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A Novel Approach to Statistical Design of Experiments in the Malaysian Latex Glove Industry

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See Toh's report on 'Statistical Designed Experiments in Rubber Compounding' filled the gap in the literature on this technique, detailing specific experimental work on full factorial design, fractional factorial design, and rotatable central composite design for rubber product manufacturing. In the latex technology area, Ng, et al.[2] *gives specific details on the use of design of experiment (DOX) in latex compounding. Despite these authors' efforts in promoting the use of DOX adoption of their techniques has not been encouraging. To bridge the gap between theory and practice, the authors described the detailed steps in DOX practice, and describe how R statistical computing language and environment allow wider adoption by practitioners. Emphasis has been placed on graphical presentation and wider scope involving equipment, latex types, and compounding ingredients.*

Keywords: Statistical design of experiments; factorial design; rotatable central composite design; glove industry; R statistical computing

Malaysian Rubber Board (MRB) is the primary source of technical information on the use of rubber in products manufactured from dry rubber and latex. In recent years the use of natural rubber latex has increased tremendously, surpassing the use of dry rubber. Malaysia is now the largest producer and exporter of gloves made from natural rubber latex, XNBR latex, and other synthetic latices. Therefore, it is important for Malaysian manufacturers to be active in R&D work, such as improving the glove manufacturing process, in order to maintain as the industry leader. With regards to this, one R&D area that can be further enhanced is in the application of statistically design of experiment technique in optimising glove manufacturing process.

See Toh's report[1] filled the gap in the literature on this technique, detailing specific experimental work on full factorial design, fractional factorial design, and rotatable central composite design for rubber product manufacturing, and providing detailed steps for calculating main effects and interactions. More specifically he chose to concentrate on designing tyre tread compounds based on natural rubber and natural rubber blend, carbon black, and rubber process oil.

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In latex glove application, Ng *et al*.[2] gave specific details on the use of design of experiment (DOX) in latex compounding and their research supplemented See Toh's earlier work[1]. However, from technical service visits and discussion by the authors with chemists and engineers of the Malaysian owned major producers of gloves, the authors concluded that, despite the availability of these two reports, DOX was not adopted at all. Possible reasons could be that See Toh[1] and Ng *et al*.[2] do not provide a single computer function or procedure to perform calculations and display results graphically. See Toh[1] mentioned MBasic as his chosen language (which lacks plotting capability).

The authors in this current research adopt open source statistical computing to write the necessary functions (R refers software procedures as functions). Model datasets from a classic text by Cochran and Cox[3], and Lenth[4] were extensively tested and validated using these functions. By writing functions and demonstrating their use in specific latex applications, can overcome the difficulties faced by practitioners in the industry in understanding DOX from books and generic journal articles devoted to other industries.

Screening and Optimising Design

In DOX, factors (also known as independent variables) may be categorical data or quantitative data. Examples of categorical data are types of synthetic rubber (XNBR, polychloroprene) or methods of grinding (pearl milling, ball milling). Examples of quantitative data are physical or chemical properties (tensile strength, swelling index, combined sulphur) or data derived from categorical data (different blend ratios of NR and XNBR latices, or number of grinding cycles for calcium carbonate). The advantages of statistical design over varying one factor at a time, while keeping other factors constant have been well documented[3,5,6]. In one factor at a time (OFAT) experiments one factor out of many factors is varied while other factors are kept constant to give desirable response such as higher production yield, minimum defect or optimal property. This factor is then kept at the new desirable level while another factor is varied to give desirable response. In OFAT the interaction effects of two or more factors are not detected.

In a designed experiment, all possible combinations of factors deemed to have an influence on the response are tested. The effect of a factor is defined as the change in response produced by a change in the level of the factor and this effect is termed the main effect. The difference between the levels of one factor is not the same at all levels of the other factors. When this occurs there is an interaction between the factors. The number of experiments needed to run combinations of factors at two levels is 2^n where n denotes the number of factors. A full factorial design for 2, 3, and 4 has 4, 8, and 16 experiments. Fortunately a fractional factorial design can be used to keep the number of experiments at 8 when the number of factors is 4, 5, 6, and 7.

Characteristics of Natural Rubber Latex

Natural rubber (NR) latex is a complex aqueous dispersion of polyisoprene latex. The technology to concentrate by centrifugation[7], creaming[8,9], and evaporation[10] has been well documented, to yield latex concentrate of 60% dry rubber content (DRC). The specific surface area[11] of NR latex has been determined by sodium dodecyl sulphate (SDS). The colloidal stability of NR latex increases with increasing higher fatty acid (HFA)[12] in the first 28 days, thereafter the stability and HFA content plateau off. To counteract the deleterious effects of bacteria, various combinations

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of bactericides[13] have been used including ammonia, hydroxylamine neutral sulphate (HNS), zinc diethyl dithiocarbamate (ZDC), sodium diethyl dithiocarbamate (SDC)[14], tetramethyl thiuram disulphide (TMTD)[15], sodium pentachlorophenol (SPP) and other chemicals yet to be commercialised[16]. Despite the various origins of field latex, preservation systems, and methods of concentration, national and international quality standards[17] have been drawn up to ensure the quality of latex concentrate used in product manufacturing.

Glove Industry

NR latex needs additional chemicals for preparation of latex compounds[18] suitable for its end application in latex foam, dipped gloves and latex thread manufacturing. These chemicals may be classified as colloidal stabilisers, curatives and activators, and protective agents[18]. Solid chemicals like ZDC, ZnO, TMTD and sulphur require grinding and dispersion through ball mill, sand/bead mill, or attritor to micron sizes to facilitate suspension in aqueous medium and easy migration to NR latex. Low melting point solid or liquid requires an emulsion step to produce stable emulsion.

Van Gils[19] studied and postulated that sulphur dissolves in aqueous solution *via* its reaction with sulphuryl protein. Poor oxidation resistance of skim latex produced from TMTD−ZnO preserved field latex prompted a systematic study by Ng[20]. He found that when dithiocarbamyl compounds were added to latex, copper dithiocarbamates were formed by the naturally present copper in the serum with these dithiocarbamyl compounds. Morris and Thomas[21] studied the diffusion of sulphur and ZDC in rubber by immersing solid chemicals below their respective melting point or in molten form at temperatures above their melting point in peroxide-vulcanised NR compound. Their study confirmed the diffusion process that transported sulphur and ZDC into rubber compound. This is a further confirmation of solubility of sulphur and ZDC in polyisoprene molecules in NR, whether in latex concentrate or in solid rubber form.

In recent years we have seen the emergence of gloves that have two or more layers[22]. Each layer is targeted at serving specific function or possessing specific properties. The complexity of latex compound design for specific properties, the choice of polymer for economic and technical reasons, coupled with the multitude of manufacturing processes and auxiliary chemicals used dictates that research and development in the laboratory and in-process validation must be conducted systematically.

EXPERIMENTAL

Materials and Methods

The high ammonia (HA) latex was purchased from Getahindus. Commercial grades XNBR were obtained from Malaysian agents of the latices – Synthomer X6617 and Zeon LX550L. Aqueous dispersions of sulphur, zinc oxide and ZDBC were prepared by ball milling under standard conditions in MRB latex laboratory and by bead milling in horizontal mill filled with 1.2 mm beads in a median size commercial dispersion plant. All of these materials are of industrial grade.

Preparation of Latex Compound

The HA and XNBR were compounded according to formulations for the various experimental designs. The stabiliser sodium dodecyl sulphate (SDS) was added to the XNBR before the pH of the latex was raised, followed by the addition of vulcanising ingredients.

Preparation of Films

NR Film. Unglazed porcelain plates were first heated above 60ºC and dipped into coagulant (15 % calcium nitrate solution) for 5 seconds. The plates were then dried in oven at 60ºC and then dipped into the latex compound for 10 seconds. The resulting deposit was wet leached at 60ºC for 2 minutes. Wet gel was then vulcanised at 90ºC in oven for 10 min followed by 100ºC in oven for 10 minutes.

XNBR Film. In the preparation of dipped films, the total solids content of the XNBR was reduced to 20%. Unglazed porcelain plates were first heated to 70ºC before dipping into a 20% calcium nitrate solution. The plates were oven dried in an air oven set at 70ºC before dipping into the latex compound for 10 seconds. The resulting wet films were air dried under room conditions for 10 min before being subjected to leaching in distilled water for 2 minutes. The leached films were then dried in the oven set at 80 ± 5ºC for 10 min before heating up to 100 ± 5ºC and then again to 110 ± 5ºC for 10 min respectively. The films were then removed from the oven and cooled to room temperature before being powdered with USP grade corn starch and stripped off the plates.

Mechanical Properties of Films

The tensile properties of the unaged films and heat aged films at 70ºC for seven days were determined using an Instron 5565 testing machine according to the *ASTM D412*[23] with a crosshead speed of 500 mm/min. The test was conducted under room temperature (25 ± 1ºC).

The tear strength values of the unaged and aged films were obtained by tearing prepared test samples using an Instron 5565 testing machine according to the *ISO 34*[24]. The test was conducted under room temperature using a crosshead speed of 100 mm/min.

