Optimization of Physical and Mechanical Properties of Rubber Compounds by a Response Surface Methodological Approach

V. SRIDHAR,[1] K. PRASAD,[2] S. CHOE,[3] P. P. KUNDU[1,3]

[1] Department of Chemical Technology, Sant Longowal Institute of Engineering & Technology, Longowal, Sangrur-148106, India

[2] Department of Food Technology, Sant Longowal Institute of Engineering & Technology, Longowal, Sangrur-148106, India

[3] Department of Chemical Engineering, Inha University, Inchon 402-751, Korea

Received 25 October 2000; accepted 23 January 2001

ABSTRACT: Response surface methodology was used for optimizing the ratio of vegetable oil and carbon black and occluded volume fraction of rubber in the compound. Central composite design for two variables was chosen as the experimental design. The data obtained from measurement of properties was fitted as a two variable second-order equation, and were plotted as contours using software developed from MATLAB v.5.1. From contours it is observed that at the ratio of 0.06 of vegetable oil and carbon black, there is maximum coupling, and a further increment in vegetable oil and carbon black ratio shows less coupling and more plasticizing effect. The ultimate failure properties like tensile and tear strength and elongation decreases with an increase in occluded volume fraction, reaches a minima at the central region, followed by an increase, whereas 300% modulus and hardness decreases throughout. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 997–1005, 2001

Key words: reponse surface methodology; ratio of vegetable oil and carbon black; occluded volume fraction of rubber; contour plots

INTRODUCTION

A statistically designed set of experiments are a collection of methods patterned in such a way so as to provide clear answers to ambiguous questions. In a conventional experimentation technique the experimental procedure was to hold all but one variable as constant while methodically changing one at a time. This technique is called one variable at a time, or OVAT. The traditional OVAT technique used for an optimizing variable fails to find a true optimum process condition, and it cannot quantitatively explore the influence of interactive effects on the response and have experimentation inefficiency. Response Surface Methodology (RSM) is a collection of techniques for exploring empirical relationships. This includes experimental designs, model fitting, and diagnosing techniques. RSM in general is discussed elaborately by Box et al.,[1] Davies,[2] Gunst et al.,[3] and Montgomery.[4] RSM for rubber compounding was extensively reviewed by Derringer.[5] RSM in rubber compounding was successively used by Bhagawan et al.[6] and Sridhar et al.[7] with good accuracy. If Y is the response of a

Correspondence to: P.P. Kundu (ppk923@yahoo.com; on leave at Inha University, Korea).

Contract grant sponsor: Council for Scientific and Industrial Research, New Delhi; contract grant number: 22(295)/99 EMR-II.

Journal of Applied Polymer Science, Vol. 82, 997–1005 (2001)

process dependent on the levels of k factors (x_1, x_2 . . . x_k), which can be precisely measured and controlled, then the model for combinations of these factor levels is given by:

$$Y_u = \phi(x_{1u}, x_{2u}, x_{3u} \ldots x_{ku}) + \varepsilon_u$$

where $u = 1, 2, 3 \ldots N$; N = number of experiments; ϕ is the functional relationship between all the factors and response; and ϵ is the error involved. Response surfaces are used in Rubber Science & Technology in the form of ISOPLETH diagrams commonly known as contour plots. A contour plot can be defined as a series of curves that identify values of factors for which the response is constant. A response surface can be defined as a geometric representation obtained when a response variable is plotted as a function of other variables. The sequence of operations involved in RSM are: (a) identify the variables, (b) find a suitable experimental design, (c) run experiments as dictated by design, (d) fit equations to the data, and (e) construct contours and response surfaces. Kundu[8,9] has reported the coupling action of vegetable oils in rubber compounds using the conventional OVAT procedure.

It is found from Scanning Electron Micrographs and 3D models of carbon black aggregates[10] that carbon black has a considerable void space within each aggregates. Medalia[11] has proposed that in a carbon black–rubber system the rubber that fills the void space within each aggregate is occluded and immobilized, and thus acts as a part of filler rather than as a part of deformable matrix. Medalia has reported that volume of rubber occluded in the carbon black particles is related to its Dibutyl Phthalate (DBP) absorption by the following equation:[12]

$$\text{Occluded volume/volume of carbon black} = (\phi' - \phi)/\phi = (\text{DBP} - 21.5)/68.26 \quad (1)$$

The DBP absorption value is constant for a definite carbon black like for HAF carbon black DBP absorption is 102 cc/100 g, then from eq. (1)

$$\text{Occluded volume fraction of rubber} = \text{Volume fraction of carbon black} \times 1.17931 \quad (2)$$

It is reported elsewhere[13] that the optimization of doses of vegetable oil and carbon black has been carried out using response surface methodology by taking these as independent parameters in a Central Composite Design (CCD). The objectives of this study is to quantitatively find the relationships between the ratio of vegetable oil and carbon black and occluded volume fraction of rubber and their effect on various properties like hardness, tensile strength, tear strength, elongation at break, and modulus, and to find the optimum level of vegetable oil/carbon black ratio.

