# Synthesis of Formaldehyde Free Amino Resin to Produce Green Eco-Labelled Leather with Improved Retanning Properties

by
Muhammad Naveed Ashraf[a]*, Shahzad Maqsood Khan[a], Shahid Munir[b], and Rashid Saleem[c]
[a]Department of Polymer Engineering and Technology, University of the Punjab, Lahore, 54000 Pakistan
[b]University of Jhang, 35200 Pakistan
[c]GC University Katchery Road Lahore 54000 Pakistan/ SRC (Pvt) Ltd, Lahore, 54000 Pakistan

## Abstract

Formaldehyde has many applications in the chemical industry including synthesis of amino resins which are used in leather processing. After application in leather, these resins are hydrolyzed under certain conditions to release free formaldehyde which has high environmental concerns due to its proven carcinogenic effects. The objective of this work is to develop a formaldehyde free melamine-based resin to produce green leather with improved retanning properties and thermal stability. The optimum melamine resin was synthesized by condensing melamine with glyoxal instead of formaldehyde. Further, the water solubility and improved thermal stability of synthesized melamine resins were achieved by introduction of sulfanilic acid in resin structure. Synthesized resin was used in leather retanning in comparison with commercially available melamine resin as a control. Both leathers were tested for mechanical properties, organoleptic properties, grain surface and fiber structure analysis. Comparative free formaldehyde content was measured in resultant leathers. Effluents of retanning baths were comparatively analyzed. Optimum resin was also characterized by thermo gravimetric analysis and FTIR. The results of this study showed that the experimental resin has imparted significant improvement in mechanical and organoleptic properties of leather as compared to the control resin. Analysis of free formaldehyde content confirmed the absence of free formaldehyde in leather treated with optimum resin while 141 mg/kg formaldehyde was detected in leather treated with control resin. Free formaldehyde was also absent in effluent of experimental resin while 305 mg/kg formaldehyde was detected in effluent of control resin. Moreover, percentage efficiency in COD, TDS and TSS load of effluent was observed as 9.62, 7.2 and 6.31 respectively. Resultant leather was free from formaldehyde making it safe for human along with reduction in pollution load of tannery.

## Introduction

The transformation of animal hides and skins into various useful articles is one of the oldest technologies. In leather making, tanning is the main process by which hides and skins are converted into a non-putrescible and stable material by improving the crosslinking of collagen.[1] Vegetable tanning is a primitive method of tanning which involve the treatment of hides with plant extracts.[2] Whereas chrome tanning is the most effective method being used today to enhance thermal stability and physio-mechanical characteristics of leather.[3, 4] Chrome tanning is also playing an active role in contributing hexavalent chrome in tannery waste.[5, 6] Another type of tanning is aldehyde tanning which can be used to make chrome free leather at the cost of poor physical-mechanical properties. Further, the modified glutaraldehyde may decompose under certain conditions and lead to release free formaldehyde[7] which is a humane carcinogen.[8]

A key step in leather processing is retanning which is used to improve the physical and chemical properties of leather. A variety of polymers like polyacrylic acid, polyurethane, phenolic resin and amino resins are used as retanning agent.[9] Amino based resins including urea, melamine and dicyandiamide – formaldehyde condensate are the most viable class of retanning agents which are supportive in improving the color of leather along with uniform distribution and better filling action in loose belly parts of skin.[10] Production of amino resins involves the condensation of amino precursors with formaldehyde. The retanning of leather with these resins result in generation of free formaldehyde in leather which is a carcinogenic moiety.[11, 12] As per legislation the permissible limit of free formaldehyde contents in leather good for adults is 75mg/kg by weight of leather.[13, 14] Air emissions of free formaldehyde have also been reported as carcinogenic.[15]

Environmental impact of urea formaldehyde resin on ecotoxicity and human toxicity was described and three main sources of formaldehyde emission were identified as: (a) air emission of free formaldehyde during production of formaldehyde based amino resin; (b) unreacted formaldehyde present in amino resin; (c) release of free formaldehyde by hydrolysis of amino resins under certain conditions.[16, 17] It was noticed that the manufacturing step of resin synthesis had potential impact on ecotoxicity and humane toxicity as a result of local emissions of formaldehyde.[18] Airborne emission