Determination of Crosslink Density

NR Films - Linear Swelling Index. Glass plates were first dipped into a coagulant (10% calcium nitrate) and dried at 70ºC in an oven. The glass plates were next dipped into the latex compound. The resulting wet gel was dried by blowing dry air (room temperature) until a completely dried film was produced. Circular test pieces with diameter of 23 mm were cut next and the test pieces were soaked in cyclohexane for 30 minutes. The procedure was repeated for every few hours for 72 hours. The linear swelling index of the films was calculated using the following equation:

$$\textit{Linear swelling index} = \frac{L_2}{L_1} \qquad \ldots 1$$

where L_1 is the initial length of the film (cm);
L_2 is the swollen length of the film (cm).

XNBR Films. The crosslink density of the film was determined by equilibrium swelling a pre-weighed test sample in acetone, based on the Flory-Rehner equation[25]. The detail experimental procedure is described elsewhere[26].

Factorial Design

Terminology for factorial design is in accordance to Cochran *et al*. and Montgomery[3,5]. However, there is a subtle difference between categorical and quantitative data. Factors are coded as -1, 0 (centre point), +1, –α and +α. Zero (for centre point) is chosen for the desired input factor at a

certain measured value (*e.g.* 0.6 phr sulphur, calcium carbonate of 2μ size, 28-day old NR latex). Experimental unit is the increment or decrement value (*e.g.* 0.2 phr sulphur, 1 μ calcium carbonate size, 10-day old latex) so that the -1, 0, and +1 levels are centre value – experimental unit, centre value and centre value + experimental unit, respectively. In the above examples, the -1, 0, and +1 factor values are now 0.4, 0.6 and 0.8 phr sulphur; 1μ, 2μ, and 3μ size calcium carbonate; and 18-day, 28-day and 38-day old NR latex, respectively. In screening factorial design, the response results are plotted as linear response formed by the -1 and +1 factor input. In quadratic design as in central composite rotatable design, these two points plus centre points and two other points (called axial points) formed by centre points ± α times the experimental units provide a curvilinear plots. 'α' normally lies between 1.414 and 2.

For categorical data, the conceptualisation of factor levels is slightly different from quantitative data. For -1 and +1 the data can be two different ingredients such as XNBR latex from Nippon Zeon and Synthomer (seen later in the paper), absence/presence of a condition or an ingredient (*e.g.* xanthan gum viscosity thickener or a secondary rubber accelerator, ZMBT) or mutually exclusive and incompatible methods (ball milling with ¾ inch pebble balls, pearl mill with 1.2 mm zirconia oxide pearl). In many cases, categorical data factorial design will provide answers to their choices in subsequent factorial design. If xanthan gum viscosity thickener has no noticeable difference in the response, it would then be eliminated in subsequent trial. In other cases, the categorical factor can be treated as quantitative in a subsequent design. Two compatible latices could be blended at ratios of 1:3, 1:1, 3:1 corresponding to -1, 0 and +1 level, but the weight of each blend is the same when compounded with other ingredients.

Data Analysis

In the initial stage of the current investigation, open source software (OpenOffice) was used to enter data and display the results in graphic form. This procedure is interactive, manual and prone to error. Each set of display chart properties need to be configured. It is a useful introduction to calculations in DOX. For advanced users, the productivity of this procedure is low.

In terms of complexity and costs, commercially available statistical packages (often referred to as close source software; main implementations are SAS, SPSS, Stata and Minitab) or open source software implementing DOX are highly capable of generating factorial design and providing graphic output. Groemping provides a summary of available R software[27] running DOX[28]. These include RcmdrPlugin.DoE and Lenth Response Surface Methodology.

However, the authors' experience with DOX has shown that migrating from the simpler OpenOffice approach to commercial packages or open source packages often presents a challenge for beginners. Migrating from OpenOffice spreadsheet to R functions represents a less daunting task. An example of 'R' function is given in *Appendix 1*: 'Screening Experiments involving seven factors at two levels'.

By varying this basic structure of the codes in *Appendix 1*, other necessary functions written for calculating and printing bar plots are listed as follows:

1. Interaction of variables
2. Lenth's *pseudo standard error*[4]
3. Central composite design involving four variables in 31 experimental runs and the simpler curvature plots for each of the four variables[3,5].

All the functions have been fully tested and yield same results as the original calculations given in Cochran and Cox[3] and Lenth[4]. All results and plots produced in this research were generated from R functions written by the authors.

RESULTS AND DISCUSSION

Screening Experiments

Screening experiments are suitable both for quantitative and categorical data as explained earlier. In this particular experiment, milling methods (categorical data) were compared.

Ball milling has been practised for years in the latex product manufacturing. In this method, chemicals are loaded into a horizontal porcelain cylindrical pot charged with balls of various sizes and made of wear-resistant material. Ball milling produces micron-size chemicals but the process is time consuming, limited by small batch size since larger ball mills are prohibitive in cost. Ball milling has been superseded by the more efficient horizontal or vertical mills, such as pearl or bead mills. Pearl or bead mills grind materials in a number of passes to achieve the final micron size; while zinc oxide (ZnO), titanium dioxide (TiO_2), and zinc diethyl dithiocarbamate (ZDC) and zinc dibutyl dithiocarbamate (ZDBC) are ground in a single pass. The coarser sulphur and Wingstay L are ground in two or three passes to achieve acceptable size reduction. This screening experiment was designed to test seven chemicals, each of which was either ground in ball mill or bead mill. All seven sets of chemicals are designated as x_1: x_7 (*Tables 1* and *2*).

Swelling was performed using cyclohexane and results were reported as percentage increase in length rather than area (*Table 2*).

It can be seen from *Table 3* that the results for factor x_1 may be grouped into x_1 = +1 (E2, E4, E6, E8) and x_1 = -1 (E1, E3, E5, E7). Contrast is calculated as the difference of mean values for x_1 (+1) and x_1 (-1), consistent with the definition given in the literature. In classical analysis of variance model, an effect is defined as the difference between the high mean and the grand mean[4]. It can be seen for any of the factors calculated at +1 level, the other six factors are equally distributed at two +1 and two -1 levels, so that the effects of other factors will cancel out. Designs with this property are called orthogonal.

Result for tensile strength is presented in *Figure 1*. It can be seen that the absolute contrast (magnitude) is most marked for x_2, x_7, x_6, x_1, in that decreasing order. Superior properties were obtained for ball-milled S (x_1), ZDC (x_2),

TABLE 1. FRACTIONAL FACTORIAL EXPERIMENTS INVOLVING SEVEN VARIABLES (X1:X7) IN EIGHT EXPERIMENTS (E1:E8)

Factor / Exp	E1	E2	E3	E4	E5	E6	E7	E8
x_1	-1	+1	-1	+1	-1	+1	-1	+1
x_2	-1	-1	+1	+1	-1	-1	+1	+1
x_3	-1	-1	-1	-1	+1	+1	+1	+1
x_4	-1	+1	+1	-1	+1	-1	-1	+1
x_5	+1	-1	-1	+1	+1	-1	-1	+1
x_6	+1	-1	+1	-1	-1	+1	-1	+1
x_7	+1	+1	-1	-1	-1	-1	+1	+1

TABLE 2. SCREENING EXPERIMENTS INVOLVING SEVEN VARIABLES

Chemical / Exp	E1	E2	E3	E4	E5	E6	E7	E8
HA latex	100	100	100	100	100	100	100	100
KOH	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Potassium laurate	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
x_1 BM Sulphur		1.1		1.1		1.1		1.1
PM Sulphur	1.1		1.1		1.1		1.1	
x_2 BM ZDC			0.4	0.4			0.4	0.4
PM ZDC	0.4	0.4			0.4	0.4		
x_3 BM ZDBC					0.2	0.2	0.2	0.2
PM ZDBC	0.2	0.2	0.2	0.2				
x_4 BM ZMBT		0.1	0.1		0.1			0.1
PM ZMBT	0.1			0.1		0.1	0.1	
x_5 BM ZnO	0.6			0.6	0.6			0.6
PM ZnO		0.6	0.6			0.6	0.6	
x_6 BM Antioxidant	0.75		0.75			0.75		0.75
PM Antioxidant		0.75		0.75	0.75		0.75	
x_7 BM TiO_2	0.3	0.3					0.3	0.3
PM TiO_2			0.3	0.3	0.3	0.3		
pH	11.31	11.32	11.27	11.18	10.99	11.23	11.66	11.72
Viscosity (centipoise)	90	95	285	350	220	360	155	200
Swell ratio, % increase in length	86.9	52.1	91.3	82.6	65.2	82.6	86.9	86.9
TS (MPa)	28.48	28.95	36.55	33.72	29.98	35.00	30.73	34.67
EB (%)	830	850	830	830	800	870	870	830
Tear (N/mm)	12.39	18.58	18.31	19.6	26.61	18.02	19.40	24.01