EXPERIMENTAL

Experimental Design

A Central Composite Design (CCD) was chosen as the experimental design. CCD is an efficient and proven design, especially for two factors. CCD is also rotatable, which means that all the points in the design area are at equal distance from center. This leads to distribution of errors among all points equally. The number of design points in CCD are based upon a complete 2k factorial. The total number of experiments are:

$$N = 2^k + 2k + m \quad (3)$$

where N = total number of experiments, k = number of factors, m = number of replicates. Multiple linear regression analysis was used, and the data was fitted as a second-order equation. The general equation that was fitted is:

$$y = \text{const} + a_1x_1 + a_2x_2 + a_3x_1^2 + a_4x_2^2 + a_5x_1x_2 \quad (4)$$

The number of coefficients in the above equation are 6. The redundancy factor of the experimental design R_f = number of experiments/number of coefficients. For a CCD, the number of experiments are 10, and the number of coefficients are 6. Therefore, the redundancy factor is 1.667. The lower limits of the two variables were fixed based on the previous experimental work carried out by Kundu.[8,9] The vegetable oil of higher Iodine value was taken for this study. Higher Iodine value indicates more unsaturation, which implies more double bonds in the oil, thus giving much greater scope for bond formation between carbon black and rubber interfaces.

Materials Used

The materials used were: natural rubber (RMA 1X): moisture content 1%, ash content 0.4%, spe-

Table I Two Variable Design Matrix for Ratio of Vegetable Oil and Carbon Black and Occluded Volume Fraction of Rubber in the Compound

S No.	Coded Level for Ratio of Vegetable Oil and Carbon Black	Coded Level for Occluded Volume Fraction of Rubber	Uncoded Levels for Ratio of Vegetable Oil and Carbon Black	Uncoded Levels for Occluded Volume Fraction of Rubber
1	0	−1.414	0.064	0.1831
2	+1	−1	0.104	0.1833
3	−1	−1	0.021	0.1877
4	+1.414	0	0.116	0.1876
5	0	0	0.060	0.1908
6	−1.414	0	0.003	0.1941
7	+1	+1	0.096	0.1938
8	−1	+1	0.020	0.1985
9	0	+1.414	0.056	0.1982
10	0	0	0.060	0.1908

The carbon black (HAF) was varied from 48.00 to 52.83 phr, and vegetable oil was varied from 0.17 to 5.83 phr in a Central Composite Rotatable Design. The other fixed ingredients in the compounds are: NR(RMA-1X): 70, PBR: 30, ZnO: 4.5, Stearic acid: 1.5, 6 PPD: 1, H. S. Beads (Antioxidant): 1.5, Parafin wax: 2, Cyclohexyl Benzsulphenamide (accelarator): 1, Sulphur: 1.5.

cific gravity 0.85, and Mooney viscosity (ML_{1+4} at 100°C) 60; Polybutadiene rubber: moisture content 1%, ash content 1.5%, specific gravity 0.93, and Mooney viscosity (ML_{1+4} at 100°C) 45; HAF carbon black: DBP absorption 102 cc/100 g, density 1.85 g/cc. Procured from Ralson Carbon, India; 6 PPD: antidegradant, M.W. 268, Procured from ICI Ltd.; Stearic acid: melting point 62°C, acid value 192–204; vegetable oil (proprietary chemical): Aniline point 22°C, more unsaturated compared to the reported one.[8]

Sample Preparation

From eq. (2), occluded volume fraction of rubber can be calculated from the known volume fraction of carbon black. The compounds are formulated as in Table I. Ten compounds were chosen from experimental design based on rotatable Central Composite Design. The experimental region extended from −1.414 to +1.414 in terms of coded levels in independent variables of the ratio of vegetable oil and carbon black and the occluded volume fraction of the rubber. The lower and higher values were based on the previous research carried by Kundu.[8,9] The formulated compounds were mixed on a two-roll mill according to standard procedure. The vegetable oil was not added separately. These were first mixed with carbon black for its pretreatment, then they were added to rubber on the mixing mill. The procedure for pretreatment of carbon black with vegetable was described elsewhere.[8] The compounds above were formulated and used for sample preparation for testing of rheometric, hardness, rebound resistance, tear, and tensile strength properties.

Molding

Molding of rubber sheet test samples were done on a hydraulic press at 160°C temperature and 15 MPa pressure for 15 min.

Table II Coefficients of Fitted Equations and Their Percentage Fit $y = \text{const.} + a_1x_1 + a_2x_2 + a_3x_1^2 + a_4x_2^2 + a_5x_1x_2$

S. No	Property	Const.	a_1	a_2	a_3	a_4	a_5	% Fit
1	Hardness	63.35	0.8596	−0.1039	−0.8313	−0.8562	−0.075	93.2
2	300% Modulus	75.3200	−1.4848	−2.0349	−9.6219	−5.8894	0.96000	94.4
3	Tensile Strength	161.56	0.0572	−0.0734	16.5713	21.5937	0.1325	95.4
4	Elongation at break	452	39.7080	−2.0349	65.375	78.375	8.5	96.6
5	Tear strength	78.15	1.9172	−2.6230	2.3494	9.0394	−1.4525	95.2

