for LPS.[1] The exceptional polysulfide chain structure is the most important feature in the properties of the final products made from this polymer. About 37% of polysulfide total weight is sulfur, which leads to low solubility of this polymer in different solvents. LPS sealants have a high chemical resistance, high resistance to solvent swelling,[2] appropriate interaction with water molecules,[3] low permeability,[4] self-repair,[5] and good adhesion to other surfaces.[6]

To design and optimize all the effective parameters in a polysulfide curing system (the amount of carbon black, filler, plasticizer, vulcanizing agents, etc.), it is necessary to establish a suitable relation between different components and the properties of the final product. Generally, economic considerations such as cost reduction,[7] cure time,[8] and ultimately the selection of an appropriate experimental design model for use in different formulations[9] are essential. Response surface methodology (RSM) was considered as the best choice for this purpose.

RSM is a collection of statistical and mathematical techniques that have been used for modeling and analyzing engineering problems. In this method, the main purpose is the optimization of surface responses. which is affected by different process parameters. Also, RSM expresses the relation between controllable entry parameters with response levels quantitatively.[10] The design procedure in RSM is as follows[11]:

1. Samples preparation and collection of a series of properties, which are obtained by accurate and reliable measurements
2. The development of a mathematical model with the best curve fittings
3. Determination of the best optimized laboratory parameters, which give the highest or lowest values
4. The presentation of direct effects and interaction parameters of the process with two- or three-dimensional curves.

When experimental results were obtained, regression analysis was carried out to determine the answer model index (a_1, $a_2 \ldots a_n$), and their standard deviations were determined [eq. (1)]. The response model consists one of the following:[12]

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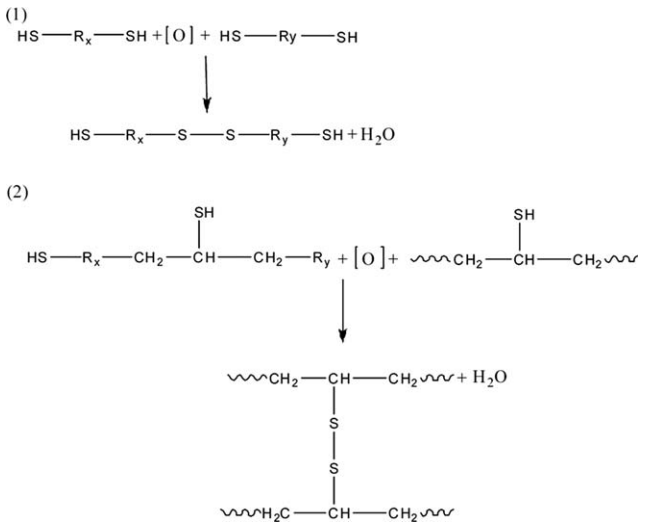

Scheme 1 The oxidative vulcanization systems for a liquid polysulfide sample.

- Linear terms for each of the variables (x_1, $x_2 \ldots x_n$)
- Square terms for each of the variables (x_1^2, $x_2^2 \ldots x_n^2$)
- Primary interaction terms for each pair (x_1x_2, $x_1x_3 \ldots x_{n-i}x_n$)

$$y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} a_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j=i+1}^{n} a_{ij} x_i x_j, \quad (1)$$

In this equation, a_0 is a constant number.

In this study, a discussion and analysis of optimized oxidative curing formulation for polysulfide sealants were carried out by considering the most important independent variables. It was tried to get the best curing system and optimized amounts of each component such as semi-reinforcing furnace carbon black (SRF), vulcanizing agent (MnO_2, $Na_2Cr_2O_7$, and PbO_2), calcium carbonate ($CaCO_3$), CAB-O-SIL® fumed silica, and chlorinated paraffin on the basis of the experimental results. Also, a comprehensive and accurate model for every effective parameter was predicted until there was best agreement with the results. Using RSM/D-optimal method, optimized functions were taken for all the amounts of effective parameters to obtain suitable answers. This method is applicable for many other polymeric systems, with their effective variables, and is a novel approach in this field.

MATERIALS AND METHODS

Experimental

The experimental plan was carried out by using Design Expert V.6 (Stat-Easy Inc., Minneapolis, MN). Table I shows the five main effective independent parameters SRF, vulcanizing agent, $CaCO_3$, CAB-O-SIL, and chlorinated paraffin, which are represented, respectively, by x_1, x_2, x_3, x_4, and x_5. Factors x_1–x_5 are shown as coded and numeric formats in two actual surfaces. The curing system is represented by x_6, which is a categorical factor, and, finally, the most suitable choice is selected. Table II gives the experimental design results, which were obtained by D-optimal in 43 runs with the analytical data of the tests. On this basis, the effects of all the parameters (x_1–x_5) for all the answers (y_1–y_8) were investigated. Finally, for each response, a linear or polynomial model on the basis of effective parameters and their interactions are fixed and represented as a generalized scheme.

Materials

LPS resin (grade NVB-2, density 1.28 g/cm^3, viscosity at 25°C, 7.50–11 Pa sec, mass fraction of S—H groups 3–4%, and molecular weight 1650–2200 g/mol) was obtained from Kazan Synthetic Rubber Plant Co., Russian federation. Carbon black (SRF) (amorphous, with particle diameter 0.1–3 mm) was received from Pars Carbon, Iran. Coated calcium carbonate was supplied by Windavar Co., Ltd., Iran. CAB-O-SIL fumed silica was obtained from Cabot Corp., US. Chlorinated paraffin was obtained from C. P. Hall, US. Oxidative vulcanizing agents, MnO_2, $Na_2Cr_2O_7$, and PbO_2 were received from Kaiyvan Chemical Co., Ltd., Tianjin Kingshine International Trade Co., Ltd., and Shijia Zhuang Xintai Longjiang Chemical Import and Export Co., Ltd., China, respectively. The other ingredients were of technical grade and were purchased from Germany and Malaysia.

TABLE I
The Range of Independent Variables and Coded Level for Experimental Design

Factor	Name	Type	Low actual	High actual	Low coded	High coded
x_1	Carbon black (SRF)	Numeric	0	45	−1	1
x_2	Vulcanizing agent	Numeric	1	7	−1	1
x_3	$CaCO_3$	Numeric	10	30	−1	1
x_4	CAB-O-SIL®	Numeric	0	20	−1	1
x_5	Chlorinated paraffin	Numeric	5	20	−1	1
x_6	Curing system	Categorical	MnO_2	$Na_2Cr_2O_7$	PbO_2	–

TABLE II
D-Optimal Design to Study the Effects of Carbon Black (SRF) (x_1), Vulcanizing Agent (x_2), $CaCO_3$ (x_3), CAB-O-SIL® (x_4), Chlorinated Paraffin (x_5), and Curing System (x_6) on the Tensile Strength (TS) (y_1), Elongation at Break (EB) (y_2), Hardness (Shore A) (y_3), Lap Shear Strength (y_4), Peel Strength (y_5), Viscosity (y_6), Optimum Cure Time (t_{90}) (y_7), and Swelling (y_8) of Vulcanized Polysulfide