TABLE 3. CONTRASTS FOR TENSILE STRENGTH FOR SEVEN VARIABLES

	Mean for $+x_i$	*Mean for* $-x_i$	*Contrast for* x_i
x_1	¼(E2+E4+E6+E8)=33.09	¼(E1+E3+E5+E7)=31.46	1.65
x_2	¼(E3+E4+E7+E8)=33.92	¼(E1+E2+E5+E6)=30.60	3.32
x_3	¼(E5+E6+E7+E8)=32.60	¼(E1+E2+E3+E4)=31.93	0.67
x_4	¼(E2+E3+E5+E8)=32.54	¼(E1+E4+E6+E7)=31.98	0.56
x_5	¼(E1+E4+E5+E8)=31.71	¼(E2+E3+E6+E7)=32.81	-1.10
x_6	¼(E1+E3+E6+E8)=33.68	¼(E2+E4+E5+E7)=30.85	2.83
x_7	¼(E1+E2+E7+E8)=30.71	¼(E3+E4+E5+E6)=33.81	-3.11

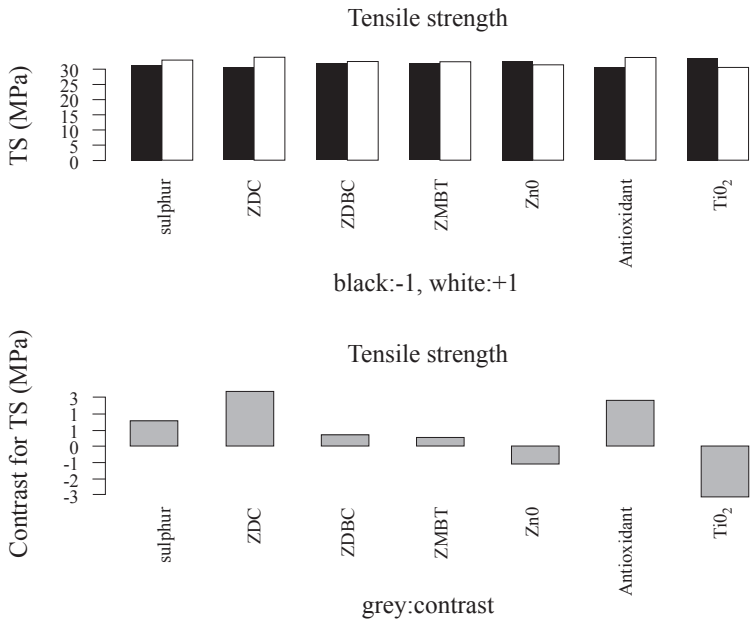

Figure 1. Tensile strength of (a) Ball-milled versus (b) Pearl-milled chemicals.

antioxidant (x_6) and pearl-milled TiO_2 (x_7). The usefulness of this screening experiment is in the ability to detect the influence of each chemical affected by the milling method and the direction of the influence.

According to See Toh[1], situations where the screening experiment in rubber product manufacturing are most useful are: finding problematic ingredients, substitution of ingredients, new ingredients, formula simplification and compound sensitivity. The screening factorial design experiment described here can be generalised to tackle the above listed objectives. These above mentioned situations are discussed in details.

Problematic ingredients arise from closure of manufacturing facilities or regulatory body new directives. In 2013, when Ishihara Sangyo Kaisha[29] closed its Singapore titanium dioxide plant in Singapore, existing customers have either to source titanium dioxide from Ishihara's Japan plant or other manufacturers; either choice necessitated revalidation.

Substitution of ingredients arise from regulations due to environmental or health concern, or cost reduction. REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) is the EU's major regulation for chemicals. Many existing compounding materials are not REACH-compliant, causing manufacturers to look for alternatives. Aromatic rubber process oils are substituted by the naphthenic or paraffinic oil and phthalates[30] are substituted by adipates or sebacates. Blends of titanium dioxide with other opacifying agents (calcium carbonate[31], calcined kaolin, barium sulphate) have been adopted as alternative to titanium dioxide.

New ingredients arise from innovations by manufacturers. In recent years, synthetic

polyisoprene (being protein-free), nitrosoamine-free accelerator combinations[32], zinc oxide-encapsulated calcium carbonate[33] are some examples of new ingredients. Formulation simplification is necessary to revalidate existing formulations which are often culmination of years of changes in ingredients, where each addition was designed to tackle an immediate problem. Often the problems at hand are combinations of the above situations. The technique described here can be used to systematically evaluate quantitative or categorical factor or combinations of both.

Interaction

According to Montgomery[5], a screening experiment must be examined for interaction. When an interaction is large, the corresponding main effects have little practical meaning. That is, knowledge of the interaction between two factors is more useful than knowledge of the main effect. Interaction of chemicals in rubber compounding is very common. Primary accelerators are often blended with secondary and tertiary accelerators to confer synergistic effects, minimise blooming, and minimising product costs. Peroxide and co-agent curing system is often used in peroxide curing system. Commercial accelerator blends for EPDM can have four individual accelerators. Reinforcement of rubber by silica filler needs the presence of a silane coupling agent in tyre tread formulation.

As screening factorial design involving 3 to 7 factor input requires eight experiments only seven effects can be calculated. For 3- factor (in which case a full factorial design is used) three main effects are calculated, three 2-factor interactions (x_1x_2, x_2x_3, x_3x_1) and one 3-factor interaction can also be calculated[1]. In the other extreme case, 7-factor fractional factorial design only a graphical method to display interaction is possible and the technique is demonstrated here.

To calculate the interaction effect of sulphur and ZDC, the following calculating steps are shown. Factor x_1 (sulphur) shows contrast between ball-milled sulphur (+1) and pearl-milled sulphur (-1). Factor x_1 (+1) there are two at level +1 (E4 and E8), and two at level -1 (E2 and E6). For x_1 (-1) there are two at level +1 (E3 and E7), and two at level -1 (E1 and E5) for factor x_2. *Table 4* shows the calculations to obtain the resolution of the results into x_1 and x_2 at two separate levels.

This procedure of subdividing four results for x_1 at +1 level into two each for x_2 = -1 and x_2 = +1 is repeated for x_2, to x_7. Plots of the four data points for x_1x_2, x_1x_3 …x_1x_7 are shown in *Figures 5−10*. Three distinct patterns are often encountered in plots of this nature depicting the interaction between two chemicals, ranging from parallel lines, non-intersecting diverging or converging lines, and intersecting lines. When the two lines are parallel there is no interaction, and intersecting lines indicate complex interaction.

The interpretation of non-interaction for sulphur and ZDC is shown in *Figure 5*. Ball-milled ZDC is superior to pearl-milled ZDC. For each of the two lines, result for pearl-mill sulphur is inferior and ball-mill sulphur is superior, represented by positively slope of the two lines. There is no interaction.

The interpretation of complex interaction for sulphur and ZDBC is shown in *Figure 6* and the contrast results for ZDBC in *Table 4* (32.59 MPa for ball-milled and 31.92 MPa for pearl-milled). However when ball-milled sulphur and ball-milled ZDBC are used together there is a marked increase in the tensile strength.

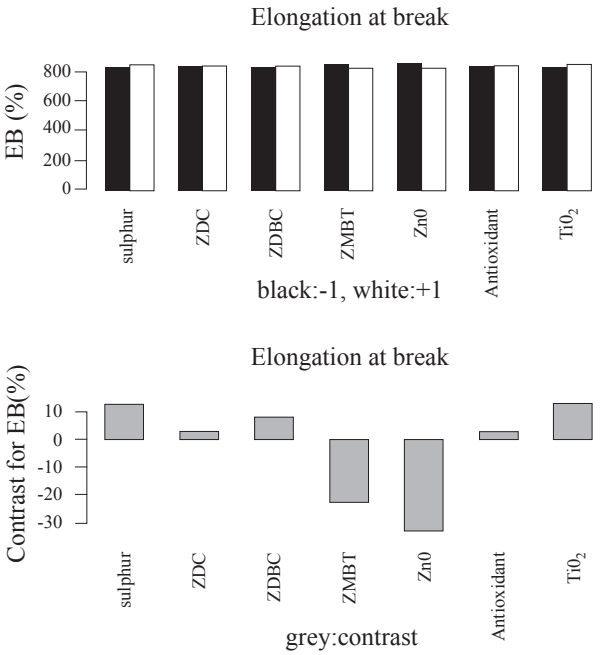

Figure 2. Elongation at break of (a) Ball-milled (b) Pearl-milled chemicals.

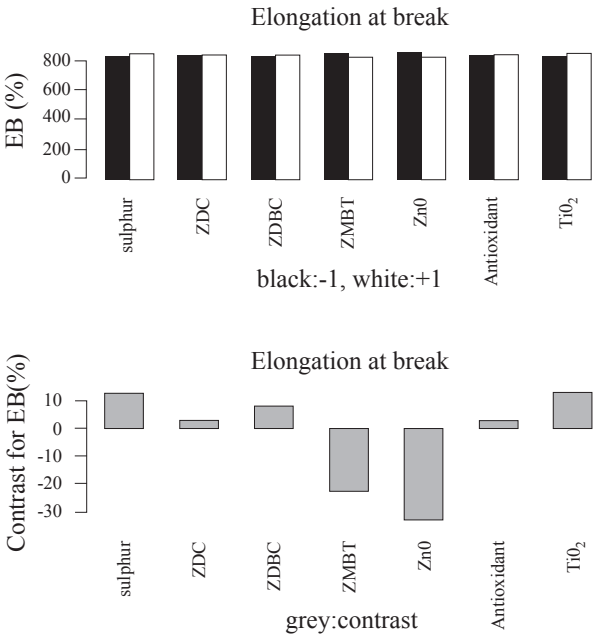

Figure 3. Tear strength of (a) Ball-milled versus (b) Pearl-milled chemicals.