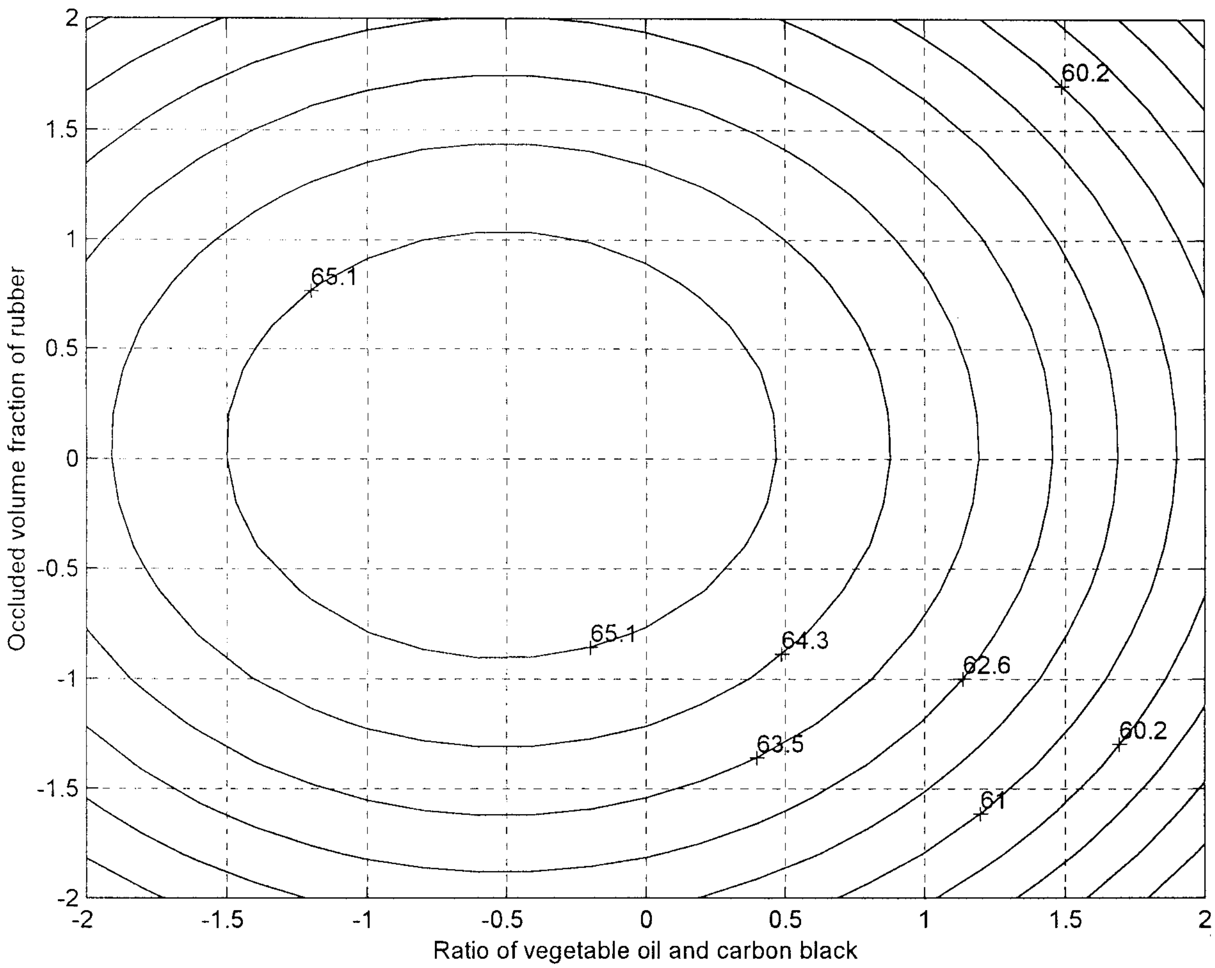

Figure 1 Contour plot showing variation in hardness, shore A with occluded volume fraction of rubber, and ratio of vegetable oil and carbon black.

Testing

Hardness

It was tested on a Shore-A durometer according to ASTM- D- 2240.

Tensile Properties

Dumbbell-shaped test samples were punched out from the molded sheets. The thickness was measured with a bench thickness gauge. These were measured on a Universal Tensile Testing Machine according to ASTM-D-412-51 at 25°C and at a crosshead speed of 500 mm/min.

Tear Strength

They were measured on a tensile tester according to ASTM D 624.

Rebound Resilience

It was tested in a pendulum rebound apparatus according to ASTM D 1054.

Curing Test

The curing tests were performed on a Monsanto Moving Disc Rheometer (MDR-2000) at 150°C, according to ASTM D 2084-81.

