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Development of Novel Formaldehyde-Free Melamine Resin for Retanning of Leather and Reduced Effluent Discharge in Water

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Abstract: The objective of this study was to develop a novel melamine-based resin suitable for producing formaldehyde-free leather with improved retanning properties. The resin was prepared by optimized condensation of melamine, glyoxal and metanilic acid. The novel resin was compared with a commercial resin against different parameters. Functional group analysis of the polymer structure and the route of synthesis was verified with the help of FT-IR spectroscopy. A Leica metallurgical microscope coupled with a CCD camera was used for SEM analysis. The results revealed that the mechanical and organoleptic properties of the novel resin were better than those of the commercial melamine resin. Tensile strength, tear strength and percentage elongation of leather were increased by 17.43%, 10.41% and 8.62%, respectively, in the direction parallel to the backbone, while the increases in these parameters were 15.17%, 9.79% and 6.0%, respectively, in the direction perpendicular to the backbone at the same dose. We observed a 100% reduction in free formaldehyde content in retanned leather as well as in effluent produced by the novel melamine resin. Pollution load study of effluent showed reductions in chemical oxygen demand, total suspended solids and total dissolved solids by 9.21%, 5.60% and 6.97%, respectively, for the novel melamine resin, reflecting its improved exhaustion. The fiber structure of the leather produced by the novel melamine resin was more orderly arranged, showing its improved retanning. These results prove that the novel melamine resin is an effective retanning agent suitable for producing formaldehyde-free leather with a reduction in effluent pollution load. This work introduces an alternative to formaldehyde for amino resins to address its carcinogenic effects.

Keywords: formaldehyde-free; melamine; glyoxal; retanning; pollution

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1. Introduction

The production of eco-labeled leather goods has gained importance due to increasing demand by customers and international brands [1]. Free formaldehyde is one of the notorious chemicals on the list of restricted and harmful substances. The European Union has included formaldehyde in carcinogenic category 3 [2]. As per legislation, the permissible limit of free formaldehyde content in leather goods for adults is 75 mg/kg by weight of leather. Air emissions of free formaldehyde have also been reported as carcinogenic [3].

The toxic effects of formaldehyde on humane health and environment have been studied, and key contributors of free formaldehyde air emissions were identified as (i) the emission of free formaldehyde in the production stage of formaldehyde-based resins, (ii) unreacted formaldehyde retained in resins and (iii) hydrolytic cleavage of resins under certain conditions to release free formaldehyde [4,5]. It was observed that the production of formaldehyde-based resin had a strong environmental impact due to emissions of formaldehyde [6]. In humans, adverse effects of airborne emissions of free formaldehyde at concentrations above 0.1 ppm have been reported [7,8].

Amino-based resins constitute an important class of retanning and are used to improve the color of leather with uniform distribution and filling action of resins in the belly parts of animal hides and skins [9]. Amino-based resins are produced by condensation reactions of amino compounds such as dicyandiamide, melamine and urea with formaldehyde. Processing leather with these resins results in the continuous release of free formaldehyde in post-tanning stages and in leather articles [10–12]. The existence of free formaldehyde in leather and leather goods is one of the major environmental concerns [13].

Moreover, the production of these resins generates formaldehyde air emissions, which affect the health conditions of workers. The short-term exposure limit (STEL) of formaldehyde has been declared as 0.3–2 ppm, and it varies from country to country. Resin manufacturers are advised to control workers' formaldehyde exposure limit to below 0.5 ppm to prevent eye irritant effects [14]. The use of formaldehyde in resin synthesis also results in increasing water pollution due to vessel washing practices [3]. Due to the limited reactivity of formaldehyde-based resins with collagen, these tanning materials fail to exhaust completely and remain unreacted in resultant effluent to increase its pollution load [15].

The carcinogenic effects of formaldehyde have forced tanneries to take measures to guarantee the existence of formaldehyde content in leather below the allowable limits, or it should be completely excluded [16]. Environmental concerns regarding free formaldehyde content are also compelling researchers to find suitable solutions to combat the issues raised due to formaldehyde [17,18].

Various practices have been exercised to lower the formaldehyde content in leather. An attempt was made to reduce the free formaldehyde content in leather articles by reducing the formaldehyde to melamine ratio during resin synthesis [19]. In another work, leather retanned with amino resins was further treated with formaldehyde scavenging materials such as pyrogallol, gallic acid and ethylene urea to minimize the free formaldehyde in resultant leather [20]. It was also investigated that plant polyphenols had the ability to reduce the formaldehyde content in leather that was previously retanned with amino resins [18]. Some authors have tried to replace formaldehyde with natural products derived from periodic oxidation of sodium alginate and sodium metabisulfite for preparing melamine resins [21], but none were able to eliminate the issue of formaldehyde completely. Moreover, the use of formaldehyde scavenging materials and plant polyphenols lowered the quality of leather and increased its production cost [20].

