

## **Impact of modified DMDHEU and copolymer acrylic resin using spraying treatment before and after an enzymatic washing on the mechanical properties of Denim cotton fabric**

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**Abstract:** *In this paper, The principal purpose is to investigate the impact of modified DMDHEU and acrylic resin using spraying treatment of denim cotton fabric on mechanical properties loss (tear strength, grab strength loss and elongation loss) and others textile properties effect, such as, 3D rank evaluation and 3D thickness. All results are obtained for two of finishing process state; before and after an enzymatic washing and in warp and weft direction fabric. It has obtain that before and after washing, the modified DMDHEU resin effect more than acrylic resin the mechanical properties, (breaking strength, breaking elongation and tear strength) especially, for fabric 100% cotton compared to different fabric (weft composition contain Elasthanne 5% or Polyester). For the 3D rank of treated fabric with dissimilar resins, results clarify that enzymatic washing one of many factors cause increase of 3D rank level and more than their level before washing. It was established that the acrylic resin and resin spray application are significant factors in 3D thickness variation of treated fabrics.*

**Keywords:** *Mechanical properties, cotton, modified DMDHEU, acrylic resin, 3D ranks, enzymatic washing*

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### **I. Introduction**

Resin is a chemical solution that fills into the amorphous area of a fibre, penetrates thoroughly by drying and curing and polymerizes inside the fibres. The resin amount, fixation temperature, pH and process time are the critical parameters of a proper resin application on denim fabric. A post curing can activate the resin after garment production [1,3]. Resin application is a process that is applied to denim garments to give dry and luster appearance, to improve the rubbing fastness, to give 3D effects, to provide stiff and firm handle and to reduce pilling. Generally, resin application is the first step of dry processes. This process can be applied on denim garments in different ways including by spraying the resin solution or dipping the garment in resin solution. Different resin solutions give denim garments different effects. After resin application, jeans must be cured in ovens at the right temperatures and time to get the perfect result. Resin can be applied on jeans manually with a brush and with a sponge for partial applications. After resin application, the jeans are manually folded to obtain whole garment crush, partial crush or special streaky effects. The creases are formed on the high, hip and back knee or over the ankle to get 3D effects with different methods. After creasing, the jeans should be dried manually with a hot press and then must be cured in an oven at right temperature [2, 3]. Enzyme washing is an alternative method and has almost replaced stone washing. In denim fabrics, due to enzymatic abrasion, dye is released from yarns, giving contrasts in the blue colour. The fibrillation produced during ageing process is a result of the action of cellulases and mechanical action. The pumice stones damage the washer drum and reduce the fabric strength due to abrasion in the stone washing process. The application of cellulases prevents damage to the machine and garments. Moreover, the use of cellulases results in a softer fabric hand, and strength loss is lower when compared with stone washing. [3, 11]

The curing temperature and time are important variables to control so as to obtain good cross linking and low formaldehyde release in treated cotton fabrics. Fabrics treated with urea-formaldehyde and dihydroxymethylethyleneurea are easy to cure; however, cotton fabrics treated with these reactants need to be cured as soon as the fabric is dried, so that the reactants will not self crosslink. DMDHEU and carbamate are in the hard-to-cure category where fabric curing temperature must exceed 130 °C therefore, fabrics can be left for a long time before post curing [7, 8]. Selecting the proper catalysts is important because stronger acids are required to catalyze the reaction of some less reactive crosslinking reagents, but the stronger the acid, the more damage to the cellulosic fibers through hydrolysis. The most commonly used catalysts for N-methylol compounds are zinc nitrate, magnesium chloride, or a combination of magnesium chloride and citric acid. [7, 8] The aim of this paper is to investigate the effect of modified DMDHEU and copolymer acrylic resin treatment, fabrics characteristics, resin nature and finishing conditions (resin concentration, curing temperature, curing time, drying temperature and drying time) after enzymatic washing on mechanical properties of cotton fabrics,

in warp and weft direction fabrics using design of experiments. Afterward, it evaluates the impact of this resin treatment before and after washing on 3D rank and 3D thickness of treated cotton fabric.

## II. Materials And Method

In this experimental study, we apply a resin treatment on three cotton denim fabrics (different in weft composition) among the most used in industry. More details gives in table 1.

**Table 1** Fabrics characteristics

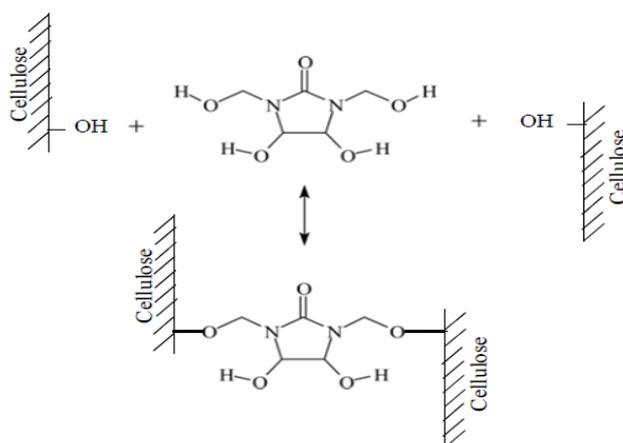
Fabric	Count Warp	Warp composition	Count Weft	Weft composition	Density (Warp/Weft)	Weight (g/m <sup>2</sup> )	Breaking strength (N)	Elongation At break (%)	Tear strength (N) (warp)	Tear strength (N) (weft)
F 1	17	100% Cotton	24	95% Cotton +5% Elasthanne	25/20	322	231,93	17,54	62,8	34,31
F 2	12,5	100% Cotton	20	24% PES +71% Cotton +5% Elasthanne	26/17	390	209,23	16,14	62,8	41,45
F 3	12,5	100% Cotton	20	100% Cotton	26/20	390	348,71	22,11	61,75	45,43

In experimental, we used two types of finishing resin and appropriate catalysts. These full chemical products are from “PROCHIMIC” company. The details of them are presented in table 2.