RESULTS AND DISCUSSION

Hardness

The variation of hardness (Shore A) with changes in ratio of vegetable oil and carbon black and occluded volume fraction of rubber is shown as contour in Figure 1. From contour it is observed

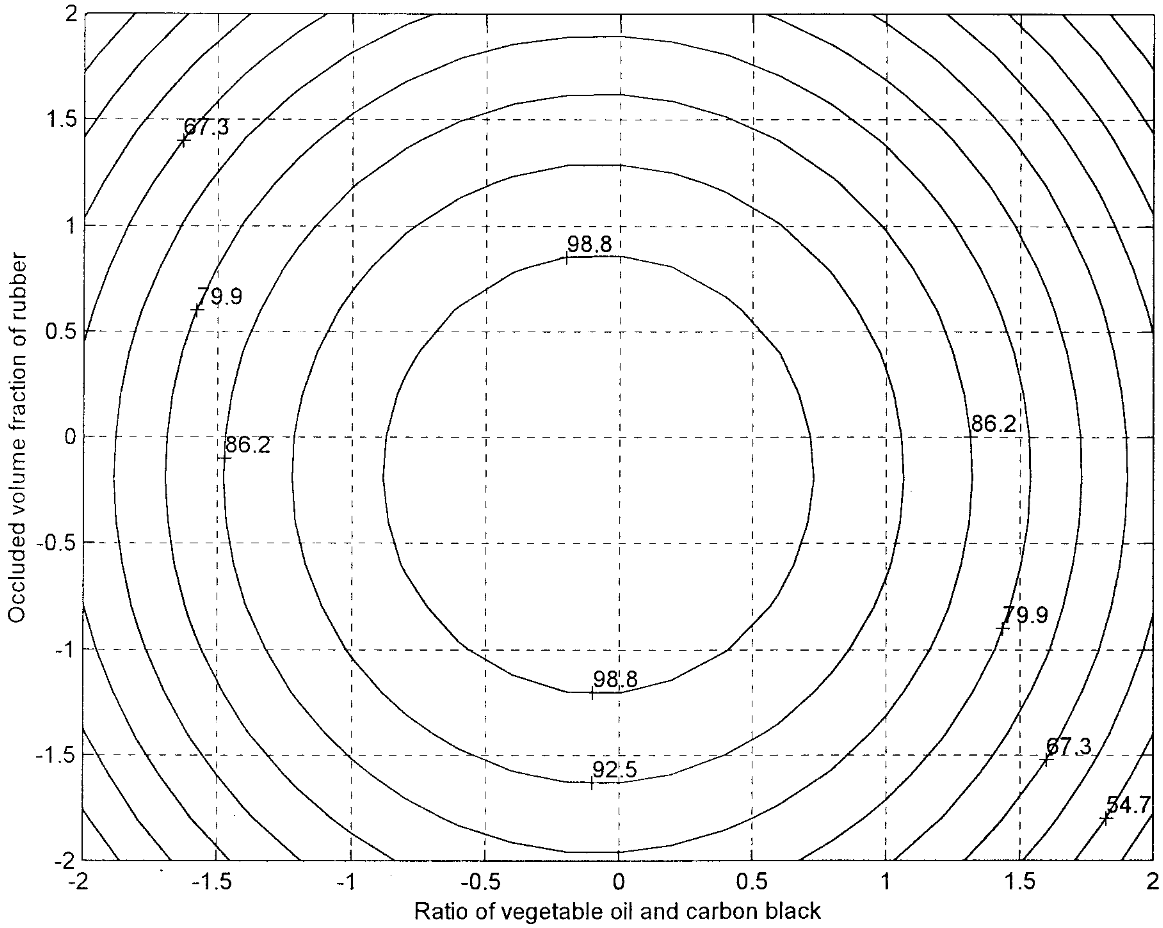

Figure 2 Contour plot showing variation in modulus, kg per sq cm with occluded volume fraction of rubber, and ratio of vegetable oil and carbon black.

that at a constant level of vegetable oil/carbon black ratio hardness increases initially up to the central point followed by its decrease with increase in occluded volume fraction. From eq. (2) it can be said that occluded volume fraction of rubber is directly proportional to the volume fraction of carbon black. So the increase in occluded volume fraction of rubber leads to an increase in carbon black volume fraction. To keep constant the ratio of vegetable oil and carbon black it is imperative that the doses of vegetable oil should increase with an increase in carbon black volume fraction. Thus, the increase in occluded volume fraction of rubber at a constant ratio of vegetable oil and carbon black will ultimately increase the doses of vegetable oil. The initial increase in hardness up to the central region may be attributed to the coupling action of vegetable oil at lower doses, which helps in formation of rubber multilayers around carbon black particles at lower occluded volume of rubber. So more volume fraction of rubber is available for penetration by the indenter during the testing of hardness. With an increase in volume fraction of rubber, hardness increases up to the central region. This is due to the replacement of multilayers by monolayers of rubber, and, thus, a lesser volume of rubber is available for penetration, which leads to higher hardness. Hardness is maximum at the central region wherein monolayers of rubber are replaced by layers of vegetable oil. This excess dose of vegetable oil in the form of layers around the carbon black will plasticize the system, leading to lowering of hardness.

With an increase in the ratio of vegetable oil and carbon black, there is an increase in hardness up to the central region, followed by its decrease. This is due to the participation of vegetable oil in curing as well as coupling at the rubber–carbon black interfaces.[8,9,12] Beyond the central point higher doses of vegetable oil acts as a plasticizer, which causes reduction in hardness.

