UNIVERSIDADE FEDERAL DE SÃO CARLOS
Centro de Ciências Exatas e de Tecnologia
Departamento de Química
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APPLICATION OF STATISTICAL TOOLS FOR EVALUATING FILMS OF STYRENE ACRYLIC EMULSION SYSTEMS

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RESUMO

APLICAÇÃO DE FERRAMENTAS ESTATÍSTICAS PARA AVALIAÇÃO DE FILMES DE EMULSÕES ESTIRENO ACRÍLICAS

Esta dissertação de Mestrado Profissional tem como objetivo a utilização de ferramentas estatísticas, tais como planejamento de experimentos (DOE) e análise de componentes principais (PCA), para a avaliação da formação de filme de emulsões estireno acrílicas (látex). A parte experimental foi realizada nos laboratórios da Dow Brasil em São Paulo. As amostras (látex + coalescente) foram caracterizadas em triplicata pelos seguintes testes: resistência à abrasão úmida, temperatura mínima de formação de filme (TMFF), tempo de secagem e viscosidade Brookfield. Na primeira etapa do trabalho foram adicionados a uma único látex 1, 2, 3 e 5% (m/m) de 4 coalescentes diferentes. Os resultados obtidos foram avaliados de forma univariada através de gráficos de resultados dos testes *versus* concentração de coalescente. Além disso, estabeleceram-se modelos para cada um dos testes. As equações matemáticas obtidas foram avaliadas pela análise de variância e foi possível estabelecer modelos para todos os testes, exceto para o tempo de secagem que não apresentou coeficientes válidos. Em seguida, foi feito um DOE do tipo Doehlert utilizando como variáveis o tipo de coalescente, a concentração de coalescente e o tipo de látex. Além disso, foram preparadas 7 amostras para serem utilizada na validação dos modelos. Modelos e análises de variância, falta de ajuste e erro puro foram feitos para cada teste. Em seguida, foram propostas equações matemáticas que representassem os mesmos. PCA foi executada para cada teste utilizando como variáveis: tipo e concentração de coalescente, tipo de látex e resultado do teste. Novamente, foi proposto um modelo, feita análise de variância, falta de ajuste e erro puro e proposta equação matemática que representasse os testes. Comparando-se os modelos / análise de variância do DOE e do DOE com PCA notou-se que o segundo foi mais eficiente em extrair informação dos dados brutos. Utilizando-se o modelo de scores da PCA e a correlação entre PC e o teste, foram obtidos gráficos de contorno. A região de maior resistência à abrasão úmida, menor TMFF e menor tempo de secagem (combinação dos resultados desejados) foi identificada, bem como a concentração de coalescente e os látexes para obtenção destes resultados (entre 1,7 e 5,0% de coalescente e látexes A e F). O resultado experimental das amostras de validação foi comparado com os resultados do modelo e, na média, houve ~80% de concordância entre os mesmos.

ABSTRACT

APPLICATION OF STATISTICAL TOOLS FOR EVALUATING FILMS OF STYRENE ACRYLIC EMULSION SYSTEMS

This dissertation is focused on using statistical tools (Design of Experiments, DOE) and Principal Component Analysis (PCA) for evaluating latex film formation. The experimental part was conducted at Dow Brasil R&D facility in São Paulo. Samples were analyzed in triplicate using the following tests: scrub resistance, minimum film formation temperature (MFFT), drying time and Brookfield viscosity. Initially, four different coalescents were added into a single emulsion system at the following concentrations: 1, 2, 3 and 5% (w/w). Plots of results against coalescent concentrations were used for comparison, as a standard coalescent evaluation approach. Subsequently the model was used to determine the numerical relationship that describes each test. Analysis of variance was done. It was possible to propose models for scrub resistance, MFFT and Brookfield viscosity. Drying time did not have valid coefficients for modeling. A Doehlert design of experiments was prepared using as variable coalescent type (X, Y and Z), coalescent concentration (0 to 5%, studied in 7 levels) and latex type (A, C, D, E and F). Additionally, seven samples were prepared for model validation. A model was run to determine the equation that describes each test. Variance, lack of fit and pure error analysis were applied. It was possible to propose models for scrub resistance, MFFT, drying time and Brookfield viscosity. For each test a PCA was performed using the following variables: coalescent concentration, coalescent type, latex type and the response of each specific test. Models were run using the first principal component scores and DOE variables. Again, variance, lack of fit and pure error analysis were applied and models were proposed. Comparing these two approaches showed that using PCA was more appropriate to extract information from raw data. Based on PC scores models, scrub resistance, MFFT and drying time contour plots were prepared. Desired results (maximum of scrub resistance, the minimum of MFFT and the shortest drying time) were highlighted in order to identify the best combination of coalescent concentration and latex type. In this case, coalescent concentration between 1.7% and 5.0% and coalescents A and/or F were optimum. Experimental results from the validation set were compared with model ones and, in average, there was about 80% of concordance between them.

SUMARY

INTRODUCTION

1 - INTRODUCTION

Productivity and quality are important goals in any industrial field and special tools are required to increase these parameters. Different approaches can be used depending on the situation, but there is a tendency to change from costly and time-consuming trial-and-error searches to the powerful, elegant and cost-effective strategies, such as statistical tools[1].

Application of statistical tools in chemical field can be noticed in many applications ranging from the development of new products to the optimization of manufacturing process[2,3]. The majority of them are described in the literature in analytical and organic area, such as multivariate calibration, pattern recognition and Design of Experiments (DOE)[4,5].

DOE may be considered as one of the most used statistical technique. Design of Experiments has been used to organize evaluation tests and to obtain the maximum amount of information from fewest numbers of experiments. There are different DOE techniques to meet different objectives. Factorial design, for example, is useful for selection of important variables. The final optimization can be carried out using response surface methodology (RSM)[6].

An important application field where increased chemistry knowledge / understanding and have many opportunities for value capture is in paints and coatings. Paints and coatings have been used for different reasons including covering a substrate, adding value to products (automobile, electronic equipments and house, e.g.) or protecting a substrate (such as pipelines and bridges). So, one of the most important requirements for these applications are that the quality of the film formation.

Coatings can be characterized based on the application (e.g. decorative, industrial or automotive), solvent (e.g. water-born solvent-based or powder) or resin type (e.g. acrylic, epoxy, or urethane)[7]. Decorative water-borne coatings are frequently composed by latex and require a coalescent for an effective and homogeneous film formation.

Coalescents have been defined by literature[8] as organic solvents with low water solubility and evaporation rate. They promote the coalescence by allowing the fusion of latex micelles and by decreasing polymer T_g (glass transition temperature)[8,9]. Coalescent selection is typically based on experimental results of film formed property measurements. Usually, these properties are analyzed using empirical methods developed by coating formulators. In order to improve coalescent selection, different statistical tools are applied and compared to the results of standard industry tests in order to show the improvements that can be obtained through the use of statistical techniques in this area.

OBJECTIVE

2 - OBJECTIVE

The aim of this Master of Dissertation was to compare the use of the standard approach with application of statistical tools for evaluating styrene acrylic emulsion system film formation. This project can be split into univariate study (coalescents evaluation at different concentrations for single latex) and the multivariate study (application of Doehlert Design of Experiments using the key variables of latex type, coalescent type, and coalescent concentration).

LITERATURE REVIEW

3 - LITERATURE REVIEW

The application of statistics is commonly confused with "quality"[1]. However statistics application can neither be summarized as quality nor process control. Statistics can be, and has been, used to plan experiments, to optimize manufacturing processes, to extract information and make multicriteria decisions[10]. Because the field of statistics is so broad, the literature review of this dissertation will focus on an overview of statistical application (mainly on design of experiments), as well as the review of some statistic concepts and their use in coating and film formation. Finally, an emulsion system film formation overview will be given.

3.1 - Statistical tools application

A common method of experimentation is one where each variable is varied while the others are fixed. This one variable at a time approach has been considered time consuming, inefficient and may induce to a false optimized condition[11]. On the other hand, there are a variety of statistical tools that can be used to investigate systems. Many of these tools allow the researcher to change variables simultaneously and while also reducing the number of experiments.

The application of statistical tools in chemical area is called Chemometric. Literature describes different examples of chemometric including Design of Experiments (DOE)[6,12], Principal Component Analysis (PCA)[13], multivariate calibration[14] and pattern recognition[15]. DOE is one of the most used statistical technique. There are a variety of DOE techniques and its selection depends on the objective one is looking for. Some of these techniques and their objectives are presented on Table 3-1.

Table 3-1: Summary of some DOE techniques and their objectives.

Technique	Objective
Factorial design	Obtain as much information as possible with fewer experiments.
Full factorial design	Evaluate the influence of variables
Minimum Square modeling	Construction of empirical models.
Simplex and Response Surface Methodology (RSM)	Optimize response within specified ranges of the factors.

One technique is not better than the other; what it is important is to use the right techniques to meet the objective. Fractional Factorial design, for example, is useful in situations where conducting large numbers of experiments are not possible, but there is a desire to identify the key independent variables in a reduced number of experiments. Full factorial design, on the other hand, is applicable in situations where the key variables are known, but their impact in the response is unknown[16]. Both techniques have restrictions, due to the fact that the variables should have the same number of levels (or values). On the contrary, Doehlert design of experiments is based on variables using different number of levels[17].

Independently on the technique used (1st or 2nd order) a model can be proposed making the correlation between variable(s) and response(s). The response can be optimized based on each variable studied. However, the optimum conditions of one response may not represent the same conditions to the other response(s). In the worst situations, conditions may be contradictory for two, or more, answers. Desirability function, for simultaneous multiple response optimization, is suggested in some studies[11,18].

Another useful chemometric tool is the principal component analysis[13]. Principal component analysis (PCA) is very useful for large datasets which contain variables which are possible correlated, reducing the dataset into uncorrelated variables, or components, while also accounting for as much variability in the dataset as possible. PCA can reduce the dataset dimension by making correlations among variables and responses[18].

The combination of both design of experiments and PCA allow the researcher to optimize conditions for more than one response and to obtain more information than using only one technique, even when running the same number of experiments.

3.2 - Statistical concepts review

Some key statistical concepts reviews are necessary, such coefficient of determination (R square) and sum of squares, in order to better understand the mathematical background used in this dissertation. This section has no intention to discuss exhaustively key statistical concept used. More information can be found in some books such as Barros *et al.*[6] or Bruns *et al.*[19]. The nomenclature used is as follows:

- i-ésima result = $_i$
- Test result = y_i
- Test result mean = $\bar{y}_i$
- Test result predicted = $\hat{y}_i$
- Number of variable levels = m
- Total number of observations = n
- Number of parameters = p
- DF_1 = number of coefficients - 1
- DF_2 = number of experiments – number of coefficients = n - p
- DF_3 = number of variables levels – number of coefficients = m - p
- DF_4 = number of experiments – number of variables levels = n – m

The regression coefficients (B) were calculated using the Equation 1 considering **X** is as the matrix containing the factorial variables coded and **Y** the matrix that has the responses.

Equation 1: $$B = (X^TX)^{-1} \times X^TY$$

Table 3-2 shows a summary of the main equations related to raw data analysis used in this dissertation.

Table 3-2: Summary of equations[6].

Equation number	Description	Equation
Equation 2	Model sum of squares (SS_{Model})	$\sum_{i}^{m}\sum_{j}^{n_i}(\hat{y}_i - \bar{y})^2$
Equation 3	Model mean square (MS_{Model})	$\frac{SS_{Model}}{DF_1}$
Equation 4	Error sum of squares (SS_{Error})	$\sum_{i}^{m}\sum_{j}^{n_i}(y_{ij} - \hat{y}_i)^2$
Equation 5	Error mean square (MS_{Error})	$\frac{\mathrm{MS}_{\mathrm{Error}}}{\mathrm{DF}_2}$
Equation 6	Calculated F_{ratio} for the model and for the lack of fit	$\frac{MS_{Model}}{MS_{Error}}$ and $\frac{MS_{LOF}}{MS_{Pure\_Error}}$
Equation 7	Error	$y_{ij} - \hat{y}_i$
Equation 8	R square (R^2)	$\frac{SS_{Model}}{SS_{Total}} = \frac{\sum(\hat{y}_i - \bar{y})^2}{\sum(y_i - \bar{y})^2}$
Equation 9	Lack of Fit sum of squares (SS_{LOF})	$\sum_{i}^{m}\sum_{j}^{n_i}(\hat{y}_i - \bar{y}_i)^2$
Equation 10	Lack of Fit mean square (MS_{LOF})	$\frac{\mathrm{MS}_{\mathrm{LOF}}}{\mathrm{DF}_3}$
Equation 11	Pure error sum of squares (SS_{PE})	$\sum_{i}^{m}\sum_{j}^{n_i}(y_{ij} - \bar{y}_i)^2$
Equation 12	Pure error mean square (MS_{PE})	$\frac{SS_{PE}}{DF_4}$

3.3 - Chemometric applied in coating and film formation

In paint and coating areas, literature describes the application of statistical tools mostly for preparing emulsion systems and optimizing coating formulation. There are some articles for exemplifying the use of chemometric for emulsion system and coating optimization. However, articles describing the application of statistical tools for understanding film formation or coalescent optimization were not found.

PRIOR *et al.*[20] used a simplex design for studying combinations of vinyl acetate with butyl acrylate, vinyl versatate and/or 2-ethyl-hexyl acrylate in order to prepare emulsion system. Emulsions were characterized by T_g, gel content, molecular weight and particle size. Paint formulations were tested by scrub resistance, gloss, and block resistance among other tests. Based on results and supporting DOE, authors could detect some tendencies, such as the use of vinyl versatate to improve scrub resistance and 2-ethyl-hexyl acrylate as a substitute for butyl acrylate to improve water resistance.

FATEMI *et al.*[21] used statistical tools to maximize the performance of traffic paint formulations. The authors used a mixture design to evaluate resin, filler and pigment impact on wet and dry paint performance. Samples were tested for hardness, adhesion, gloss, and surface drying time among others and results were compared with a commercial solvent based formulation. The best water born formulation was proposed based on results and statistical tools used.

A full factorial design was used by Emélie *et al.*[16] to study rheological behavior of the emulsion system. Thickener type and concentration, surfactant concentration and particle size were used as variables. The authors identified the rheological agent impact on coating formulation, but not in the emulsion system. A correlation among rheological agent and total latex surface was also found.

3.4 - Latex film formation

Latex can be defined as an aqueous colloidal dispersion of polymer particles (usually spherical)[8]. Film formation has been used to describe the entire process which the latex becomes a continuous film or forms different phases in the process[9,22,23,24]. Coalescence can be defined as the phase which two particles join each other in order to reduce particles total surface area[8]. So, coalescence can be considered as a part of film formation.

Film formation mechanisms have been exhaustively studied and discussed in the literature[8,9,23,24,25]. In 1973, IMOTO[23] reviewed scientific literature and concluded that a final model to explain film formation for emulsion system was not available. In the same year, Wanderhoff *et al.*[24] proposed a model for film formation considering three steps: (1) the particles move randomly with few contacts with each other and the water evaporates (from the latex) at the same rate as pure water evaporates; (2) the particles come into irreversible contact with each other and the water evaporation rate decreases; (3) the film is formed (particle joined each other) and water evaporation rate drops off.

Since the 1973, many studies have been carried out[26,27] and models have been proposed[8,28,29] with the objective of understanding the driving forces for film formation and optimizing through the use of additives. Although the stage names and the number of phases differ among authors, the following three principal stages can be considered for film formation[23,26,29]:

Stage 1: The polymer particles move independently. Water starts evaporating and particle concentration increases.

