IOSR Journal of Engineering (IOSRJEN) **www.iosrjen.org**
ISSN (e): 2250-3021, ISSN (p): 2278-8719
Vol. 05, Issue 03 (March. 2015), ||V1|| PP 27-32

Synergistic Effects of Varing Combined Mass Of Catalyst ($Mgcl_2$ And Citric Acid) On The Rheological Properties Of Urea And Melamine Formaldehyde Resinated Cotton Fabrics

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***Abstract:* -** Tri and tetra methylol urea, penta and hexa methylol melamine resins were synthesized at various combined mass of catalyst ($MgCl_2$ and citric acid) and the rheological properties were investigated. The results show that the refractive index of 10% tri and tetra methylol urea resins gave maximum values of 1.339 and 1.336, 10% penta and hexa methylol melamine resins gave maximum values of 1.340 and 1.335 at 1.0 and 0.5g mass of catalyst. Melting point results of 10% tri and tetra methylol urea resins gave maximum values of 215^{o}C and 175°C,while10% penta and hexa methylol melamine resinated cotton fabrics gave maximum values of 250°C and 200°C at l.0 and 0.5g mass of catalyst .Dry crease recovery angle of 10% tri and tetra methylol urea gave maximum values of 76^0 and 65^o, while that of 10% penta and hexa methylol melamine gave maximum values of 77 and 80° at 0.5g of catalyst mass in weft direction. In warp direction, the dry crease recovery angle of tri and tetra methylol urea resin gave maximum values of 80° and 65^o at 0.5 and 1.50g of catalyst mass respectively, while penta and hexa methylol melamine resinated cotton fabrics samples gave maximum values of 83° and 68° at 0.7 and 1.50g of catalyst. The result of the breaking load experiment revealed a gradual increase in tear strength of resinated fabrics as the degree of substitution and mass of catalyst increases. Tri and tetra methylol urea gave maximum values of 8.0kgf and 5.2kgf, while penta and hexa gave l0.0 kgf and 5.8kgf, at l.0g mass of catalyst in weft direction .In warp direction, tri and tetra urea methylol resinated fabrics gave maximum values of 9.2kgf and 5.2kgf at 0.75 and 0.5g of catalyst mass, while the results of penta and hexa melamine methylol resinated samples gave maximum values of l0.0 kgf and of 6.0kgf at catalyst mass of 1.50g. The catalyst proved friendly on cotton samples even at higher concentrations. The overall results suggest that cotton fabrics may be resinnated with combined catalyst mass to impact synergistic properties.

Key words: *Combined Catalyst Mass, Refractive Index, Dry Crease Recovery, Breaking Load, and Synergistic Effect.*

I. INTRODUCTION

Methylol urea and Melamine named for their common synthetic pathways and overall structure is a transparent thermosetting resin made from condensation reaction between the nucleophilic nitrogen of urea and melamine and the electrophilic carbonyl carbon of formaldehyde (Wikipedia, 2007), in the presence of catalyst to form a branch copolymer. The presence of catalyst in the reaction increases the number of collision between active centres and monomers. These lead to the production of resins with a higher molecular mass viscosity, refractive index and density (Othman, 1978). When the catalysts are added, there is a new path hence a different activation energy barrier. Acid catalyses the reaction of the N- methylol compounds with cellulose. The stronger the acid, the faster the reaction. Maxwell-boltzmann (2002), explained that catalyst provides an alternative route for reaction. That alternative route has lower activation energy, The new reaction path corresponds to a new mechanism that permits the reaction to occur via the different activated complex, thus particles can get over the new lowered energy barrier and the rate of reaction increase (Ezeribe and Bello, 2007). The most common catalyst for N-methylol compounds are Zinc nitrate, magnesium chloride, potassium dihydrogen phosphate, citric acid or combination of magnesium chloride and citric acid (Cook *et al*, 1982). Each of the catalyst type has one advantage over the other but a combination may lead to synergistic effect on the rheological properties of methylol resins on treated cotton fabric (Peterson, 1987) Naturally, cellulose fabric is prone to crease thus distorting aesthetic appeal on the surface of fabric (Ezeribe and Bello, 2007). These make resin-finishing treatment an important operation. In addition, it confers smooth drying, high strength greater elasticity and smoothness of fabrics (Ezeribe, 2007). Hypothetically, the hydroxyl group in methylol resin may react with the Hydroxyl group in the cellulose. The reaction forms a resin fibre - net work during curing process. The cross linkage formed between the resin and the fibre provide excellent anchorage in the substrates.