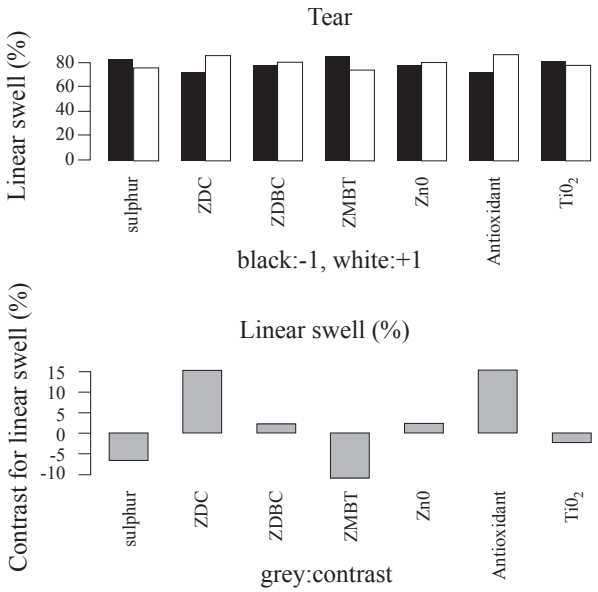

Figure 4. Linear swell of (a) Ball-milled versus (b) Pearl-milled chemicals.

TABLE 4. CALCULATING INTERACTIONS FOR SULPHUR (X1) AND ZDC (X2)

x_1 at +1		x_1 at -1	
x_2 at +1	x_2 at -1	x_2 at +1	x_2 at -1
E4 and E8	E2 and E6	E3 and E7	E1 and E5
½(33.72+34.67)	½(28.95+35.00)	½(36.55+30.73)	½(28.48+29.98)
=34.20	=31.98	=33.65	=29.26

Pseudo-standard Error

Statistical designed experiments are designed to evaluate the main effects and interactions between variables. To measure the significance of factors (x_1: x_7) it is necessary to have an estimate of the standard error ($sd = \sqrt{variance}$). It is customary to replicate the experiments at the centre point (0) for all factors. However it is often too tedious, time-consuming or expensive to replicate experiments at the centre point. There is therefore a need to have an alternative, but robust method to provide an estimate of the standard error (*sd*). Daniel[34] used semi-normal plots. However, Lenth[4] has provided an alternative robust method for estimating the standard error (*sd*). He calculated standard error based on the absolute contrasts for main, and interactions among the factors. Pseudo standard error (pse) is easier to calculate and display graphically; in four factor at two level design, all 16 absolute contrasts were ordered and median absolute contrast was taken and multiplied by 1.5 to obtain pse. Detailed steps for calculating pse are given by Lenth[4].

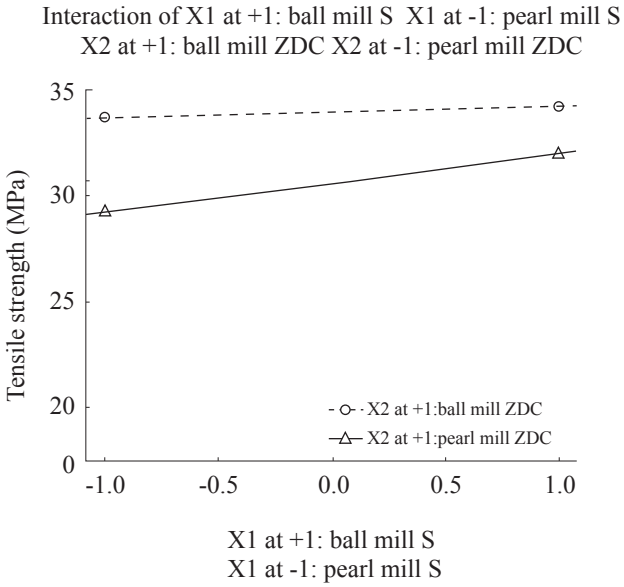

Figure 5. Interaction between sulphur and ZDC.

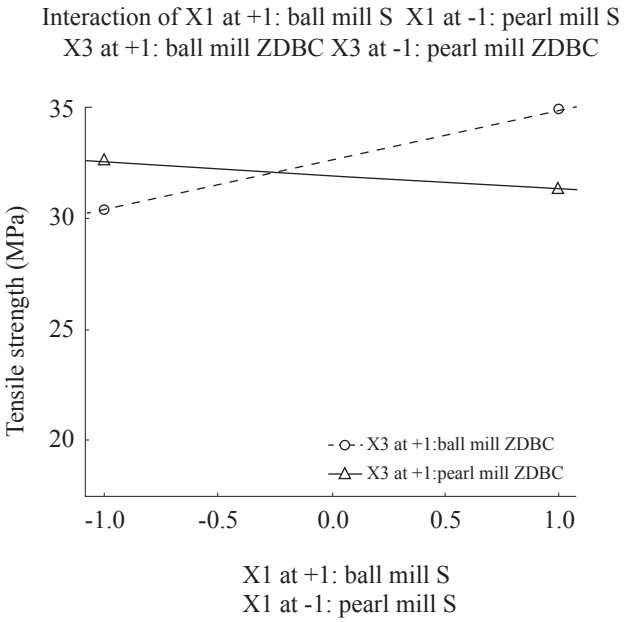

Figure 6. Interaction between sulphur and ZDBC.

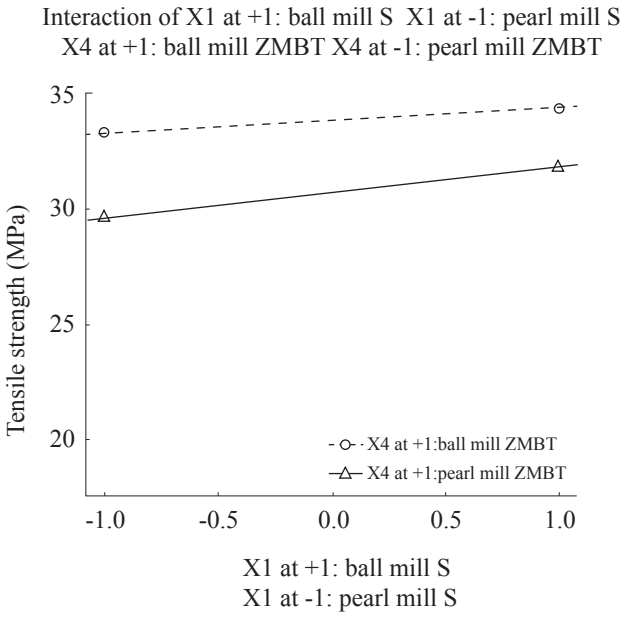

Figure 7. Interaction between sulphur and ZMBT.

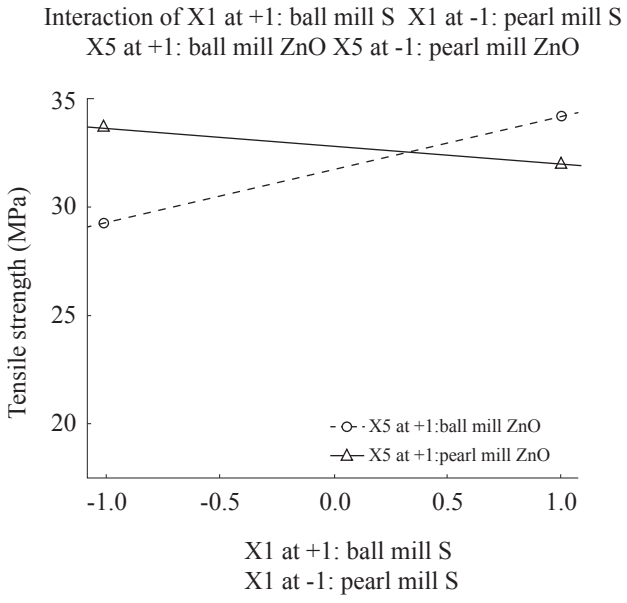

Figure 8. Interaction between sulphur and ZnO.

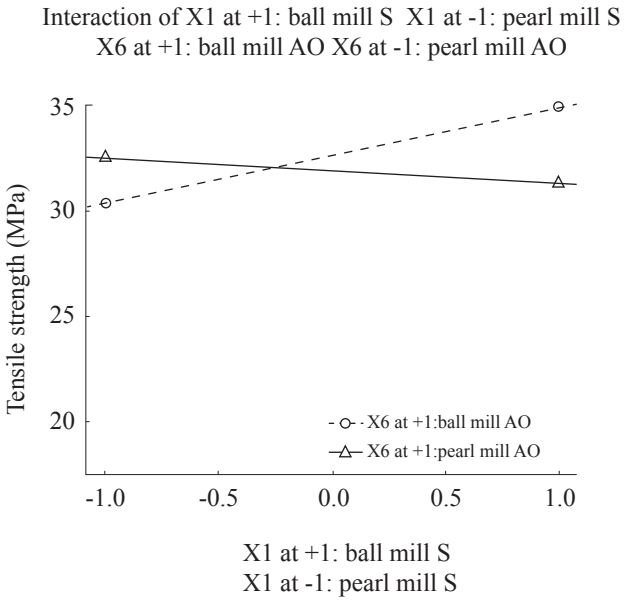

Figure 9. Interaction between sulphur and antioxidant (Wingstay L).