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*Corresponding author E-mail: Naveed.ashraf@src.com.pk
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limit of free formaldehyde has been reported as 0.1 ppm. An increase in airborne emissions above this value produces adverse effects in human beings like nausea, watery eyes and irritation in eyes and throat.[19] Environmental concerns regarding free formaldehyde content are compelling researchers to find suitable solutions to combat the formaldehyde issue.[20]

An effort was made to minimize the generation of free formaldehyde content in leather by reducing formaldehyde to melamine mole ratio in resins.[21] It was investigated in a study that formaldehyde scavengers like pyrogallol, gallic acid and ethylene urea can be used to reduce the formaldehyde in leather produced through resin tannage.[22] It was also worked out that the polyphenols of vegetable origins had the tendency to reduce the formaldehyde in leather which was produced by retanning with amino resins.[23] All efforts done in previous work were only supportive in reduction of free formaldehyde in the leather without its complete elimination. Moreover, the use of formaldehyde scavengers and plant polyphenols also resulted in increasing production cost and lowering quality of leather.[24]

The best possible approach could be to find some alternate condensing agent to replace formaldehyde in synthesis of amino resins to make them formaldehyde free. One suggested alternative is glyoxal (OHC-CHO), which is a non-volatile and less toxic (LD50 mouse >1280 mg/kg, LD50 rat >2960 mg/kg) dialdehyde as compared to formaldehyde (LD50 mouse >42 mg/kg, LD50 rat >100 mg/kg.[25] In literature the use of glyoxal as leather tannin[26] and in wood adhesives has been reported.[27] The use of glyoxylated melamine resins in paper making has also been worked out to achieve water resistant properties.[28] The use of melamine-glyoxal resin without any sulfonation has been reported to check their tanning action but such resin exhibited limited water solubility even at higher glyoxal/melamine ratio. Further, due to absence of sulphonating agent water solubility of this resin was poor. [29]

In another attempt, melamine-glyoxal resin was prepared using sulfamic acid as a sulfonating agent[30] with improved water solubility. This resin has limited shelf life due to its production at higher melamine to glyoxal mole ratio 1:5.

The aim of this research work is to synthesize melamine resin with lower melamine to glyoxal mole ratio 1:2 and sulfonation with sulfanilic acid to impart improved shelf life in liquid form, better retanning properties and higher thermal stability. The resin exhibited better affinity with leather collagen during leather tanning process resulting in improved exhaustion. The resulting tanned leather will be green and free from formaldehyde. The development of formaldehyde free melamine resin and its use as ecofriendly retanning agent would be helpful in the clean production of leather with environmental protection.

## Experimental

### Materials and Methods

Goat wet-blue (Commercial grade) was purchased from Hafeez Shafi Tannery of Pakistan. Sulfanilic acid (Food grade, 99%) was arranged from Kevin India, Melamine powder (99.8%) was purchased from Royal DSM. Glyoxal (w/w 40% commercial grade) was bought from local Pakistan market. Sodium Hydroxide (AR, Merck) was used for resin synthesis. Commercially used melamine-formaldehyde resin was used as control in comparative study. All other chemicals used for leather processing were of commercial grade. Leather processing[31] was performed by using well water. Distilled water and analytical reagents from Merck were used for estimation of free formaldehyde and other related analysis.

### Synthesis of Glyoxylated Melamine Resins using Sulfanilic Acid as Condensing Agent

In a round-bottom flask fitted with a condenser and thermometer, requisite quantity of water and 0.5-3 mole sodium hydroxide was charged and mixed to make solution. Then 0.5-3 mole sulfanilic acid was added into flask while mixing to make solution. After getting clear solution, 2-6 moles of glyoxal (40% aqueous solution) was charged into the reaction flask and its pH was adjusted at $7.5 \pm 0.25$ by adding sodium hydroxide solution (0.5N). Then, 1mole of melamine was charged with mixing and reaction mixture was heated up to 75°C for 2 hours duration. Then the reaction mass was cooled to $30 \pm 2$°C.

The dry content of each synthesized resin was determined by heating a known mass of resin for one hour in an oven at 103 - 105°C according to standard procedure,[32] the solid content of resin was adjusted to $38 \pm 0.25\%$ by adding distilled water. Series of designed experiments were performed under optimized conditions at various reactant mole ratios. Physical characteristics of synthesized resins were measured as given in Table I.