The most favorable solution to control the emission of free formaldehyde in leather is to find a condensing agent other than formaldehyde. One option could be glyoxal (OHC-CHO), a non-volatile dialdehyde with adequate biodegradability [22,23]. Its toxicity is much less (LD50 mouse > 1280 mg/kg, LD50 rat > 2960 mg/kg) than that of formaldehyde (LD50 mouse > 42 mg/kg, LD50 rat > 100 mg/kg [24]. The use of glyoxal has been reported as tannin in leather [25] and as a condensing agent in adhesives for making wood panels [26]. Synthesis of glyoxalated melamine resin has also been evaluated for its use in making paper water-resistant [27,28].

The tanning properties of melamine–glyoxal resin have been studied, but the water solubility and shelf-life stability of this resin were found to be poor due to the absence of sulfonation during synthesis [29]. This resin was produced at a glyoxal to melamine mole ratio of 5:1 while using high quantities of glyoxal in synthesis.

Another effort was made to prepare sulfonated melamine–glyoxal resin by using sulfamic acid to improve its water solubility. This resin was also produced at a higher glyoxal to melamine mole ratio of 5:1, and it exhibited limited shelf life [30]. The consumption of a high mole ratio of glyoxal may have toxic effects.

In view of the aforementioned issues, the present study was designed to produce formaldehyde-free melamine resin (melamine–glyoxal–metanilic acid (MGMNA)) as a Retanning agent. This resin is optimized at a comparatively low glyoxal to melamine ratio (3:1) to further reduce the toxic effects of glyoxal along with cost. The use of formaldehyde has been eliminated in this work to protect factory workers from exposure. The novel melamine-based resin would be helpful in the clean production of leather with improved retanning properties, zero formaldehyde content and reduced pollution load.

2. Materials and Methods

2.1. Materials

Melamine powder (99.8%, Royal DSM, Mumbai, India), metanilic acid (99%, Kevin, Maharashtra, India), Glyoxal (*w/w* 40%, commercial) and sodium hydroxide (AR, Merck, Lahore, Pakistan) were used as received.

Commercial goat wet blue was received from Hafeez Shafi Tannery Pakistan, along with melamine–formaldehyde resin for a comparative study. Leather processing chemicals including sodium format, sodium bicarbonate and formic acid were purchased from a local market. Leather processing was carried out using well water. For the determination of free formaldehyde, distilled water and analytical-grade reagents, including sodium dodecylsulphonate, ammonium acetate, glacial acetic acid, acetyl acetone and dimedone from Merck, were used.

2.2. Methods

2.2.1. Synthesis of Novel Melamine Resin

First, we placed 85 gm of distilled water in a round-bottom three-necked flask fitted with a thermometer and a condenser. Then, 54.37 gm of (0.375 mole) glyoxal 40% aqueous solution was added to the flask while stirring. Next, 32.65 gm (0.187 mole) of metanilic acid and 16 gm (0.20 mole) of sodium hydroxide (aqueous solution 50%) were added to form sodium salt of metanilic acid, and pH was adjusted to 7.5 ± 0.25 by adding sodium hydroxide solution (0.5 N). Then, 15.76 gm (0.125 mole) of melamine was added while mixing, and the reaction mixture was heated to 70 °C while mixing for 2 h. Then, the reaction mass was cooled to 30 ± 2 °C.

2.2.2. Determination of Dry Content

The dry content of the synthesized resin was determined by heating a known mass of the resin in an oven at 103–105 °C for one hour while following the standard procedure [31]; the solid content was adjusted to 38 ± 0.25% by adding distilled water.

2.2.3. Measurement of Molecular Weight

Viscosity average molecular weight (M_v) of the synthesized resin was calculated by a viscometry technique using a Cannon Ubbelohde viscometer. The time of flow of distilled water as a solvent and MGMNA resin solutions was noted at a constant temperature of 27 ± 0.1 °C at different concentrations. The relative viscosity, specific viscosity and intrinsic viscosity of each concentration were calculated from the date of time of flows. Finally, the molecular weight of the polymers was calculated by using the Mark Houwink equation [32] as follows: $[\eta] = K\,[M]^a$.

2.2.4. Thermogravimetric Analysis (TGA) of Resin

Thermogravimetric analysis (TGA) is a technique used to measure the change in the mass of a polymeric substance as a function of temperature or time. TGA is helpful in understanding the decomposition behavior of a polymer, along with its thermal stability.

Thermogravimetric analysis of novel resins was carried out by using the SDT Q 600 machine by Universal V4.5A TA Instruments (Waters TA, New Castle, DE, USA). A platinum pan was used to perform TGA analysis of samples in an inert environment having a nitrogen gas flow rate of 50 mL/min. TGA was performed by changing the temperature from ambient temperature (25 °C) to 600 °C with a gradient of 10 °C per minute. Percent (%) mass loss in the sample was recorded with the change in temperature [33].