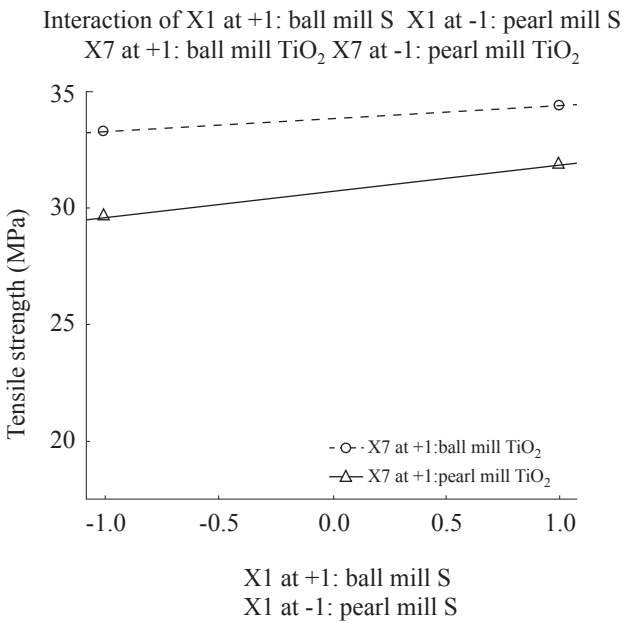

Figure 10. Interaction between sulphur and TiO_2.

TABLE 5. FULL FACTORIAL DESIGN OF FOUR FACTORS AT TWO LEVELS

Factor / Exp	E1	E2	E3	E4	E5	E6	E7	E8
x_1	-1	+1	-1	+1	-1	+1	-1	+1
x_2	-1	-1	+1	+1	-1	-1	+1	+1
x_3	-1	-1	-1	-1	+1	+1	+1	+1
x_4	-1	+1	+1	-1	+1	-1	-1	+1
Factor / Exp	E9	E10	E11	E12	E13	E14	E15	E16
x_1	-1	+1	-1	+1	-1	+1	-1	+1
x_2	-1	-1	+1	+1	-1	-1	+1	+1
x_3	-1	-1	-1	-1	+1	+1	+1	+1
x_4	+1	-1	-1	+1	-1	+1	+1	-1

TABLE 6. DETAILED CHEMICAL ADDITIONS AND PHYSICAL PROPERTIES

Chemical / Exp	E1	E2	E3	E4	E5	E6	E7	E8
10% SDS	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
5% KOH	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
x_1 Synthomer X6617		100		100		100		100
Zeon LX550L	100		100		100		100	
x_2 S Canada			1	1			1	1
S Thailand	1	1			1	1		
x_3 ZDBC Weiling					1	1	1	1
ZDBC Perkacit	1	1	1	1				
x_4 ZnO Normal		1.5	1.5		1.5			1.5
ZnO Active	1.5			1.5		1.5	1.5	
TS (MPa)	34.2	39.1	34.2	33.1	28.7	39.9	32.1	36.8
EB (%)	602	520	608	452	554	452	550	480
Tear (N/mm)	3.28	3.21	4.17	2.47	3.16	2.62	2.59	2.38
pH	11.35	10.4	10.56	10.49	11.3	10.54	11.46	10.5
Visco	6	6	6	6	7	7	6	6
V_r (X10^{-3})	1.78	0.77	1.33	0.78	1.48	0.56	1.28	0.53
Chemical / Exp	E9	E10	E11	E12	E13	E14	E15	E16
10% SDS	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
5% KOH	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
x_1 Synthomer X6617		100		100		100		100
Zeon LX550L	100		100		100		100	
x_2 S Canada			1	1			1	1
S Thailand	1	1			1	1		
x_3 ZDBC Weiling					1	1	1	1
ZDBC Perkacit	1	1	1	1				
x_4 ZnO Normal	1.5			1.5		1.5	1.5	
ZnO Active		1.5	1.5		1.5			1.5
TS (MPa)	35.6	32.9	38.6	31.3	33	36	30.2	35.7
EB (%)	594	478	570	514	566	450	575	450
Tear (N/mm)	3.35	2.84	2.88	2.79	2.73	2.87	3.36	2.87
pH	11.29	10.59	11.38	10.55	11.29	10.46	11.26	10.51
Visco	7	6	6	6	7	6	6	6
V_r (X10^{-3})	1.10	0.65	1.30	0.57	1.33	0.55	1.03	0.58

In this series of experiments comprising of four factors, the full factorial (2^4) experiments, a total of 15 (16-1 degrees of freedom) contrasts can be calculated – four main effects, six 2-factor interactions, four 3-factor interactions, one 4-factor interaction are calculated, by subtracting the -1 results from the +1 results. Pseudo standard error (pse) is calculated as 1.5 times of the median absolute contrasts.

The key difference between Lenth's pse for examining interaction from the above graphical method for examining interaction in 7-factor eight experiments is that the former is based on calculation of the absolute contrasts and statistical significance is justifiable. Meanwhile, the latter is based on visual examination of the two lines, and interpretation of non-intersecting lines is more subjective.

An XNBR formulation was chosen for studying pse. The choice of factor at -1 and +1 is again categorical rather than quantitative. Two grades of carboxylated butadiene-acrylonitrile copolymer latex were obtained directly from the suppliers and were used without further characterisation. ZDBC was sourced from the local agent for a European brand (Perkacit), and the other a People Republic of China brand (Weiling). Zinc oxide was obtained from two local agents – one labelled as normal while the other was labelled as active. The results were shown in *Figure 11*. The top charts represent the -1 and +1 for each of the 15 effects (main and interaction). The bottom chart is an expanded view of the contrast (taken as the difference between +1 and -1) together with *pse* line drawn across the bar charts. For tensile strength, the contrasts for main effect, and interaction (for two-, three-, and four-factor) are calculated and shown in *Table 7*. The absolute contrast can be ordered as 0.14, 0.24, 0.26, 0.44, 0.46, 0.56, 0.91, 1.04, 1.74, 1.91, 2.28, 2.41, 2.51, 2.68 and 3.38. Thus the 8th absolute contrast (1.04) was multiplied by 1.50 to yield 1.56.

It can be inferred from *Table 7* that polymer type (Zeon LX550L *vs* Synthomer X6617); polymer-ZDBC, polymer-ZnO and polymer-sulphur interactions are significant (denoted with *), since the absolute contrasts exceed the pse for tensile strength (=1.56 MPa). Technical data sheet from Synthomer indicates high acrylonitrile content for Synthomer X6617 so the high tensile could be interpreted as due to this high acrylonitrile content. *Figures 12* to *14* are bar plots for all other parameters.

Factorial experiments are intended to bring out the difference (contrast) in physical properties measured due to particular factors (main effect), interactions of factors or combinations of main and interactions. Interpretations of these effects can only be done through confirmatory tests.

A summary of all the variables with the contrasts for the respective main, and interaction together with their pse is given in *Table 8*.

Rotatable Central Composite Design

The full factorial experiment and the fractional factorial experiment cover the factorial points for main effects, and interaction effects. The Box-Wilson[5] central composite design or simply abbreviated as the central composite design (CCD) contains an embedded factorial or fractional factorial design with centre points that is augmented with a group of star points or axial points that allow estimation of curvature (*Figure 15*). Response surface methods describe traditional second order designs with more than one factor at more than two levels. We have chosen a design of four factors, with the axial and star points[5].

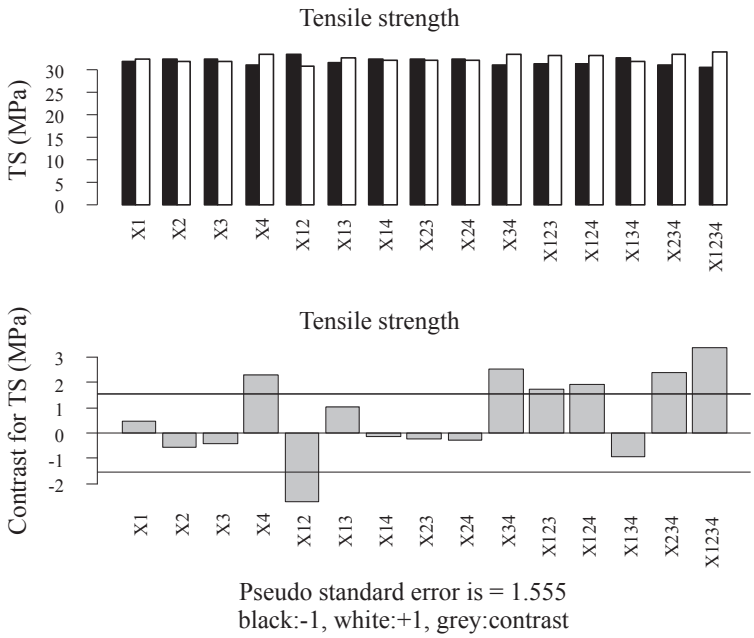

Figure 11. Tensile strength: main effects, interaction of 2nd, 3rd and 4th order for four factors at two levels.