**Table 2** Properties of used resin

Resin	pH (20°C)	Viscosity (cPo) (20°C)	Density	Agent description	Catalysts	Catalyst description
Modified DMDHEU	3 - 5,5	184	1,3	Modified DMDHEU (diethylene glycol 15 – 22 % and Formaldehyde < 0,1%, and methanol < 0,5 %) crosslinks at 140°C	MG	Contains magnesium chloride : MgCl <sub>2</sub>
Acrylic	5,5 -7,5	107	1	Copolymer self cross linked, crosslinks at 100°C	PAZ	Water dispersion anionic, soluble of reticulate agent .It's totally y free of thoxylate alkylphenoles, plasticizing agents.

These resins selected are usually used for resin treatments of denim garments, permanent press and wash and wear treatments and to improve the durable press properties of fabrics. DMDHEU is an accepted resin widely used in wash-and-wear and Durable Press treatments. This resin used in the current experiments was with the ultra low amount of free formaldehyde [5]. The Cross linkage of cellulose with the modified DMDHEU resin, in presence of acid catalyst shown in Fig. 1. In addition, acrylic resin may form ester links with cellulose chains. [4]



**Fig. 1** Crosslinkage of cellulose with the modified DMDHEU resin in presence of acid catalysts MgCl<sub>2</sub> at 140-160°C for 5 min

**Finishing process**

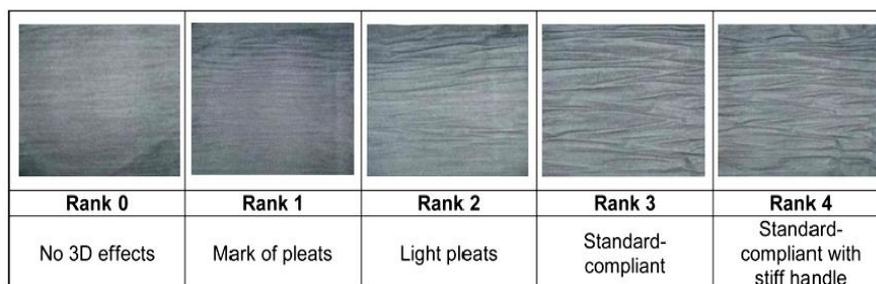
Spraying is different from the exhaustion method by applying the chemical only to the surface and to the desired parts of the denim garment. Air pressurised hand guns are used to spray the chemical on the surface of garments, which are placed on inflated vertical mannequins. Different chemicals are sprayed for different purposes. Instead of manual spraying, spray robot machines are now widely used in the laundries. [2, 3]. In our case, it sprays a resin solution manually with guns. In this experimental study of resin treatment, firstly we prepare the resin solution to pulverization, with defined finishing condition. The resin solution contains resin (or crosslinking agent), catalyst (with proportion of 20% from resin weight), water and others additives to improve the crosslinking. After a lot of test to control resin parameters (pH solution, pick-up % of treated fabric.), we fixed the cotton fabric on a special bracket to obtain fashioned 3D rank on different place of fabric. Finally, we use a spraying method to applied resin solution on the preformed denim fabric at ambient temperature room 25 ° C. After resin treatment, the treated fabrics samples, collectively, were desized with amylase “Ecoprep” 2g.l<sup>-1</sup> and softened with “CHTTACC” 1g.l<sup>-1</sup> for 10 min at 50°C, washed with enzyme “Novasi ultra MC/M” 2g.l<sup>-1</sup> for 20 min at 50°C. Finally, the treated fabrics are dried collectively for 20 min at 90°C and conditioned. The design of experiments DOE applied is presented in table 3.

**Table 3.** Design of experiments plan

Condition index (Si)	Resin code	Resin name	Pick up %	Resin Concentration (g.l <sup>-1</sup> )	Drying temperature (°C) TS	Drying time (min) DS	Curing temperature (°C) TP	Curing time (min) DP
1	1	Modified DMDHEU	67	60	80	10	110	15
2	1	Modified DMDHEU	80	150	80	10	110	15
3	1	Modified DMDHEU	69	60	100	10	110	15
4	1	Modified DMDHEU	74	60	80	5	110	15
5	1	Modified DMDHEU	78	60	80	10	140	15
6	1	Modified DMDHEU	76	60	80	10	110	30
7	2	Acrylic Resacryl M	70	60	80	10	110	15
8	2	Acrylic Resacryl M	88	150	80	10	110	15
9	2	Acrylic Resacryl M	71	60	100	10	110	15
10	2	Acrylic Resacryl M	77	60	80	5	110	15
11	2	Acrylic Resacryl M	75	60	80	10	140	15
12	2	Acrylic Resacryl M	73	60	80	10	110	30

To investigate the influence of resin characteristic on the surface properties of treated cotton fabrics, the surface morphology of untreated cotton and treated samples with used resins obtain after washing, were examined with SEM (Scanning Electronic Microscopy) ‘Hitachi SU 3500’. A sputter coater was used to pre-coat conductive gold onto the surface before observing the microstructure at 22 kV. All samples have morphology of 1500 times magnification.

For the mechanical properties including (grab strength and breaking elongation) of treated samples are evaluated in warp and weft direction with the LLYOD LS5 tensile tester according to the standard ISO 2062 (2014). For the tear strength properties is determinate with a ballistic method according to ISO 13937-1 using apparel “Elmendorf 275A”. The samples are conditioned during 24 hours in the relaxed state (22°C, 60% RH) according to the norm ISO 13934-1. For the 3D thickness is according to ISO 5084. The 3D ranks were evaluated by fastness to wash, the maximal thickness of the area preformed [10]. It is estimate by rating the appearance of specimen in comparison with appropriate reference standards made with the association of an industrial panel as described in Fig. 2. Rank 3 is the desired effect: it is standard compliant.