Stage 2: The particles start to come into contact with each other and the water continues to evaporate. The contact become irreversible and particles start deforming into polyhedra under the action of interfacial and capillary forces. Film formation initiates.

Stage 3: While the film is being formed, some particles are still deforming in order to join with the other particles. The remaining water escapes by diffusion through capillary channels between the deformed spheres or through the polymer itself. Coalescent evaporates after this stage.

Independent of the number and name of stages or model used to describe the process, film formation remains important for coating manufactures and raw material suppliers[27]. “Good” film formation is usually defined as when the latex is ideally transformed into a continuous crack-free, transparent and non-porous polymeric film[22,28].

It is considered that film formation will be obtained only if the T_g of the polymer(s) (of which the latex particles are comprised), is lower than the temperature at which drying occurs during the film formation process[22]. In some cases, when the T_g of the polymer is higher than the application temperature, a coalescent is required. The coalescent decreases the Minimum Film Formation Temperature (MFFT) and promotes film formation.

There are many ways to evaluate film formation, for example, scrub resistance. In this case, the latex is applied under panels then scrubbed with a bristle brush and an abrasive scrub. The amount of cycles necessary to remove the film, in one continuous thin line across the shim, is called “scrub resistance” [30].

MFFT is another important parameter. Based on the work of Protzman and Brown (1960), the standard ASTM D2354 was prepared to measure the MFFT, defined as the lowest possible temperature at which film formation can occur as determined by visual observation of cracking or whitening[8,31].

Drying time is a measure of how long it takes a film to form under some application conditions. From the technological point of view, it is important to avoid applications issues related to flowing over and the necessity of waiting for long drying times between applications. During the film formation, polymer particle mobility is a key factor, therefore for this dissertation; viscosity was measured using a Brookfield viscometer in order to understand the rheological behavior of the samples.

Therefore, this dissertation will use the following parameters to evaluate coalescent performance: scrub resistance, MFFT, drying time and Brookfield viscosity. The key variables in this study are coalescent type, coalescent concentration and latex type.

EXPERIMENTAL PART

4 - EXPERIMENTAL PART

In order to protect confidential information all substances used in this dissertation were coded. Coalescents were selected among the most popular products used in Brazilian's water born decorative formulations. They were named as following X, Y, Z and W. The differences between the coalescents are chemical function, evaporation rate and water solubility. Latexes were identified by the following letters: A, C, D, E and F and differ from MFFT and particle size. All of them are the styrene acrylic type and are representatives of Brazilian decorative coating market.

Samples were identified by latex type, coalescent type and coalescent concentration. The sample AX1, for example, means that it was prepared with latex A, coalescent X at 1% (w/w) of concentration.

According to the information (latex, type and concentration of coalescent) available in the next section samples were prepared by mixing coalescent with latex. Formulations were homogenized for 5 minutes in a Red Devil mixer. Sample analyses were performed, at least, 24 hours after sample preparation and parameters were measured three times for each sample. The whole experimental step was carried out at Dow Brasil, São Paulo R&D facility. Raw data were split into two groups as described in more detail below.

4.1 - Univariate study.

This group of data was composed by samples prepared only with the latex A and with four different coalescents (X, Y, Z and W) in a range of concentrations (1, 2, 3 and 5%, w/w). It is a univariate study of coalescent type and its concentration. Table 4-1 shows experiments number (exp), sample identification (sample id), coalescent type (coalescent) and concentration in percentage (Coalescent conc (%) (w/w)). All samples, including neat latex (exp 1), were characterized by MFFT, scrub resistance, drying time and Brookfield viscosity.

Table 4-1: Experiments of the univariate study with experiment numbers, sample id, coalescent and concentration of coalescent.

Exp	Sample id	Coalescent	Coalescent conc (%) (w/w)
1	A0	Not applicable	0
2	AX1	X	1
3	AX2		2
4	AX3		3
5	AX5		5
6	AY1	Y	1
7	AY2		2
8	AY3		3
9	AY5		5
10	AZ1	Z	1
11	AZ2		2
12	AZ3		3
13	AZ5		5
14	AW1	W	1
15	AW2		2
16	AW3		3
17	AW5		5

4.2 - Multivariate study.

This group presents as Doehlert DOE[17] which was prepared using the following variables: coalescent type (X, Y and Z), coalescent concentration (from 0 to 5%, w/w, studied in 7 levels) and latex type (A, C, D, E and F). Table 4-2 describes experiment number (exp), sample identification (sample id), variables coded (V1, V2 and V3) and number of authentic replicates samples (# authentic replicates). Samples were characterized by MFFT, scrub resistance, drying time and Brookfield viscosity.

Table 4-2: Experiments table based on DOE with variables (latex type, coalescent concentration and type), its levels and number of authentic replicates.

Exp	Sample id	V1		V2		V3		# authentic replicates
		Code	**Latex type**	**Code**	**Coalescent conc (%) (w/w)**	**Code**	**Coalescent type**	
1	CY2.5	0	C	0	2.5	0	Y	2
2	EY2.5	1	E	0	2.5	0	Y	1
3	DY5	0.5	D	0.866	5.0	0	Y	2
4	DZ3.3	0.5	D	0.289	3.3	0.817	Z	2
5	FY2.5	-1	F	0	2.5	0	Y	1
6	AY0	-0.5	A	-0.866	0.0	0	Y	2
7	AX1.7	-0.5	A	-0.289	1.7	-0.817	X	2
8	DY0	0.5	D	-0.866	0.0	0	Y	2
9	DX1.7	0.5	D	-0.289	1.7	-0.817	X	2
10	AY5	-0.5	A	0.866	5.0	0	Y	2
11	CX4.2	0	C	0.577	4.2	-0.817	X	1
12	AZ3.3	-0.5	A	0.289	3.3	0.817	Z	2
13	CZ0.8	0	C	-0.577	0.8	0.817	Z	1
14	C0	0	C	-0.866	0.0	0	Y	1
15	E0	1	E	-0.866	0.0	0	Y	1
17	F0	-1	F	-0.866	0.0	0	Y	1
17	E1.7Y	1	E	-0.289	1.7	0	Y	1
18	E4.2Y	1	E	0.577	4.2	0	Y	1
19	F1.7Y	-1	F	-0.289	1.7	0	Y	1
20	F4.2Y	-1	F	0.577	4.2	0	Y	1

The experiments from 1 to 13 were used to propose models. Experiments from 14 to 20 were used to evaluate them.

4.3 - Tests of performance

Tests and procedures used in this dissertation are the same as paint and coating professionals use to evaluate film formation, e.g. standard ASTM (*American Society for Testing and Materials*) and/or ABNT NBR (Associação Brasileira de Normas Técnicas / Norma Brasileira)[30-34].

4.3.1 - <u>Scrub resistance (SR)</u>

Samples were applied using 175 μm extensor in black scrub resistance panels (P 121-10N) and dried for 7 days at room temperature (~25°C). The coated panel was then scrubbed with a bristle brush and an abrasive scrub with BYK Gardner Abrasion Tester (BYK Gardner) (Figure 7.1 at Appendix 1). The amount of cycles necessary to remove the film in one continuous thin line across the shim is considered as “scrub resistance”. The scrub paste was prepared at the Dow Brasil facility according to Appendix A of standard ABNT NBR 14940[32]. Reference standards used: ASTM D 2486-06[30] and ABNT NBR 14940[32]. The high amount of cycles will mean high scrub resistance and, consequently, homogeneous film formed. The more cycles the better and it should be considered as the desired result.

4.3.2 - <u>Minimum Temperature Film Formation (MFFT)</u>

Samples were applied using 175 μm extensor in plastic films under temperature range (from 0 to 25°C) in the MFFT equipment (Modern Metalcraft Co.) (Figure 7.2 at Appendix 1). Minimum Film Formation Temperature is determined by visual inspection of cracking and whitening in the film. Reference standard used: ASTM D 2354-98[31]. Small temperatures for MFFT mean that the coalescent will be more effective to promote the film formation. So, the smaller MFFT is the desired result for this test.

4.3.3 - Drying time (DT)

Samples were applied using 175 μm extensor in glass plate and drying time equipment Dry Time DC 9610 Circular Gardner (BYK Gardner Pacific Scientific) in 360° for 1 hour (Figure 7.3 at Appendix 1). Time is recorded by a chronometer and drying time is determined when the pendulum stops stamping the film. Reference standard used: ABNT NBR 15311[33]. Quick film formation is considered as the desired result because of customer preferences towards faster application of coating in their houses.

4.3.4 - Brookfield viscosity (BV)

The viscosity was measured using ASTM D 2196-05 and Brookfield Viscometer LVT (Brookfield), spindle # 3, 50 rpm and at room temperature (~25°C). Reference standard used: ASTM 2196-05[34]. Small values of Brookfield viscosity could impact positively the coating formulation and it is the expected result.

RESULTS & DISCUSSION

5 - RESULTS & DISCUSSION

Results and discussion will be presented in groups of raw data (univariate and multivariate). Statistical evaluations, including DOE preparation and calculus, were performed using Microsoft Excel and/or JMP (version 8, from SAS Institute Inc) software. JMP is the software The Dow Chemical Company Research and Development (R&D) employees use for raw data treatment, DOE preparation and carrying out Six Sigma projects.

5.1 - Univariate study.

Based on the results of the following tests scrub resistance, MFFT, drying time and Brookfield viscosity (Appendix 2) it was possible to plot results against coalescent concentrations as described in Figure 5.1.

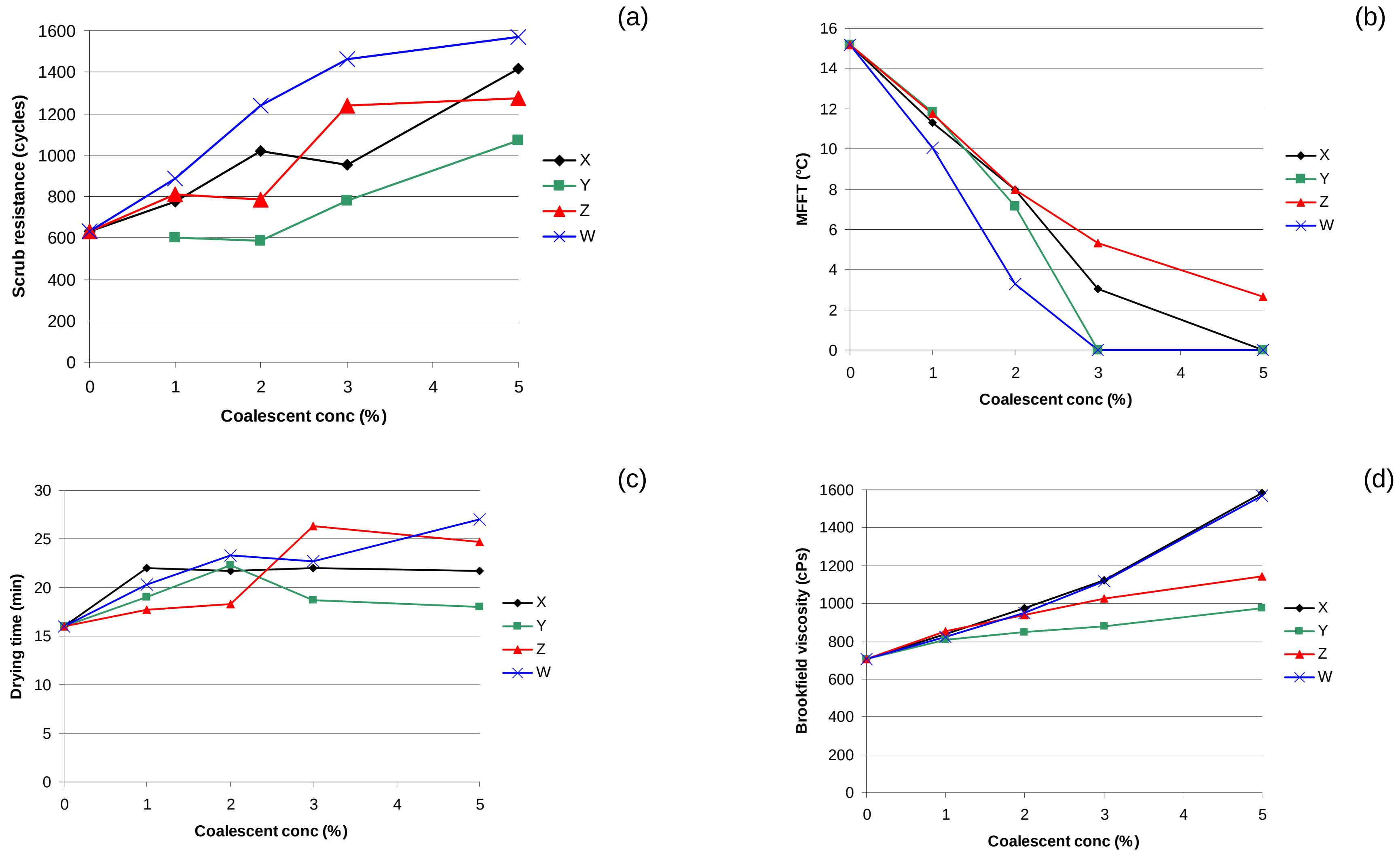

Figure 5.1: Plot of scrub resistance (a), MFFT (b), drying time (c) and Brookfield viscosity (d) results against coalescent concentrations for univariate study.

Figure 5.1 shows that scrub resistance (a), drying time (c) and Brookfield viscosity (d) increased and the MFFT (b) decreased as the concentration of coalescents (X, Y, Z and W) increased. By comparing all coalescents to each other at one specific concentration, e.g. 2% (w/w), it is noticed that coalescent W was more effective to improve scrub resistance and decrease MFFT. These results complied with the desired result. On the other hand, coalescent W increased drying time (more than the other coalescents) and increased the Brookfield viscosity (as did the other coalescents) what was not the desired result.

Coalescent Z used, at the same concentration (2%, w/w) of the others resulted in shorter drying time, presented the same performance for Brookfield viscosity, but it was not the best for scrub resistance improvement or decreasing MFFT.

This kind of approach, to compare plots of results against coalescent concentration, neither provides enough information to conclude what coalescent is the best nor the optimum concentration to be used with this emulsion system. However, it is exhaustively used for coalescent performance evaluation and is usually the traditional approach used by coating formulators.

Another type of approach is defining a model for each test (scrub resistance, MFFT, drying time and Brookfield viscosity) using raw data. Even if this evaluation is performed without any statistical plan, a table can be prepared by making correlations between coded level (-1, -0.5, 0.5 and 1) with type of coalescent (X, Y, Z and W) and coalescent concentration (1, 2, 3 and 5%, w/w). In the sequence, a model was run using the following variables alone and the interaction between them:

- coalescent type (CT)
- coalescent concentration (CC)
- coalescent type x coalescent concentration (CTCC)

The following parameters were calculated based on equations 2 to 6 described on Table 3-2: sum and mean of squares for model (SS_{Model} and MS_{Model}, respectively) and error (SS_{Error} and MS_{Error}, respectively) for models of scrub resistance, MFFT, drying time and Brookfield viscosity, as shown in Table 5-1. No authentic sample replications were available, therefore neither lack of fit or pure errors were taken into consideration for further analysis.

Table 5-1: Analysis of variance for scrub resistance, MFFT, drying time and Brookfield viscosity of univariate study.