### Measurements and Instruments

Brookfield viscometer LVDVE 230 was used to determine the viscosities of resins in aqueous state. Viscosity of each resin sample was noted at solid contents $38 \pm 0.25\%$ at temperature 25°C. Agilent instrument Cary 630 was used for FT-IR analysis of all the synthesized resins. The optimum synthesized resin, MGSNA #03, corresponding to mole ratio of reactants giving improved retanning properties and zero formaldehyde contents, was oven dried and its thermal analysis was performed by a SDT Q 600 machine of Universal V4.5ATA instruments (USA). Thermogravimetric analysis was conducted to observe percentage loss of resin with the increase of temperature.

Effluent collected from retanning processes of leather for both control and experimental resins were analyzed for determination of

**Table I**

**Mole ratio and physical characteristics of prepared MGSNA resins**

| **EXPERIMENTAL DATA** | | | | | |
|---|---|---|---|---|---|
| **Resin No** | **Glyoxal / Melamine (G/M)** | **Sulfanilic acid / Melamine (ONA/M)** | **Solid Contents (%)** | **Acid Sensitivity at pH 4-5** | **Viscosity at 25°C (cp)** |
| MGSNA #01 | 2 | 0.5 | 38 + 0.25 | Yes | Gel |
| MGSNA #02 | 2 | 1 | 38 + 0.25 | Yes | 126 |
| MGSNA #03 | 2 | 1.5 | 38 + 0.25 | Yes | 25.0 |
| MGSNA #04 | 2 | 2 | 38 + 0.25 | Yes | 21.4 |
| MGSNA #05 | 2 | 2.5 | 38 + 0.25 | No | 18.9 |
| MGSNA #06 | 2 | 3 | 38 + 0.25 | No | 17.2 |
| MGSNA #07 | 3 | 0.5 | 38 + 0.25 | Yes | Gel |
| MGSNA #08 | 3 | 1 | 38 + 0.25 | Yes | 98.7 |
| MGSNA #09 | 3 | 1.5 | 38 + 0.25 | No | 23.2 |
| MGSNA #10 | 3 | 2 | 38 + 0.25 | No | 20.6 |
| MGSNA #11 | 3 | 2.5 | 38 + 0.25 | No | 17.6 |
| MGSNA #12 | 3 | 3 | 38 + 0.25 | No | 16.5 |
| MGSNA # 3 | 4 | 0.5 | 38 + 0.25 | Yes | Gel |
| MGSNA #14 | 4 | 1 | 38 + 0.25 | Yes | 89.7 |
| MGSNA #15 | 4 | 1.5 | 38 + 0.25 | No | 22.3 |
| MGSNA #16 | 4 | 2 | 38 + 0.25 | No | 19.8 |
| MGSNA #17 | 4 | 2.5 | 38 + 0.25 | No | 16.7 |
| MGSNA #18 | 4 | 3 | 38 + 0.25 | No | 15.4 |
| MGSNA #19 | 5 | 0.5 | 38 + 0.25 | No | 252 |
| MGSNA #20 | 5 | 1 | 38 + 0.25 | No | 67 |
| MGSNA #21 | 5 | 1.5 | 38 + 0.25 | No | 21.6 |
| MGSNA #22 | 5 | 2 | 38 + 0.25 | No | 18.5 |
| MGSNA #23 | 5 | 2.5 | 38 + 0.25 | No | 15.9 |
| MGSNA #24 | 5 | 3 | 38 + 0.25 | No | 15.1 |
| MGSNA #25 | 6 | 0.5 | 38 + 0.25 | No | 148 |
| MGSNA #26 | 6 | 1 | 38 + 0.25 | No | 42 |
| MGSNA #27 | 6 | 1.5 | 38 + 0.25 | No | 20.6 |
| MGSNA #28 | 6 | 2 | 38 + 0.25 | No | 17.4 |
| MGSNA #29 | 6 | 2.5 | 38 + 0.25 | No | 14.6 |
| MGSNA #30 | 6 | 3 | 38 + 0.25 | No | 13.8 |

total dissolved solids, total suspended solids and chemical oxygen demand (COD). HANNA COD Reactor and Photometer was used for determination of COD. Comparative free formaldehyde contents were also estimated in effluents as per standard colorimetric method.[33]

Standard colorimetric method[33] was adopted to estimate free formaldehyde in leather treated with optimum resin, MGSNA #03, and commercial melamine resin as a control. Before analysis, moisture contents in both selected pieces of leather were noted and finally the free formaldehyde contents were measured on dry weight basis. Comparative free formaldehyde contents were also estimated in effluents by using the same method.