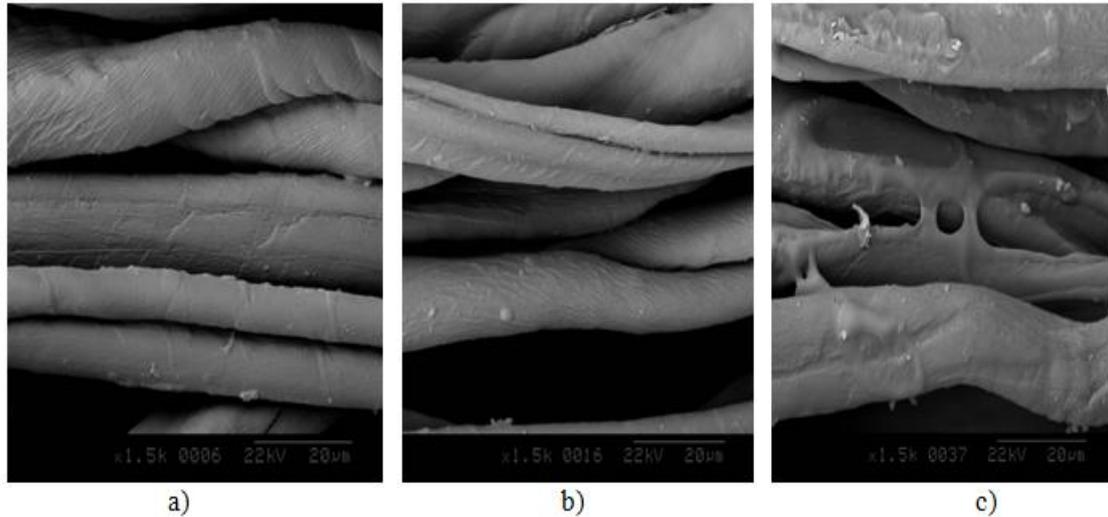


**Fig. 2** 3D standard

**III. Results and discussion**

**Analysis morphology surface with SEM**

The cotton fabrics were examined with SEM (scanning electronic microscopy) and micrographs are shown in Fig. 3.



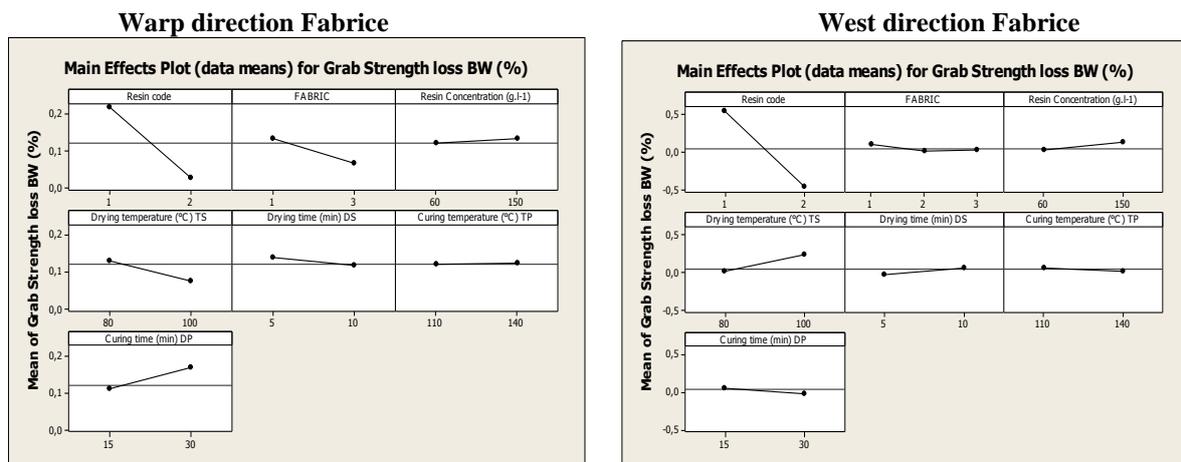
**Fig. 3** SEM micrographs: a) Untreated b) Treated with Modified glyoxalic agent c) Treated with acrylic agent (at same finishing conditions)

As can be seen in Fig. 3 (a), the untreated fibers have rough surface with a lot of grooves and imperfections on surface. When comparing (a) to (b) and (c), it could be found that fibers were coated with finishing agent and there were a lot of significant cross-linking between adjacent fibers after resin treatment. It is distinguished that hydroxyl groups in modified DMDHEU resin react with hydroxyls groups of two cellulose chains as well as those of one chain [19]. The acrylic agent covers the totality of the fibers and the spaces inter-fiber seen in Fig. 3(c) that probably is at the source of changes on the mechanical properties that will be discussed later. Copolymer acrylic resin seems to be a coating film on the surface fibers and between the fibers. [20]

**Analysis of main effect and interaction plot**

**Analysis of main effects plot**

Using Minitab software, the graphic of main effect of mechanical properties, 3D ranks and shrinkage (for warp and west direction, before and after washing) of treated fabric with all factors design of experiments is presented in Fig. (4, 6, 7, and 9)



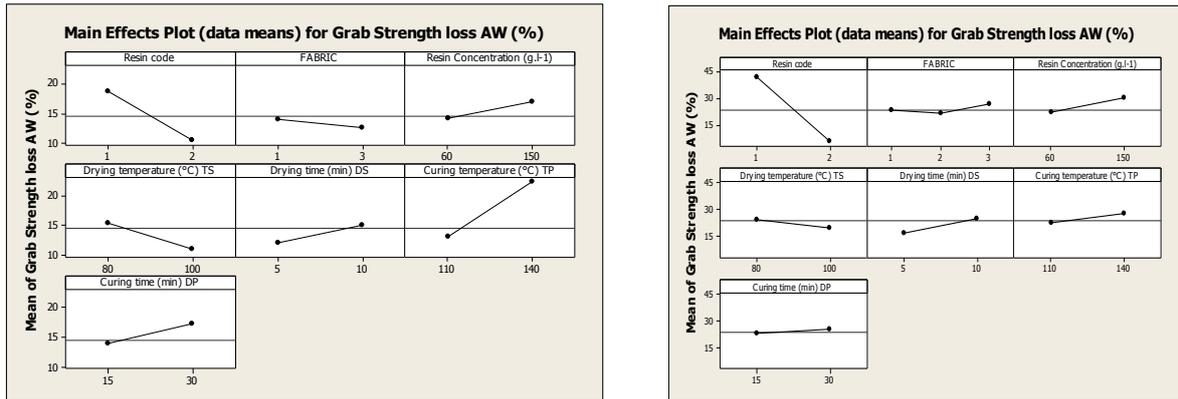


Fig. 4. Graphic main effect plot of grab strength loss before and after washing for warp and weft direction