Run	x_1	x_2	x_3	x_4	x_5	x_6	TS (MPa) (y_1)	EB (%) (y_2)	Hardness (shore A) (y_3)	Lap shear strength (MPa) (y_4)	Peel strength (kN/m) (y_5)	Viscosity (Pa sec) (y_6)	Optimum cure time (t_{90}) (min) (y_7)	Swelling (%) (y_8)
1	45	5	20	0	12	MnO_2	3.94	301	57	1.62	3.12	500	161	7.4
2	0	5	10	0	5	MnO_2	1.63	302	25	0.66	7.24	180	185	0.1
3	0	1	30	20	12	MnO_2	2.07	192	28	0.45	4.93	486	242	19.4
4	45	3	10	0	20	MnO_2	2.89	363	44	1.24	2.79	406	103	2.9
5	15	7	20	20	20	MnO_2	3.53	468	33	1.99	3.75	463	95	11.2
6	0	7	30	10	20	MnO_2	2.52	478	14	0.76	1.91	259	66	14.8
7	15	7	30	0	5	MnO_2	3.25	300	35	1.42	3.23	333	116	20.5
8	30	1	30	0	20	MnO_2	2.26	244	33	0.61	1.52	415	212	16.3
9	45	7	30	20	5	MnO_2	5.81	233	74	2.86	4.03	848	100	22.7
10	30	7	10	10	5	$Na_2Cr_2O_7$	3.25	195	61	1.67	5.04	430	285	4
11	15	7	20	20	20	$Na_2Cr_2O_7$	2.71	344	54	1.61	4.16	446	338	1
12	45	5	30	20	5	$Na_2Cr_2O_7$	3.7	118	71	2.3	5	756	65	24
13	30	7	30	0	12	$Na_2Cr_2O_7$	2.15	251	49	1.58	2.75	366	45	19
14	0	3	30	20	12	$Na_2Cr_2O_7$	1.47	165	43	1.07	3.26	429	438	21
15	45	1	20	0	20	$Na_2Cr_2O_7$	2.11	280	40	1.27	2.33	417	443	18
16	45	1	20	0	20	$Na_2Cr_2O_7$	2.11	280	40	1.27	2.33	417	443	18
17	0	3	20	0	5	$Na_2Cr_2O_7$	0.75	78	29	0.57	3.96	117	180	22
18	15	1	10	10	12	$Na_2Cr_2O_7$	1.01	186	30	0.76	3.83	170	224	24
19	0	5	30	10	20	$Na_2Cr_2O_7$	0.63	323	30	0.79	1.44	153	318	18
20	45	5	30	20	5	$Na_2Cr_2O_7$	3.7	118	71	2.3	5.00	756	65	24
21	45	7	10	0	12	$Na_2Cr_2O_7$	2.86	292	54	1.69	3.89	407	119	4
22	30	7	10	10	5	$Na_2Cr_2O_7$	3.25	195	61	1.67	5.04	430	285	4
23	0	1	30	20	12	PbO_2	1.17	85	24	0.89	4.45	494	174	33
24	45	7	10	0	12	PbO_2	2.23	382	58	1.7	5.55	513	65	7
25	30	1	20	20	5	PbO_2	1.71	56	51	1.29	4.34	693	152	35
26	45	1	20	0	20	PbO_2	1.37	137	36	1.06	2.23	481	179	29
27	15	5	20	10	12	PbO_2	1.29	200	34	0.98	2.9	336	137	28
28	30	5	30	0	20	PbO_2	1.36	240	31	1.04	0.26	407	135	26
29	15	7	20	20	20	PbO_2	2.04	424	43	1.58	3.92	501	81	2
30	30	5	10	20	5	PbO_2	1.92	146	51	1.48	8.25	667	141	21
31	30	5	10	20	5	PbO_2	1.92	146	51	1.48	8.25	667	141	21
32	0	1	10	0	5	PbO_2	0.38	80	17	0.29	5.24	166	168	33
33	45	1	30	10	5	PbO_2	1.94	43	55	1.49	3.28	676	154	38
34	30	1	20	20	5	PbO_2	1.71	56	51	1.29	4.34	693	152	35
35	0	7	20	0	5	PbO_2	1.34	358	36	1.03	3.25	242	67	10
36	0	7	30	10	20	PbO_2	1.56	425	28	1.21	2.31	297	72	4
37	15	1	30	0	5	PbO_2	0.99	55	30	0.78	2.33	337	148	37
38	15	3	10	20	20	PbO_2	1.54	351	34	1.18	4.37	419	100	13
39	15	3	30	0	5	PbO_2	1.61	236	42	1.24	3.85	379	97	17
40	0	3	10	0	5	PbO_2	0.96	261	28	0.74	6.83	208	122	14
41	30	7	30	0	12	PbO_2	2.14	371	50	1.63	3.04	497	76	10
42	45	7	30	20	5	PbO_2	2.9	332	75	2.23	4.35	885	82	15
43	45	5	10	0	20	PbO_2	1.51	251	40	1.14	2.69	423	117	21

Samples preparation

According to the samples formulations given in Table II, amounts of components x_1–x_5 for each of curing system (x_6) were mixed with 100 weight parts LPS. Samples preparations were carried out in a two-stage process. At first, vulcanizing agent (MnO_2 or $Na_2Cr_2O_7$ or PbO_2) was mixed with half of the chlorinated paraffin in a mixer at 60 rpm for 15 min at 25°C. On the other hand, LPS was mixed with carbon black (SRF), $CaCO_3$, CAB-O-SIL, stearic acid, and the rest of 50% chlorinated paraffin was added to the mixer at the same conditions. At last, the vulcanizing agents and the base compound were mixed in a mixer at 60 rpm for 20 min and then vulcanization of the compound was carried out at 60°C.

Samples characterization

Mechanical properties

Tensile strength (TS) tests of the samples were determined using a universal tensile tester, Instron Co., model 1114. The measurements were done according