	Scrub resistance	**MFFT**	**Drying time**	**Brookfield viscosity**
SS_{Model}	$2.48x10^6$	723	152	$1.58x10^6$
MS_{Model}	$8.26x10^5$	241	50.8	$5.27x10^5$
SS_{Error}	$2.24x10^6$	247	287	$1.00x10^6$
MS_{Error}	$5.08x10^4$	5.60	6.53	$2.28x10^4$
MS_{Model} / MS_{Error}	16.3	43.0	7.78	23.1

For all calculated models, Degree of Freedom (DF) for the model was 3 and error 12. In order to compare both mean of square (from the model and the error), an *F*-test with 95% confidence was performed according to Equation 6 at Table 3-2. The obtained values were compared with the tabulated $F_{3,12}$ 95% with 3 by 12 Degrees of Freedom (3.49). For all studied test (scrub resistance, MFFT, drying time and Brookfield viscosity) the ratio MS_{Model} / MS_{Error} (16.3, 43.0, 7.78 and 23.1, respectively) were higher than tabulated $F_{3,12}$ (3.49). It means that these models are valid and consistent with 95% of confidence and both MS_{Model} and MS_{Error} are from different populations.

It was possible to calculate coefficients for the model for scrub resistance, MFFT and Brookfield viscosity as the following equations describe. The MS_{Error} was used as variance and only the significant coefficients, with 95% confidence, are shown in the equations below. Drying time model had coefficients smaller than the errors, therefore it was not possible to propose a valid model for drying time.

- Equation 13: Scrub resistance (cycles) = $\underset{\pm 100}{410} + \underset{\pm 29}{101} CT + \underset{\pm 22}{133} CC$
- Equation 14: MFFT (°C) = $\underset{\pm 1.0}{13.4} - \underset{\pm 0.23}{2.59} CC$
- Equation 15: Brookfield viscosity (cPs) = $\underset{\pm 67}{674} + \underset{\pm 15}{123} CC$

From Equation 13 to 15 it is observed that coalescent type coefficient (CT) was only valid for scrub resistance. Coalescent concentration coefficient (CC) was valid in all models. The interaction between coalescent type and coalescent concentration (CTCC) was not a valid coefficient for any model.

It was possible to calculate residuals, according to Equation 7 (Table 3-2), for each sample result. Residual and observed values were plotted for scrub resistance, MFFT and Brookfield viscosity (Figure 5.2).

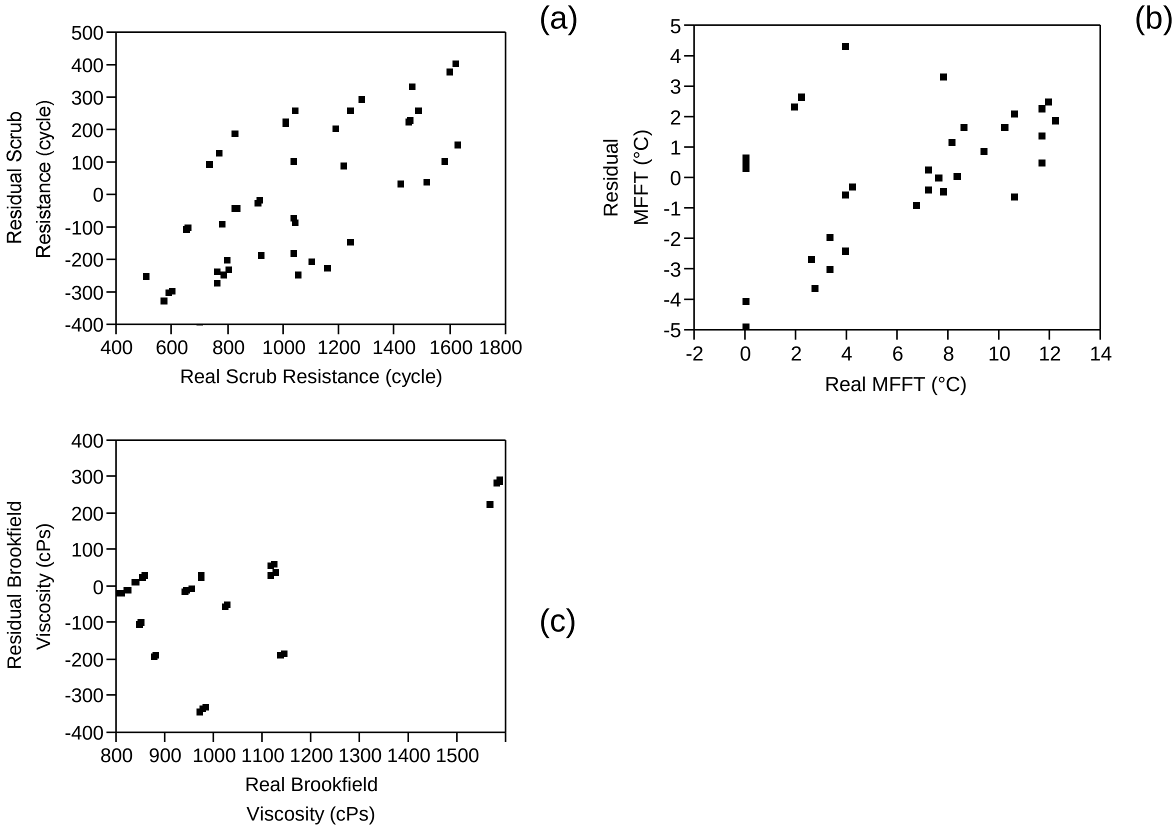

Figure 5.2: Plot of residual and observed results for scrub resistance (a), MFFT (b) and Brookfield viscosity (c) based on univariate study.

Results obtained with this first group of experiments should be analyzed carefully; because information related to the latexes was not taken into account (only one latex was tested). In addition, some models presented general linear trend (see Figure 5.2). Therefore, based on Figure 5.1 it was no possible to determine the best coalescent neither coalescent concentration. It is important to highlight that to evaluate these coalescents performance with the others latexes (C, D, E and F) it would be necessary 60 additional experiments that means a lot of resources.

5.2 - Multivariate study: DOE.

Results of each characterization are described in Appendix 3. A model using samples from 1 to 13 was run in order to propose model for each test. Coefficients used were variables alone, quadratic term and the interaction between them as described below:

- Coalescent type (CT).
- Coalescent concentration (CC).
- Latex type (LT).
- Coalescent type x Coalescent concentration (CTCC).
- Coalescent type x Latex type (CTLT).
- Coalescent concentration x Latex type (CCLT).
- Coalescent type x Coalescent type (CT^2).
- Coalescent concentration x Coalescent concentration (CC^2).
- Latex type x Latex type (LT^2).

Based on Equations 2 to 6 and 8 (Table 3-2), the parameters sum and mean of squares for model and error, the mean of squares ratio and R square (SS_{Model}, MS_{Model}, SS_{Error}, MS_{Error}, MS_{Model} / MS_{Error} and R^2, respectively) were calculated for the following tests scrub resistance, MFFT, drying time and Brookfield viscosity (Table 5-2).

Table 5-2: Analysis of variance for scrub resistance, MFFT, drying time and Brookfield viscosity of multivariate study.

	Scrub resistance	**MFFT**	**Drying time**	**Brookfield viscosity**
SS_{Model}	$5.06x10^6$	$3.10x10^3$	778	$1.03x10^8$
MS_{Model}	$5.61x10^5$	344	86.4	$1.15x10^7$
SS_{Error}	$8.89x10^5$	149	305	$9.69x10^6$
MS_{Error}	$7.41x10^4$	12.4	25.4	$8.08x10^5$
MS_{Model} / MS_{Error}	7.57	27.7	3.40	14.2
R^2	0.850	0.954	0.718	0.914

Degrees of freedom for the model and error are 9 and 12, respectively. Considering variable 1 as the MS_{Model} and variable 2 as the MS_{Error} an *F* test was performed according to the Equation 6 at Table 3-2. The obtained value was compared with the tabulated $F_{9,12}$ equal to 2.80 with 95% of confidence level. For all tests the MS_{Model} / MS_{Error} ratio (7.57, 27.7, 3.40, 14.2) were higher than the tabulated value (2.80), indicating that models are valid and consistent with 95% of confidence and both MS are from different populations.

Based on equations 9 to 12 and 6 (Table 3-2) sum and mean of squares for lack of fit and pure error and means of square ratio were calculated (SS_{LOF}, MS_{LOF}, SS_{PE}, MS_{PE} and MS_{LOF} / MS_{PE}, respectively) for scrub resistance, MFFT, drying time and Brookfield viscosity (Table 5-3).

Table 5-3: Summary of sum and mean of squares for lack of fit and pure error for scrub resistance, MFFT, drying time and Brookfield viscosity models of multivariate study.

	Scrub resistance	**MFFT**	**Drying time**	**Brookfield viscosity**
SS_{LOF}	6.82×10^5	136	227	9.69×10^6
MS_{LOF}	2.27×10^5	45.2	74.6	3.23×10^6
SS_{PE}	2.07×10^5	13.8	81.1	2.28×10^3
MS_{PE}	2.30×10^3	1.53	9.01	2.53×10^2
MS_{LOF} / MS_{PE}	9.87	29.5	8.28	1.28×10^4

Degrees of freedom for the lack of fit and pure error are 3 and 9, respectively. Considering variable 1 as MS_{LOF} and variable 2 as MS_{PE} an *F* test was performed according to the Equation 6. The obtained value was compared with the tabulated $F_{3,9}$ with 95% of confidence level.

For all model calculated the MS_{LOF} / MS_{PE} ratio (9.87, 29.5, 8.28 and 1.28×10^4) was higher than the $F_{3,9}$ tabulated (2.86), indicating that the proposed models are not well adjusted to the calculated coefficients and the MS_{LOF} must be used as variance to calculate the error for each coefficient. For Brookfield viscosity, the ratio among MS_{LOF} and MS_{PE} is relatively high (1.28×10^4). It suggests that this model is extremely poor and must be analyzed carefully.

It was possible to calculate coefficient for the model for each test as the following equations describe:

- Equation 16: Scrub resistance (cycles) = $\underset{\pm 619}{865} + \underset{\pm 326}{339} CC$
- Equation 17: MFFT (°C) = $\underset{\pm 4.6}{-10.7} CC$
- Equation 18: Drying time (min) = $\underset{\pm 11.2}{22.7}$
- Equation 19: Brookfield viscosity (cPs) = $\underset{\pm 2.34x10^3}{3.21x10^3} - \underset{\pm 3.89x10^3}{5.77x10^3} CTCC$

As shown by Equations from 16 to 19, coalescent concentration (CC) and its interaction with coalescent type (CTCC) were the only two valid coefficients with 95% of confidence. Drying time model (equation 18) has only one valid coefficient.

It was possible to calculate residuals, according to Equation 7 (Table 3-2), for each sample result. Residual and observed values were plotted for each parameter analyzed (Figure 5.3).

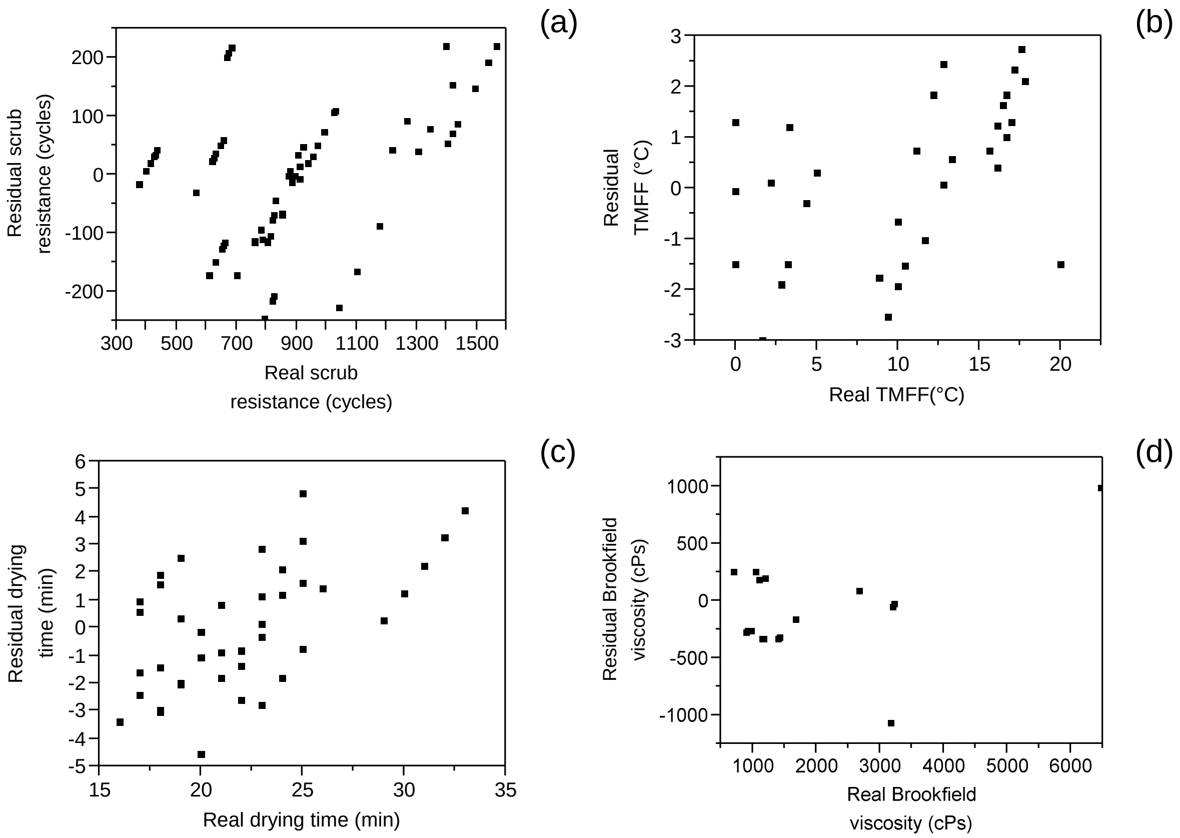

Figure 5.3: Plot of residual and observed results for scrub resistance (a), MFFT (b), drying time (c) and Brookfield viscosity (d) for multivariate study.

Figure 5.3 shows the plot of results against its residual. Based on that it is possible to notice there is some values distribution tendency. For drying time, for example, there is correlation between results and residual for high drying time values (> 25 min). A few samples had high residual (+1,000 and -1,000) for Brookfield viscosity what suggest that the model has some limitation for high viscosities (> 3,000cPs), probably because there are few data in this region.

The logarithmic in base 10 was calculated for each Brookfield viscosity results. A model was prepared with these raw data. Analyses of variance, lack of fit and pure error were run. The model had also lack of fit and it was not better adjusted than the raw data one. So, data analysis will be carried out using Brookfield viscosity raw data without any type of pre treatment.

5.3 - Multivariate study: DOE + PCA.

Models proposed by tests studied (Equation 16 to Equation 19) had lack of fit and were composed by few valid coefficients, as already discussed. In order to extract more information from this design of experiments results, a Principal Component Analysis (PCA) was performed. PCA is a least square statistical method of analysis, which makes variables with large variance have large loading[13]. As scrub resistance has larger variance than MFFT or drying time raw data were auto scaled as pre-treatment.

PCA was done using all 20 samples (1 to 13 for modeling and 14 to 20 for validation as described on Table 7-2 of Appendix 3) for each test isolated by using the following as variables: coalescent type (CT), coalescent concentration (CC), latex type (LT) and the test results. In the sequence PCA for each test studied (scrub resistance, MFFT, drying time and Brookfield viscosity) is presented.

For scrub resistance PCA the principal components, its percent of information and accumulative percent of information (Cum percent) are given in Table 5-4.

Table 5-4: Scrub resistance Principal Components (PC), percent of information for each PC (Percent) and cumulative percent (Cum Percent).