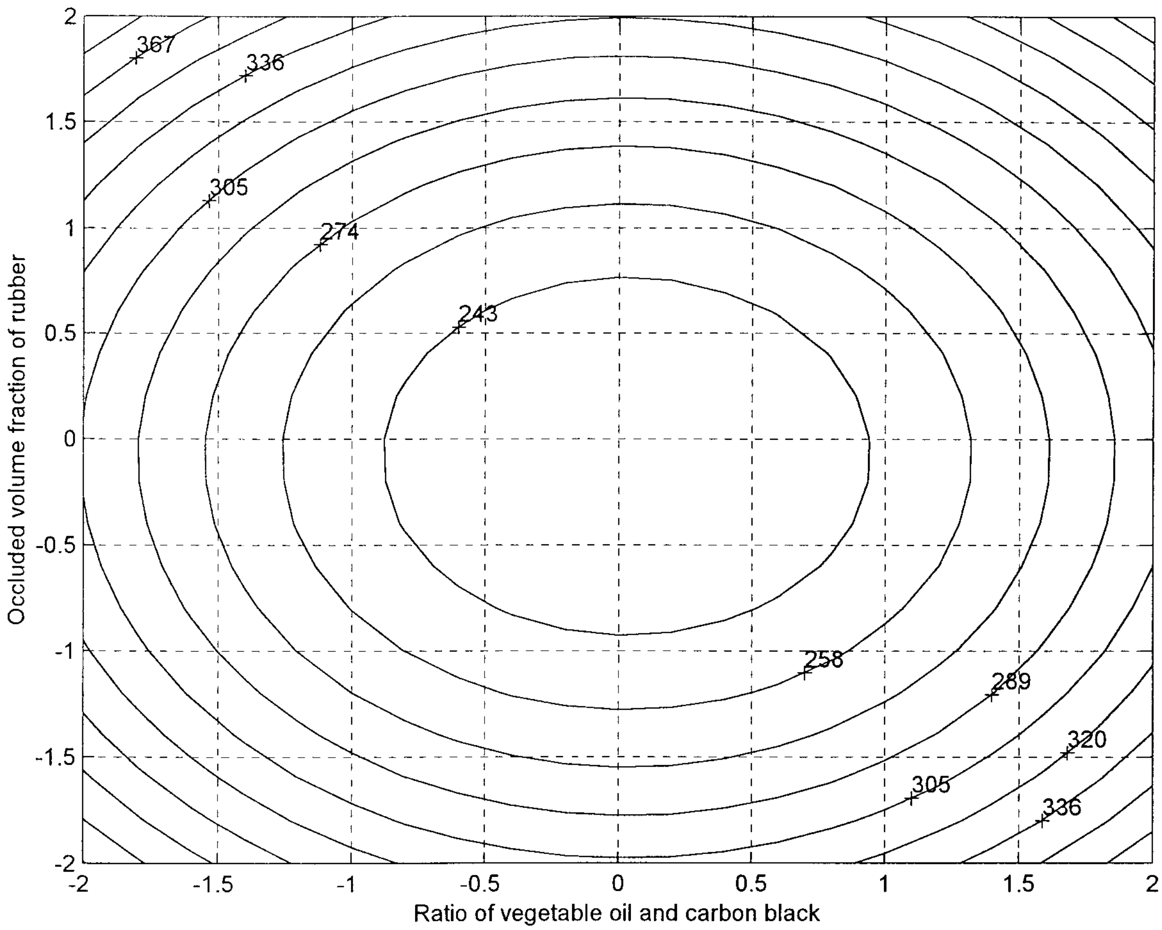

Figure 3 Contour plot showing variation in tensile strength, kg per sq cm with occluded volume fraction of rubber, and ratio of vegetable oil and carbon black.

300% Modulus

The variation of 300% modulus (kg/sq · cm) with changes in the ratio of vegetable oil and carbon black and occluded volume fraction of the rubber is shown as a contour in Figure 2. From the figure it is evident that at a fixed ratio of vegetable oil/carbon black, the modulus decreases with an increase in the occluded rubber volume fraction. At a fixed level of carbon black/vegetable oil ratio, multiple rubber layers are formed around carbon black particles through the coupling action of vegetable oil at lower doses. As the occluded volume fraction increases, the carbon black fraction increases , which facilitates formation of monolayer of rubber around carbon black. So, the effective volume of carbon black (volume fraction of carbon black + occluded volume fraction) decreases with an increase in occluded volume fraction of rubber, which leads to lowering in the modulus. Around the central level, with an increase in occluded volume fraction the monolayers of rubber are replaced by a vegetable oil monolayer followed by its multiple layers, leading to progressive lowering in the modulus.

With an increase in the vegetable oil/carbon black ratio there are increases in modulus up to the central region, followed by its decrease. This can be explained as at a lower ratio the doses of vegetable oil will be lower, and it acts as a coupling agent. This action is maximum at the central region, beyond which it acts preferably as a plasticizer. Due to the coupling action of the vegetable oil modulus increases and lowering in the modulus is due to its plasticizing action.