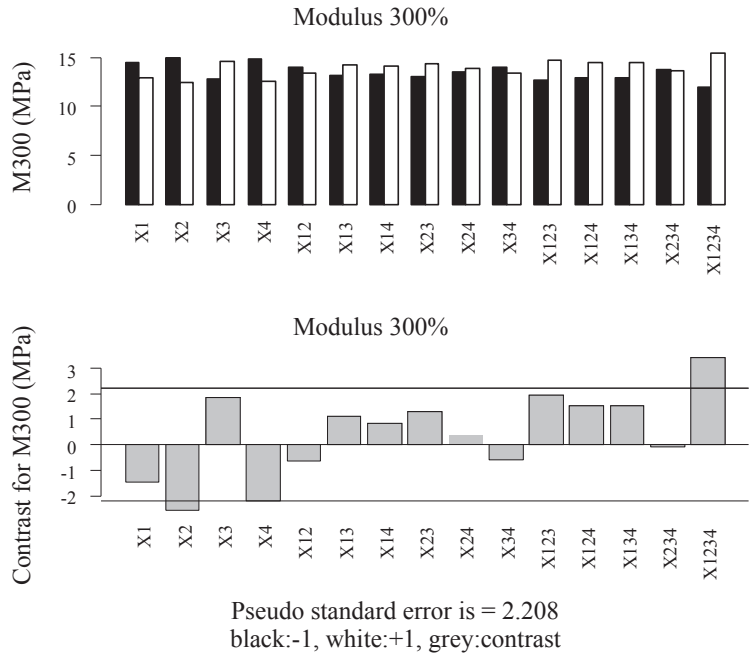

Figure 12. Modulus 300%: main effects, interaction of 2nd, 3rd and 4th order for four factors at two levels.

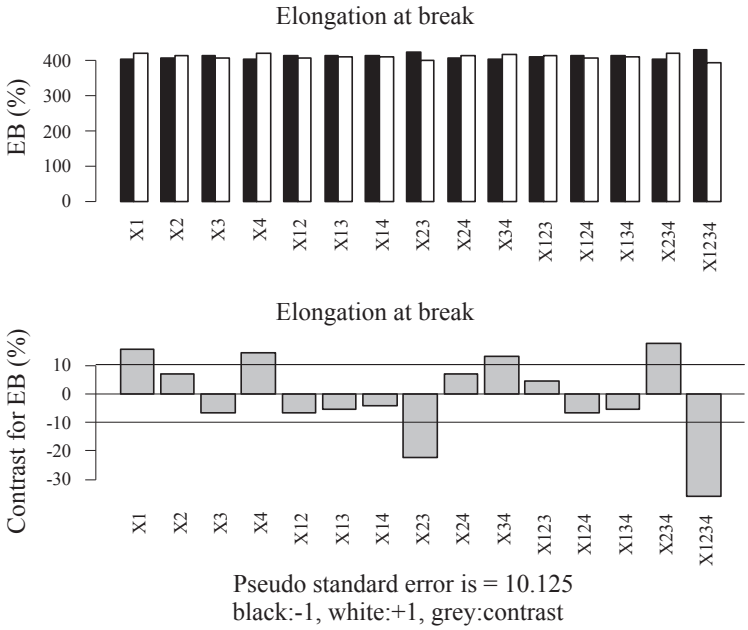

Figure 13. Elongation at break: Main effects, interaction of 2nd, 3rd and 4th order for four factors at two levels.

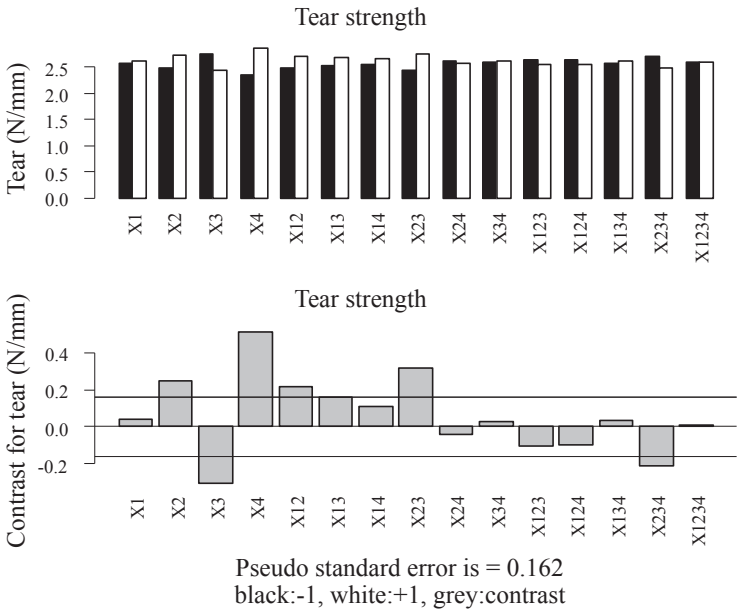

Figure 14. Tear strength: main effects, interaction of 2nd, 3rd and 4th order for four factors at two levels.

TABLE 7. MAIN EFFECTS, 2ND, 3RD AND 4TH ORDER INTERACTIONS FOR TENSILE STRENGTH

	Mean for +Xi	Mean for -Xi	Contrast for Xi *indicates significance
x_1	31.83	32.29	0.46
x_2	32.34	31.78	-0.56
x_3	32.28	31.84	-0.44
x_4	30.91	33.20	*2.28
x_{12}	33.40	30.71	*-2.68
x_{13}	31.54	32.58	1.04
x_{14}	32.13	31.98	-0.14
x_{23}	32.17	31.94	-0.24
x_{24}	32.19	31.93	-0.26
x_{34}	30.80	33.31	*2.51
x_{123}	31.19	32.93	*1.74
x_{124}	31.10	33.01	*1.91
x_{134}	32.51	31.60	-0.91
x_{234}	30.85	33.26	*2.41
x_{1234}	30.36	33.75	*3.38

TABLE 8. MAIN EFFECTS, 2ND, 3RD AND 4TH ORDER INTERACTIONS FOR ALL THE PHYSICAL PROPERTIES

	TS (MPa)	M300 (%)	EB (%)	Tear (N/mm)	Aged TS (MPa)	Aged M300 (%)	Aged EB(%)	Aged Tear (N/mm)
pse	1.56	2.21	10.1	0.16	2.01	1.93	11.3	0.18
x_1	0.46	-1.47	*15.8	0.04	1.34	*-5.24	*56.3	-0.15
x_2	-0.56	*-2.55	6.8	*0.25	*-3.18	*-2.01	7.5	0.02
x_3	-0.44	1.85	-6.8	*-0.30	0.56	*3.19	*-20.5	0.14
x_4	*2.28	-2.19	*14.3	*0.52	-1.04	-0.41	-2.5	*0.45
x_{12}	*-2.68	-0.62	-6.8	*0.22	-0.96	-0.62	1.3	0.11
x_{13}	1.04	1.13	-5.3	0.16	-1.76	1.63	*-15.8	*0.21
x_{14}	-0.14	0.84	-4.3	0.11	0.38	1.52	-11.3	-0.05
x_{23}	-0.24	1.28	*-22.3	*0.32	-0.94	0.34	-5.5	-0.02
x_{24}	-0.26	0.38	6.8	-0.04	*3.16	0.59	7.5	-0.35
x_{34}	*2.51	-0.60	*13.3	0.03	-1.34	-1.91	10.5	0.05
x_{123}	*1.74	1.96	4.3	-0.10	0.64	1.29	-6.8	0
x_{124}	*1.91	1.53	-6.8	-0.10	-1.81	1.39	*-15.3	*-0.98
x_{134}	-0.91	1.53	-5.3	0.04	1.94	-0.84	6.8	-0.12
x_{234}	*2.41	-0.10	*17.8	*-0.21	1.96	0.58	4.5	0.05
x_{1234}	*3.38	*3.43	*-35.8	0.01	-0.76	0.88	*-23.3	*0.25

This particular design is the circumscribed central composite design in that the extreme points for each of the variation are at a distance α from centre point (0 for all factors). The value α is calculated from a formula as follows:

$$\alpha = (\textit{number of factorial runs})^{1/4} \quad \ldots 4$$

Since a full factorial design is chosen for this case thus

$$\alpha = (\textit{number of factorial runs})^{1/4} = (2^4)^{1/4} = 2 \quad \ldots 5$$

The detailed design with ingredient names and phr are shown in *Tables 9* and *10*.

It can be seen from the results (*Table 11*) that the lack of fit is of equal magnitude to the first and second order terms, meaning that a second order quadratic equation does not fully fit the data. It has been demonstrated earlier that third and perhaps even the fourth order interactions are evident in physical properties of XNBR compound.