2.2.5. FTIR Analysis

Functional group analysis of the polymer structure and the route of synthesis was verified with the help of FT-IR spectroscopy. FTIR analysis of the novel MGMNA resin was performed using a Cary 630 instrument from Agilent (Santa Clara, CA, USA). The absorbance FTIR spectrum of the MGMNA resin was recorded within the scanning range of 600–4000 cm^{-1} [34].

2.2.6. Comparative Leather Application of Resins as Retanning Agent

The goat wet blue was chosen as a substrate to study the application of synthesized resin. In order to ensure the uniformity of the substrate, wet blue of the same animal was used to conduct the leather application for both MGMNA and commercial melamine resins. Two pieces of wet blue having the same size (200 mm × 150 mm) were cut along the spine. One piece was treated with MGMNA and the second piece was treated with the commercial melamine resin for comparison. The leather processing recipe [30], raw materials used and the processing conditions are given in Table 1. Chemicals were used in the retanning process of leather on a weight basis of wet blue.

Table 1. Leather processing recipe and conditions.

Process/Chemicals	%	Duration (min)	Comments
Washing			
Water	100	10	Drained
Neutralization			
Water	150		
Sodium formate	1.5	10	
Sodium bicarbonate	1	90	pH up to 5.0–5.2, drained
Washing			
Water	200	15	Drained
Retanning, dyeing and fat liquoring			
Water	100		
Novel melamine resin (MGMNA) *	10	45	
Synthetic fat 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 twice, dried by hooking and staked after conditioning

* MGMNA and commercial melamine resin were used.

2.2.7. Analysis of Leather Characteristics

The measurement of mechanical properties of both pieces of leather retanned with MGMNA and commercial melamine resins was performed as per standard procedure [35]. The resulting pieces of leathers were first conditioned for 48 h at 65 ± 2% relative humidity while maintaining a temperature of 27 ± 2 °C. Then, the leather samples were tested for tensile strength and elongation at break by using STM 566F equipment as per standard procedure [36]. Similarly, tear strength and grain strength were measured by using equipment STM 566ST and a lastometer according to the standard procedures [37].

The resulting pieces of leather after retanning were tested for softness, fullness, roundness, grain tightness (break) and grain smoothness with the help of visual observations and softness meter SL-01 by standard procedure [38]. Each property was allotted a rating on a scale of 0–10 points, where a higher point reflected better property. Both pieces of leather treated with MGMNA and commercial melamine resins were subjected to testing after proper conditioning.

2.2.8. Characterization of Retanned Leather by SEM

A Leica metallurgical microscope Q550IW (Bustleton PikeFeasterville-Trevose, PA, USA) coupled with a CCD camera (Hilkvision, Lahore, Pakistan) was used for SEM analysis. Selected swatches of retanned leathers were cut and washed with acetone to clean their surface. An ion sputter coater, JEOL Model JFC 1500, was used to obtain a uniform gold coating of thickness 300 Å on each leather swatch. Scanning electron microscopy (SEM) analysis was performed at a magnification of 50× to observe the morphologies of the grain surface and at a magnification of 500× to study the spatial arrangement of collagen fibers after the retanning process [39].

2.2.9. Determination of Free Formaldehyde Content in Leather

The determination of free formaldehyde in leather retanned with MGMNA and commercial melamine resins was performed as per the standard colorimetric method [40]. Selected swatches of leather were analyzed to calculate their moisture contents, and finally, the free formaldehyde was determined on a dry weight basis.

2.2.10. Color Difference Measurements

Data Color (Spectra Flash SF 550-USA, New York, NY, USA) was used to measure the color of both dyed leathers previously retanned with novel and commercial melamine resins. The comparative difference of shade lightness is designated as ΔL, while the difference in values "a" and "b" is indicated as Δa and Δb, where a represents the red and green axis, and b represents the yellow and blue axis. Values of ΔL, Δa, Δb and ΔC could be obtained by subtraction of the respective values of leathers retanned with novel and commercial melamine resins [2].

2.2.11. Analysis of Effluent

Effluents collected after retanning of leather with both novel and commercial melamine resins were analyzed as per APHA standard procedures [41]. For chemical oxygen demand (closed refluxed titrimetric method 5220-D), total dissolved solids (2540-D) and total suspended solids (2540-C) were used. Free formaldehyde contents were measured as per standard procedure [40].

3. Results and Discussion

The present work involves the development of formaldehyde-free melamine resin (MGMNA). The novel MGMNA resin was produced by condensation reaction of melamine and glyoxal followed by sulfonation with metanilic acid. The respective mole ratios of these reactants are listed in Table 2. The optimal mole ratio of reactants produced a novel MGMNA resin with an optimum molecular weight which improved the retanning properties. The structure of the novel MGMNA resin is shown in Figure 1.

Table 2. Mole ratio of reactants used for the preparation of novel MGMNA resin.