Tensile Strength

The variation of tensile strength (kg/sq · cm) with changes in the ratio of vegetable oil and carbon black and occluded volume fraction of the rubber is shown as a contour in Figure 3. Tensile strength is the ultimate strength at which failure of the rubber chains occurs under tensile stretch-

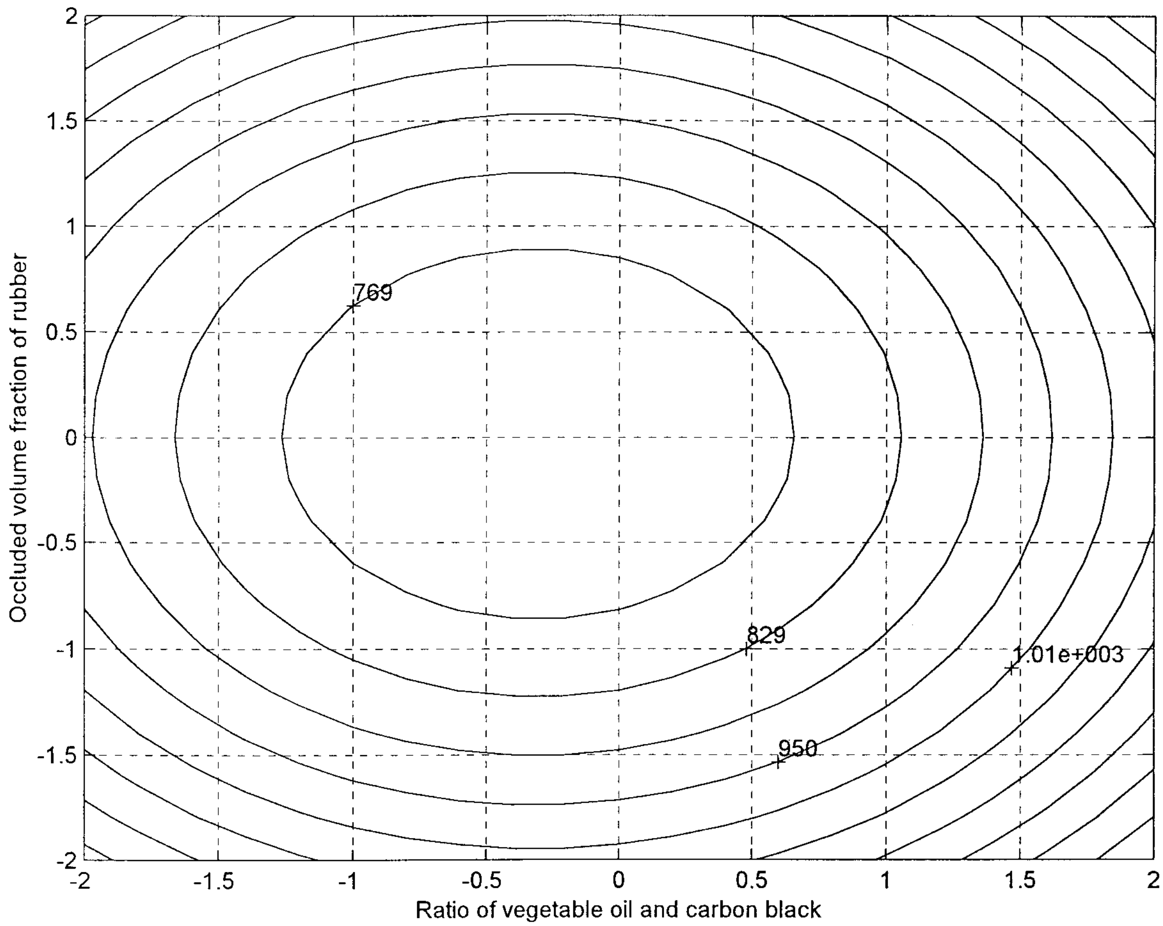

Figure 4 Contour plot showing variation in elongation at break % with occluded volume fraction of rubber, and ratio of vegetable oil and carbon black.

ing. At a lower occluded volume fraction, multiple layers of rubbers are adhered to the carbon black particles along with the embedded rubbers through the coupling action of vegetable oil. Thus, an effective volume fraction of carbon black is higher at a lower occluded volume. This leads to higher ultimate properties like tensile strength. Tensile strength decreases with an increase in the occluded volume fraction of rubber up to the central region due to the replacement of multilayers by the monolayer of the rubber, which reduces the effective volume fraction of the carbon black. This leads to lowering in the tensile strength. Beyond the central region, tensile strength increases with an increase in the occluded volume fraction of rubber. This is due to the formation of monolayers followed by multilayers of vegetable oil around the carbon black particles, leading to an effective plasticization at the carbon black–rubber interfaces. This plasticization, coupled with a little coupling action of higher doses of vegetable oil at higher occluded volumes of rubber, causes an increase in tensile strength.