Both the experimental and control resins were used comparatively in retanning process of leather. Goat wet blue skin of the same animal was used to conduct the leather retanning properties of both resins to ensure the uniformity of the substrate. Two sets of wet blue pieces of identical size (200 mm × 150 mm) were selected along the spine. One set was retanned with experimental resin and second set was retanned with a control resin for comparison. Leather processing recipe along with raw materials and processing conditions are listed in Table II. All the experimental resin exhibiting low viscosity and acid sensitivity up to pH 4 - 5 were tested for leather processing.

### Table II

**Leather processing recipe and conditions**

| Process/chemicals | % | Duration (min) | Comments |
|---|---|---|---|
| **Washing** | | | |
| Water | 100 | 10 | Drained |
| **Neutralization** | | | |
| Water | 150 | | |
| Sodium format | 1.5 | 10 | |
| Sodium bicarbonate | 1 | 90 | pH up to 5.0-5.2, drained |
| **Washing** | | | |
| Water | 200 | 15 | Washed and drained |
| **Retanning, dyeing and fat liquoring** | | | |
| Water | 100 | | |
| MGSNA Resin* | 10 | 45 | |
| Synthetic Flat liquor | 4 | 60 | Mixed in hot water |
| Acid Dye | 2 | 30 | |
| Formic acid | 1.5 | 60 | The exhaustion of the bath was checked, drained |
| Washing with water | 100 | 15 | The processed leathers were set, dried by hooking and staked after conditioning |

*All the synthesized MGSNA resins showing sensitivity up to pH 4-5 and commercial melamine resin.

Standard procedure was used for measuring the mechanical properties of the leather treated with both experimental MGSNA resin and control resin.[34] Selected swatches of leather were first conditioned at 65±2% relative humidity for 48 hours while keeping temperature 27°±2°C. The conditioned leather pieces were tested for measuring tensile strength and elongation at break by using STM 566F equipment according to standard procedure.[35] In the same way tear strength and grain strength of retanned leathers were noted by STM 566ST equipment and Lasto-meter as per standard procedures.[36]

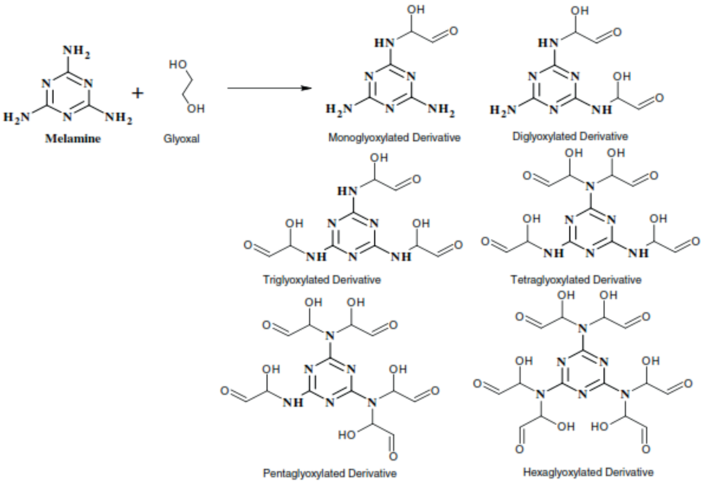
Measurement of the organoleptic properties like softness, fullness, roundness, grain tightness (break), and grain smoothness were determined by visual observation and with the help of softness meter SL-01 by standard procedure.[37] Each property was assigned a rating 0 - 5 point on a scale, with higher point showing better property. Both leathers treated with experimental resin MGSNA #03 and control resin were evaluated after proper conditioning procedure.

Scanning electron microscopy (SEM) analysis was conducted by using Lieca metallurgical microscope Q550IW coupled with CCD camera. Selected leather pieces obtained after retanning with experimental and control resin were cut into suitable size and their surface was cleaned by washing with acetone. A uniform gold coating of thickness 300Åwas applied on each leather sample by using ion sputter coater, JEOL Model JFC 1500. Micrographs of both grain surface and fiber cross section of retanned leather samples were collected at magnification 50×.