Novel Melamine-Based Resin	Melamine	Glyoxal	Metanilic Acid	Sodium Hydroxide	M_v
MGMNA	0.125 mole	0.375 mole	0.187 mole	0.2 mole	26,219.90

3.1. Molecular Weight Determination of MGMNA Resin

The molecular weight of MGMNA was determined from the relative viscosity measurements by using a Cannon Ubbelohde viscometer. The time of flow of distilled water and MGMNA resin solution was noted, and relative viscosity (ηr) and specific viscosity (ηsp) were calculated. From these values, Δ/c^2 for the MGMNA resin was calculated at various concentrations. The determination of Δ/c^2 for MGMNA at five different concentrations is given Table 3.

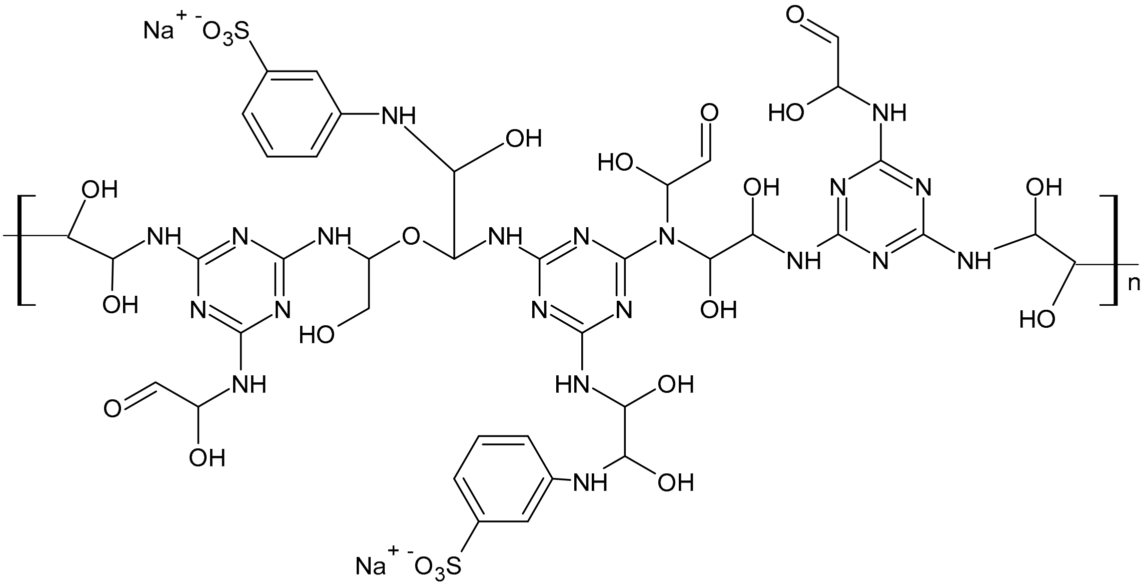

Figure 1. Structure of MGMNA.

Table 3. Dependence of flow time, relative viscosity, specific viscosity, $\Delta = \eta sp - \ln\eta r$ and Δ/c^2 on different concentrations of MGMNA.

Conc. MGMNA (g/mL)	Flow Time (Seconds)	ηr	ηsp	lnηr	Δ = ηsp − lnηr	Δ/c^2
0.008	138.2	1.161	0.161	0.149	0.012	183.422
0.007	137.2	1.153	0.153	0.142	0.011	216.312
0.006	136.7	1.149	0.149	0.138	0.010	279.146
0.005	135.2	1.136	0.136	0.127	0.008	339.197
0.004	132.5	1.113	0.113	0.107	0.006	372.949

The graph of the relationship between Δ/c^2 and concentration was extrapolated to determine the value of intrinsic viscosity [η]. The determination of intrinsic viscosity for MGMNA is shown in Figure 2.

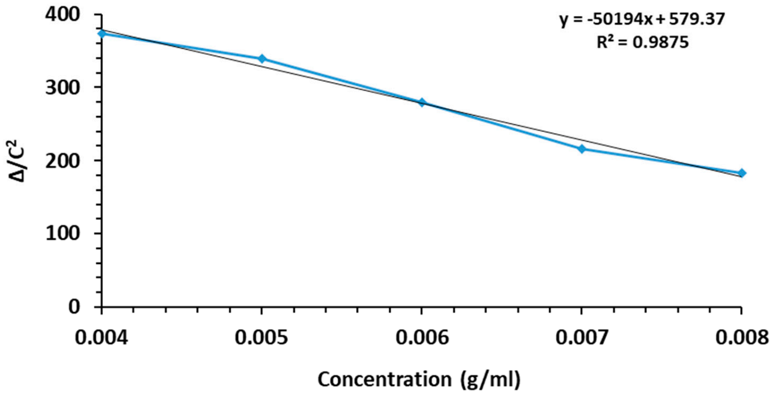

Figure 2. Dependence of Δ/c^2 on the concentration of MGMNA resin.