PC	Percent	Cum Percent
1	46.0	46.0
2	26.0	72.0
3	23.0	95.0
4	5.0	100

Table 5-4 showed that first, second and third principal components (PC1, PC2 and PC3, respectively) have around 46.0, 26.0 and 23.0% of total variance each one. The cumulative percentage of these three principal components is about 95.0%. Scores and loading were plotted for these principal components (PC1 x PC2, PC1 x PC3 and PC2 x PC3) and are given in figures from 5.4 to 5.7, respectively.

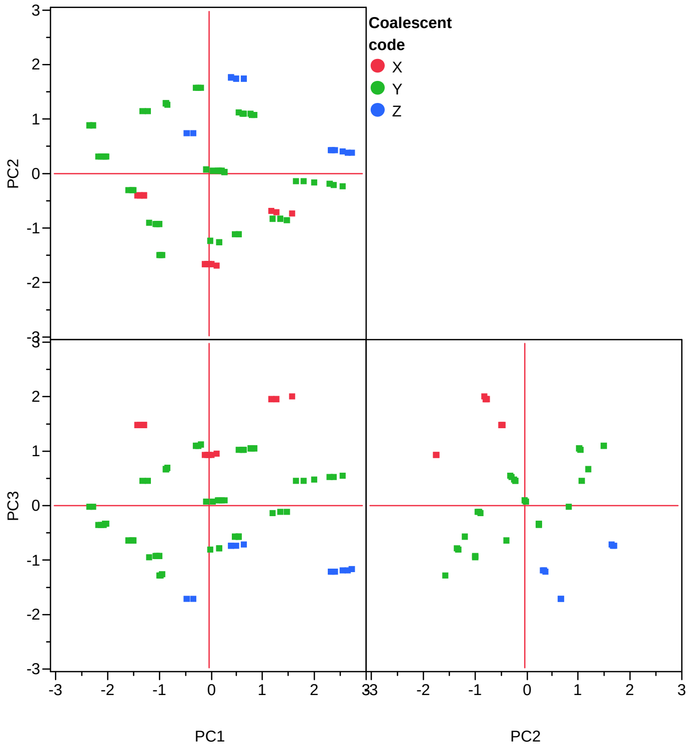

Figure 5.4: Plot of first, second and third PC scores of scrub resistance test of mutilvariate study (coalescent type class highlighted).

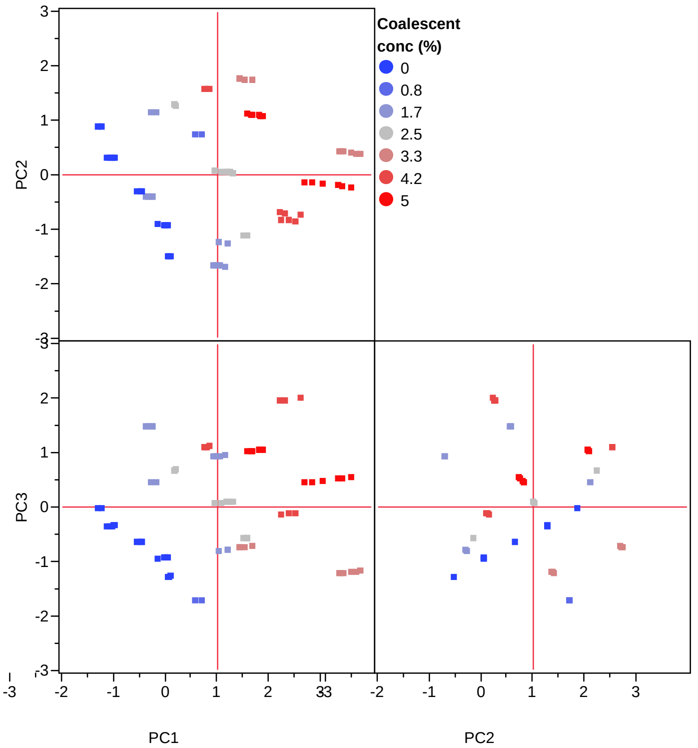

Figure 5.5: Plot of first, second and third PC scores of scrub resistance test of mutilvariate study (coalescent concentration class highlighted).

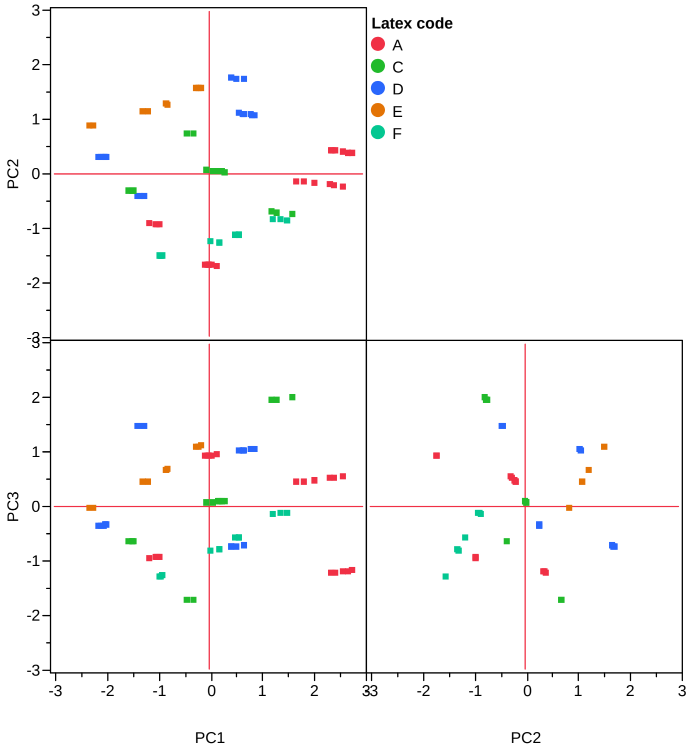

Figure 5.6: Plot of first, second and third PC scores of scrub resistance test of mutilvariate study (latex type class highlighted).

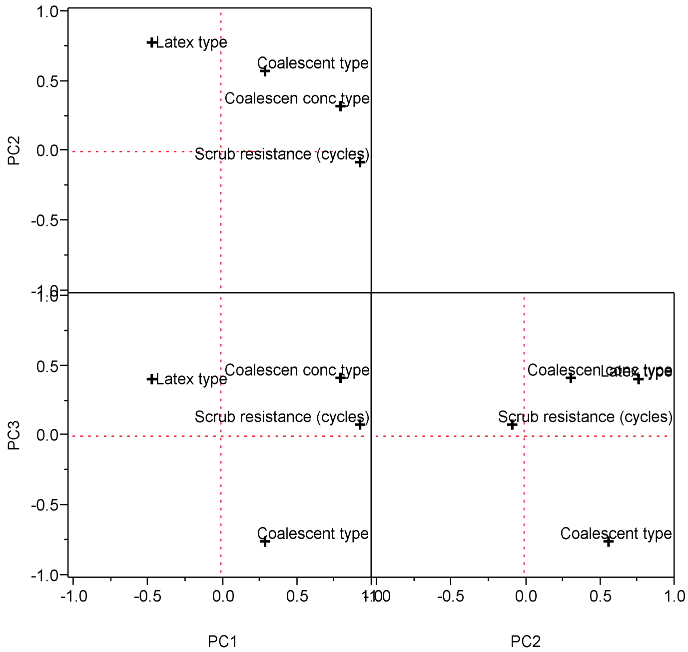

Figure 5.7: Plot of first, second and third PC loadings of scrub resistance test of mutilvariate study.

Score plots, Figure 5.4 to Figure 5.6, are highlighted by the following classes of variables: coalescent type, coalescent concentration and latex type, respectively. Based on these figures, it can be observed the first principal component was able to separate samples in groups for latex type and coalescent concentration class (Figure 5.4 and Figure 5.5). The coalescent type class did not show a clear sample separation.

Loading plots are shown in Figure 5.7 for PC1, PC2 and PC3 where show scrub resistance variable, “scrub resistance (cycles)”, had large positive loading only for PC1. For PC2 and PC3 the scrub resistance has loading around zero. It means that both principal components (PC2 and PC3) have no information about scrub resistance test.

The same procedure described for scrub resistance PCA was done for other tests (MFFT, drying time and Brookfield viscosity). All information regarding to PCA of these tests (that include principal components, its percent of variance, cumulative percent of variance, score and loading plots) are available in Appendix 4 to 6. Principal component analyses for each of the test results were quite similar to that of scrub resistance: score plots showed there is some sample separation tendency when coalescent concentration and latex type were highlighted and loading plots showed that only PC1 has high values for the test and all of them were positive.

Therefore, the first principal component scores for each test were saved and re-name with following nomenclature: PC_{SR}, PC_{MFFT}, PC_{DT} and PC_{BV} (respectively scrub resistance, MFFT, drying time and Brookfield viscosity) in order to avoid misunderstanding of principal components. PC1 score for validation samples (from 14 to 20) were excluded from the table.

A model was run using these principal components as answers and the same previously variables used for tests model (item 5.2 of this dissertation). The analysis of variance table for these models and lack of fit are given in Table 5-5 and Table 5-6, respectively.

Table 5-5: Analysis of variance for scores first principal component of scrub resistance, MFFT, drying time and Brookfield viscosity tests.

	PC_{SR}	PC_{MFFT}	PC_{DT}	PC_{BV}
SS_{Model}	115	121	91.4	80.9
MS_{Model}	12.8	13.4	10.2	8.99
SS_{Error}	5.01	1.46	10.3	3.32
MS_{Error}	$4.18x10^{-1}$	$1.22x10^{-1}$	$8.58x10^{-1}$	$2.77x10^{-2}$
MS_{Model} / MS_{Error}	30.7	110	11.9	32.5
R^2	0.958	0.988	0.899	0.961

Degrees of freedom for the model and error are 9 and 12, respectively. For all calculated model the MS_{Model} / MS_{Error} (30.7, 110, 11.9 and 32.5) was higher than the $F_{9,12}$ tabulated (2.80). So, all models were valid and consistent with 95% of confidence and both MS are from different populations.

Table 5-6: Summary of sum and mean of squares for lack of fit and pure error for scores first principal components for scrub resistance, MFFT, drying time and Brookfield viscosity tests.

	PC_{SR}	PC_{MFFT}	PC_{DT}	PC_{BV}
SS_{LOF}	3.84	1.32	7.56	3.32
MS_{LOF}	1.28	$4.41x10^{-1}$	2.52	1.11
SS_{PE}	1.17	$1.35x10^{-1}$	2.74	$7.83x10^{-4}$
MS_{PE}	$1.30x10^{-2}$	$1.50x10^{-2}$	$3.04x10^{-1}$	$8.70x10^{-5}$
MS_{LOF} / MS_{PE}	9.85	29.4	8.28	$1.24x10^{4}$

Degrees of freedom for the lack of fit and pure error are 3 and 9, respectively (Table 5-6). For all calculated model the MS_{Model} / MS_{Error} ratio (9.85, 29.4, 8.28 and $1.24x10^4$) was higher than the $F_{3,9}$ tabulated (2.86). This lack of fit was equal to that obtained for raw data. Therefore proposed models are not well adjusted to the calculated coefficients. Consequently, the MS_{LOF} must be used as variance to calculate the error for each coefficient.

Based on that, it was possible to calculate coefficient for the model for each test as the following equations describe:

- Equation 20: PC_{SR} = $\underset{\pm 0.78}{1.80}CC - \underset{\pm 0.85}{1.20}LT$
- Equation 21: PC_{MFFT} = $-\underset{\pm 0.46}{2.15}CC + \underset{\pm 0.498}{0.814}LT$
- Equation 22: PC_{DT} = $\underset{\pm 1.09}{1.21}CC + \underset{\pm 1.19}{1.68}LT$
- Equation 23: PC_{BV} = $\underset{\pm 0.76}{1.18}CT + \underset{\pm 0.79}{1.09}LT - \underset{\pm 2.28}{3.38}CTCC$

In order to compare both approaches (DOE and DOE + PCA) the analysis of variance tables, from the raw data model and scores principal components model, were summarized in Table 5-7 and Table 5-8, respectively.

Table 5-7: Comparisons of analysis of variance tables between models obtained from raw data and principal components scores.

	Scrub resistance	**PC_{SR}**	**MFFT**	**PC_{MFFT}**	**Drying time**	**PC_{DT}**	**Brookfield viscosity**	**PC_{BV}**
SS_{Model}	$5.06x10^6$	115	$3.10x10^3$	121	778	91.4	$1.03x10^8$	80.9
MS_{Model}	$5.61x10^5$	12.8	344	13.4	86.4	10.2	$1.15x10^7$	8.99
SS_{Error}	$8.89x10^5$	5.01	149	1.46	305	10.3	$9.69x10^6$	3.32
MS_{Error}	$7.41x10^4$	$4.18x10^{-1}$	12.4	$1.22x10^{-1}$	25.4	$8.58x10^{-1}$	$8.08x10^5$	$2.77x10^{-2}$
MS_{Model} / MS_{Error}	7.57	30.7	27.7	110	3.40	11.9	14.2	32.5
R^2	0.850	0.958	0.954	0.988	0.718	0.899	0.914	0.961

Table 5-8: Comparisons of lack of fit tables between models obtained from raw data and principal components scores.

	Scrub resistance	**PC_{SR}**	**MFFT**	**PC_{MFFT}**	**Drying time**	**PC_{DT}**	**Brookfield viscosity**	**PC_{BV}**
SS_{LOF}	$6.82x10^5$	3.84	136	1.32	227	7.56	$9.69x10^6$	3.32
MS_{LOF}	$2.27x10^5$	1.28	45.2	$4.41x10^{-1}$	74.6	2.52	$3.23x10^6$	1.11
SS_{PE}	$2.07x10^5$	1.17	13.8	$1.35x10^{-1}$	81.1	2.74	$2.28x10^3$	$7.83x10^{-4}$
MS_{PE}	$2.30x10^3$	$1.30x10^{-2}$	1.53	$1.50x10^{-2}$	9.01	$3.04x10^{-1}$	$2.53x10^2$	$8.70x10^{-5}$
MS_{LOF} / MS_{PE}	9.87	9.85	29.5	29.4	8.28	8.28	$1.28x10^4$	$1.24x10^4$

Table 5-7 showed the MS_{Model} / MS_{Error} ratio increased when the first principal component scores were used for proposing a model, independently of the test. For scrub resistance MS_{Model} / MS_{Error} ratio went up from 7.57 to 30.7. It represented about 306% of improvement. MS_{Model} / MS_{Error} ratio increased from 27.2 to 110 (~297% of improvement) for MFFT, changed from 3.40 to 11.9 (around 250%) for drying time and rose from 14.2 to 32.5 (~129%) for Brookfield viscosity.

R square (R^2), which is the ratio between sum of squares of model and total variance, increased for both scrub resistance and drying time (0.850 to 0.958 and 0.718 to 0.899, respectively). Both situations suggest that models prepared by PC scores have more information than the previous proposed models based on raw data. It means the principal component analysis allow extracting more information from raw data.

Lack of fit is still present in all proposed models, based on raw data or PC scores. MS_{LOF} / MS_{PE} ratio keep the same for models independently of data used (from raw data or PC scores). Model equations for tests were also summarized for comparisons in the following table (Table 5-9).

Table 5-9: Comparisons of model equations between raw data and principal components scores models.