Referred to Fig. 5, it's cleared that before BW and after AW enzymatic washing in warp and weft direction; the grab strength loss is important with modified DMDHEU resin (1) that with acrylic resin (2). In addition, all fabrics F1, F2 and F3 are slightly affected in warp and weft direction. Before washing BW, the fabric F3 resist more than F2 and F1 to the resin action in terms of grab strength loss ( $F3 > F2 > F1$ ), while, after wash AW, we have a opposing result ( $F1 \approx F2 > F3$ ), this result is probably due to the enzyme and additives products effect on fabric structure (F3 is 100% cotton w/w). For resin concentration and curing temperature have the action on breaking strength in warp the same as warp direction BW and increases proportionally AW in warp and weft direction. After wash, drying time increase and drying temperature decrease respectively, with the garb strength loss for the warp and weft direction of all fabrics. In warp direction of fabric and before BW and after wash AW, the grab strength loss increase about (5%), it is effecting by the curing time increase. Whereas, in weft direction, the grab strength loss showed unaffected at what time the curing time increase.

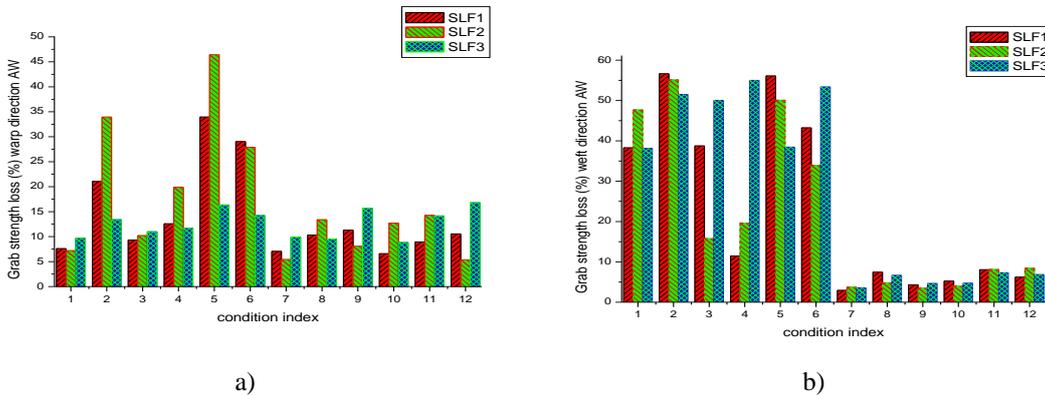


Fig.5 The grab strength loss (SL) variation after wash AW in warp direction (a) and weft direction (b)

Shown to Fig. 5, that offered the grab strength loss (SL) of three treated fabrics according to condition index, in warp and weft direction after wash AW. It's clear that the equivalent result obtained, in warp and weft direction fabric; the fabrics (F1, F2, F3) have the higher value of strength loss under effect of modified DMDHEU resin in conditions (2, 5 and 6) explained the consequence of high curing temperature, higher curing time and important resin concentration, respectively. Also, the same result is obtained with effect of acrylic resin for the conditions (8, 11 and 12). In reality, there are many reasons for strength loss, and most of the reasons are directly related to mechanical and chemical washing processes. Synthetic stone sizes, oxidizing agents, enzymes, acids, chemical agents, resin application, sanding and brushing strength, incorrect grinding and destruction and laser intensity are the possible reasons for strength loss. Cellulose fibre can be degraded chemically by action of oxidizing or reducing agents and acids. These chemicals attack the structure of the polymer, and so the polymer is destroyed and strength loss occurs [2]. Physical forces such as extreme abrasive processes may also reduce the strength of some parts of the garment. The influence of resin treatment, permanganate spray, bleach, stone washing, enzyme washing, combined washing (stone + enzyme) and final finishing procedures on the mechanical properties of denim fabrics has been studied [3, 12], and it was found that washing processes reduce the mechanical properties especially of the warp yarns of the fabrics. Resin treatment is found the most degrading treatment, which reduces both tearing and breaking strength of denim fabrics.