It is evident from the figure that with an increase in the ratio of vegetable oil and carbon black, the tensile strength increases up to the central region, followed by its decrease. This is due to the coupling action of vegetable oil as well as its participation in curing at lower doses. Beyond the central region vegetable oil acts preferably as a plasticizer, thereby causing a decrease in tensile strength.

Elongation at Break

The variation of elongation at break (%) with changes in the ratio of vegetable oil and carbon black and occluded volume fraction of the rubber is shown as a contour in Figure 4. Elongation at break is the ultimate tensile stretch at which failure occurs. At a constant ratio of vegetable oil and carbon black it is observed that elongation decreases with an increase in the occluded volume fraction. This reinforces the argument about formation of multiple layers of rubber around the carbon black at a lower occluded volume fraction

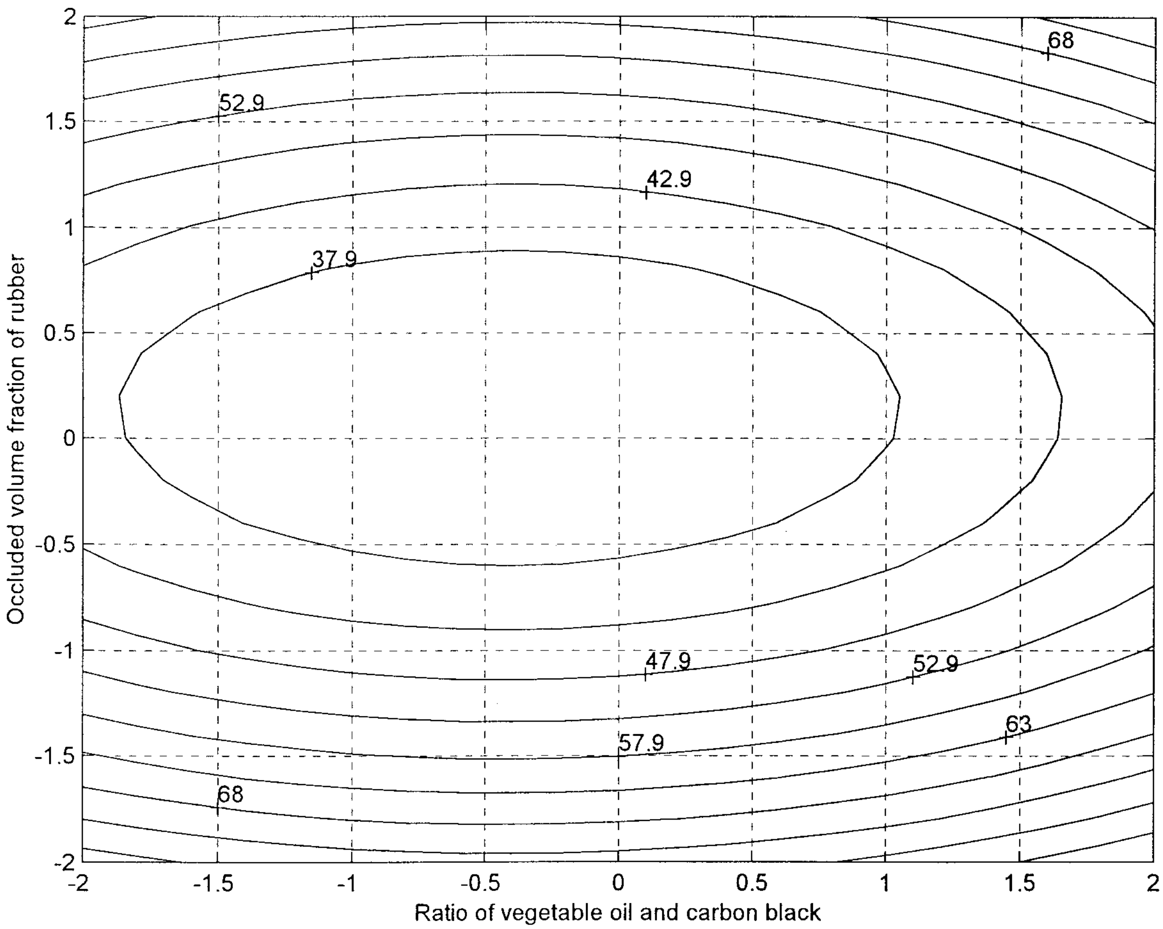

Figure 5 Contour plot showing variation in tear strength, kg per sq cm with occluded volume fraction of rubber, and ratio of vegetable oil and carbon black.

of the rubber. There is a progressive decrease in elongation as the occluded volume increases with a minimum around the central region where multiple layers are replaced by monolayers of rubber. Beyond this region the increase in elongation is caused by the replacement of rubber layers around the carbon black particles by that of vegetable oil. This is due to effective plasticization of vegetable oil at the rubber–carbon black interfaces.

With a variation in the vegetable oil/carbon black ratio, an initial decrease in elongation up to the central region followed by an increase is observed. The lowering in elongation is caused by coupling action at the carbon black–rubber interfaces as well as participation in curing by the vegetable oil. Beyond the central region the increase in elongation is caused by the plasticization effect of vegetable oil.