The plot provided the value of 1/2 [η] 2 at a concentration of 0, which was found to be 579.37, while the intrinsic viscosity was calculated as 34.04. The viscosity average molecular weight of the MGMNA was calculated by using the Mark Houwink equation with the help of intrinsic viscosity and was found to be 26,219.90.

3.2. Thermogravimetric Analysis (TGA)

Thermal degradation graphs of the novel MGMNA resin and the commercial melamine resin are displayed in Figure 3. At a higher temperature, the cross-linking ability of the novel MGMNA resin increased while forming a stable composite mass to improve its thermal stability. A resin having more tendency to cross-link with collagen fibers would enhance the thermal stability of leather. It is clear from the graph that the thermal stability of the MGMNA resin is better than control resin. The mass loss of both resins at 70–150 °C was a result of moisture removal, whereas mass loss at 150–250 °C was due to the release of certain moieties during condensation reactions of the novel resin in this temperature range. Mass loss above 250 °C was due to thermal decomposition of resins. Reduced mass loss was noticed for the MGMNA resin at 250–650 °C, showing its improved thermal stability by 10.6% as compared to control.

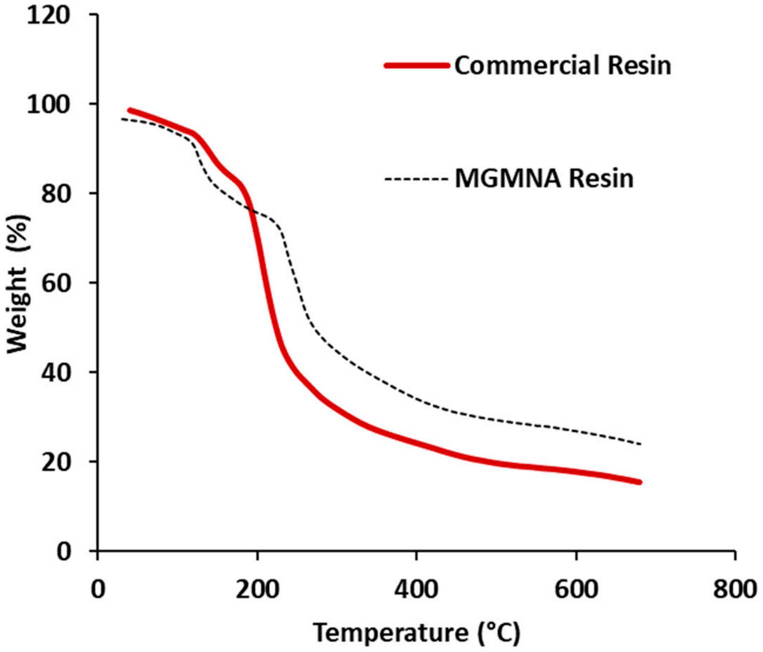

Figure 3. TGA of MGMNA resin and commercial melamine resin.

3.3. FTIR Analysis

FTIR spectrum of the MGMNA resin is shown in Figure 4. Two absorption peaks at 3468 cm^{-1} and 3417 cm^{-1}, due to asymmetric stretching vibrations of $–NH_2$ groups of melamine, are absent in the FTIR spectrum of the MGMNA resin, showing complete incorporation of melamine in the MGMNA resin. Similarly, a characteristic peak at 1630 cm^{-1} responsible for the –CHO group of glyoxal was also absent in the spectrum of the MGMNA resin. Absence of both these FTIR signals confirmed the completion of the condensation reaction. The existence of a broad peak at 3320 cm^{-1} indicated the formation of –NH and –OH groups produced by a reaction of melamine and glyoxal. The FTIR signal at 1560 cm^{-1} appeared due to asymmetric stretching of C–N. The FTIR signal at 1020 cm^{-1} indicated the stretching of C–O in the resin structure. The existence of a peak at 990 cm^{-1} was due to ether linkage. A signal at 805 cm^{-1} was due to the triazine ring of melamine, while the signal at 780 cm^{-1} was due to the meta disubstituted aromatic ring of metanilic acid. The peak located at 1170 cm^{-1} corresponds to the asymmetric stretching of the $R\text{-}SO_3$- group, confirming the completion of the sulfonation reaction. FTIR analysis confirmed that the melamine reacted with glyoxal, followed by sulfonation with metanilic acid.