Central composite design can be used for plotting physical properties and is used for optimisation purpose. The present work bridges the gap between the highly sophisticated response surface plots by providing a simpler interpretation of the central composite design. In this work, plots for physical properties versus the levels for each of the treatments (at '0' level for the other treatments) are shown in *Figures 16-19*. The results for 0 are obtained from the replicate '0' level, the +1 and -1 are obtained from the main effects, while the -2 and +2 are obtained from unreplicated 2 experiments (all other factors are kept at '0').

Sulphur at -2 level produces low tensile strength, M300 for both unaged and aged, while at this level it does not affect EB and tear (unaged and aged). Zinc oxide at -2 level parallels sulphur in that lower M300 is obtained but the tensile strength is high compared to sulphur at -2 level. Thus covalent bond (sulphur crosslinking) contributing to tensile property is significant, whereas low ionic bond (low zinc oxide) contribution to tensile property is less marked. ZDBC level does not significantly affect the strength or the moduli (at 100% and 300%) whereas aged properties (tensile, moduli at 100% and 300% appear to be affected by low level of ZDBC (-2 level). ZMBT shows a levelling effect at levels of ZMBT. In addition, it confers protection against ageing even at low level of ZMBT (-2).

TABLE 9. CENTRAL COMPOSITE DESIGN IN 31 EXPERIMENTS

Factor	Exp E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11	E12	E13	E14	E15	E16
x_1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1
x_2	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1
x_3	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	1	1	1	1
x_4	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	1
Factor	E17	E18	E19	E20	E21	E22	E23	E24	E25	E26	E27	E28	E29	E30	E31	
x_1	-2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	
x_2	0	0	-2	2	0	0	0	0	0	0	0	0	0	0	0	
x_3	0	0	0	0	-2	2	0	0	0	0	0	0	0	0	0	
x_4	0	0	0	0	0	0	-2	2	0	0	0	0	0	0	0	

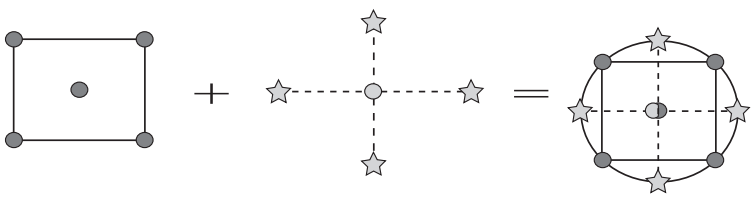

Figure 15. Axial and star points.

TABLE 10. CCD WITH ACTUAL DOSAGE AND PHYSICAL PROPERTIES

Factor	Ingredients (dry weight)	Exp E1	E2	E3	E4	E5	E6	E7	E8
	Synthomer X6617	100	100	100	100	100	100	100	100
	KOH	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
	SDS	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
x_1	Sulphur	1.2	2.0	1.2	2.0	1.2	2.0	1.2	2.0
x_2	ZDBC	0.71	0.71	1.18	1.18	0.71	0.71	1.18	1.18
x_3	ZMBT	0.30	0.30	0.30	0.30	0.50	0.50	0.50	0.50
x_4	ZnO	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22
TS (MPa)		33.7	32.1	28.4	32.7	37.6	28.8	34.3	38
M300 (MPa)		11.07	12.31	14.7	17.28	11.07	10.17	9	15.34
EB (%)		460	400	380	400	400	420	480	420
Tear (N/mm)		2.26	2.87	2.92	2.69	3.35	3.49	2.74	2.48
$V_r(\times 10^{-3})$		7.78	4.96	5.33	8.13	3.97	8.59	8.42	4.37
		E9	E10	E11	E12	E13	E14	E15	E16
	Synthomer X6617	100	100	100	100	100	100	100	100
	KOH	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
	SDS	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
x_1	Sulphur	1.20	2.0	1.20	2.0	1.20	2.0	1.20	2.0
x_2	ZDBC	0.71	0.71	1.18	1.18	0.71	0.71	1.18	1.18
x_3	ZMBT	0.30	0.30	0.30	0.30	0.50	0.50	0.50	0.50
x_4	ZnO	2.04	2.04	2.04	2.04	2.04	2.04	2.04	2.04
TS (MPa)		33.5	27.4	30.6	36.3	28.6	32.5	31.6	26.8
M300 (MPa)		14.35	13.16	13.23	20.99	11.55	15.82	18.84	10.52
EB (%)		420	416	420	380	430	384	376	420
Tear (N/mm)		2.12	2.38	2.23	2.06	2.79	2.47	2.5	2.13
$V_r(\times 10^{-3})$		6.65	9.89	36.35	4.39	4.91	5.39	2.83	6.56
		E17	E18	E19	E20	E21	E22	E23	E24
	Synthomer X6617	100	100	100	100	100	100	100	100
	KOH	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
	SDS	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
x_1	Sulphur	0.80	2.40	1.60	1.60	1.60	1.60	1.60	1.60
x_2	ZDBC	0.95	0.95	0.47	1.421	0.95	0.95	0.95	0.95
x_3	ZMBT	0.40	0.40	0.40	0.40	0.20	0.60	0.40	0.40
x_4	ZnO	1.63	1.63	1.63	1.63	1.63	1.63	0.82	2.46
TS (MPa)		18.2	28.9	35.4	33.8	35	34.1	39.7	30.2
M300 (MPa)		7.37	11.33	13.93	13.33	17.12	16.11	10.78	16.94
EB (%)		400	440	430	450	402	392	460	384
Tear (N/mm)		3.58	2.06	2.55	2.87	2.7	2.64	2.64	2.16
$V_r(\times 10^{-3})$		4.17	7.56	4.77	4.93	3.75	7.62	2.55	6.55

TABLE 10 (CONT.). CCD WITH ACTUAL DOSAGE AND PHYSICAL PROPERTIES (SPLIT INTO FOUR TABLES FOR EASY VIEWING)

Factor	Ingredients	Exp						
		E25	E26	E27	E28	E29	E30	E31
	Synthomer X6617	100	100	100	100	100	100	100
	KOH	1.8	1.8	1.8	1.8	1.8	1.8	1.8
	SDS	0.2	0.2	0.2	0.2	0.2	0.2	0.2
x1	Sulphur	1.60	1.60	1.60	1.60	1.60	1.60	1.604
x2	ZDBC	0.95	0.95	0.95	0.95	0.95	0.95	0.95
x3	ZMBT	0.40	0.40	0.40	0.40	0.40	0.40	0.40
x4	ZnO	1.63	1.63	1.63	1.63	1.63	1.63	1.63
TS (MPa)		33.2	36.4	38.4	31.7	35.5	35.5	28.6
M300 (MPa)		16.08	14.55	17.26	14.64	15.76	16.33	11.46
EB (%)		400	440	415	408	420	408	420
Tear (N/mm)		2.22	2.41	2.08	2.11	2.22	2.37	2.24
$V_r(\times 10^{-3})$		6.67	5.45	4.24	4.81	4.15	4.82	3.95

TABLE 11. MEAN SQUARE FOR 1ST ORDER, 2ND ORDER TERMS TOGETHER WITH LACK OF FIT AND ERROR TERMS (ACCORDING TO COCHRAN AND COX)

SS.terms	df	SS	MS
First order term	4	71.22	17.80
Second order terms	10	270.77	27.08
Lack of fit	6	156.61	26.10
Error	6	64.47	10.74
Total	30	563.06	18.77
Column	y total	coefficient	coef values
1	1007.5	b0	34.19
2	17.7	b1	0.74
3	1.3	b2	0.05
4	1.7	b3	0.07
5	-37.3	b4	-1.55
6	701.3	b11	-2.64
7	789.7	b22	0.13
8	789.3	b33	0.11
9	792.5	b44	0.21
10	0.0	b12	1.34
11	-8.3	b13	-0.52
12	1.1	b14	0.07
13	1.9	b23	0.12
14	2.1	b24	0.13
15	-20.1	b34	-1.26

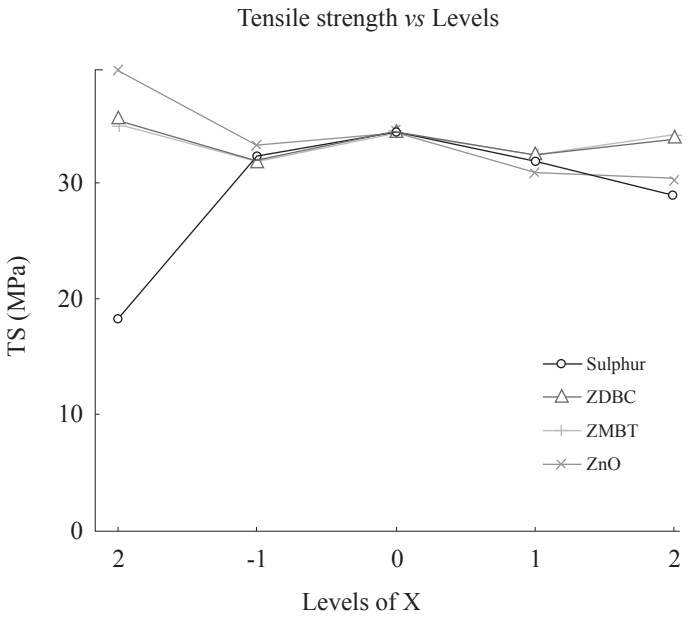

Figure 16. Curvature plots for tensile strength. For any one factor varying, all other factors are held at zero level.