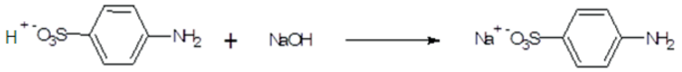
## Results and Discussion

### Schematic Route of Synthesis

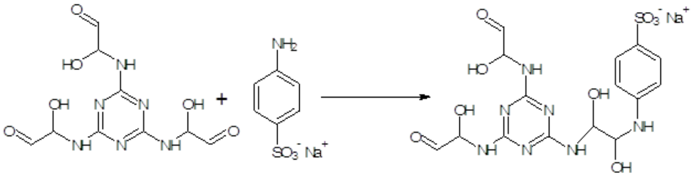
Amino group of melamine attacks on carbonyl group of glyoxal through nucleophilic substitution reaction in basic media to produce mono-, di-, tri-, tetra-, penta- and hexa- glyoxylated derivatives of melamine. Resulting glyoxylated derivatives of melamine were sulfonated with sodium salt of sulfanilic acid. In condensation step, sulfonated glyoxylated derivatives react with each other to form a bigger polymer as shown in scheme.



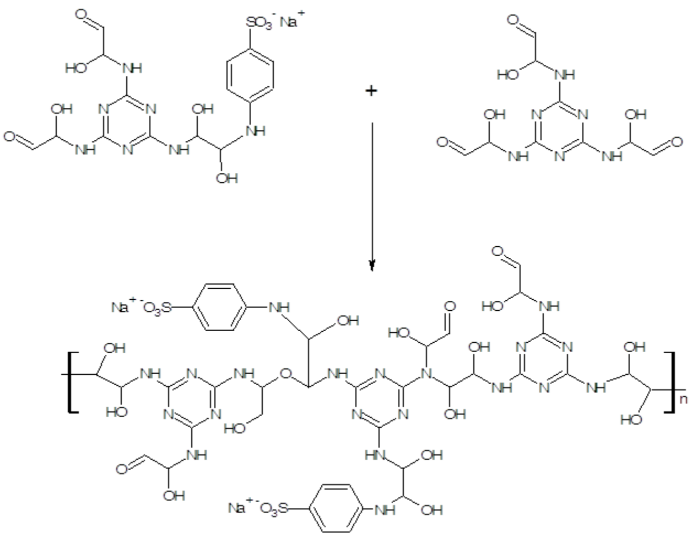
**Scheme 1.** Formation of glyoxylated derivatives of melamine[30]



**Scheme 2.** Preparation of sodium salt of sulfanilic acid



**Scheme 3.** Sulfonation of glyoxylated melamine



**Scheme 4.** Condensation of monomers to produce polymer

### Rheology of Resins

It was observed that there was a decreasing trend of viscosities in a series of synthesized resins with increase of sulfanilic acid/melamine (SNA/M) mole ratio. The decrease in viscosity trend can be attributed to creation of more anionic sites in polymer structure with increase of SNA/M ratio. The introduction of anionic sites produces sliding action between the polymer chains due to repulsion, thus reducing the viscosities of aqueous polymer resins with enhancement in their water solubility. Sulfonation takes place at hydroxyl group (-OH), thus increase in degree of sulfonation results in reducing free hydroxyl groups responsible for H- bonding and tend to lower the viscosity.

Further, an increase of glyoxal/melamine (G/M) ratio from 2 to 3 results in increase in number of free hydroxyl and inter-molecular H-bonding thus increasing the viscosity of the resins. On the other hand, further increase of G/M ratio from 4 to 6 lead to lower the viscosity. The reason is decrease in inter-molecular H-bonding and increases of intra-molecular H-bonding due to formation of bigger polymer structure; no doubt the increase in number of hydroxyl groups is still there.