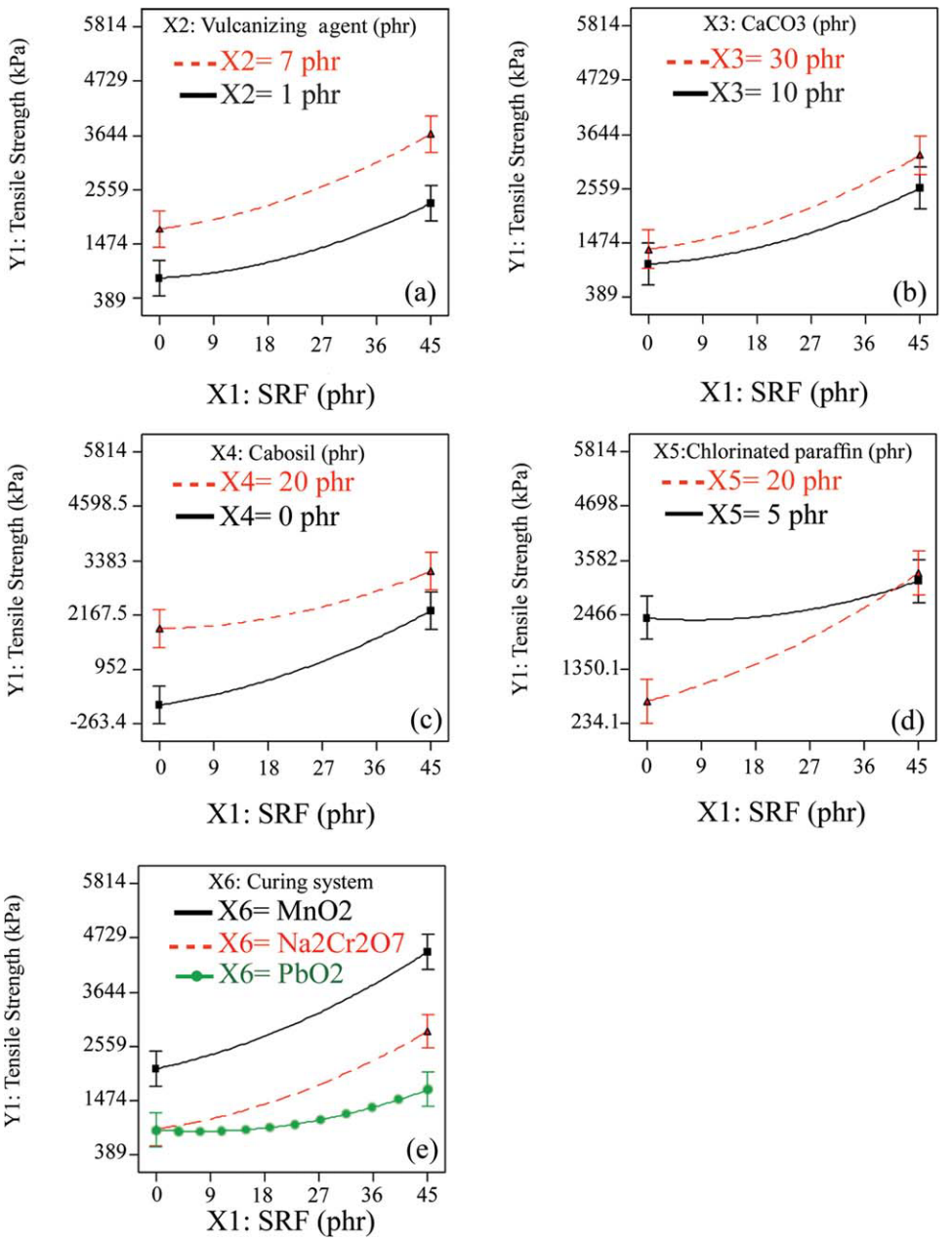

Figure 1 Variations in tensile strength with effective independent factors and their interactions in the liquid polysulfide samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to ASTM D412 with a cross-head speed of 100 mm/min, using die (C) (CCSi UltraLife Specimen Cutting Dies, Akron, OH). TS and elongation at break (EB) results were obtained from stress–strain curves. The hardness (shore A) of the samples was determined according to the standard test method, ASTM D2240, using a durometer hardness tester model 3100 (Zwick Co., Germany). The mean values for five samples were recorded with a deviation less than 5% for each test.

Lap shear strength

This test was carried out according to ASTM D3165-95 (a standard test for the determination of adhesives strength against tensile stress for single-lap-joint laminated assemblies). Aluminum plaques were glued together with different samples and then subjected to a tensile load. The universal tensile machine was set to maintain the rate of loading of about 1.27 mm/min on the cross-head to create a constant rate of loading on the aluminum plaques.

Peel strength

This test was done according to ASTM D903. The peel test measures the strength required to pull apart the bonded surfaces. This test is useful in evaluating adhesives, adhesive tapes, sealants, and other attached

surfaces. After the sample was measured for thickness, it was placed in a fixture in the universal tester. The specimen was pulled at the rate of 50 mm/min until either the part or the bond failed. Two 6 in. × 1 in. aluminum plaques were superimposed on one another and bonded by the prepared compounds in the center.

Viscometry

The viscosity of polysulfide compounds were determined by filling a 250 cm^3 cylindrical container up to about 1.5 cm from the top. After about 2 hr, the contents of this container were stirred with the needle No. 6 in a Brookfield viscometer model RVF at 2 rpm. The maximum number after 1–3 min was recorded as the viscosity (Pa sec) of the sample. This test was done according to ASTM D1439-03.

Optimum cure time measurement

The optimum cure time (t_{90}) of the samples was determined using a rheometer, model MDR 2000 (Flexy Co., England), at 60°C. This test was done according to ASTM D2084.

Swelling test

Polysulfide sealants have found special uses in fuel tanks coatings.[13] Therefore, chemical resistance and weight reduction of the samples in the selected jet fuel environment JP-4 for a period of 1 week were determined. JP-4 is a mixed compound composed primarily of hydrocarbons (i.e., alkanes, cycloalkanes, alkylbenzenes, indan/tetralins, and naphthalenes). According to eq. (2), w_1 and w_2 were the weight of the sample before and after the immersion in the above fuel, respectively. The percentage of the sample weight reduction is calculated as follows:

$$\text{Weight loss} = \Delta w = (w_2 - w_1)/w_1 \times 100, \qquad (2)$$

RESULTS AND DISCUSSION

Using the D-optimal design method, the experimental results obtained on the samples from TS, EB, hardness, lap shear and peel strengths, viscosity, optimum cure time (t_{90}), and solvent swelling tests were investigated. Carbon black is the most important component in the LPS compound because of its good reinforcing effects in the oxidative curing system such as MnO_2,[14] and its interaction with other effective parameters such as vulcanizing agent, $CaCO_3$, CAB-O-SIL, and chlorinated paraffin were investigated. Also, all the factors have interaction with each other, and their effects in all the results are considered.

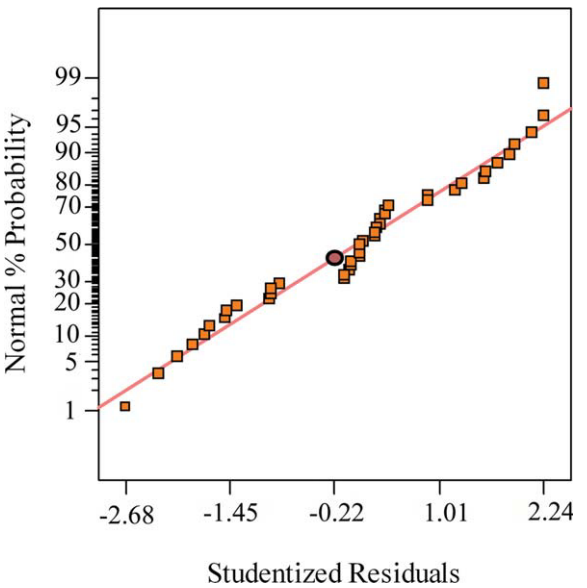

Figure 2 Relation between experimental and predicted values of TS using eq. (3) with $R^2 = 0.99$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effects of parameters on tensile and elongation properties

Figure 1(a–e) shows the interaction effects of carbon black (SRF) alone and also on each of the other independent effective variables on TS results. As it can be seen in Figure 1, increase in carbon black amount in the samples leads to an increase in the TS. Also, increasing carbon black results in an increase in elastic properties, which increase the TS of the samples. Figure 1(a) shows the interaction of two parameters carbon black and vulcanizing agent at the lowest and highest levels in the samples. In this work, by analyzing all the curves, other main parameters are kept at a mean value and constant. Oxidative vulcanizing agents MnO_2, $Na_2Cr_2O_7$, and PbO_2[15] along with carbon black increases elastic properties of the samples. On the other hand, according to physical and mechanical properties of the polymers,[16] the relation between TS and EB variations are opposite to each other. Therefore, by increasing the percentages of carbon black or vulcanizing agent, a decrease in EB is observed for the samples. The most important property of polysulfide sealants is their high elastic properties.[17] According to Figure 1(b), by increasing $CaCO_3$ from 10 to 30 phr for constant amount of carbon black, the increase in TS is not considerable relative to vulcanizing agent effect. Also, in Figure 1(a,b), higher values of TS for carbon black increases are observed. This behavior is known as noninteraction.[18] From statistical calculations, increase in TS for vulcanizing agent and $CaCO_3$ for all the phr of carbon black were about 124% and 27.9%, respectively. Similarly, Figure 1(c) shows that