II. EXPERIMENTAL PROCEDURES

Fabrics Purification

The fabrics were chemically purified and pre treated by scouring, bleaching, mercerization and then resinated with methylol urea and melamine.

Resins preparation

Preparation of methylol urea and melamine resins

Polymerization of urea and melamine formaldehyde resins were carried out in two stages (Trotman, 1975). The low molecular mass fusible and soluble resins were prepared by reacting 1 mole of urea with $90cm^3$ and $120cm^3$ formaldehyde to yield tri and tetra methylol urea resins respectively, in 0.5g, 0.75g, l.0g 1.25g, and 1.50g of magnesium chloride and citric acid. Few drops of sodium carbonate solution were added to maintain the pH at about 8-7 at 40°C for 8-12 hours. The resulting syrup was dried in the oven for 2 hours at 40° C.

Preparation of methylol melamine resins

I mole of Melamine was reacted with 5 and 6 moles of formaldehyde to produce penta and hexa-methylol melamine respectively. Here, melamine weighing 126g was dissolved in $90cm^3$ and $120cm^3$ of formaldehyde to produce penta and hexa-methylol melamine respectively in 0.5g, 0.7g, l.0g 1.25g and 1.50g of magnesium chloride and citric acid. Few drops of sodium carbonate were also added to maintain the pH at about 7-8, at 40°C for 8-12 hours. 10% resins of four substitutions of tri, tetra methylol urea and penta and hexa methylol melamine resins were prepared by dissolving l0g of each sample in 100ml of distilled water and were thoroughly mixed together using a magnetic stirrer on an electric hot plate at 40°C for 30 minutes (Trotman, 1975).

Refractive Index determination

The test samples were diluted to 10% and dropped at the lower lens of Abee Refractometer and spread evenly using a glass rod. Then the lens was sealed with the upper lens and the refractive index was determined through the eyes piece-lens. The refractive index is a point at which the velocity of light changes as it moves from less dense medium to denser medium. The refractive index is given by;

Sin i /Sin r = refractive index (Rl)

Melting point Determination

The melting point apparatus was switched on and allowed to warm up for 20 minutes. The already dried 10% resin samples were packed in a capillary tube. Each of tri and tetra methylol urea and penta and hexa melamine formaldehyde resins at various catalysts mass was inserted together with thermometer into their respective compartments. The melting temperature of each sample was taken and recorded in degrees.

Resin Application (Pad-dry-cure method)

The mercerized cotton samples were impregnated with 30mls each of 10% 0.5g to 1.50g of Magnesium Citrate ($C_6H_60_7Mg$) catalyzed tri, tetra methylol urea and penta and hexa methylol melamine for 30minutes followed by occasional padding on a smooth surface to achieve even treatment and also to remove excess resins. The samples were dried in the oven at 100°C for 45 minutes and cured at 150°C for 45 minutes

Breaking Load

Testometric tester model 220D, was calibrated and allowed to warm up for 20 minutes. The cotton sample measuring 1cm x 5.0cm both warp and weft directions were mounted on the instrument. The instrument was operated at a speed of 0l0mm/minute and the load extension values of the instrument were recorded for various 10% tri and tetra substituted methylol urea and melamine resinated cotton fabrics in (kgf) .