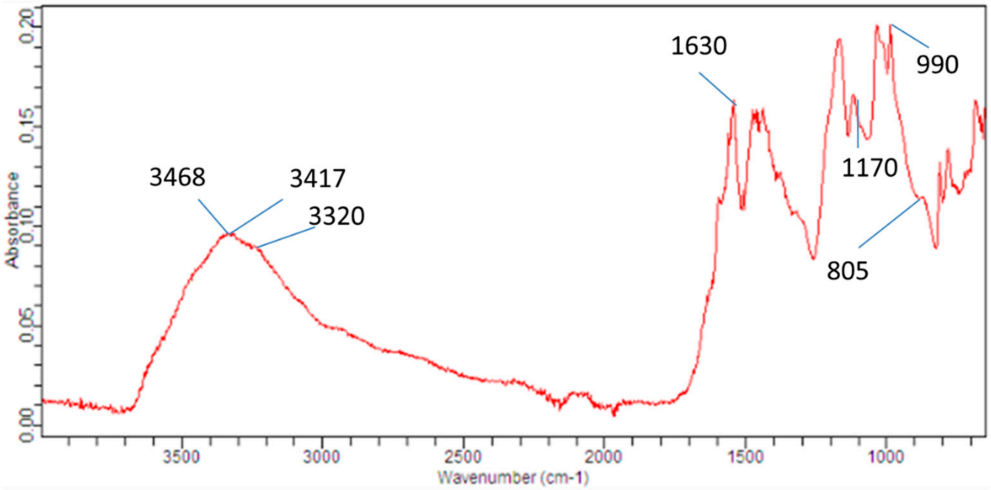

Figure 4. FTIR of MGMNA resin.

3.4. Mechanical Characteristics of Retanned Leather

As displayed in Table 4, the increase in mechanical properties of leather treated with MGMNA was more obvious as compared to the conventional melamine resin. The comparative increases in percentage elongation, tear strength and tensile strength were 8.62%, 10.41% and 17.43%, respectively, in the direction parallel to the backbone for MGMNA. The comparative increases in percentage elongation, tear strength and tensile strength values were 6.0%, 9.79% and 15.17%, respectively, in the direction perpendicular to the backbone. Similarly, the recorded increase in grain distension at cracking was 5.84% and grain distension at burst was 5.51% for leather retanned with the MGMNA resin.

Table 4. Mechanical characteristics of leather retanned with MGMNA and commercial melamine resin.

Parameter	Commercial Melamine-Based Resin	Novel Melamine-Based Resin (MGMNA)	Percentage Increase
Tensile strength (N/cm^2) parallel to backbone	1354	1590	17.43
Tensile strength (N/cm^2) perpendicular to backbone	1094	1260	15.17
Tear strength (N/cm) parallel to backbone	317	350	10.41
Tear strength (N/cm) perpendicular to backbone	378	415	9.79
% Elongation parallel to backbone	58	63	8.62
% Elongation perpendicular to backbone	50	53	6.0
Distension at grain cracking (mm)	8.9	9.42	5.84
Distension at burst (mm)	10.88	11.48	5.51

The MGMNA developed more reactive sites in its structure and exhibited improved ability to undergo cross-linking with collagen fibers in treated leather. Therefore, the stronger interactions developed between collagen and the MGMNA resin compelled the collagen fibers to arrange in a more orderly fashion to improve the mechanical properties [42].

3.5. Effect of Melamine Resins on Organoleptic Properties

The results revealed that the retanning with the MGMNA resin improved the organoleptic properties of the leather significantly as compared to the commercial melamine resin (Figure 5).

The ability of MGMNA to form hydrogen bonding with collagen fiber fixed the collagen fibers tightly to hinder the fiber motion, which resulted in a slight reduction in softness [42]. Moreover, a stable complex formed through intermolecular hydrogen bonding of the MGMNA resin would exist in collagen fibers to enlarge the fiber gaps while improving the fullness of leather. Furthermore, the extended structure of the MGMNA resin developed the entanglements with various nearby fibers to form stronger linkages to improve roundness, smoothness and tightness in the grain structure of leather.

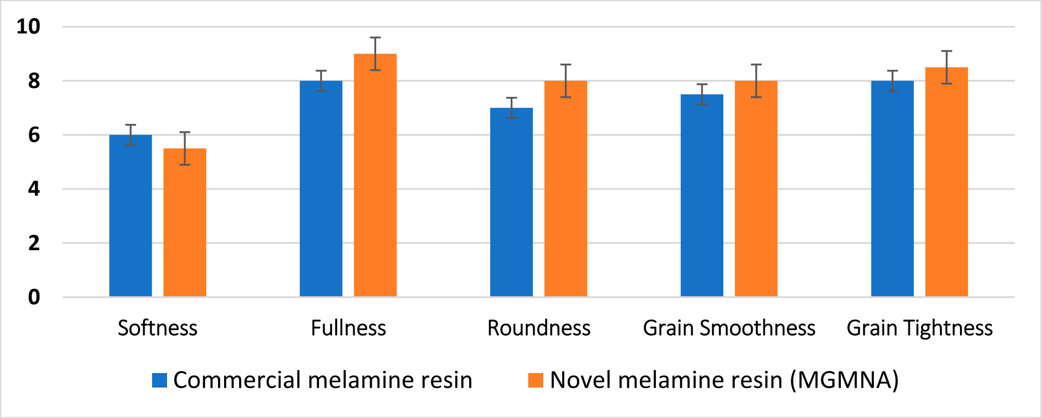

Figure 5. Organoleptic properties of leather treated with MGMNA and commercial resin.