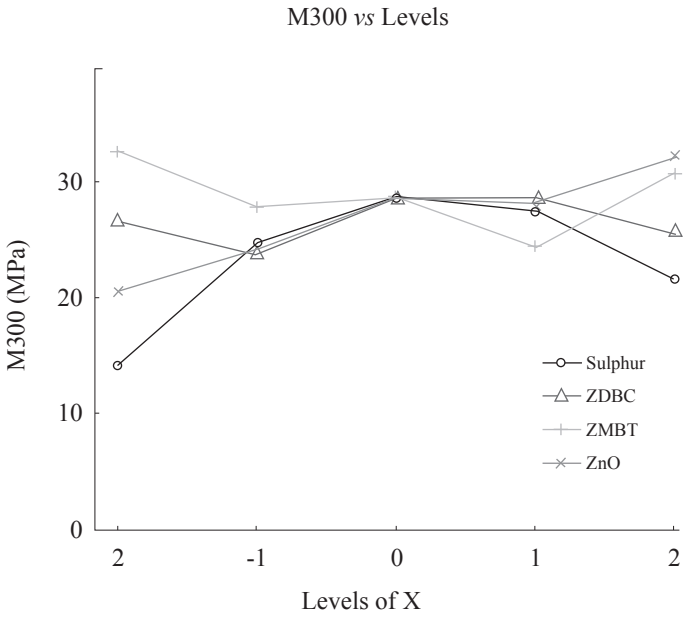

Figure 17. Curvature plots for M300. For any one factor varying, all other factors are held at zero level.

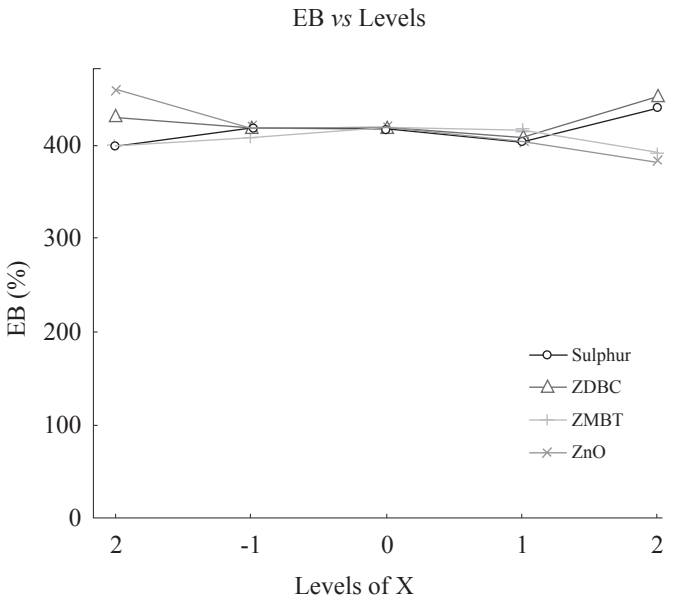

Figure 18. Curvature plots for EB. For any one factor varying, all other factors are held at zero level.

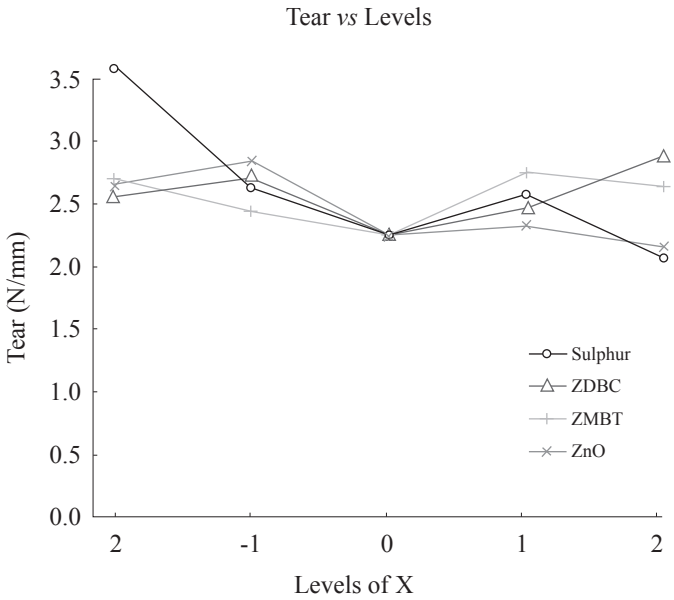

Figure 19. Curvature plots for tear strength. For any one factor varying, all other factors are held at zero level.

CONCLUSION

The paper provides additional resources to the two earlier papers on DOX. It expands on the use of categorical data. It departs from the approach taken in the first two papers in that it covers more latex types and ingredients in diverse applications, instead of systematic treatment of one single latex or ingredients, and sequential steps in screening and progressing to central composite design as in See Toh[1]. It emphasizes on the use of graphical capability of R statistical computing, and enhances the visual presentation of results. All results presented have been produced by functions written by the authors and pre-tested against data from published sources. Lenth's pseudo standard error is introduced for the first time in latex DOX application. The experimental steps outlined in this paper can be adopted by latex product manufacturers and tailored for their own research requirement.

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Appendix 1

Screening experiments involving seven factors at two levels

```
function (E, main, xlab, ylab)
# function: X1.X7.contrast.function.IRC, version is 19 January 2014
# E is a data frame with row names E1, E2, E3…E8, columns are results for pH, VC, TS, EB…..
# This data set is downloadable from jpspartners.com, file name: ball.pearl.1)
# X1.X7.contrast.function.IRC (ball.pearl.1$TS, 'Tensile Strength \n Pearl vs Ball Mill', '+1 : Ball Mill \n -1
Pearl', 'TS (MPa)')
```

Separate calculations for mean (plus) and mean (minus)

```
# Calculate X1 (-1, +1)
X1m <- 1/4 * (E[1] + E[3] + E[5] + E[7])
X1p <- 1/4 * (E[2] + E[4] + E[6] + E[8])

# Calculate X2 (-1, +1)
X2m <- 1/4 * (E [1] + E [2] + E[5] + E[6])
X2p <- 1/4 * (E[3] + E[4] + E [7] + E[8])

# Calculate X3 (-1, +1)
X3m <- 1/4 * (E[1] + E[2] + E[3] + E[4])
X3p <- 1/4 * (E[5] + E[6] + E[7] + E[8])

# Calculate X4 (-1, +1)
X4m <- 1/4 * (E[1] + E[4] + E[6] + E[7])
X4p <- 1/4 * (E[2] + E[3] + E[5] + E[8])

# Calculate X5 (-1, +1)
X5m <- 1/4 * (E[2] + E[3] + E[6] + E[7])
X5p <- 1/4 * (E[1] + E[4] + E[5] + E[8])

# Calculate X6 (-1, +1)
X6m <- 1/4 * (E[2] + E[4] + E[5] + E[7])
X6p <- 1/4 * (E[1] + E[3] + E[6] + E[8])

# Calculate X7 (-1, +1)
X7m <- 1/4 * (E[3] + E[4] + E[5] + E[6])
X7p <- 1/4 * (E[1] + E[2] + E[7] + E[8])
```

Calculate Xi (m)minus and (p)plus

```
Xi.minus <- c (X1m, X2m, X3m, X4m, X5m, X6m, X7m)
Xi.plus <- c (X1p, X2p, X3p, X4p, X5p, X6p, X7p)
Xi.contrast <- Xi.plus - Xi.minus # Reversed minus plus
X1.X7.contrast <- data.frame (Xi.minus, Xi.plus, Xi.contrast)
row.names (X1.X7.contrast) <- c ('X1', 'X2', 'X3', 'X4', 'X5', 'X6', 'X7')
print (round(X1.X7.contrast,2))
par (mfrow = c (2,1))
barplot (t(X1.X7.contrast[,1:2]), beside = TRUE, col = c ('red', 'blue'), main = main, xlab = xlab, ylab = ylab, las = 2)
barplot (t(X1.X7.contrast$Xi.contrast), names.arg = row.names (X1.X7.contrast), beside = TRUE, col = 'yellow', main = main, xlab = xlab, ylab = ylab, las =2)
par (mfrow = c (1,1))
```

Output from running the above function:

```
X1.X7.contrast.function.IRC (ball.pearl.1$TS, 'Tensile Strength \n Pearl vs Ball Mill', '+1 : Ball Mill \n -1 Pearl', 'TS (MPa)')
```

	Xi.minus	Xi.plus	Xi.contrast
X1	31.44	33.09	1.65
X2	30.60	33.92	3.32
X3	31.92	32.59	0.67
X4	31.98	32.54	0.55
X5	32.81	31.71	-1.09
X6	30.85	33.67	2.83
X7	33.81	30.71	-3.11