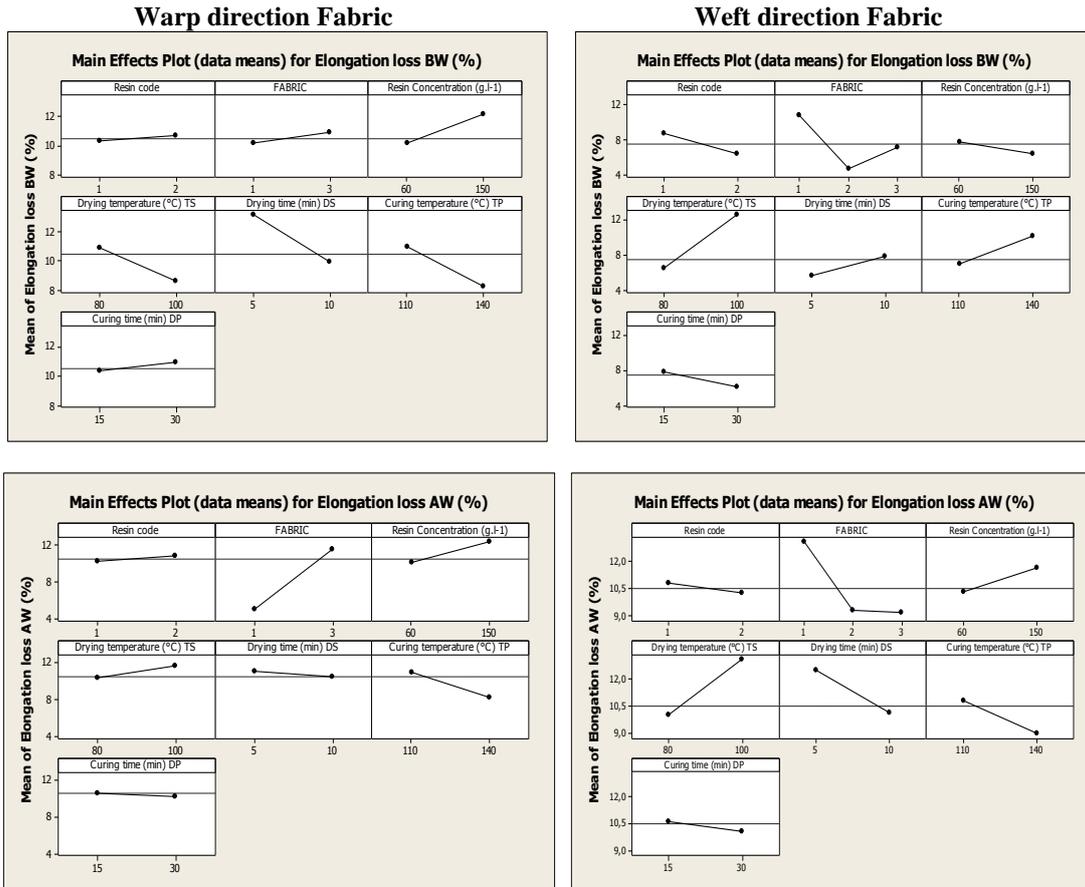
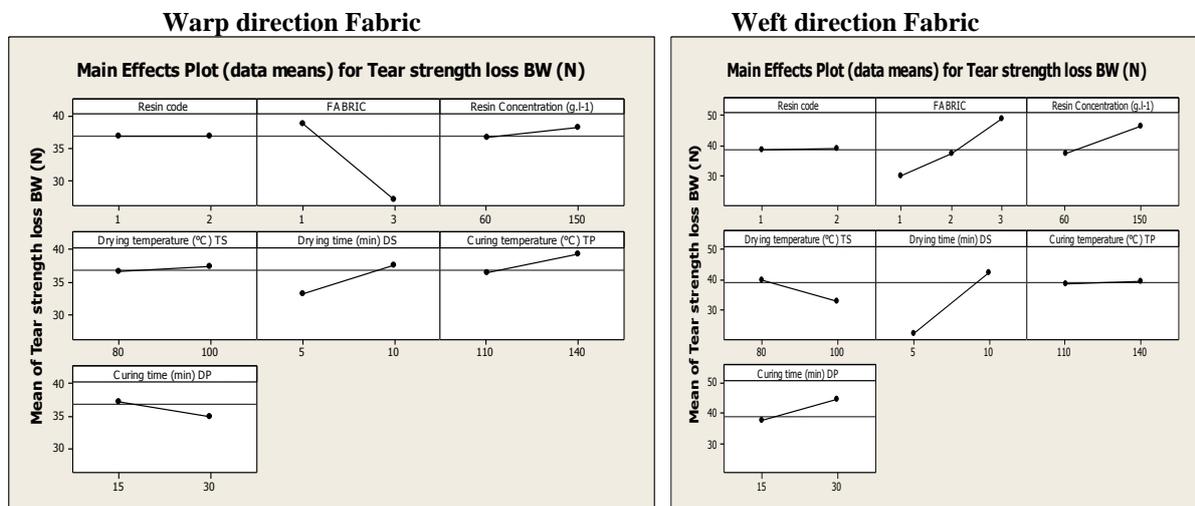


Fig.6 Graphic main effect plot of elongation loss before and after washing for warp and weft direction

Referred to Fig. 6 that present graphic main effect plot of elongation loss before and after washing for warp and weft direction, it's clear that BW, all factors experiments (curing temperature, curing time, drying temperature and drying time and resin concentration) progress in warp direction opposing to the same factors in weft direction as soon as these factors effect on elongation loss by increase or decrease. In addition, after wash AW, in warp direction, only the factor time (drying and curing) has slightly effect on the elongation loss variation. Nevertheless, after wash AW, in weft direction, all factors have persuaded on elongation loss value (%) of treated fabric. In warp direction, the fabric elongation loss is different ( $F3 > F2 > F1$ ), because the distinction of weft account, fabric composition and density. However, in weft direction, the elasticity of fabric (weft composition) has an effect on the elongation loss variation. So, the result showed that ( $F1 > F2 \approx F3$ ) in term elongation loss.



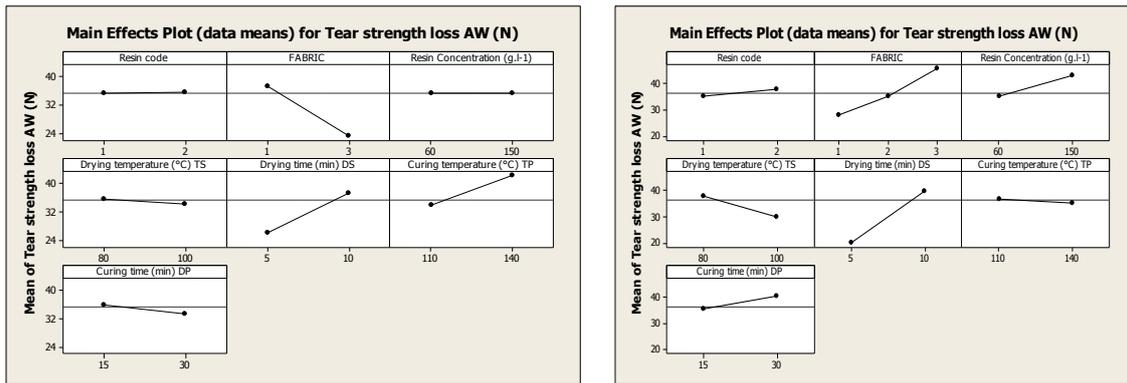


Fig. 7 Graphic main effect plot of tear strength before and after washing for warp and weft direction