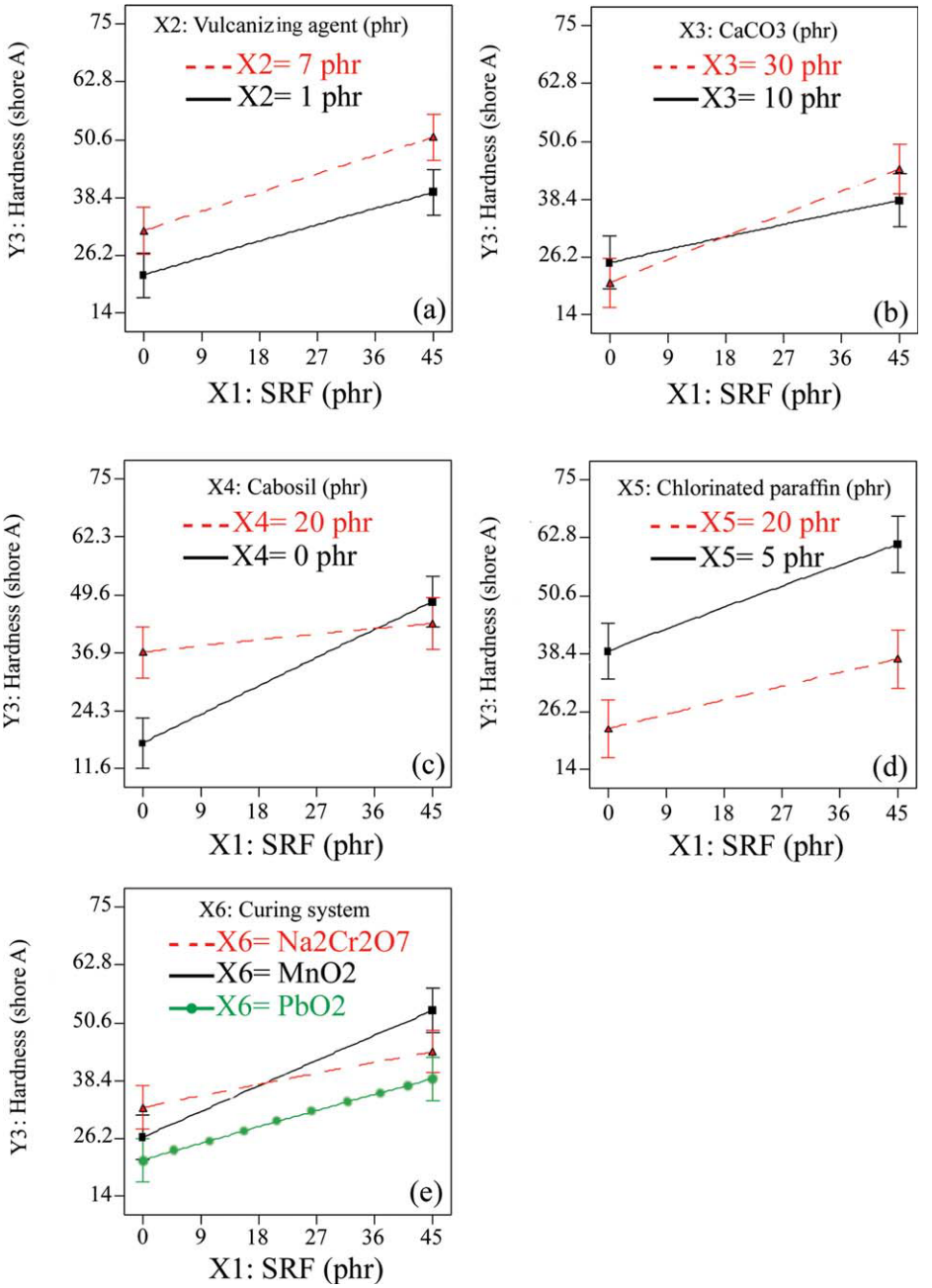

Figure 3 Variations in hardness with effective independent factors and their interactions in the liquid polysulfide samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as CAB-O-SIL percentage is increased TS increases. For instance, 39% increase in TS occurs when 20 phr CAB-O-SIL and 45 phr carbon black are added to the system. A completely different behavior in Figure 1(d) relative to Figure 1(a–c) is observed. So that, when chlorinated paraffin in the system is reduced to about 5 phr, TS is increased. This behavior is due to the lower mobility of polysulfide chains and their higher elasticity. But, for values of carbon black higher than 40 phr, the behavior is changed and, because of its high percentages in the system despite a high level of the plasticizer (20 phr), higher TS relative to 5 phr chlorinated paraffin is observed. This behavior in the curves is called antagonistic.[18] In Figure 1(e), MnO_2 curing system has the highest TS, which is considered as the most suitable curing system for polysulfide sealants.

Figure 2 shows normal probability curve against studentized residuals, which explain the difference between actual and predicted values divided by standard error for each point. The normal probability curve indicates whether the residuals follow a normal distribution, in which case, the points will follow a straight line.