Dry Crease Recovery Angle

The test was carried out in accordance with the British Standard Specification. The device was calibrated and balanced to face the 0° mark. Resinated samples were folded end to end and held by tweezers, gripping not more than 5mm from the ends. The samples were then placed on the marked area of the lower plate of the loading device and the load gently applied to it. This was done face-to- face, back-to-back of samples. The samples were kept under this load for 5minutes. After which the load was removed and samples were allowed to recover for 5 minutes. The recovered samples were transferred to crease recovery tester in warp and weft directions. The crease recovery angle was then read and recorded in degrees.

III. RESULTS

Figure 1 shows the graph of varying combined mass of catalyst on the refractive index of 10% solution of tri, tetra urea methylol; penta and hexa methylol melamine resin. Figure 2 shows the graph of varying combined mass of catalyst on melting point of 10% tri, tetra methylol urea, and penta, hexa methylol melamine resins. Figure 3 shows the graph of varying combined mass of catalyst on dry crease recovery angle (DCRA) of 10% tri, tetra urea, and penta, hexa methylol melamine resinated cotton fabrics (weft) direction. Figure 4 shows the graph of varying combined mass of catalyst on DCRA of 10% tri, tetra methylol urea, and penta, hexa methylol melamine resinated cotton fabrics (warp) direction. Figure 5 shows the graph of varying combined mass of catalyst on the breaking load (kgf) of 10% tri, tetra methylol urea, and penta and hexa melamine methylol resin (weft) direction. Figure 6 shows the graph of varying combined mass of catalyst on the breaking load (kgf) of the 10% tri, tetra methylol urea, and penta, hexa methylol melamine resinated cotton fabrics (warp) direction.

IV. DISCUSSION

Effects of combined mass of catalyst on refractive index of 10 % tri, tetra methylol urea and 10% penta, hexa methylol melamine resins.

Resins are known to have varying degrees of opacity or transparency depending on the amount of light transmitted or reflected from the surface of resins. The gloss of resins is a function of refractive index of the surface and particle size (Barminas and Osemeahon, 2006). Also the gloss of resin is a function of refractive index of the surface, the angle of incident light, nature of light and the material (Trezza and Krochta, 2001). The effect of combined mass of catalyst on the refractive index of methylol urea and melamine resins is shown in figure l.