Tear Strength

The variation of tear strength (kg/cm) with changes in the ratio of vegetable oil and carbon black and occluded volume fraction of rubber is shown as a contour in Figure 5. Tear strength is the ultimate failure property at which rubber chains are teared under stretch. This is due to initiation of cracks developed by friction mainly at the rubber–carbon black interfaces as well as at the rubber–rubber interfaces. Tear strength can be improved by the formation of rubber layers around carbon black through the coupling action of vegetable oil at its lower doses as well as formation of a vegetable oil layer as plasticizer at its higher doses. At a fixed ratio of vegetable oil and carbon black, with an increase in the occluded volume fraction of rubber, tear strength decreases up to the central region followed by its increase. As the rubber occluded volume is directly proportional to the carbon black volume fraction, it is apparent from this fact that tear strength should increase with increase in the occluded volume of rubber. But the figure shows just the opposite trend up to the central region. This may be explained as the occluded volume of rubber may form a multilayer around the carbon black particles along with filling the intermittent voids of the carbon black. As the occluded volume of rubber increases, doses of the vegetable oil will also increase to keep the ratio of vegetable oil and carbon black constant. Therefore, at a lower occluded volume fraction, tear strength will be higher due to the formation of a multilayer of rubber around the carbon black caused by the coupling action of vegetable oil..[8,9,12] But, as the occluded volume increases, at fixed level of vegetable oil/carbon black ratio multiple layers will be diminished into monolayers around the central region, thus reducing the tear strength due to lowering of the effective volume of the carbon black (occluded volume + volume fraction of carbon black). Beyond the central region the monolayers of rubber will be replaced by monolayers of vegetable oil as the dosage of vegetable oil increases to keep constant the ratio of vegetable oil and carbon black. Therefore, at this region vegetable oil behaves primarily as a plasticizer in comparison with the coupling action. Tear strength increases with an increase in vegetable oil due to formation of the multiple layers of vegetable oil around the carbon black particles, which facilitates the increase in tear strength.

It is observed from the figure that the tear strength is almost constant with the increase in the ratio of vegetable oil and carbon black up to the central region followed by a slight increase. This is primarily due to the plasticization action of vegetable oil at higher doses coupled with a little coupling action.

CONCLUSION

It can be concluded that response surface methodology can be successfully used to optimize the ratio of vegetable oil and carbon black and occluded volume fraction of rubber. The experimental points were designed as a rotatable Central Composite Design (CCD). The data obtained was fit as a two variable second-order equation. The obtained equations were plotted as contours. From the data obtained and contour plots, it may be concluded that increasing the ratio of vegetable oil and carbon black as well as the occluded volume fraction of rubber will have a tremendous effect on the physical and tensile properties. From contours it is observed that at a value of 0.06 of vegetable oil and carbon black ratio, there is coupling action, and further increment in vegetable oil and carbon black ratio shows less coupling and more plasticising effect. The ultimate failure properties like tensile and tear strength and elongation decreases with an increase in the occluded volume fraction, reaches a minima at the central region, followed by an increase, whereas 300% modulus and hardness decreases throughout. Thus, it can be concluded that desirable properties of the compounds will be achieved around 0.1982 of the occluded volume fraction of rubber and 0.056 of the ratio of vegetable oil and carbon black.

The authors (P.P.K. and V.S.) give thanks to the Council for Scientific and Industrial Research, New Delhi, for their gracious grant [Grant No. 22(295)/99 EMR-II].

REFERENCES

1. Box, G. E. P.; Hunter, W. G.; Hunter, S. S. Statistics for Experimenters; John Wiley: New York, 1978, p. 453.
2. Davies, O. L. Design & Analysis of Industrial Experiments; John Wiley: New York, 1967.
3. Gunst, R. F.; Mason, R. L.; James, L. H. Statistical Analysis & Design of Experiments; John Wiley: New York, 1989, p. 204.
4. Montgomery, D. C. Design and Analysis of Experiments; John Wiley: New York, 1984, p. 445.
5. Derringer, G. C. Rubber Chem Technol 1990, 61, 377.
6. Bhagawan, S. S.; Rao, M. S.; Muraleekrishnan. R.; Jain, P. Response Surface Methodology—A Tool for Developing Low Styrene Butadiene Rubber Compounds, Macromolecules: New Frontiers; John Wiley: New Delhi, 1996, p. 1058.
7. Sridhar, V.; Bhagawan; S. S.; Rao; S. S.; Muraleekrishnan, R. Optimisation of NBR/CR Blends for Low Temperature Applications by Response Surface Methodology; International Chemical Conference (CHEMCON), Vishakapatnam, India, 1998, p. 238.
8. Kundu, P. P. J Appl Polym Sci 2000, 75, 735.
9. Kundu, P. P.; Kukreja, T.R. J Appl Polym Sci , communicated.
10. Medalia, A. I. J Colloid Interface Sci 1967, 24,293.
11. Medalia, A. I. Rubber Chem Technol. 1972, 45, 1171.
12. Sridhar, V.; Kukreja, T. R.; Kundu, P. P. Polymer, communicated.