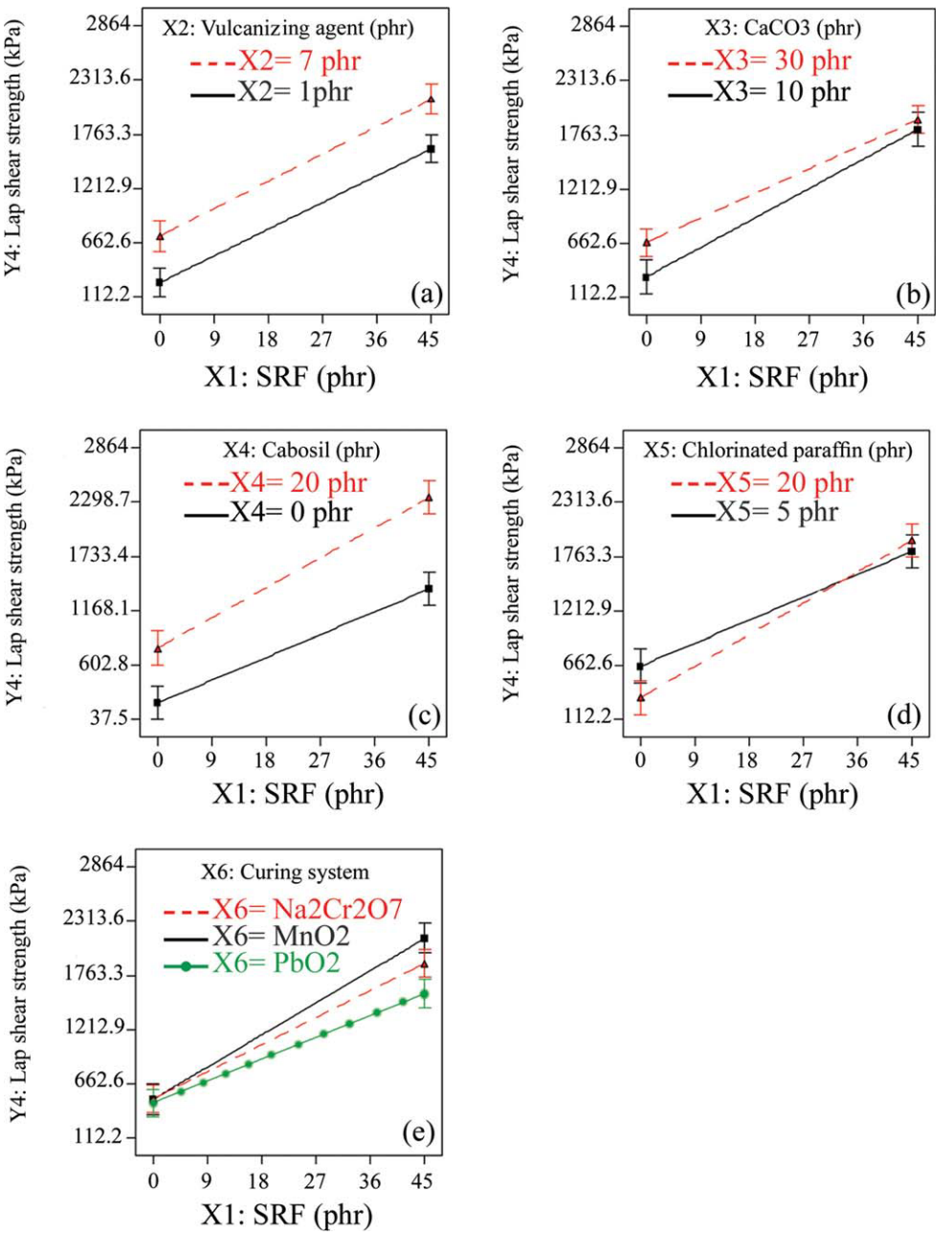

Figure 4 Variations in lap shear strength with effective independent factors and their interactions in the liquid polysulfide samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In TS test, the proposed equation is a polynomial with a standard deviation 90.53 and $R^2 = 0.9982$, which is of reduced quadratic type of equation. MnO_2 curing system provides the best levels of answers for TS and EB; therefore, eqs. (3) and (4) on the basis of this system are as follows:

$$y_1 = 769.68 - 13.33 \times x_1 + 188.69 \times x_2 + 47.4 \times x_3 + 165.19 \times x_4 - 150.65 \times x_5 + 0.61 \times {x_1}^2 - 2.65 \times {x_4}^2 + 0.68 \times x_1x_2 + 3.29 \times x_1x_5 + 4.24 \times x_2x_5 - 1.85 \times x_3x_4 + 0.99 \times x_3x_5 \quad (3)$$

$$y_2 = 105.74 - 0.96 \times x_1 + 30.73 \times x_2 - 2.53 \times x_3 + 0.20 \times x_4 + 15.49 \times x_5 - 0.06 \times x_1x_5 - 0.09 \times x_3x_5 - 0.1 \times x_4x_5 \quad (4)$$

Equation (3) is a polynomial for TS test (y_1), and eq. (4) as a linear relation two-factor interaction (2FI) is for EB test (y_2). Generally, every parameter that is eliminated in these equations is because of their unimportance effects on the answers; they had a P-value >0.05.

Effects of parameters on hardness responses

Figure 3(a–e) shows the variations of hardness properties of polysulfide samples with effective different

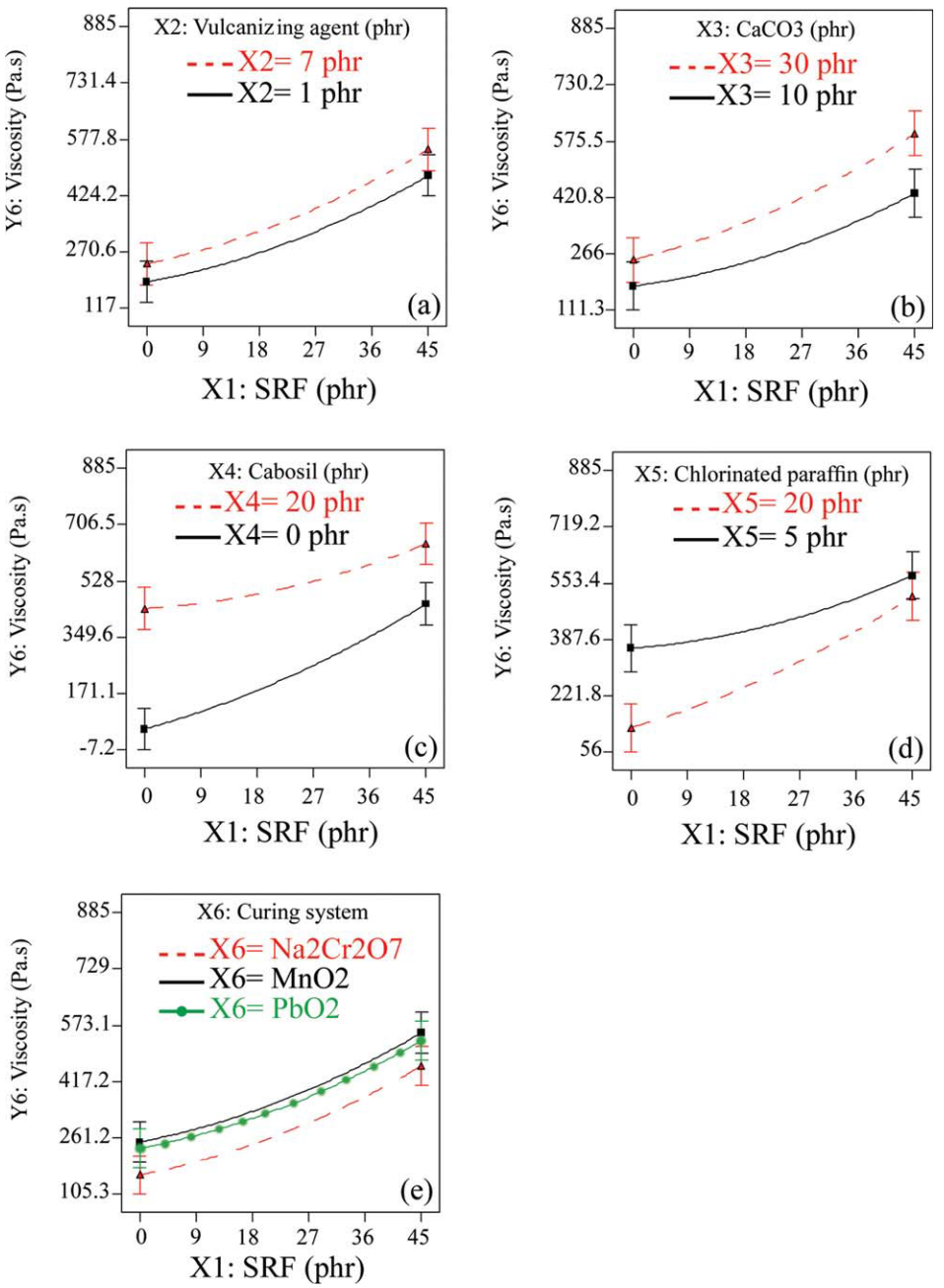

Figure 5 Variations in viscosity with effective independent factors and their interactions in the liquid polysulfide samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