Fig. 7 presents the main effect plot of tear strength before and after washing for warp and weft direction. We showed that tear strength in warp and weft directions increases with the increase of the concentration of modified DMDHEU resin or acrylic resin. However, the tear strength is affected at the same degree with used crosslinking agent in warp and weft direction before or after wash, correspondingly. Acrylic resin has a small effect on the response and a small increase is noted from a concentration over  $60g.l^{-1}$ , While for modified DMDHEU resin has a significant effect on the response from a concentration over  $60g.l^{-1}$ . The warp direction is more affected and this is may be due to the effect that the finish solution is sprayed on the right side of the denim fabric, so that the warp yarns are more apparent in twill construction. Cellulose fibers cross linked become more bottled by the restriction of stress distribution within the fibers due to their rigid cross linking by monomeric resins, so, flexibility and extensibility responsible for strength is reduced [21, 22]. The problems related to resin applied products are strength loss and tear, and for this reason the physical properties of the selected denim fabric should be very good. Before resin application, the denim fabric must have sufficient strength to resist (40– 50%) loss in tensile and tear strength. The application of resin must be homogeneous, otherwise colour differences and stains occur on treated fabric. In addition, the fabric must have excellent absorbency to allow resin to penetrate into the very interior of the fibres, and for this reason a high degree of size removal is essential before resin application [2]. After resin application, the fixing temperature and time in the oven must be situate same for all repeated resin solution, in order to conserve mechanical properties.

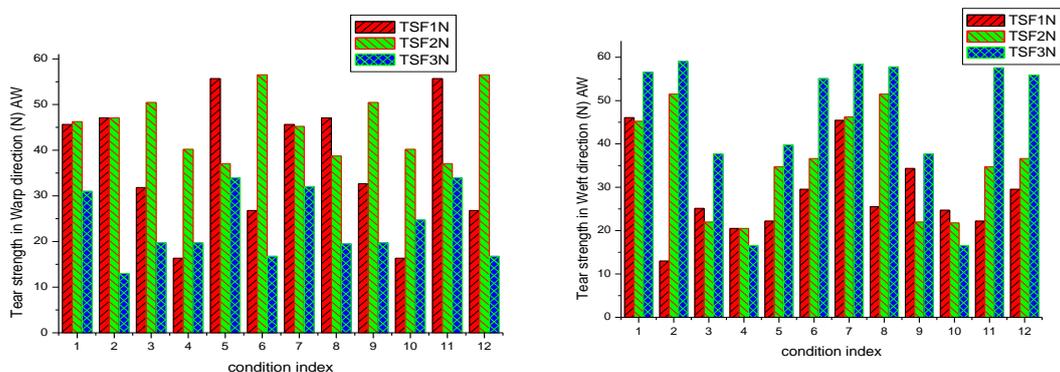
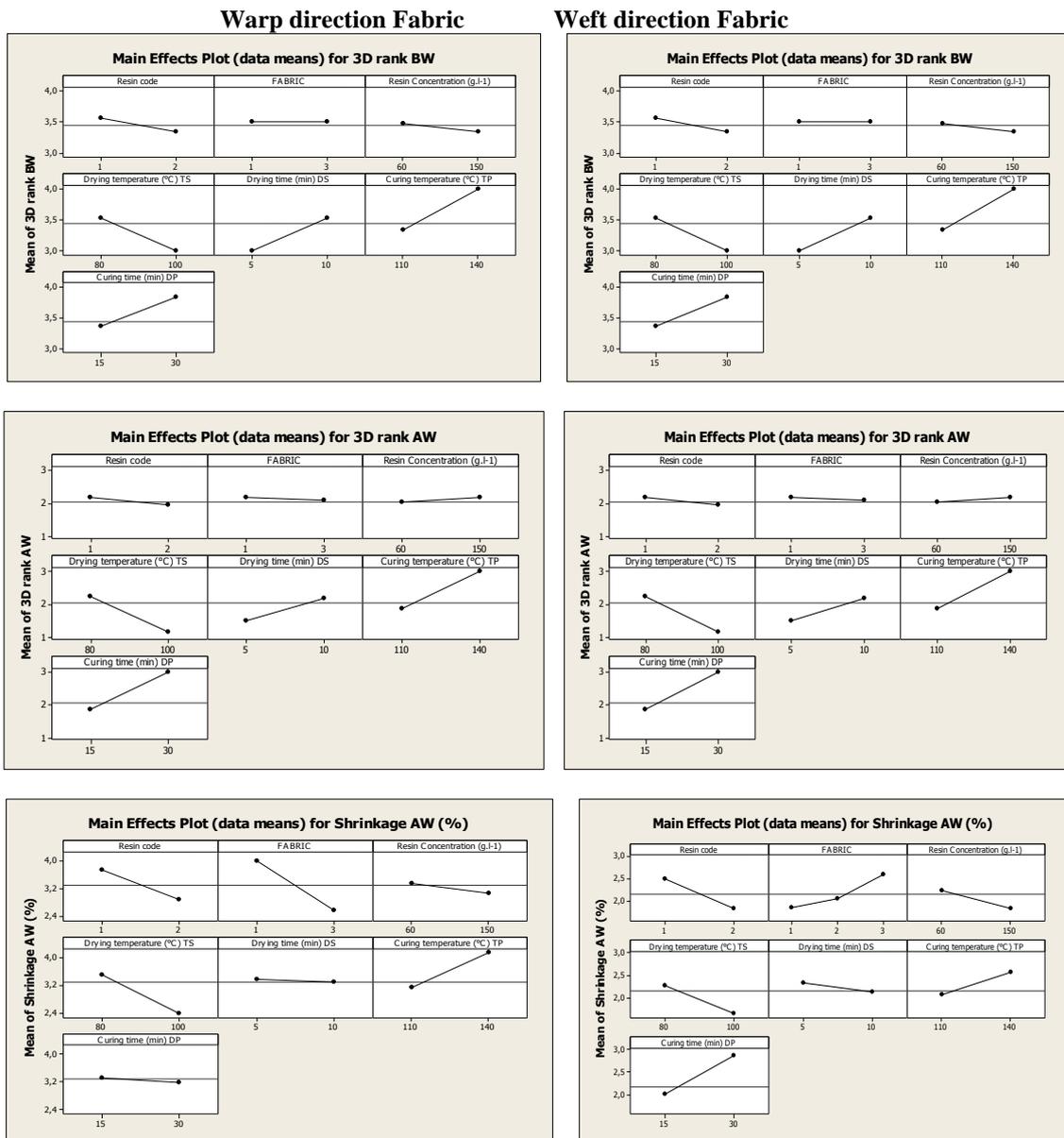