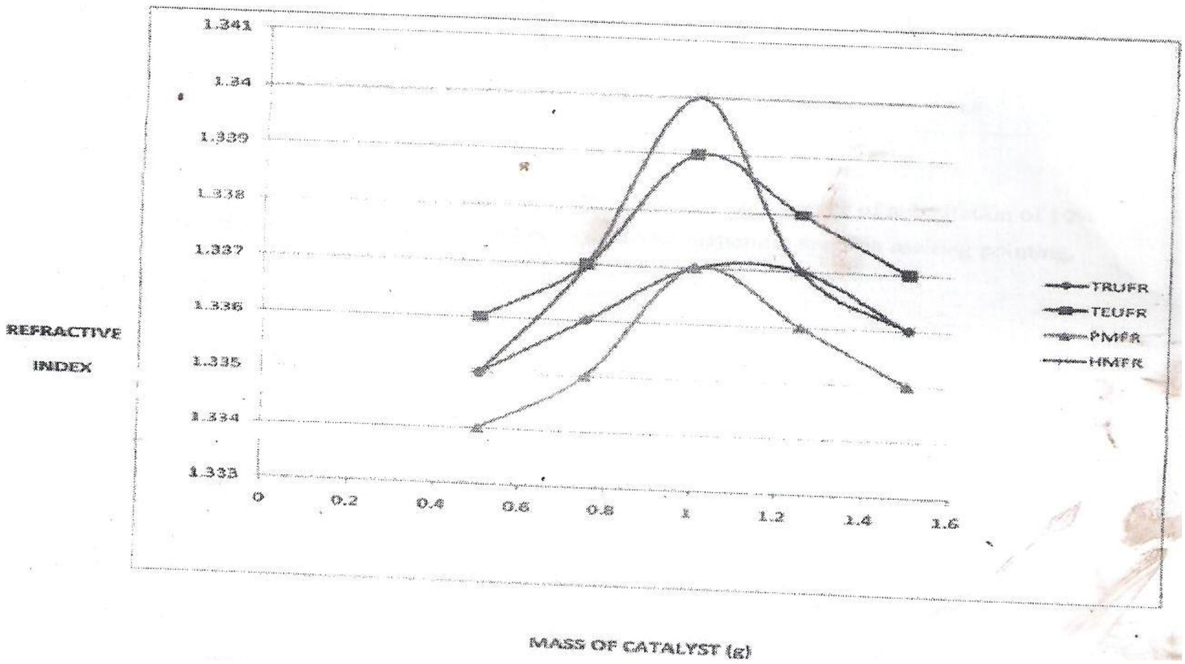

Figure 1: Effect of combined mass of catalyst and degree of substitution of 10% tri,tetra methylol urea,penta and penta, hexa methylol melamine resin on refractive index

It is observed from figure 1 that refractive index of tri-substituted methylol urea showed a gradual increase from 1.335 to 1.339 with increases in mass of catalyst from 0.5g to l.0g and decrease with further increase in mass of catalyst. The result of 10% tetra substitution of the same resin also revealed an increase in refractive index from 1.336 to 1.340 as catalyst mass increase from 0.5 to l.0g and thereafter decreases with further increase in catalyst mass. 10% penta methylol melamine resins gave an increase in refractive index from 1.334 to 1.337 and 10 % hexa substitutions an increase from 1.335 to 1.338 as mass of catalyst increase from 0.5 to l.0g, then decreases with further increase in mass of catalyst in both substitutions. The higher values of refractive index observed in hexa methylol melamine may be due to difference in molecular weight and features of the copolymer (Trezza and Krochta, 2001). The decrease in refractive index with further increase in catalyst mass is attributed to micro phase separation between the resins, mass of catalyst and interaction with light (Gupta *et al.,* 2001).

Effects of combined mass of catalyst on melting point of 10 % tri, tetra methylol urea and 10% penta, hexa methylol melamine resins.

The melting point of a polymer resin has a direct bearing on its thermal property, molecular weight, degree of cross linking and the level of rigidity (Osemeahon *et al,* 2007). Figure 2. Shows the effect of combined