parameters and their interactions with each other. As it can be seen, hardness variations have a linear relation with SRF phr values and contrary to TS results. This is the reason that SRF variations have a less-sensitive behavior compared with TS results. Figure 3(a) represents the hardness results with respect to interaction variations of SRF and vulcanizing agent and two other parameters SRF and chlorinated paraffin [Fig. 3(d)], which is similar to TS behavior. On the other hand, Figure 3(b,c) shows the antagonistic behavior of SRF/$CaCO_3$ and SRF/CAB-O-SIL. This means that for a specific percentage of SRF, the hardness behavior with maximum and minimum amount of $CaCO_3$ and CAB-O-SIL are changed. Figure 3(b) shows that the position of antagonistic behavior for hardness in the presence of $CaCO_3$ for SRF is equal to 18 phr, and also Figure 3(c) shows that this behavior in the presence of CAB-O-SIL happens at 36 phr SRF. Because of significant variations in the elastic properties of the samples for higher and lower critical values of SRF in the presence of any other parameter, the role of $CaCO_3$ and CAB-O-SIL with different percentages as a filler or reinforcing agent is

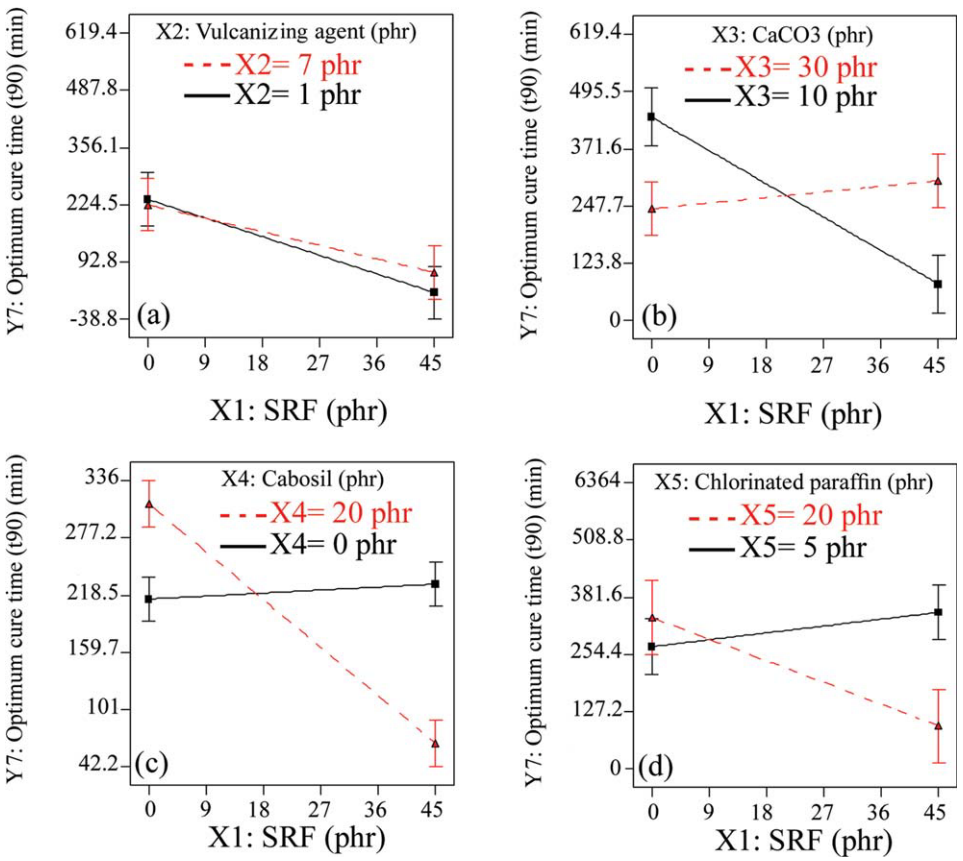

Figure 6 Variations in optimum cure time with effective independent factors and their interactions in the liquid polysulfide samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

changed completely, which has a direct effect on the final hardness of the samples. Figure 3(e) shows that to have MnO_2 as the best curing system for the samples, SRF amounts must be more than 18 phr, which leads to suitable hardness for polysulfide sealants compared with the two other $Na_2Cr_2O_7$ and PbO_2 curing systems. The suggested eq. (5) about this answer for the best correlation with its level is a reduced quadratic equation represented as follows:

$$y_3 = 21.68 + 0.9 \times x_1 + 0.05 \times x_2 + 1.10 \times x_3 + 0.72 \times x_4 - 1.8 \times x_5 - 0.02 \times {x_3}^2 + 0.02 \times {x_5}^2 - 7.56 \times 10^{-3} \times x_1 x_4 \quad (5)$$

The regression of this equation is calculated as $R^2 = 0.9985$.

Variations of lap shear and peel strengths

For elastic sealants, high values of lap shear strength and peel strength are the most important properties. Figure 4(a–c) shows that by increasing SRF content, the amount of oxidative vulcanizing agent parameter (x_1), $CaCO_3$ (x_2), and CAB-O-SIL (x_3) are increased; consequently, the lap shear strength of the samples are increased. Figure 4(b) is about SRF/$CaCO_3$ interactions with a synergistic property. On the other hand, lap shear strength of the samples with SRF/chlorinated paraffin interactions has an antagonistic property [Fig. 4(d)], as for SRF values about 36 phr a variable property is observed in the results. As it can be seen in Figure 4(d), for carbon black values higher than 36 phr, the elastic property of polysulfide sealants is increased sharply. Therefore, 20 phr chlorinated paraffin plasticizer has no effect in lap shear strength reduction. For the whole range of SRF values (0–45 phr), it can be seen in Figure 4(e) that the lap shear strength of the samples for MnO_2 curing system is higher than the other two curing systems under investigation.

In the analysis of variance[19] studies in the D-optimal experimental design, no significant interaction between the main parameters (x_1–x_5) for peel strength were observed, because for all the interactions, the *P*-values were much more than the assumed 0.05 probability value; therefore, the only suitable equation for the effect of parameter as one factor is a linear equation. Equations (6) and (7) represent functions 2FI and linear on the response surfaces lap shear strength (y_5), which have R^2 values of 0.9917 and 0.7780, respectively, from the fitted models.