### Mechanical characteristics of retanned leather

Mechanical properties of the leathers retanned with selected synthesized MGSNA resins are shown in Table III. All the MGSNA resins showed improved mechanical properties but the increase in mechanicals properties of resin MGSNA #03 were more obvious as compared to the conventional melamine formaldehyde resin. The optimal resin MGSNA #03 formulated at mole ratios G/M=2 and SNA/M=2, reflected the improved crosslinking ability of the resin with collagen fibers. Therefore, the stronger interactions developed between collagen and MGSNA #03 resin compelled the collagen fibers to arrange more orderly to enhance the physical properties. The results showed that the leather retanned with optimal resin MGSNA #03 exhibited significant improvement in mechanical properties in comparison with control resin. Results of resin MGSNA #14 were observed to be less than control as this sample was produced at comparative higher glyoxal/melamine (G/M) and low sulfanilic acid/melamine (SNA/M) ratio creating low charge density on molecules and finally low affinity with collagen fibers. Less reactivity of resin resulted in its poor exhaustion and reduction of physical properties of leather.

### Organoleptic properties

Comparative organoleptic properties of both leathers retanned with experimental MGSNA #03 and control resin are given in Figure 1. It is clear from the results that the retanning with experimental resin MGSNA #03 has improved the organoleptic properties of the resultant leather as compared to the leather obtained from control resin.

The optimum resin MGSNA #03 succeeded to develop stronger interactions with leather fibers by locking their position and resulted to minimize the fiber motions over each other, thus reducing the softness of leather. Moreover, in the structure of experimental resin more reactive sights has been developed which get entangled with

**Table III**

**Physical properties of leather retanned with resins MGSNA.**

| Experimental Resins | Parallel to backbone | | | Perpendicular to backbone | | | Distension at Grain Cracking |
|---|---|---|---|---|---|---|---|
| | Tensile Strength (N/cm2) | Tear Strength (N/cm) | % Elongation | Tensile Strength (N/cm2) | Tear Strength (N/cm) | % Elongation | (mm) |
| MGSNA #02 | 1425.3±78.21 | 398.7±29.47 | 62± 4.66 | 1209.7±72.32 | 329.2±18.21 | 56±27.29 | 9.49±1.99 |
| MGSNA #03 | 1610.4±39.12 | 425.3±12.21 | 64±2.27 | 1276.5±26.22 | 352.9±14.25 | 57±2.15 | 9.79±1.69 |
| MGSNA #04 | 1329.4±26.44 | 327.3±12.85 | 61±3.17 | 1185.1±55.28 | 315.4±31.44 | 55±7.73 | 9.43±1.58 |
| MGSNA #08 | 1585.7±34.41 | 410.2±42.16 | 62±1.35 | 1235.2±25.65 | 341.4±15.28 | 56±3.21 | 9.56±1.92 |
| MGSNA #14 | 1210.9±61.22 | 280.2±22.41 | 61±1.43 | 1107.4±21.31 | 308.4±48.58 | 54±1.79 | 9.10±1.43 |
| Commercial melamine resin | 1375.2±62.22 | 320.4±11.56 | 62±3.72 | 1160.3±4.11 | 310.2±23.16 | 56±2.51 | 9.48±1.62 |