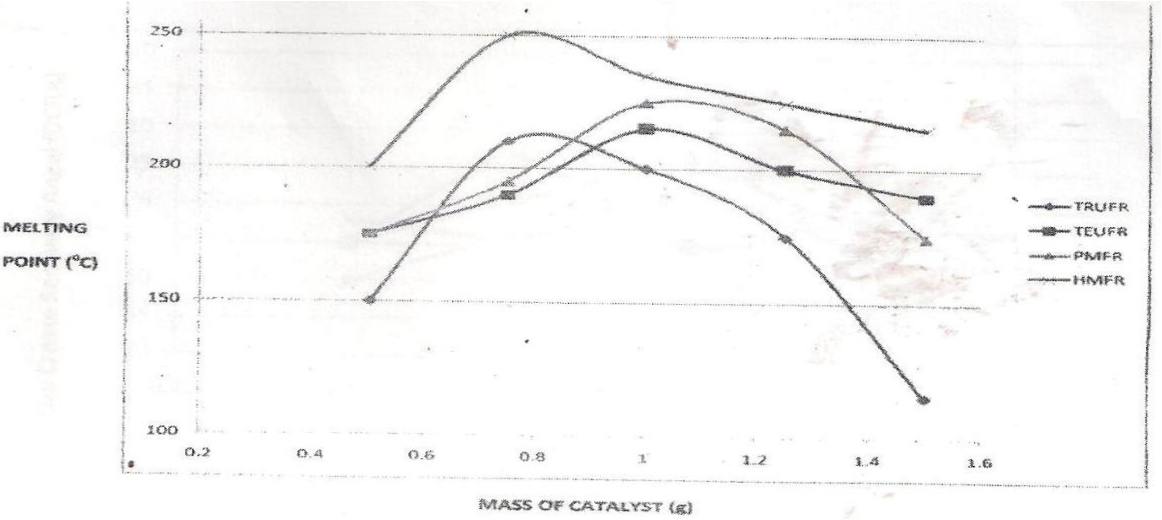

Figure 2: Effect of combined mass of catalyst and degree of substitution of 10% tri,tetra methylol urea and penta, hexa methylol melamine resin on melting point.

mass of catalyst on melting point of 10% tri and tetra methylol -urea resin and 10% methylol melamine. The graph of 10 % tri methylol urea resin shows increase in melting point from 150°C to 210°C, 10 % tetra methylol urea resin, increase in melting point from 175 to 225°C, while the 10 % penta methylol melamine resin, gave a gradual increase in melting point from 175°C to 275°C with increase in mass of catalyst mass from 0.5g - 1.0g and then decrease from 275°C to 165°C as the mass of catalyst increase from l.0g to 1.5g. The graph of 10% hexa-methylol melamine resin shows a progressive increase in the melting point from 200 to 250°C with increase in mass of catalyst of 0.5g to 0.75g and decreases with further increase in mass of catalyst. This trend can be explain in term of inherent nature of resin which is semi solid at cure state (Osemeahon and Barminas, 2006)

Effects of combined mass of catalyst and degree of substitution on dry crease recovery angle of 10% Tri, Tetra methylol urea and Penta, Hexa methylol melamine resinated cotton fabrics

Crease recovery is the ability of resinated fabric to regain its normal shape when stressed. The angle formed when stress is removed is known as angle of crease recovery. The results obtained as shown in figure 3, gave a gradual increase in dry crease recovery angle with maximum values of 75 and 76, 77 and 80° for tri, tetra urea methylol and penta, hexa substituted methylol melamine resinated cotton fabrics with increase in mass of catalyst between 0.75g and 1.0g in weft direction. The result also showed increase in crease recovery angle values of 78, 80° in tri and tetra substituted urea methylol resinated cotton fabrics and 78 and 73° for penta and hexa methylol melamine resinated cotton fabrics with increase in mass of catalyst of 0.5 and l.0g respectively at 150°C in warp