3.6. SEM Analysis

Micrographs of grain surface and fiber cross-section of retanned leathers are shown in Figure 6. It is clear from comparing Figure 6a,b that a fine grain surface could be seen on leather treated with MGMNA, showing uniform penetration and distribution of resin during the retanning process. Similarly, a more orderly arranged fiber structure could be seen in leather treated with the MGMNA resin as compared to the commercial melamine resin, as shown in Figure 6c,d, which might be an indication of improved retanning properties of resultant leather due to strong bonding between collagen fibers and the MGMNA resin. Moreover, the collagen fibers were empty in control leather, whereas compact fibers with a higher weave angle were noticed in leather treated with the MGMNA resin [43].

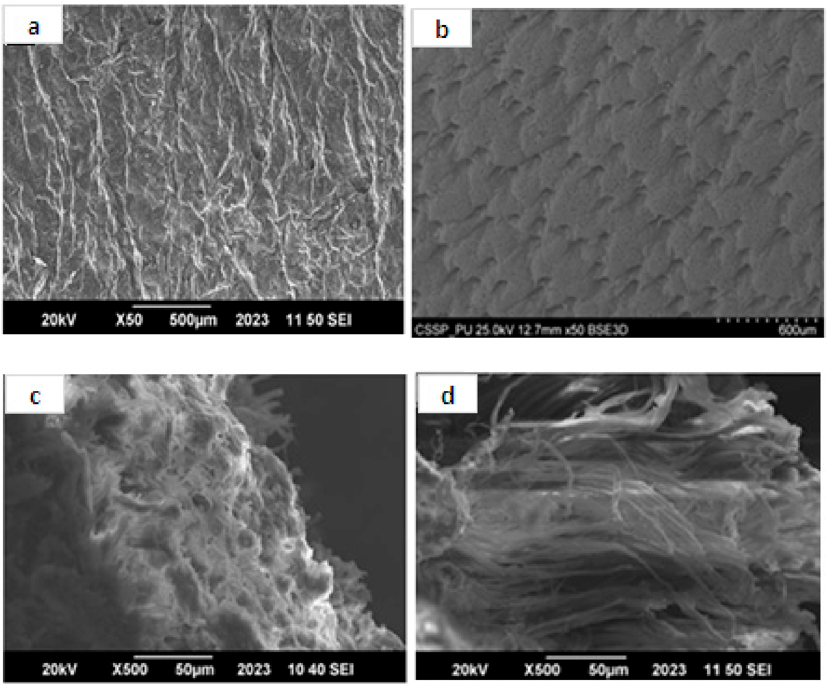

Figure 6. Scanning electron micrographs of cross-section of grain surface (×50) and collagen fiber (×500): (**a**) grain surface of leather treated with commercial melamine resin; (**b**) grain surface of leather treated with MGMNA resin; (**c**) fiber cross-section of leather treated with commercial melamine resin; (**d**) fiber cross-section of leather treated with MGMNA resin.

3.7. Quantitative Determination of Free Formaldehyde Contents in Leather

The free formaldehyde content in leather treated with the commercial melamine resin was found to be 145 mg/kg of leather, while no formaldehyde was detected in leather treated with the MGMNA resin, as reflected in Figure 7. The permissible limit of formaldehyde in leather and leather goods is 75 mg/kg of leather. This development has succeeded in producing formaldehyde-free leather.