Fig.8 a) Tear strength loss (%) in warp direction AW Fig.8 b) Tear strength loss (%) in weft direction AW

Fig.8 The tear strength loss of treated fabric in warp and weft direction after washing. Fig 8. Present the tear strength loss of treated fabric in warp and weft direction after washing. It's clear that, the tear strength loss of fabric F1 (stretched weft yarn) is more affected in warp direction; minimum 15% for condition 4 and 57% for conditions 5 and 11 (Fig 8 b). This results confirmed that the predisposition of F1 at modified DMDHEU resin concentration or copolymer acrylic resin for higher curing temperature  $140^{\circ}C$ , while in weft direction, tear strength loss is more affected (45% and 46%) in condition 1 and 7 respectively (Fig 8 b). In warp direction, for the fabric F2 that has a weft yarn composition contain 24% polyester gives disadvantage to the tear strength more affected. However, in weft direction, it's clearly that the tear strength loss values under the tear strength loss values for fabric F3 (100% cotton). We conclude that, the factors higher curing temperature (for conditions 5, 11) higher curing time (for conditions 6, 12) and resin concentration (for conditions 2, 7) are the most significant factor on tear strength of finished fabric with modified DMDHEU resin concentration and/or

copolymer acrylic resin. In addition stretched yarn (weft), play a important position on tear strength of finished fabric. This variation of tear strength is probably do the no uniformity of resin application on surface treated fabric as well due to the using of spray method parameters, also the enzyme wash effect ,as well the drying and curing conditions. Researchers announced that, pointed out the tearing phenomenon in textiles are a complex and hard problem due to the fact that the parameters of stretched as well as tearing thread system influenced the tearing process. Durable press finishing is one of the most important processes to improve the wearing properties, especially, of the cotton garment. However, the durable press finishing would negatively affect the tearing strength of cotton woven fabrics [13-15]. As a result, it is worth to investigate the relationship of durable press performance and tearing strength of the cotton woven fabrics [16, 17]. Researchers announced that, the analysis and the mechanism of the cotton woven fabric tearing strength after durable press finished. They were indicated that keeping or enhancing yarn extension and crimping which lead to a higher (variation of tear)  $\Delta L$  during fabric tearing process is of critical important to maintain durable finished fabric tearing strength. [18].



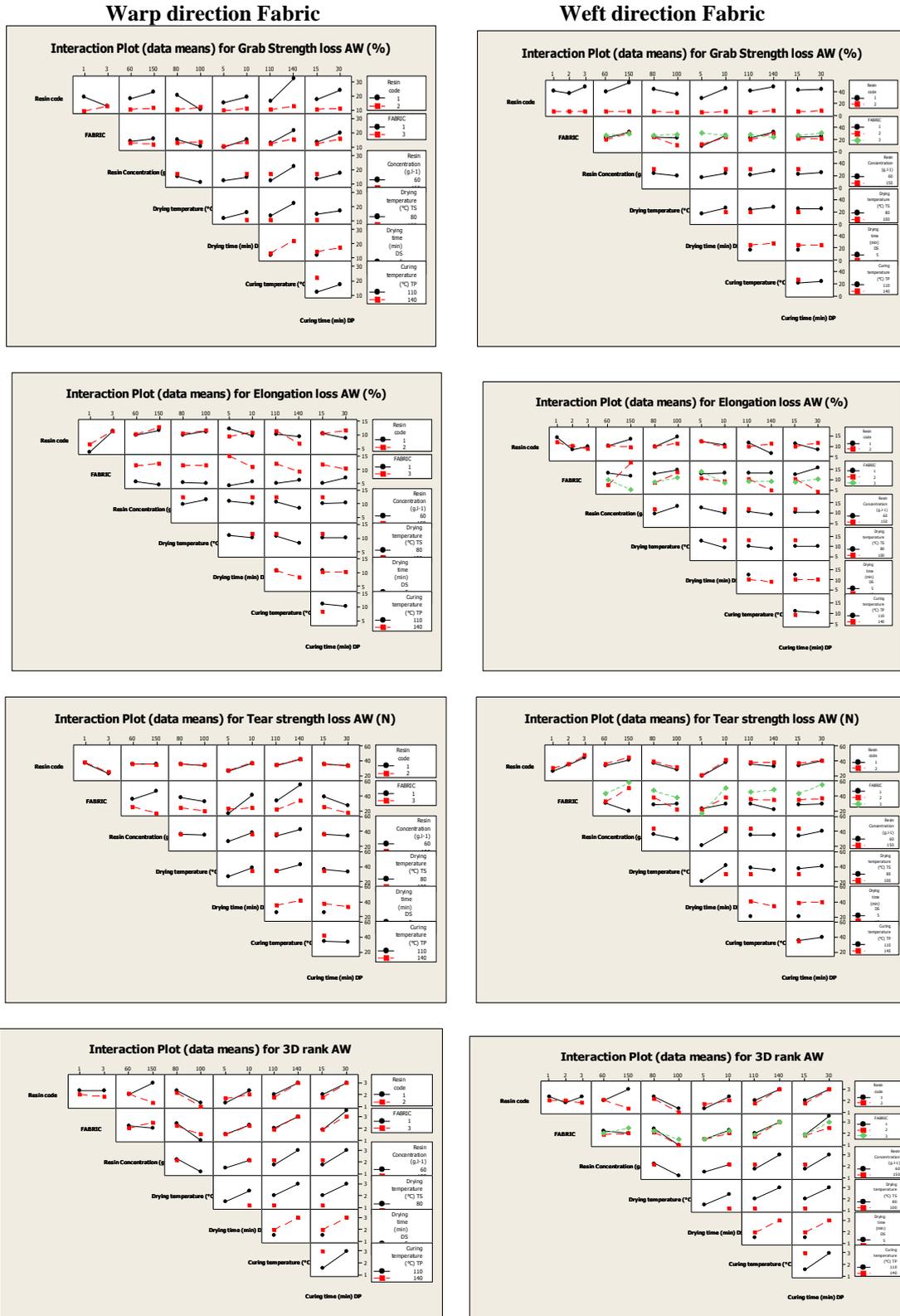
**Fig. 9** Graphic main effect plot of 3D rank, shrinkage before and after washing in warp and weft direction