	Raw data model	**PC scores model**
Scrub resistance (cycles) / PC_{SR}	$\underset{\pm 619}{865} + \underset{\pm 326}{339}\,CC$	$\underset{\pm 0.78}{1.80}\,CC - \underset{\pm 0.85}{1.20}\,LT$
MFFT (°C) / PC_{MFFT}	$-\underset{\pm 4.6}{10.7}\,CC$	$-\underset{\pm 0.46}{2.15}\,CC + \underset{\pm 0.498}{0.814}\,LT$
Drying time (min) / PC_{DT}	$\underset{\pm 11.2}{22.7}$	$\underset{\pm 1.09}{1.21}\,CC + \underset{\pm 1.19}{1.68}\,LT$
Brookfield viscosity (cPs) / PC_{BV}	$\underset{\pm 2.34x10^3}{3.21x10^3} - \underset{\pm 3.89x10^3}{5.77x10^3}\,CTCC$	$\underset{\pm 0.76}{1.18}\,CT + \underset{\pm 0.79}{1.09}\,LT - \underset{\pm 2.28}{3.38}\,CTCC$

Table 5-9 shows model equations for all tests of this dissertation. Coalescent concentration (CC) and latex type (LT) alone were variables presented in all models proposed by PC scores. The model for Brookfield viscosity also contained the interaction between coalescent type and concentration (CTCC). The number of coefficients increased for all tests when equations from raw data and PC scores models are compared.

For scrub resistance, MFFT and Brookfield viscosity latex type variable (LT) became significant when PC scores were used for proposing a model. The most significant change was noticed for the response drying time that only had the intercept in the raw data model ($\underset{\pm 11.2}{22.7}$) and coalescent concentration and latex type variable for PC scores model ($\underset{\pm 1.09}{1.21}CC + \underset{\pm 1.19}{1.68}LT$).

There is a correlation between these principal component scores and tests results. In order to determine this relationship, test results against the related PC scores were plotted (Figure 7.16 on Appendix 7) and a linear regression for each data was calculated (Equation 24 to Equation 27).

- Equation 24: Scrub resistance (cycles) = $837 + 211PC_{SR}$, $R^2 = 0.897$
- Equation 25: MFFT (°C) = $9.25 + 5.03PC_{TMFF}$, $R^2 = 0.951$
- Equation 26: Drying time (min) = $21.2 + 3.04PC_{TS}$, $R^2 = 0.868$
- Equation 27: Brookfield viscosity (cPs) = $1.79x10^3 + 9.42PC_{VB}$, $R^2 = 0.662$

R squares (R^2) and Figure 7.16 (section 7.7 - Appendix 7) show that there was a direct correlation between test results and the first principal component scores (R^2 equal to 0.897, 0.951 and 0.868 for scrub resistance, MFFT and drying time, respectively), except for Brookfield viscosity that presented poor relationship (R^2 = 0.662).

Therefore, contour plots were prepared only for scrub resistance, MFFT and drying time based on direct correlation between the test results and first principal component scores and the commonality that these tests had the same variable (coalescent concentration and latex type) for PC scores models (Figure 5.8).

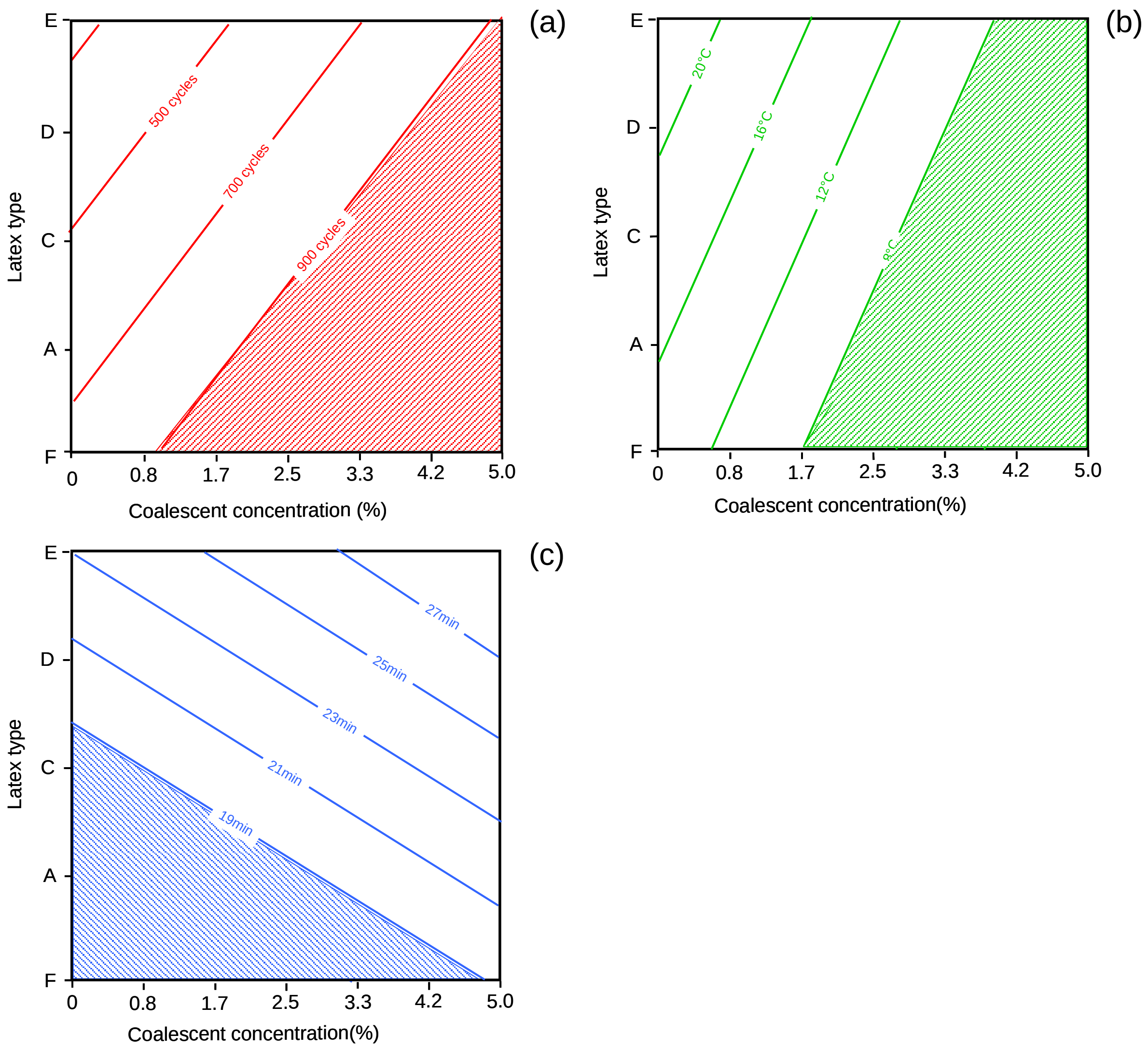

Figure 5.8: Contour plots for scrub resistance (a), MFFT (b) and drying time (c) with desired results highlighted.

Figure 5.8 presents contour plots for each response variable evaluated (scrub resistance, MFFT and drying time). Highlighted areas represent the desired results for each variable. Figure 5.8 (a), for example, is the scrub resistance plot and the highlighted inferior right corner represents the desired situation. These regions were defined according to the Brazilian market preferences. This area is composed by high levels of the variable coalescent concentration and low levels of the variable latex type. It means that high amount of coalescent (around 1.7 to 5.0%) and latex F, A and/or C according to design of experiments for group 2 (Table 4-2) gave high values for scrub resistance.

Scrub resistance, MFFT and drying time plots are at the same scale and have the same variables (coalescent concentration and latex type), so it was possible to overlay its plot in order to determine the best zone considered the desired result for the three tests. Figure 5.9 shows the overlaid plot.

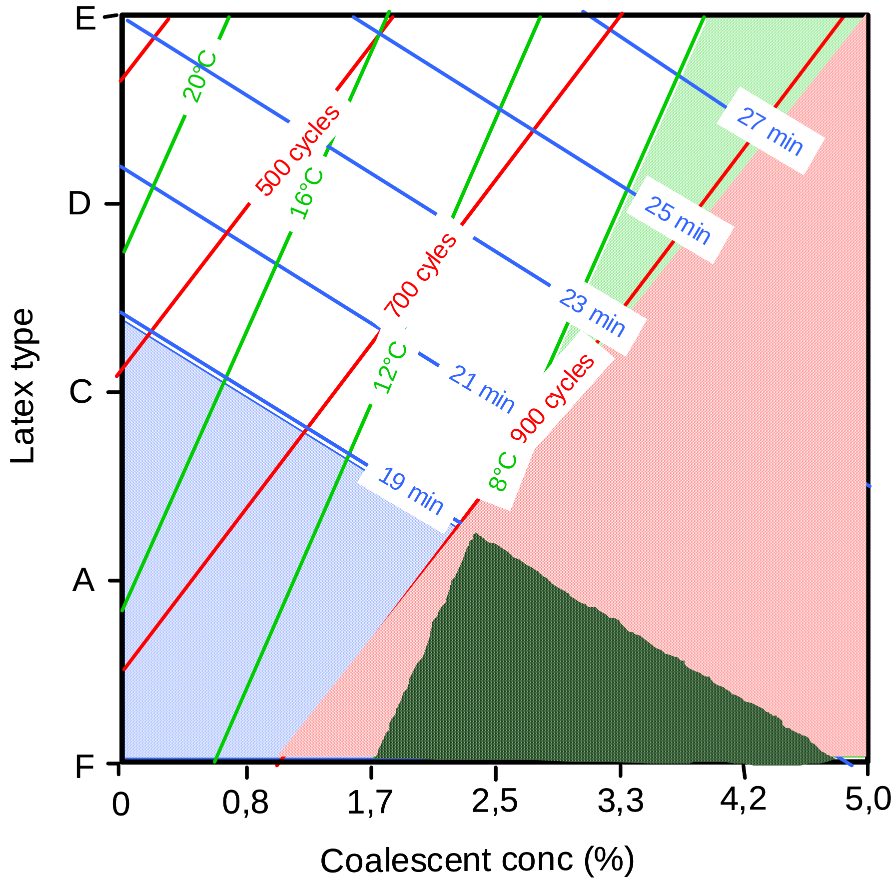

Figure 5.9: Plot of overlaid contour plots of scrub resistance, MFFT and drying time results with desired resulted highlighted.

Figure 5.9Figure 5.9 shows the overlaid contour plots for scrub resistance, MFFT and drying time. The desired result for each test was highlighted with a triangle. The three tests overlap is around intermediate coalescent concentration and low levels of latex type. The criterion to select the coalescent concentration and latex type will depend on the desired result; however the anticipated ideal concentrations are from 1.7 to ~5% of one of the following latexes A or F.

5.3.1 - Multivariate study: DOE + PCA model validation.

Samples 14 to 20, described on Table 4-2, were used to validate scrub resistance, MFFT and drying time PCA models. PC1 scores and its standard deviation were calculated for each sample using equations 20 to 22. PC1 scores were become in test results by equations 28 to 30. These ones were obtained based the linear regression of test results against the related PC scores for validation samples only (Figure 7.17 on Appendix 8).

- Equation 28: Scrub resistance (cycles) = $730 + 135PC_{SR}$, $R^2 = 0.954$.
- Equation 29: MFFT (°C) = $8.42 + 4.87PC_{MFFT}$, $R^2 = 0.985$.
- Equation 30: Drying time (min) = $20.9 + 1.80PC_{DT}$, $R^2 = 0.705$.

The average and its deviations were calculated for experimental results too. These deviations were multiplied by 1.96 to have 95% of confidence and to be compared with standard deviation from model results. Tables 7-6 to 7-8 on Appendix 9 describe these values.

Based on that, coalescent concentration against latex type contour plot was done and validation sample, both experimental and PCA model for scrub resistance, MFFT and drying time (Figure 5.10 to Figure 5.12) results were added into plots. Validation samples were identified as spheres, experimental range results were represented as rectangles and PCA Model range results were as lines. 95% of confidence standard deviation for each result is represented by rectangle or line length. Results were added beside each rectangle / line.

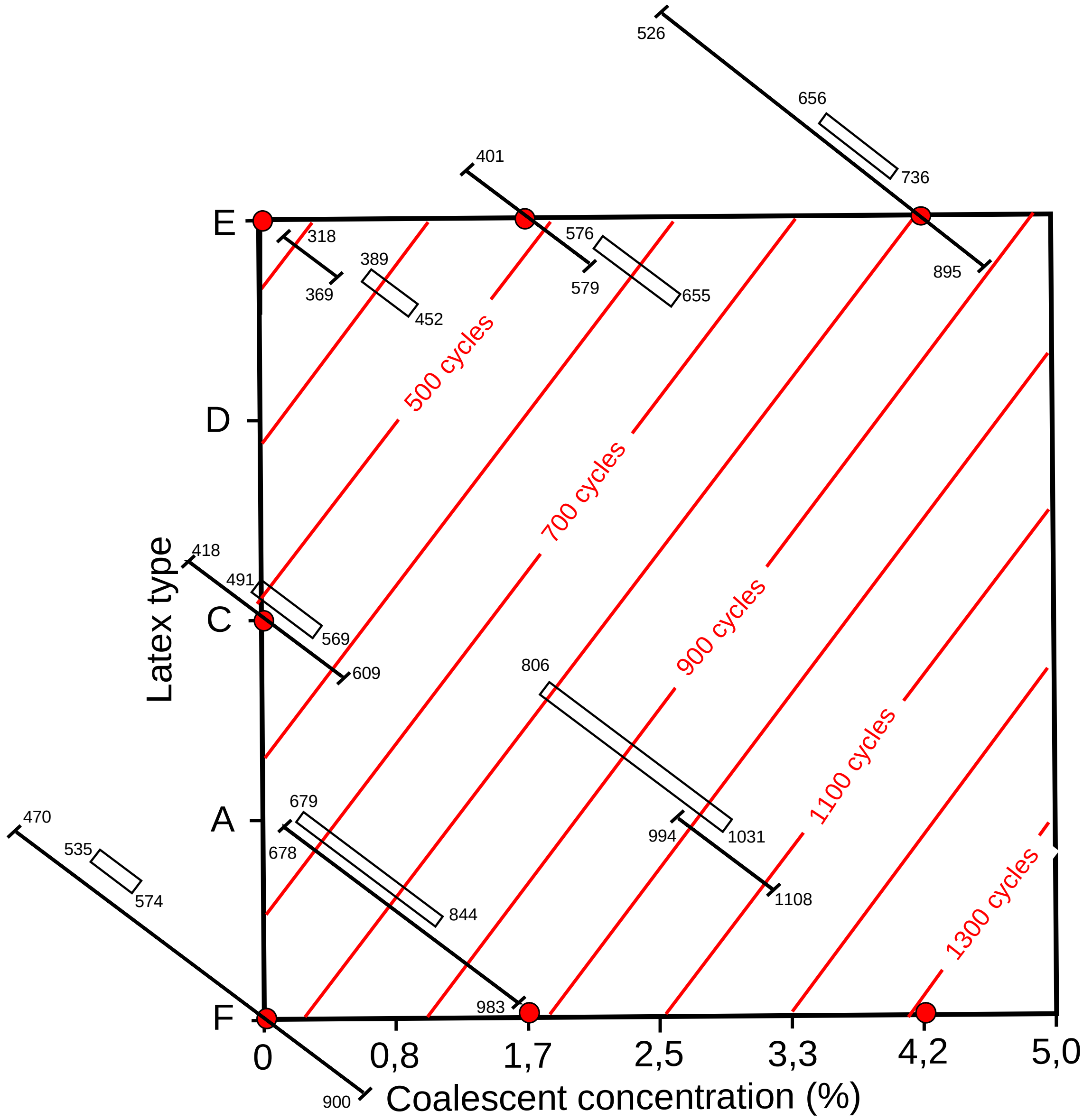

Figure 5.10: Contour plot of coalescent concentration against latex type with scrub resistance experimental results (rectangles) and model results (range lines) for validation samples (spheres).

Figure 5.10 shows coalescent concentration *versus* latex type contour plot with both experimental (rectangles) and PCA model scrub resistance (range lines), for scrub resistance, results for validation samples (spheres). All validation samples had overlapping between experimental and PCA model results, except for E0 sample. These ones had results with significant differences between experimental and model. It means about 86% of concordance among experimental and PCA model results.