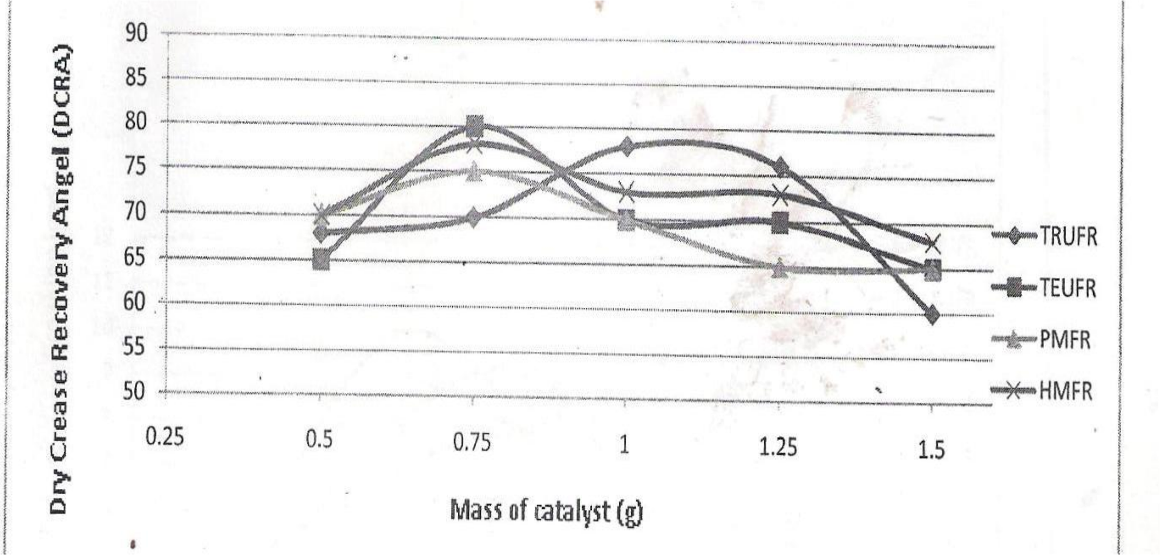

Figure 3: Graph of combine mass of catalyst and degree of substitution on dry crease recovery angle (SCRA) of 10% methylol urea/melamine resonated cotton fabrics (weft) cured at 150°C

direction. This increase in crease recovery angle is due to lowering of activation energy of reactant molecules thereby allowing more molecules of resin to participate in reaction. Creasing is due to weak Van der Waal forces which characterized amorphous region of cotton fabrics. It was observed that angle of relaxation in warp direction is greater than angle of relaxation in weft direction. This is chiefly due to numbers of threads present in both directions. The higher the number of thread count, the lower the recovery angle and vice-versa. Increase in DCRA is also not infinite since there are finite numbers of glucose residue per unit of cellulose molecules (Moji, 2000). This reason may account for the gradual decrease in DCRA as mass of catalyst increase. This result is consisted with the result of Ajayi *et al*.., (2001).

Effects of combined mass of catalyst and degree of substitution on breaking load of 10 % Tri, Tetra methylol urea and Penta, Hexa methylol melamine resinated cotton fabrics.

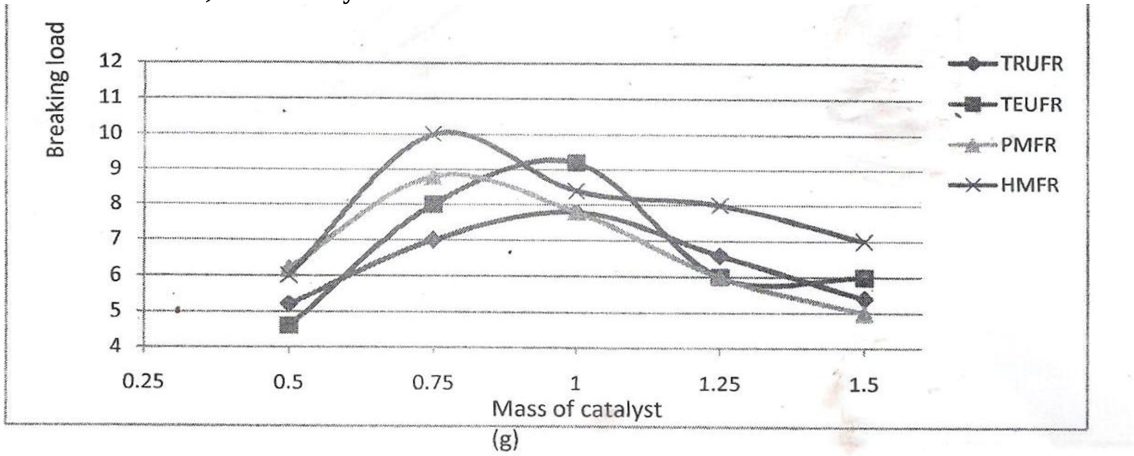

Figure 4: Combined mass of catalyst and degree of substitution on breaking load (Kgf) of 10 % Tri, Tetra methylol urea and Penta, Hexa methylol melamine resinated cotton fabric (weft) cured at 150°C

Effects of catalyst mass and degree of substitution on breaking load of 10 % methylol urea and melamine resinated cotton fabrics in weft and warp directions are as shown in figure 4 and 5. The results revealed that breaking load of tri and tetra urea methylol gave highest breaking load values of 7.8kgf and 9.2kgf, while penta and hexa substituted methylol melamine gave 7.0 kgf and 8.0kgf at l.0g of catalyst mass in weft directions respectively.