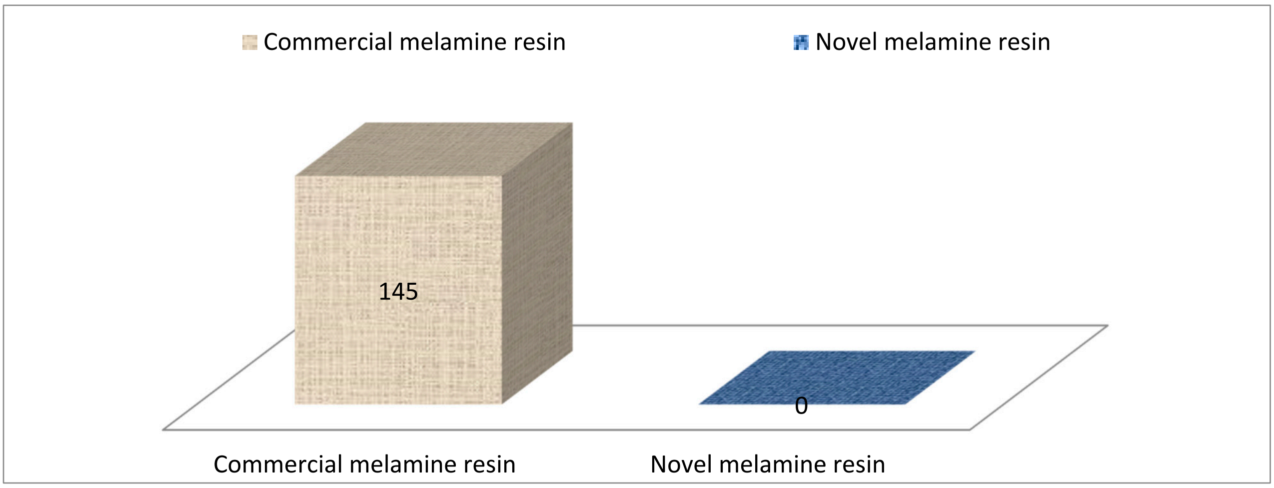

Figure 7. Free formaldehyde content in retanned leathers (mg/kg).

3.8. Color Difference Measurements

Measurements of the color values for both dyed leathers retanned with novel and commercial melamine resins are shown in Table 5. Leather treated with the novel melamine resin showed a negative value of ΔL, which could be an indication of a darker shade. The overall value of color difference observed for both resins was 3.48. Moreover, the leather retanned with the MGMNA resin exhibited improved uniformity of the dye shade, which reflected the improved dispersing and leveling properties of the novel melamine resin as compared to the commercial resin.

Table 5. Color difference measurements of leathers.

Commercial Melamine Formaldehyde-Based Retanned Leather			
Illuminant D65	L 73.43	a −0.24	b 30.23
MGMNA Resin-Based Retanned Leather			
Illuminant D65	L 69.95	a 1.41	b 37.60
Distinction of Experimental Leather			
Illuminant D65	ΔL −3.48	Δa 1.65	Δb 7.37
	Darker	Red	Yellow

3.9. Effluent Analysis

The effluents collected after comparative retanning of both the MGMNA resin and the control resin were analyzed by measuring free formaldehyde content, total dissolved solids (TDS), total suspended solids (TSS) and chemical oxygen demand (COD). The observed values of these parameters are listed in Table 6. It is clear from the results that the novel MGMNA resin had not contributed any free formaldehyde in effluent, while 295 ppm free formaldehyde had been generated by the commercial melamine resin [44–46]. Significant reductions in COD, TDS and TSS load were observed in the effluent of the MGMNA resin. A 9.21% reduction in COD was observed in the effluent from MGMNA, which could be attributed to the reduced quantity of un-exhausted resin in the tanning bath by improved fixation of the novel resin due to its in situ polymerization and more reactive groups in the structure. Similarly, a 6.97% reduction in TDS was noted in the effluent of novel melamine resin due to the in situ cross-linking ability of the MGMNA resin with collagen. Moreover, the observed reduction in TSS was 5.60%, which was due to the absence of any insoluble carriers in the novel resin as compared to the commercial resin [45,47,48].

Table 6. Comparative characteristics of effluent for leathers retanned with MGMNA resin and commercial melamine resin.

Parameter	Commercial Melamine Formaldehyde Resin	(MGMNA)	Percentage Efficiency
Formaldehyde content (ppm)	295	0	100
Chemical oxygen demand (ppm)	14,340	13,020	9.21
Total dissolved solids (TDS)	23,627	21,980	6.97
Total suspended solids (TSS))	16,526	15,600	5.60

4. Conclusions

In this research, a novel formaldehyde-free melamine resin was produced at a glyoxal to melamine ratio of 3:1. This resin in comparison with the commercial resin has improved mechanical and organoleptic properties in the leather tanning due to availability of more reactive sites in the molecules. Color measurements of the dyed leather confirmed that the novel melamine resin had adequate leveling and penetration properties to ensure uniform dyeing with better exhaustion. The use of an aromatic sulfonating agent improved the thermal stability of the novel resin by 10.6%. The optimum molecular size of melamine–glyoxal–metanilic acid (MGMNA) resin exhibited improved penetration in leather, and its ability to undergo in situ polymerization improved its exhaustion, leaving minimum unfixed resin in the bath. Furthermore, the production process cut the pollution load in effluent by 9.21% of COD, 6.97% of TDS and 5.6% of TSS. Furthermore, free formaldehyde contents in finished leather were observed to be zero, making it formaldehyde-free. Therefore, the novel MGMNA resin is proven to be a suitable resin for producing green leather with 100% reduction in formaldehyde. In the future, production-scale applications will help to protect the environment, workers and public health from the harmful effects of formaldehyde.

Author Contributions: Conceptualization, M.N.A. and A.A.; methodology, M.N.A. and A.A.; Laboratory analyses and investigation, S.R.A., M.N.A., A.A. and S.-E.O.; writing original draft reparation, M.N.A. and A.A.; writing review and editing, A.A., F.H. and M.B.S.; Laboratory equipment and material acquisition or other resources, M.N.A. and A.A. All authors have read and agreed to the published version of the manuscript.

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