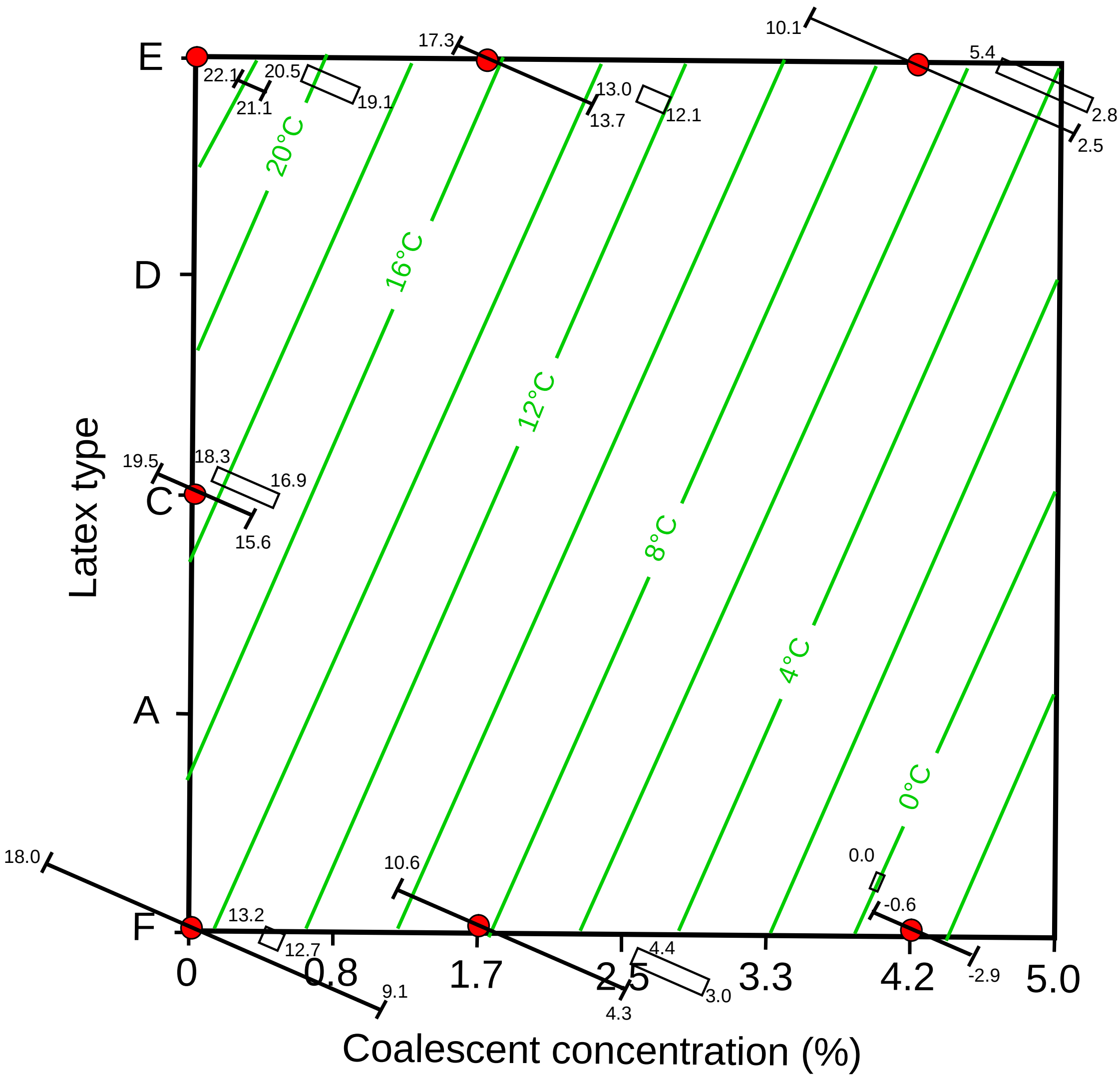

Figure 5.11: Contour plot of coalescent concentration against latex type with MFFT experimental results (rectangles) and model results (range lines) for validation samples (spheres).

Figure 5.11 shows coalescent concentration *versus* latex type contour plot with both experimental and PCA model MFFT results. All validation samples had overlapping between experimental and PCA model results, except for samples E0, E1.7Y and F4.2Y. These ones had results with significant differences between experimental and model. It means about 57% of concordance among experimental and PCA model results.

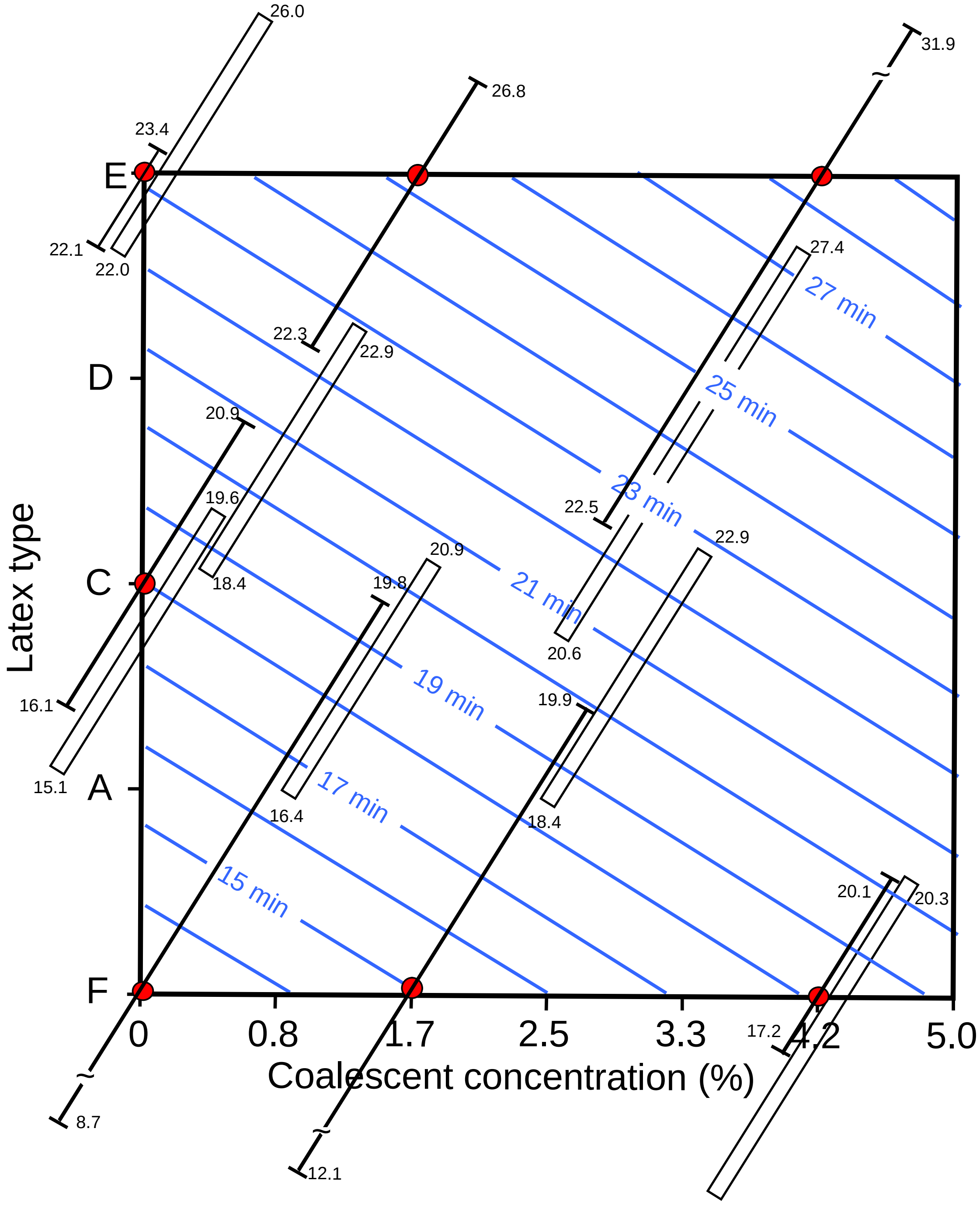

Figure 5.12: Contour plot of coalescent concentration against latex type with drying time experimental results (rectangles) and model results (range lines) for validation samples (spheres).

Figure 5.12 shows coalescent concentration *versus* latex type contour plot with both experimental and PCA model drying time results. All validation samples had overlapping between experimental and PCA model results. It means 100% of concordance among experimental and PCA model results.

CONCLUSION

6 - CONCLUSION

Two experimental approaches were evaluated and compared to study emulsion system film formation: experimentally varying one variable at a time and use of Doehlert design of experiments, comparing results obtained with linear regression with Principal Component Analysis. Coalescent type, coalescent concentration and latex type were the independent variables. Scrub resistance, Minimum Film Formation Temperature, drying time and Brookfield viscosity were the responses (samples analyze).

By comparing both experimentation methodologies, it was possible to notice using the standard approach it was difficult to select the best coalescent or concentration to be used. By using Doehlert DOE that a (relative) few number of experiments allow propose valid models for all tests.

PCA was done with Doehlert DOE raw data. The first principal component scores were used for proposing models for each test. By using DOE and PCA the following MS_{Model} / MS_{Error}, r^2 and the number of valid coefficients increased. It means PCA was more effective at explaining the variability in the data as compared with the linear regression models.

Based on this PC1 scores models, scrub resistance, MFFT and drying time contour plots were prepared. Desired results for the three tests were highlighted in order to identify the best combination of coalescent type and concentration and latex type to obtain the maximum of scrub resistance, the minimum of MFFT and the shortest drying time. It may be from 1.7 to 5.0% of coalescent and latex A or F.

This coalescent optimization, regarding to these latexes, result in selecting the amount of coalescent addition, without excess, to promote the film formation. Due to no coalescent excess the following items odor, environmental impact and cost's coating may decrease. Based on this study and A and F latexes better understanding new products (latexes and coalescents) will be developed and offered to Brazilian decorative coating market.

Validation samples were used to check the PCA proposed model of scrub resistance, MFFT and drying time. By comparing the experimental results with PCA model ones it was possible to notice there was around 80% of concordance in average.

APPENDICES

7 - APPENDICES

7.1 - Appendix 1 – Equipment

Figure 7.1: Scrub resistance test equipment.

Figure 7.2: Minimum Film Formation Temperature test equipment.

Figure 7.3: Drying time test equipment.

7.2 - Appendix 2 – Univariate study: results of scrub resistance, MFFT, drying time and Brookfield viscosity tests.

Table 7-1: Univariate study results of scrub resistance, MFFT, drying time and Brookfield viscosity tests.

Exp	Sample id	Coalescent type	Coalescent conc (%) (w/w)	Measure	Scrub Resistance (cycle)	MFFT (°C)	Drying Time (min)	Brookfield Viscosity (cPs)
1	A0	NA	0	a	640	16.7	16	706
				b	625	13.3	16	706
				c	630	15.6	16	706
2	AX1	X	1	a	828	11.7	23	841
				b	769	11.7	25	838
				c	733	10.6	18	840
3	AX2		2	a	1044	7.8	20	974
				b	1007	8.3	22	974
				c	1004	7.8	23	972
4	AX3		3	a	1034	3.3	24	1122
				b	912	3.3	21	1118
				c	905	2.6	21	1122
5	AX5		5	a	1596	0	22	1580
				b	1036	0	20	1588
				c	1621	0	23	1586
6	AY1	Y	1	a	648	11.7	19	810
				b	654	12.2	18	808
				c	506	11.7	20	810
7	AY2		2	a	568	6.7	24	845
				b	589	7.2	22	850
				c	596	7.6	21	850

NA: not applicable

Table 7-1: Univariate study results of scrub resistance, MFFT, drying time and Brookfield viscosity tests (cont.)

Exp	Sample id	Coalescent type	Coalescent conc (%) (w/w)	Measure	Scrub Resistance (cycle)	MFFT (°C)	Drying Time (min)	Brookfield Viscosity (cPs)
8	AY3	Y	3	a	783	0	18	880
				b	760	0	19	876
				c	800	0	19	876
9	AY5		5	a	1056	0	17	976
				b	1098	0	18	970
				c	1055	0	19	982
10	AZ1	Z	1	a	777	11.7	17	854
				b	828	11.7	18	858
				c	829	11.9	18	854
11	AZ2		2	a	762	8.6	20	942
				b	799	7.2	18	942
				c	799	8.1	17	940
12	AZ3		3	a	1464	7.8	28	1024
				b	1040	4.2	26	1028
				c	1215	3.9	25	1028
13	AZ5		5	a	1242	3.9	23	1142
				b	1159	1.9	25	1138
				c	1420	2.2	26	1144
14	AW1	W	1	a	921	9.4	20	822
				b	1033	10.6	22	820
				c	700	10.2	19	820
15	AW2		2	a	1190	3.9	24	952
				b	1242	2.7	23	952
				c	1280	3.3	23	952

Table 7-1: Univariate study results of scrub resistance, MFFT, drying time and Brookfield viscosity tests tests (cont.)

Exp	Sample id	Coalescent type	Coalescent conc (%) (w/w)	Measure	Scrub Resistance (cycle)	MFFT (°C)	Drying Time (min)	Brookfield Viscosity (cPs)
16	AW3	W	3	a	1455	0	22	1126
				b	1487	0	23	1116
				c	1452	0	23	1116
17	AW5		5	a	1624	0	27	1568
				b	1513	0	26	1568
				c	1577	0	28	1568

7.3 - Appendix 3 – Multivariate study: results of scrub resistance, MFFT, drying time and Brookfield viscosity tests.

Table 7-2: Multivariate study results of scrub resistance, MFFT, drying time and Brookfield viscosity tests.

Exp	Sample id	Coalescent type	Coalescent conc (%) (w/w)	Latex type	Measure	Scrub resistance (cycles)	MFFT (°C)	Drying time (min)	Brookfield viscosity (cPs)
1	CY2.5	Y	2.5	C	a	780	5	23	3192
					b	908	4.4	21	3188
					c	880	4.4	23	3188
	CY2.5r				a	922	4.4	22	3220
					b	829	4.4	23	3224
					c	872	5	24	3220
2	EY2.5	Y	2.5	E	a	666	8.9	26	2660
					b	682	10	22	2664
					c	673	10	20	2662
3	DY5	Y	5	D	a	828	0	32	1168
					b	787	0	31	1164
					c	821	0	31	1164

Table 7-2: Multivariate study results of scrub resistance, MFFT, drying time and Brookfield viscosity test (cont).

Exp	Sample id	Coalescent type	Coalescent conc (%) (w/w)	Latex type	Measure	Scrub resistance (cycles)	MFFT (°C)	Drying time (min)	Brookfield viscosity (cPs)
3	DY5r	Y	5	D	a	912	0	29	1160
					b	885	0	30	1160
					c	897	0	33	1160
4	DZ3.3	Z	3.3	D	a	814	12.8	18	1188
					b	803	11.1	19	1188
					c	806	12.8	20	1188
	DZ3.3r				a	851	11.1	19	1188
					b	913	12.2	20	1192
					c	853	12.8	20	1192
5	FY2.5	Y	2.5	F	a	820	3.3	17	1678
					b	828	2.2	18	1674
					c	791	3.3	18	1678
6	A0	Y	0	A	a	619	16.7	17	690
					b	566	16.1	17	690
					c	633	16.7	18	690
	A0r				a	656	17.8	16	692
					b	625	17.8	17	692
					c	646	17	16	692
7	AX1.7	X	1.7	A	a	1028	10.4	17	916
					b	1031	10	18	916
					c	994	10	18	918
	AX1.7r				a	953	10	18	910
					b	971	10	19	906
					c	941	9.4	17	906
8	D0	Y	0	D	a	414	20	23	1108
					b	428	20	25	1104
					c	435	20	23	1104

Table 7-2: Multivariate study results of scrub resistance, MFFT, drying time and Brookfield viscosity test (cont).