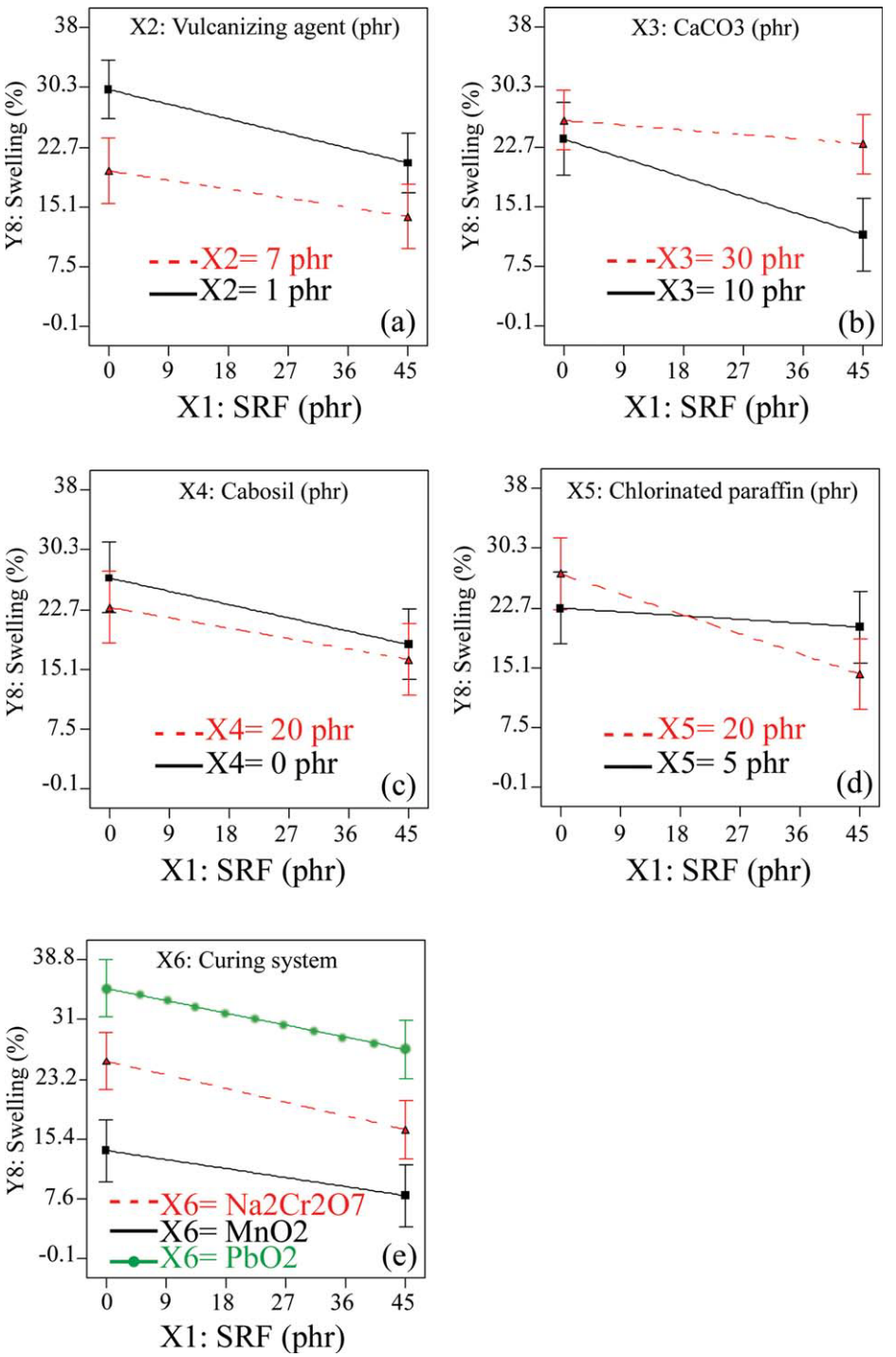

Figure 7 Variations in swelling with effective independent factors and their interactions in the liquid polysulfide samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$y_4 = -169.17 + 22.47 \times x_1 + 176.88 \times x_2 - 0.21 \times x_3 + 38.78 \times x_4 - 23.17 \times x_5 + 0.47 \times x_1 x_5 \quad (6)$$

$$y_5 = 7459.26 - 6.31 \times x_1 + 40.62 \times x_2 - 112.36 \times x_3 + 72.37 \times x_4 - 139.15 \times x_5 \quad (7)$$

Viscosity, optimum cure time, and swelling

Figures 5(a–e), 6(a–d), and 7(a–e) show the behavior of viscosity, optimum cure time (t_{90}), and swelling responses for polysulfide samples, respectively. Viscosity tests are important for the fluidability of the samples, which show a climbing pattern with increasing SRF [Fig. 5(a–e)]. Viscosity increase for CAB-O-

TABLE III
Analysis of Variance for Surface Response Linear and Polynomial Models

Index	Response	Model	Adj-R^2	Pred-R^2
y_1	TS	Reduced quadratic	0.9911	0.9726
y_2	EB	Reduced 2FI	0.9950	0.9867
y_3	Hardness	Reduced quadratic	0.9924	0.9695
y_4	Lap shear strength	Reduced 2FI	0.9777	0.9370
y_5	Peel strength	Linear	0.7335	0.6689
y_6	Viscosity	Reduced quadratic	0.9948	0.9916
y_7	Optimum cure time	Reduced quadratic	0.8496	0.7375
y_8	Swelling	Reduced 2FI	0.9398	0.8809

SIL has the highest value. In other words, with the increase in the added CAB-O-SIL fumed silica from 0 to 20 phr to the samples, a sharp increase in the viscosity is observed. Because of the silica (SiO_2) in CAB-O-SIL, a good interaction and compatibility occurs between S—H and S—S groups from polysulfide with Si, which will reduce the mobility of polymer chains and increase viscosity. For higher values of SiO_2 in the CAB-O-SIL, interactions are stronger.[20] This behavior is dependent on the percentages of water content in these inorganic particles.

The fluctuations in optimum cure time (t_{90}) of the samples are dependent on the factors such as carbon black percentage and vulcanizing agent in the formulation, acidic or basic environment,[21] and other similar factors. From Figure 6(a–d) it can be seen that for t_{90} behavior, with the interactions of parameters in a compound, certain percentage of SRF is antagonistic. In Figure 6(a), for carbon black percentages about 45 phr and the amount of vulcanizing agent of 7 and 1, a minimum value for t_{90} is observed. Of course, the low value of t_{90} alone is not a good evidence for selecting curing system, but it must be studied along with other answers.

Figure 7(a–d) shows a reduction in the swelling of the samples in JP4 fuel. For harder samples, more reduction in the swelling because of their higher cross-linked structure was observed. Figure 7(e) shows a confirmation of MnO_2-optimized cure system. Equations (8)–(10) for each of the responses, viscosity (y_6), t_{90} (y_7), and swelling (y_8), are generalized as follows:

$$y_6 = 256.91 + 6.15 \times x_1 + 5.56 \times x_2 + 0.34 \times x_3 + 9.34 \times x_4 - 28.24 \times x_5 + 0.03 \times {x_1}^2 + 0.6 \times {x_4}^2 + 0.64 \times {x_5}^2 + 0.08 \times x_1x_3 - 0.26 \times x_1x_4 + 0.23 \times x_3x_5 - 0.23 \times x_4x_5 \quad (8)$$

$$y_7 = 400.5 - 1.63 \times x_1 - 5.41 \times x_2 + 7.1 \times x_3 + 29.63 \times x_4 - 53.62 \times x_5 - 0.35 \times {x_3}^2 + 1.88 \times {x_5}^2 + 0.25 \times x_1x_3 - 0.93 \times x_1x_4 + 0.92 \times x_2x_4 - 1.1 \times x_4x_5 \quad (9)$$

$$y_8 = -4.86 - 0.04 \times x_1 - 0.6 \times x_2 + 0.97 \times x_3 - 0.13 \times x_4 + 0.54 \times x_5 + 0.01 \times x_1x_2 + 5.04 \times 10^{-3} \times x_1x_3 - 0.012 \times x_1x_5 - 0.02 \times x_3x_5 \quad (10)$$

In these equations, the proposed models based on reduced quadratic for viscosity response, optimum cure time, and 2FI for swelling response arranged, for each R^2 respectively, were 0.9986, 0.9443, and 0.9849, which indicates a suitable approximation of good relations between different "x," their interactions, and "y" values.