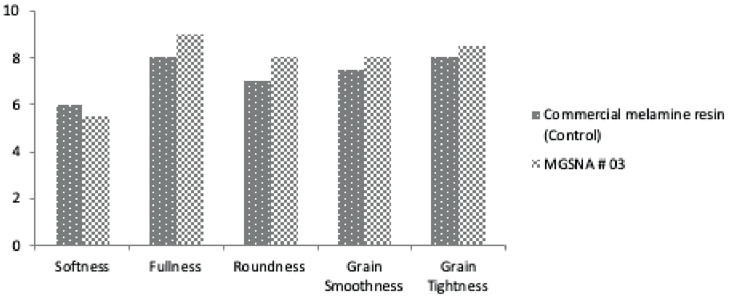


**Figure 1.** Organoleptic properties of leathers retanned with experimental resin MGSNA #03 and control resin

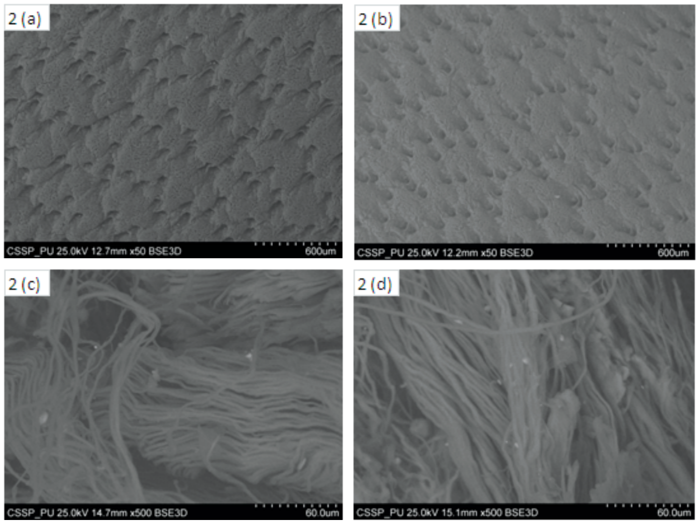


**Figure 2.** Scanning electron micrographs of cross section of grain surface (50×) and collagen fiber (500×): **2 (a)** grain surface of leather retanned with MGSNA#03 resin: **2 (b)** grain surface of leather retanned with commercial melamine resin: **2 (c)** fiber cross section of leather retanned with MGSNA #03 resin: **2 (d)** fiber cross section of leather retanned with commercial melamine resin.

fibers in neighborhood and resulted in improvement of fullness, roundness, grain smoothness and grain tightness of resultant leather.

### SEM Analysis (JEOL 6490)

Micrographs of fiber cross section and grain surface of treated leathers are shown in Figure 2. Comparison of grain surface monographs showed the presence of fine grain and smooth surface on leather treated with experimental resin MGSNA #03. Moreover, the experimental resin produced more orderly arranged fiber structure due to better crosslinking of resin with collagen to improve the retanning properties of the leather.

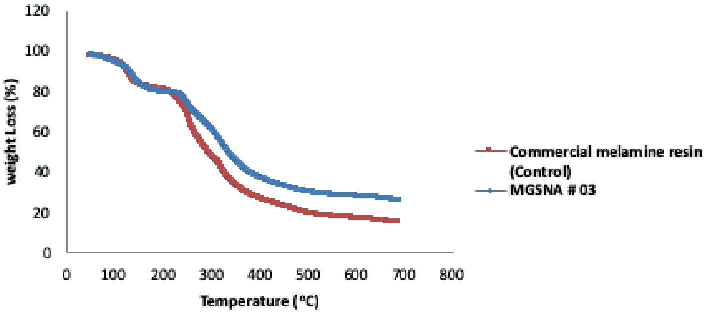


**Figure 3.** TGA of optimized MGSNA #03 and commercial melamine formaldehyde resin

### Quantitative determination of Free Formaldehyde Contents in Leather

100% reduction in free formaldehyde was observed in leather processed with experimental resin MGSNA #03, whereas the free formaldehyde content measured in leather treated with control resin was 141 mg/kg. The reported allowed limit of free formaldehyde in leather goods for adults is 75 mg/kg of leather.

### Thermogravimetric Analysis

At higher temperature cross linking of the resin has increased to form a stable cross-linked mass leading to improve the thermal stability. Polymers showing more tendencies to crosslink with collagen would tend to increase the thermal stability of leather. Comparison of thermal degradation of newly synthesized MGSNA #03 resin and control resin is shown in Figure 3. The graph has shown that the comparative thermal stability of resin MGSNA #03 was better than the commercial resin. Mass loss in both resins at 160-170°C was due to loss of moisture while mass loss above 240°C was due to thermal decomposition of polymers. The percent mass loss of MGSNA #03 resin at temperature range 250-650°C was 12.4% lower than the commercial resin which indicated improved thermal stability of synthetic resin.

### Structural Elucidation

An FTIR spectrum of the synthesized MGSNA #03 resin is shown in Figure 4. A broad peak was seen at 3342cm$^{-1}$ due to NH and OH formed by the reaction of melamine and glyoxal. Formation of