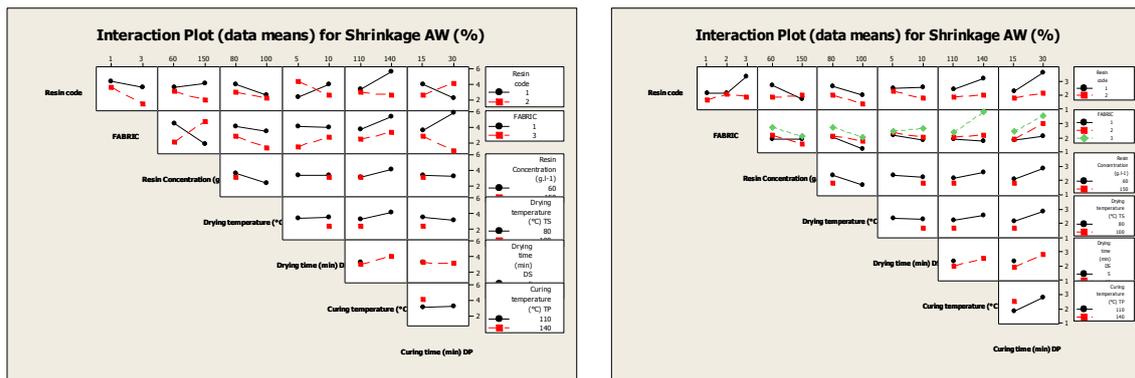
Referred to Fig. 9 that present graphic main effect plot of 3D rank, shrinkage before and after washing in warp and weft direction, it's clear that for response 3D rank of treated fabrics, in warp and weft direction has the same progress before or after wash according to the variation of majority of factors. In fact, to achieve a permanent 3D (rank) effect in certain areas of a garment, the application of cross linking agents in combination with acrylic resins is a common practice. The use of the e-flow technology to apply the resin solution will have

important benefits in terms of water and chemical wastage in comparison with the conventional garment application systems. [3].

**Analysis of interaction plot**

The graphic of interaction plot of mechanical properties, 3D ranks and shrinkage (in warp and weft direction) of treated fabric with all factors design of experiments is presented in Fig. 10





**Fig. 10** Graphic interaction plot of mechanical properties, 3D rank, fabric shrinkage with factors DOE in warp and weft direction after wash

The interaction plot is a representation of the answers information averages for every factor level. The level of the second factor remained constant. This plot is useful to judge the presence of interaction. An interaction is present if the answer for a parameters level depends on/or the other parameters levels. In a diagram of the interaction, some parallel lines indicate the absence of interaction [9]. More the lines depart from the parallel; more the degree of interaction is raised. Refereed to Fig. 10 which present graphic of interaction plot of mechanical properties loss (grab strength, elongation loss and tear strength), 3D ranks and treated fabric shrinkage, we obtain an interaction for all responses with all factors of DOE. It determines that, the curing temperature, curing time, resin concentration and resin nature are the most influencing factors for modified DMDHEU and acrylic resin treatment. Also a significant interaction connects these four parameters. There is a significant interaction between the curing time and the resin concentration which is relatively logical because if we increase the resin concentration, it requires more time to complete the polymerization. Also there is an interaction between the curing temperature, resin concentration and the catalyst concentration because it accelerates the reaction and then it reduces the curing time. From previous results, we can conclude that, the curing temperature, curing time and resin concentration are the primary factors which greatly affect mechanical properties loss, the quality of 3D rank, 3D thickness variation and fabric shrinkage in terms of fabric direction (warp /weft), characteristic (yarns account have dissimilar composition) and the significant effect of enzymatic washing.

#### IV. Conclusion

To recapitulate this paper, it has clarified that modified DMDHEU and acrylic resin using spraying treatment is related directly too many finishing parameters. In essential, the curing temperature, curing time and resin concentration are the great influencing parameters of resin treatment process. Obtained results clarify that before and after washing the modified DMDHEU resin effect more than acrylic resin the mechanical properties, (breaking strength, breaking elongation and tear strength) especially, for F1 (100% cotton) compared to others fabric F2,F3 (weft composition contain Polyester or 5% Elasthanne). For the 3D rank of treated fabric with dissimilar resins, results make clear that enzymatic washing one of many factors cause increase of 3D rank level and more than before washing level. It conclude that, the curing temperature, curing time and resin concentration are the primary factors which greatly affect mechanical properties loss, the quality of 3D rank, 3D thickness variation and fabric increase of shrinkage in terms of fabric direction (warp /weft), fabric characteristic (yarns account composition) and the significant effect of the enzymatic washing on surface fabric.

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