Table III shows a summary of responses y_1–y_8 and a suitable proposed model for each of the response surfaces in which MnO_2 as an appropriate system for the cure of LPS sealants are calculated.

Three-dimensional graphs of the surface responses for MnO_2 curing system

After analyzing the parameters and their interactions with each other for individual responses, determining the best curing system, paying attention to the point that properties such as TS, lap shear strength, and peel strength must have high values and t_{90} and swelling must have lower values as far as possible, and considering the equations obtained, the best percentages of each effective parameter along with the responses for the oxidative curing system of MnO_2 are given in Table IV. Also, for a better comparison, Table IV shows similar results for the other two curing systems, $Na_2Cr_2O_7$ and PbO_2. The final conclusion is that MnO_2 produced the best results. Also, for the distinction of each response behavior, their surface at optimum percentages according to two parameters such as SRF and vulcanizing agent MnO_2, which are arranged in Table IV, were plotted,

TABLE IV
The Optimized Effective Independent Variables and Surface Responses for MnO_2, $Na_2Cr_2O_7$, and PbO_2 as Curing Systems Using D-Optimal Design Method

Factor	Lower	Upper	Optimization
Carbon black (SRF)	0	45	44
MnO_2	1	7	7
$CaCO_3$	10	30	10
Fumed silica (CAB-O-SIL®)	0	20	20
Chlorinated paraffin	5	20	5
Optimized curing system	MnO_2	$Na_2Cr_2O_7$	PbO_2
Tensile (TS) (MPa)	5.4	4.2	2.3
Elongation at break (EB) (%)	305	148	149
Hardness (shore A)	70	68	60
Lap shear strength (MPa)	2.8	2	1.6
Peel strength (kN/m)	7.1	6.5	6.7
Viscosity (Pa sec)	730	654	730
Optimum cure time (t_{90}) (min)	~7	~23	~90
Swelling (%)	0.3	9.3	22.1

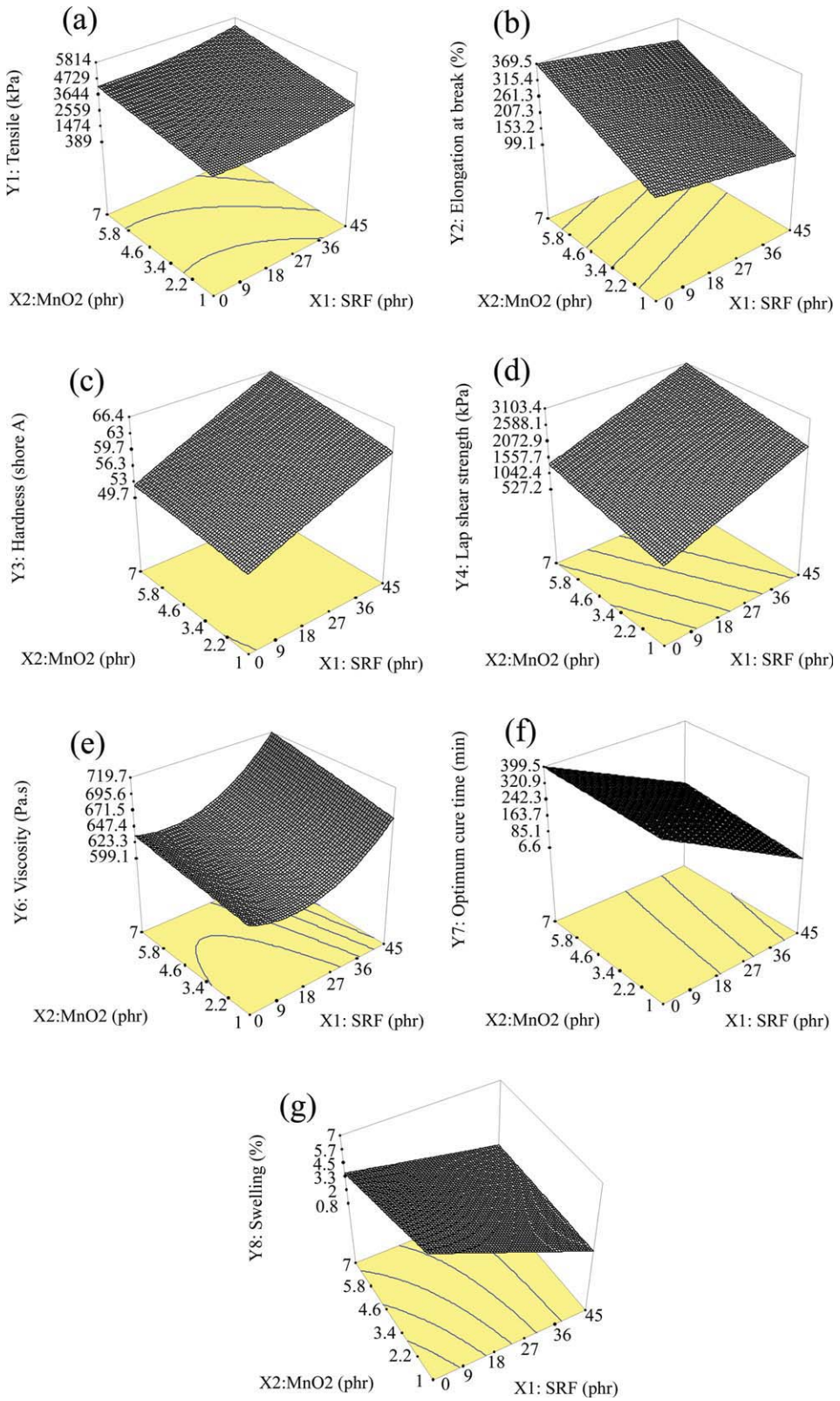

Figure 8 Three-dimensional graphs of surface responses results against carbon black (SRF) and MnO_2 as the optimized curing system for liquid polysulfide samples: (a) tensile strength, (b) elongation at break, (c) hardness, (d) lap shear strength, (e) viscosity, (f) optimum cure time, and (g) swelling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which represent a suitable view of the work done [Fig. 8(a–g)].

CONCLUSIONS

In this study, LPS sealant samples with oxidative curing systems MnO_2, $Na_2Cr_2O_7$, and PbO_2 were investigated. Using RSM/D-optimal design method and considering five independent effective parameters, carbon black (SRF), vulcanizing agent, $CaCO_3$, CAB-O-SIL, and chlorinated paraffin were studied. Also, eight responses, TS, EB, hardness, lap shear strength, peel strength, viscosity, optimum cure time, and swelling, all together 43 runs were carried out. For responses evaluations, using analysis of variance method and considering the meaningfulness of each factor by choosing the best model on the surface responses were studied. Consequently, for each of the responses y_1–y_8, curves of polynomial reduced quadratic type, 2FI, and also linear graph for above tests were generalized. Considering the modeling that was carried out, it was determined that the best curing system for LPS sealants is MnO_2. With the assumption that the maximum TS and minimum optimum cure time for the optimized LPS sample were 5.4 MPa and 7 min, respectively, the analysis of the response surface indicated the following amounts for each component: carbon black (SRF) about 44 phr, MnO_2 7 phr, $CaCO_3$ 10 phr, fumed silica (CAB-O-SIL) 20 phr, and chlorinated paraffin 5 phr.

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