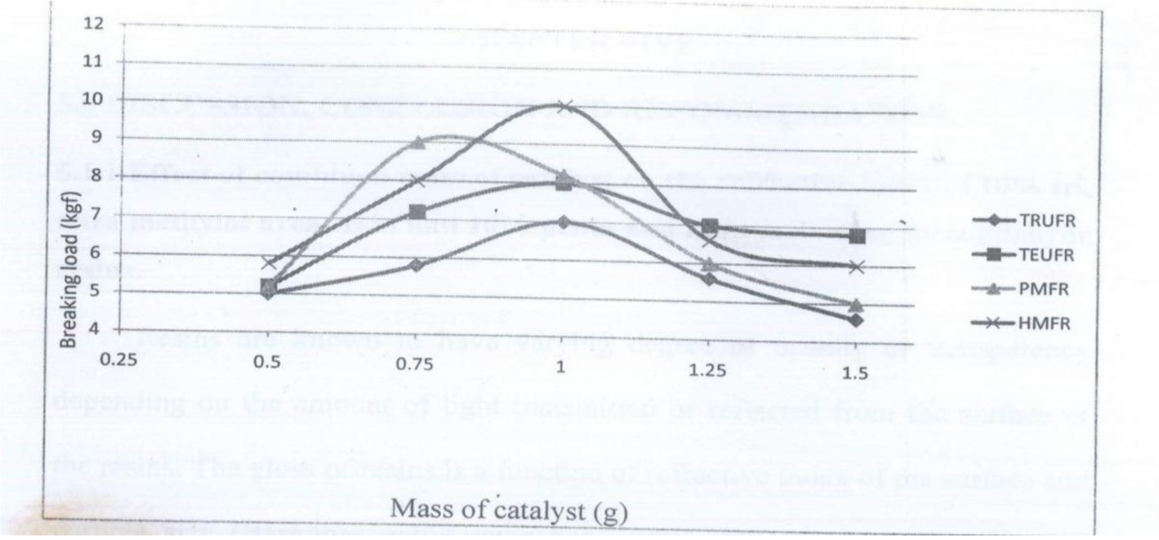

Figure 5: Graph of combined mass f catalyst and degree of substitution on the breaking load of 10% tri, tetra and penta and hexa methylol resonated cotton fabric (warp) cured at 150°C

While penta and hexa methylol melamine have values of 8.8kgf, 10.0kgf and 9.0kgf and l0.0kgf at 0.75g and l.0g catalyst mass in weft and warp directions respectively. Amorphous region of cellulose are filled up with resins and strengthened by chemical cross-linking between cellulose and resins molecules (Norma *et al.*, 1979). Cross-linking provides anchoring points for chains in the network (Ajayi *et al.*, 2001). The higher breaking load of methylol melamine resinated samples cured at150°C can be ascribed to longer chain length of melamine compared to urea formaldehyde resins. This improves flexibility in cotton fibre with improved mechanical properties (Andrews, 1995).

V. CONCLUSION

The effects of catalyst mass were visible throughout the experiment. High breaking load values and angle of relaxation achieved was due to high catalytic activities of mixtures of $MgCl_2$ and Citric acid, most probably influence by synergistic effect of combined catalyst for better performance of resins in the investigated areas, synthesis of resin should be carried out with combined mass of catalyst. This is because a fabric sample resinated with excess of catalyst mixture does not lead to fabric degradation compared with acid catalyst (KH_2P0_4) which can causes distortion of cellulose fabrics especially at higher concentrations.

Recommendation

From the result obtained so far, using combined catalyst ($MgCl_2$ and Citric acid), We hereby recommend that combined catalyst should be used for preparation of methylol urea resins used in treatment of cotton fabrics for the following reasons: It does not degrade or change colour to cotton fabrics during resination, unlike zinc nitrate catalyst but also increases angle of relaxation of cotton fabrics.

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