Exp	Sample id	Coalescent type	Coalescent conc (%) (w/w)	Latex type	Measure	Scrub resistance (cycles)	MFFT (°C)	Drying time (min)	Brookfield viscosity (cPs)
8	D0r	Y	0	D	a	378	20	20	1104
					b	400	20	23	1100
					c	426	20	21	1100
9	DX1.7	X	1.7	D	a	654	17.2	25	1408
					b	660	17.6	24	1408
					c	607	15.6	24	1408
	DX1.7r				a	608	16.1	25	1416
					b	631	16.7	23	1416
					c	664	16.5	23	1416
10	AY5	Y	5	A	a	1421	0	18	970
					b	1345	0	18	970
					c	1305	0	18	972
	AY5r				a	1179	0	19	960
					b	1100	0	18	958
					c	1040	0	19	958
11	CX4.2	X	4.2	C	a	1268	0	23	6480
					b	1219	0	22	6472
					c	1397	0	25	6480
12	AZ3.3	Z	3.3	A	a	1570	1.7	25	1050
					b	1436	2.8	21	1048
					c	1542	2.8	23	1048
	AZ3.3r				a	1403	3.2	23	1044
					b	1421	2.8	24	1044
					c	1497	3.2	24	1044
13	CZ0.8	Z	0.8	C	a	761	11.7	19	3180
					b	759	13.3	17	3172
					c	701	12.8	19	3172

Table 7-2: Multivariate study results of scrub resistance, MFFT, drying time and Brookfield viscosity tes (cont)

Exp	Sample id	Coalescent type	Coalescent conc (%) (w/w)	Latex type	Measure	Scrub resistance (cycles)	MFFT (°C)	Drying time (min)	Brookfield viscosity (cPs)
14	C0	NA	0	C	a	546	17.8	16	2712
					b	508	17.2	18	2700
					c	537	17.8	18	2704
15	E0	NA	0	E	a	439	19.4	24	2840
					b	414	20	25	2834
					c	409	20	23	2834
16	F0	NA	0	F	a	545	13	18	1672
					b	565	12.8	20	1672
					c	553	13	18	1670
17	E1.7Y	Y	1.7	E	a	605	12.8	22	2816
					b	639	12.4	20	2816
					c	603	12.4	20	2816
18	E4.2Y	Y	4.2	E	a	675	3.9	26	2640
					b	697	3.5	23	2640
					c	716	4.8	23	2632
19	F1.7Y	Y	1.7	F	a	783	3.9	20	1840
					b	789	3.9	20	1840
					c	713	3.3	22	1840
20	F4.2Y	Y	4.2	F	a	861	0	17	2008
					b	976	0	16	2008
					c	918	0	19	2008

7.4 - Appendix 4 - PCA for MFFT test.

Table 7-3: MFFT Principal Components (PC), percent of information for each PC (Percent) and accumulative percent (Cum Percent).

PC	Percent	Cum Percent
1	48.9	48.9
2	25.8	74.7
3	23.7	98.4
4	1.60	100

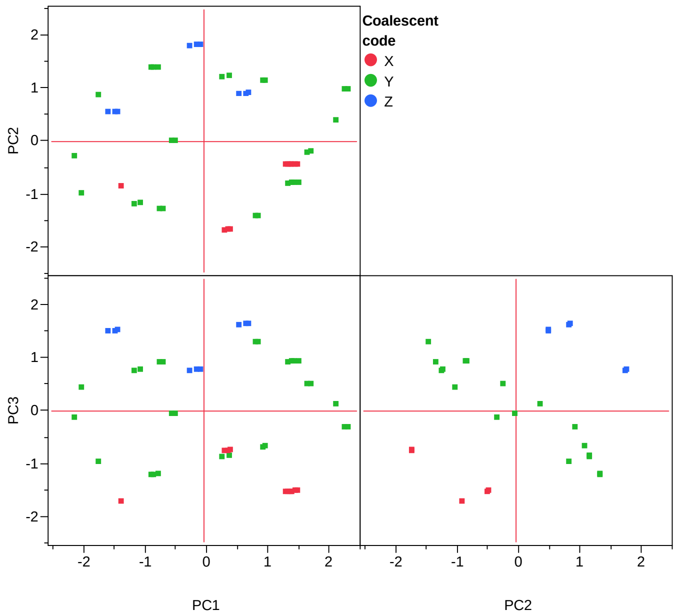

Figure 7.4: Plot of first, second and third PC scores of MFFT test of mutilvariate study (coalescent type class highlighted).

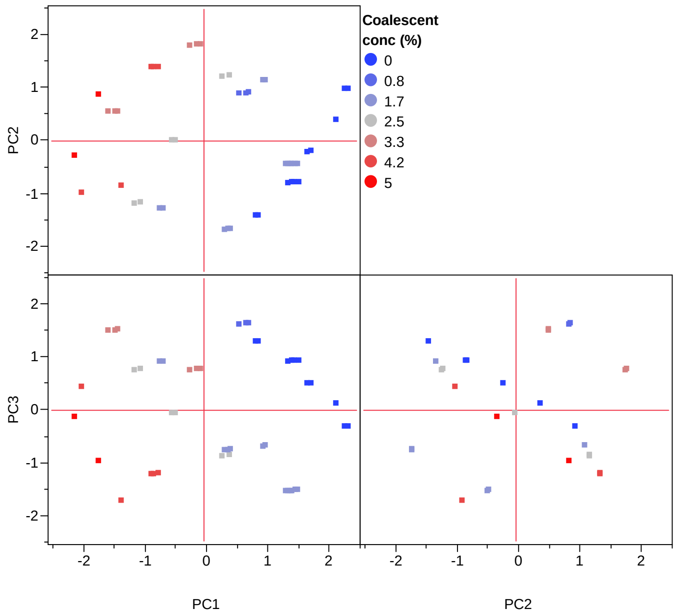

Figure 7.5: Plot of first, second and third PC scores of MFFT test of mutilvariate study (coalescent concentration class highlighted).

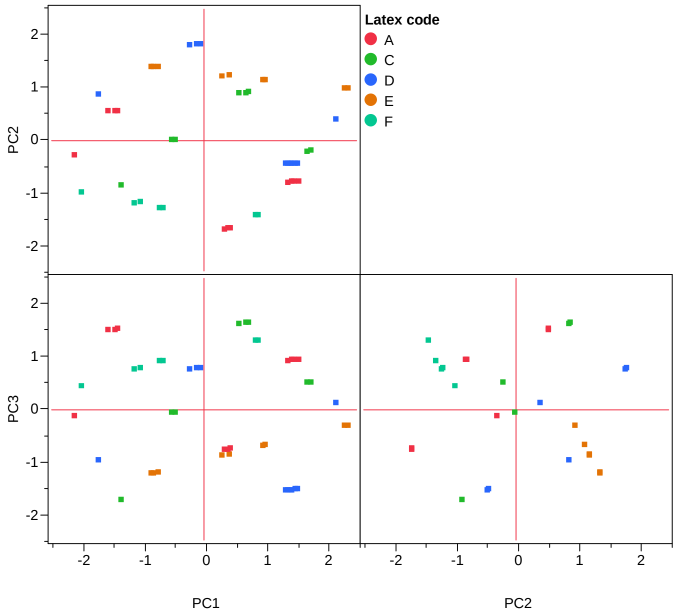

Figure 7.6: Plot of first, second and third PC scores of MFFT test of mutilvariate study (latex type class highlighted).

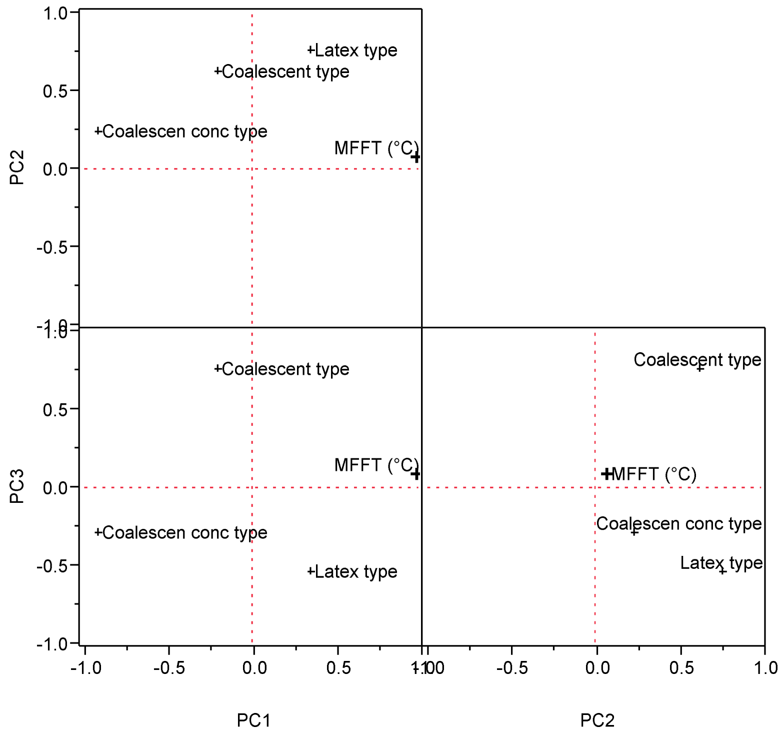

Figure 7.7: Plot of first, second and third PC loadings of MFFT test of mutilvariate study.

7.5 - Appendix 5 – PCA for drying time test.

Table 7-4: Drying time Principal Components (PC), percent of information for each PC (Percent) and accumulative percent (Cum Percent).

PC	Percent	Cum Percent
1	50.4	50.4
2	27.4	77.8
3	22.2	100.0

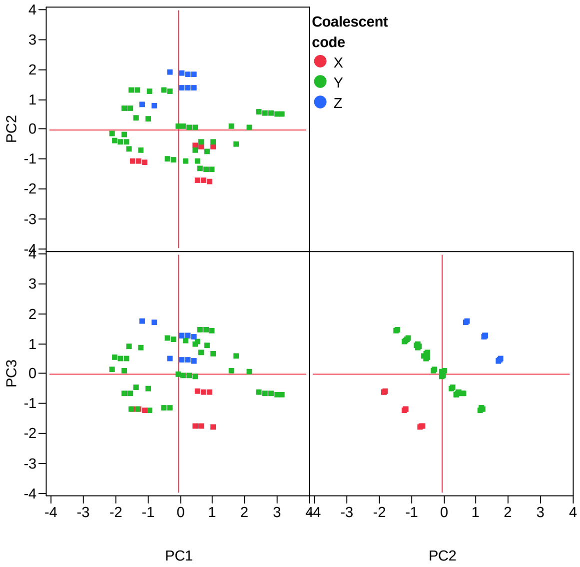

Figure 7.8: Plot of first, second and third PC scores of drying time test of mutilvariate study (coalescent type class highlighted).

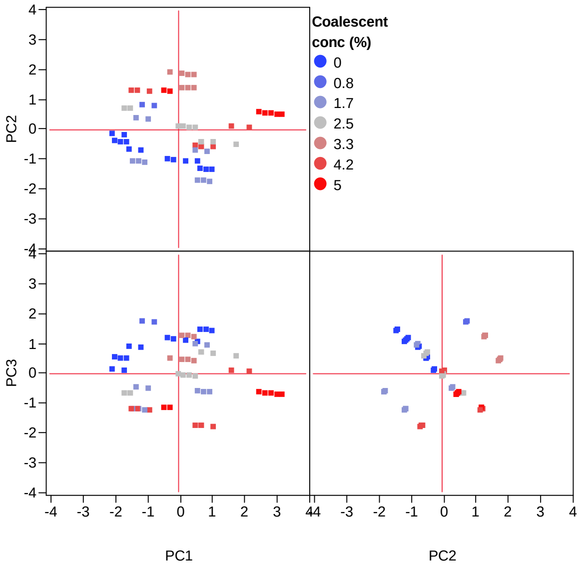

Figure 7.9: Plot of first, second and third PC scores of drying time test of mutilvariate study (coalescent concentration class highlighted).

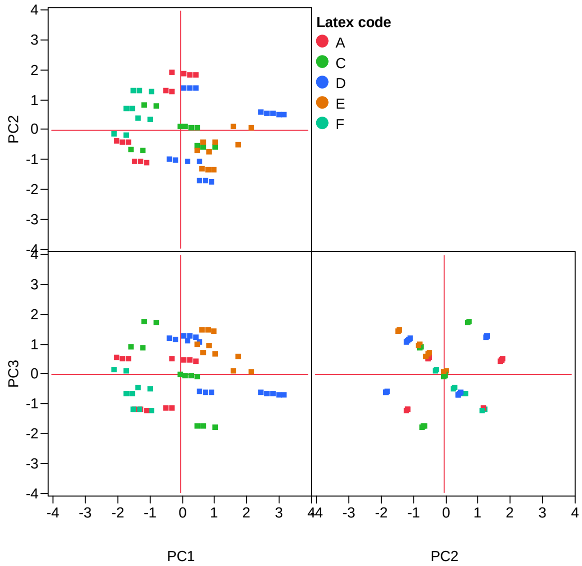

Figure 7.10: Plot of first, second and third PC scores of drying time test of mutilvariate study (latex type class highlighted).

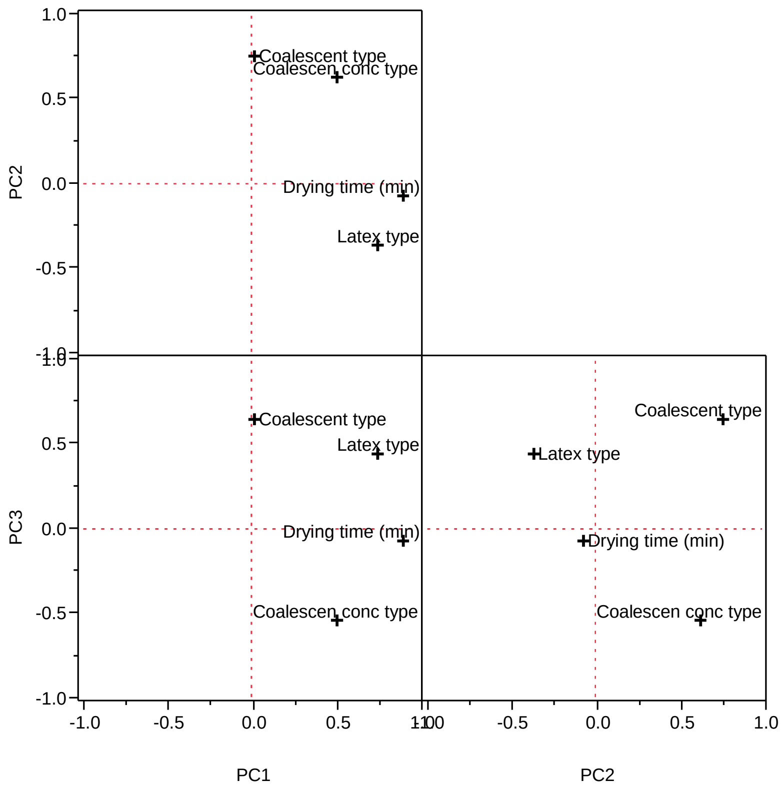

Figure 7.11: Plot of first, second and third PC loadings of drying time test of mutilvariate study

7.6 - Appendix 6 – PCA of Brookfield viscosity test.