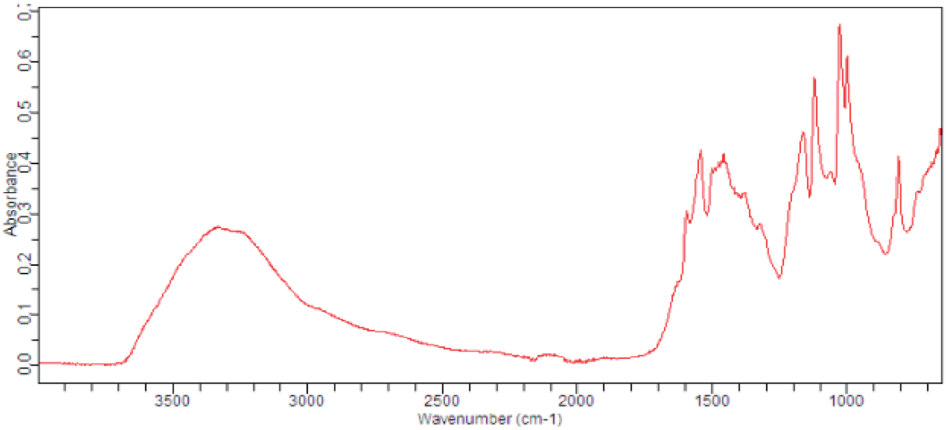


**Figure 4.** FTIR of MGSNA # 03 resin

ether linkage was confirmed by peak at 1026cm$^{-1}$. Presence of 1, 3, 5-triazine ring in resin structure showed a signal at 804.3234cm$^{-1}$. IR stretching at 1589.34cm$^{-1}$ appear due to C=N group. R-$SO_3^-$ group in polymer was indicated by IR peak at 1192.2cm$^{-1}$.

**Effluent Analysis**

The Effluent collected after retanning processes of experimental resin and control resin were analyzed for measuring total dissolved solids (TDS), total suspended solids (TSS) and chemical oxygen demand (COD). The observed values of parameters are listed in Table IV. Significant reduction in TDS, TSS and COD load was observed in spent liquor collected from bath treated with experimental formaldehyde free amino resin MGSNA #03. The optimized degree of sulfonation and molecular size of the experimental resin MGSNA #03 resulted in improved penetration of resin in leather leaving its least quantity in bath. Further, at the tanning pH conditions, impregnated resin MGSNA #03 showed in situ polymerization to form composite mass which was unable to bleed into bath after fixation. Moreover, being formaldehyde free, no formaldehyde was detected in spent liquor of experimental resin while 305mg/kg formaldehyde was analyzed in spent liquor of commercial melamine resin.

### Table IV

**Comparative characteristics of effluent after retanning with experimental and commercial melamine resin**

| Parameter | Commercial melamine formaldehyde resin | Experimental melamine-based resin (MGSNA#03) | Percentage efficiency |
|---|---|---|---|
| Formaldehyde content (mg/kg) | 305 | 0 | 100 |
| Chemical oxygen demand, COD (ppm) | 14340 | 12960 | 9.62 |
| Total dissolved solids, TDS (ppm) | 22421 | 20806 | 7.20 |
| Total suspended solids, TSS (ppm) | 17124 | 16044 | 6.31 |

## Conclusions

The results of this research work have shown that the sulfanilic acid modified melamine-glyoxal resin can be produced to use as an effective retanning agent for producing environment friendly leather. Various resins were produced at different mole ratio of reactants, but the resin MGSNA #03, designed at mole ratios G/M=2 and SNA/M =2 was proved as an optimum resin because at this mole ratio suitable/controlled molecular size was attained which was supportive in achieving improved retanning properties and stability . This optimum resin showed significant improvement in mechanical and organoleptic properties of the resultant leather in comparison with control resin. The SEM analysis of leather treated with optimum resin showed the existence of compact and aligned fiber structures reflecting stronger interactions of resin with collagen fibers to give improved retanning properties. Comparative determination of free formaldehyde in both experimental and controlled leathers confirmed that the optimum resin was ecofriendly without releasing any free formaldehyde in leather while the free formaldehyde content released by control resin was 141 mg/kg of leather. The use of optimum resin MGSNA #03 has resulted in 100% reduction of formaldehyde contents in effluent as compared to the control resin which generated 305 mg/kg formaldehyde due to unfixed resin. Further the percentage efficiency of spent liquor parameters like COD, TDS and TSS were observed to be improved by 9.62, 7.25 and 6.31 for optimum resin MGSNA #03 as compared to the control resin. The comparative thermo gravimetric analysis revealed the improved thermal properties of the optimum resin with refection of longer life cycle of leather articles. This research work has succeeded to produce formaldehyde free melamine resin to produce green eco-labeled leather with improved retanning effects and pollution load.

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