Table 7-5: Brookfield viscosity Principal Components (PC), percent of information for each PC (Percent) and accumulative percent (Cum Percent).

PC	Percent	Cum Percent
1	32.1	32.1
2	27.6	59.7
3	23.2	82.8
4	17.2	100

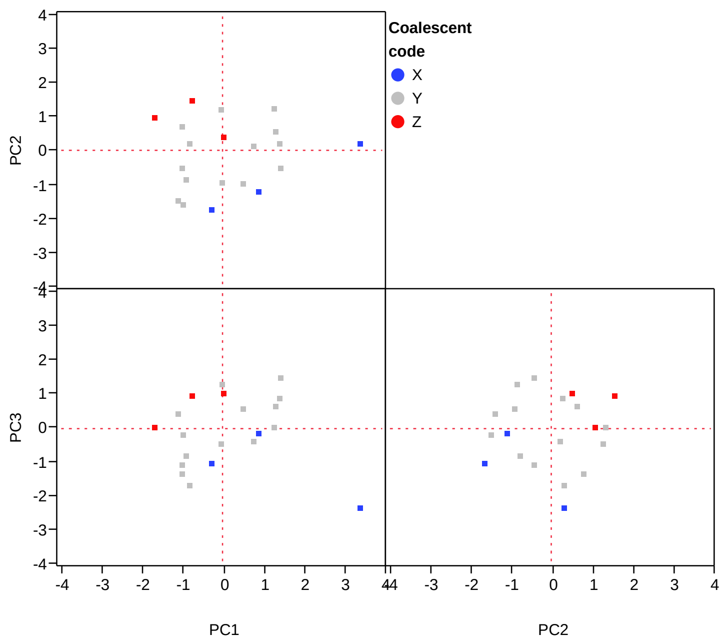

Figure 7.12: Plot of first, second and third PC scores of Brookfield viscosity test of mutilvariate study (coalescent type class highlighted).

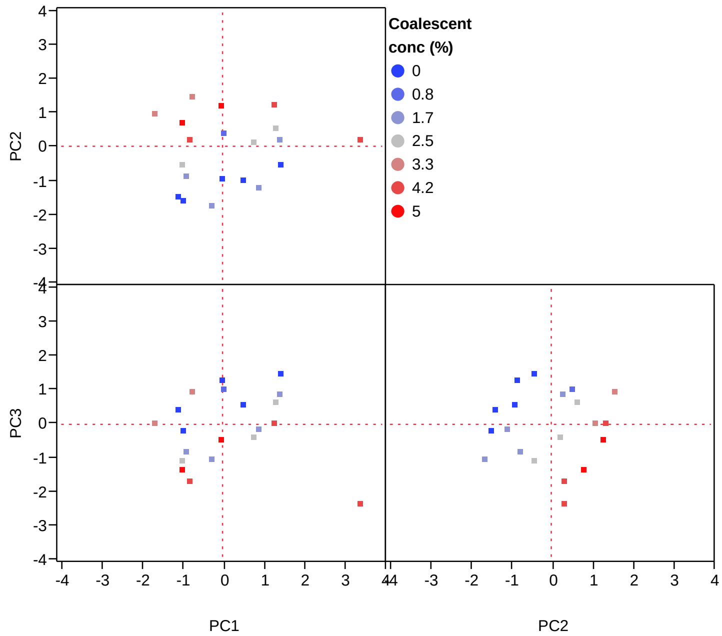

Figure 7.13: Plot of first, second and third PC scores of Brookfield viscosity test of mutilvariate study (coalescent concentration class highlighted).

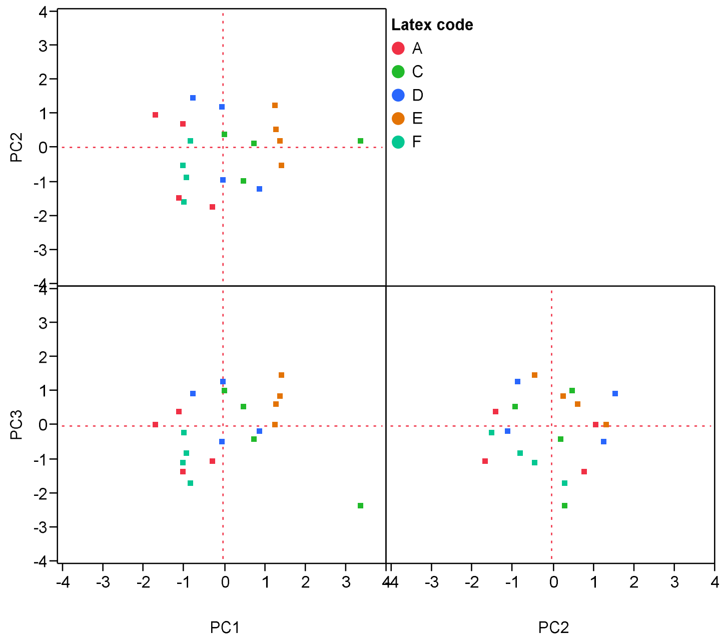

Figure 7.14: Plot of first, second and third PC scores of Brookfield viscosity test of mutilvariate study (latex type class highlighted).

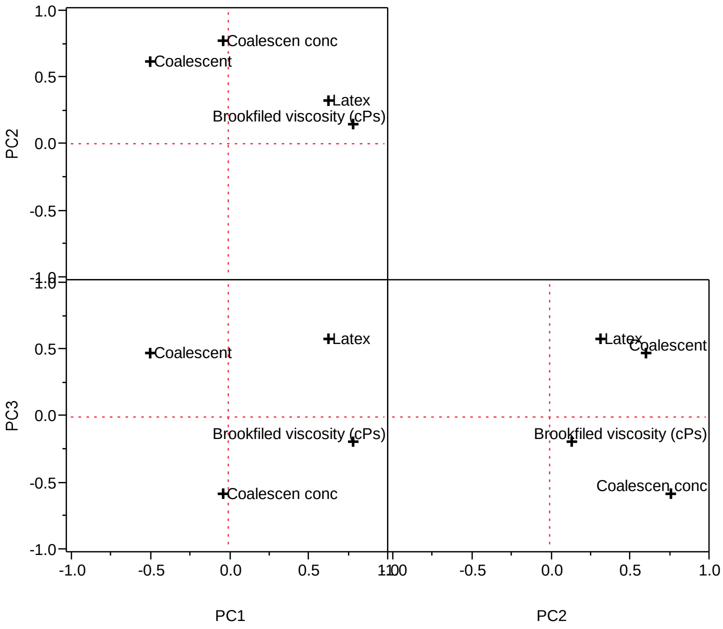

Figure 7.15: Plot of first, second and third PC loadings of Brookfield viscosity test of mutilvariate study.

7.7 - Appendix 7 – Relationship between results and first PC scores for model samples for scrub resistance, MFFT, drying time and Brookfield viscosity.

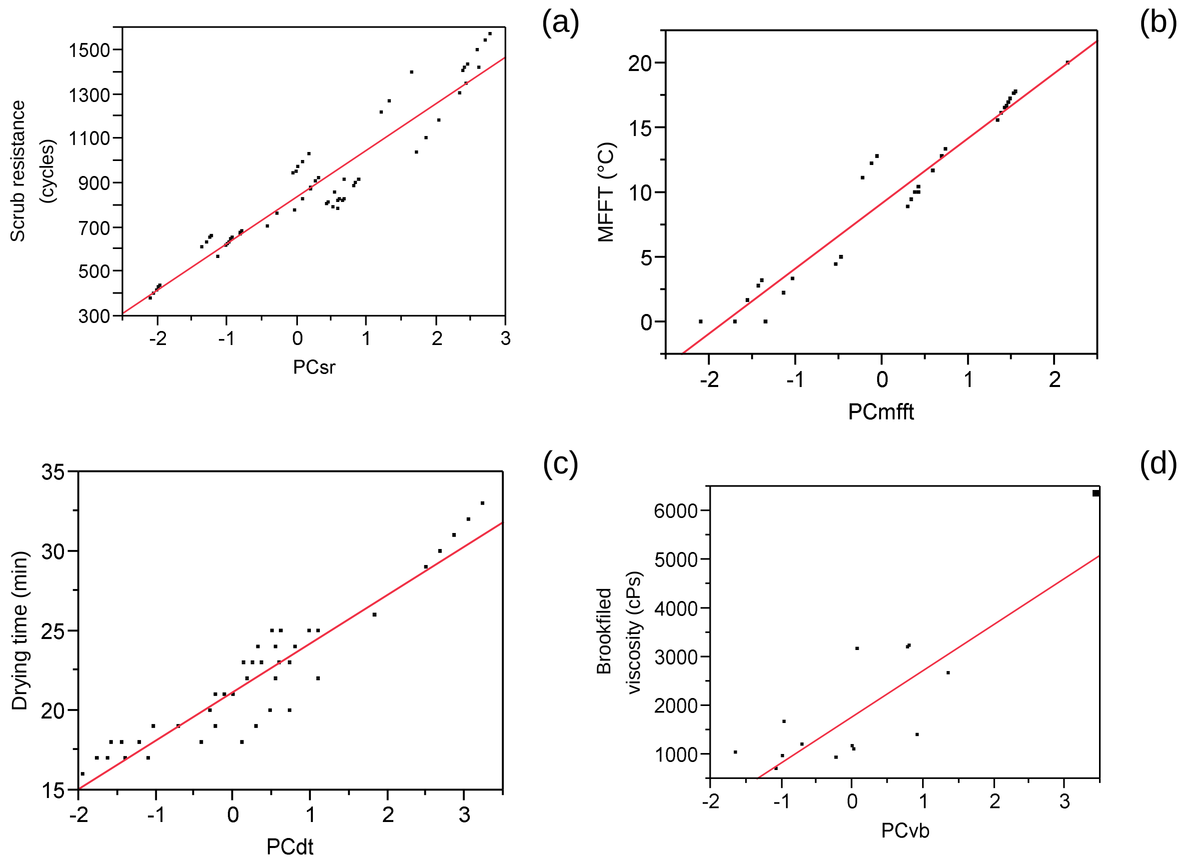

Figure 7.16: Plot of test results against first PC scores for model samples for scrub resistance (a), MFFT (b), drying time (c) and Brookfield viscosity (d).

7.8 - Appendix 8 – Relationship between results and first PC scores for validation samples for scrub resistance, MFFT and drying time.

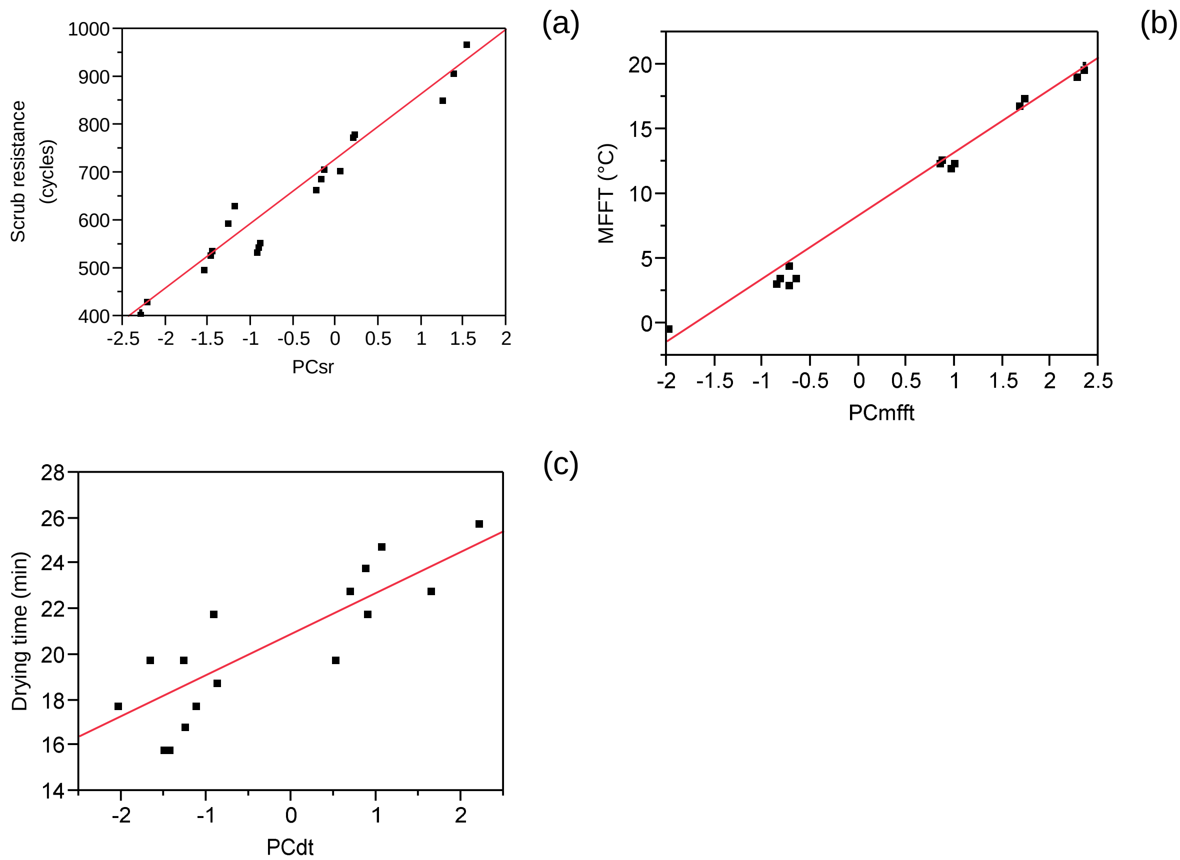

Figure 7.17: Plot of test results against first PC scores for validation samples for scrub resistance (a), MFFT (b) and drying time (c).

7.9 - Appendix 9 – Scrub resistance, MFFT and Drying time experimental results, PCA model results and its 95% of confidence of standard deviation.

Table 7-6: Scrub resistance experimental and PCA model average results and its standard deviations with 95% of confidence.

Exp #	Sample id	Experimental results (cycles)		PCA model results (cycles)	
		Average	Standard deviation	Average	Standard deviation
14	C0	530	39	514	95
15	E0	421	32	343	25
16	F0	554	20	684	216
17	E1.7Y	616	40	490	89
18	E4.2Y	696	40	711	184
19	F1.7Y	762	83	831	153
20	F4.2Y	918	113	1051	57

Table 7-7: MFFT experimental and PCA model average results and its standard deviations with 95% of confidence.

Exp #	Sample id	Experimental results (°C)		PCA model results (°C)	
		Average	Standard deviation	Average	Standard deviation
14	C0	17.6	0.7	17.6	2.0
15	E0	19.8	0.7	21.6	0.5
16	F0	12.9	0.2	13.5	4.5
17	E1.7Y	12.5	0.5	15.5	1.8
18	E4.2Y	4.1	1.3	6.3	3.8
19	F1.7Y	3.7	0.7	7.4	3.1
20	F4.2Y	0.0	0.0	-1.8	1.2

Table 7-8: Drying time experimental and PCA model average results and its standard deviations with 95% of confidence.

Exp #	Sample id	Experimental results (min)		PCA model results (min)	
		Average	Standard deviation	Average	Standard deviation
14	C0	17.3	2.3	18.5	2.4
15	E0	24.0	2.0	22.8	0.6
16	F0	18.7	2.3	14.2	5.5
17	E1.7Y	20.7	2.3	24.5	2.3
18	E4.2Y	24.0	3.4	27.2	4.7
19	F1.7Y	20.7	2.3	16.0	3.9
20	F4.2Y	17.3	3.0	18.7	1.5

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