



Investigation of Flame Retardant Effects of Resins on the Flammability of Leather

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ABSTRACT

Natural leather products, which are by-products of the meat industry, are used because of their high air vapor permeability and elegant appearance compared to synthetic leather. The production of flame retardant leather is important for some leather types such as motorcyclist jackets, flight or automotive upholstery leathers, military boots. It is frequently mentioned in the literature that resinous chemicals create flame retardant effects in textile materials due to their nitrogen content. Urea, melamine and dicyandiamide resins are always used in the traditional retanning process of cattle leathers. It has been investigated which of these resins has the highest flame retardant effect on the leather. In the study, 2%, 3% and 4% ratios were studied for these three resins; flame resistance of the leathers were investigated by LOI and TGA analysis. The study also examined the chemical effects of resin deposition on the leather surface with FTIR and SEM analyses.

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1. INTRODUCTION

Natural leather products, which are by-products of the meat industry, are used because of their high water vapor permeability and elegant appearance compared to synthetic leather. The production of flame retardant leather is important for some leather types such as motorcyclist jackets, flight or automotive upholstery leathers, military boots [1]. It is frequently mentioned in the literature that resinous chemicals create flame retardant effects in textile materials due to their nitrogen content.

During the last 10–15 years there has been a constant trend in engineering plastics to move from traditional halogenated flame retardant polymers (FRP's) towards non-halogenated alternatives [2-8].

The drive to change from halogenated FRP's, due to toxicology and environmental concerns, came about in the middle of the last decade driven by the introduction of three regulations, RoHS (Restriction of Hazardous substances)

[9], REACH (Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals), specifically SVHC (substances of very high concern) and the WEEE (Waste Electric and Electronical Equipment). These regulations basically pushed the additive suppliers, the compounders and the E & E industry to act, innovate and control the type of additive systems used in their formulations. Today these regulations, or very similar regulations, have circumnavigated the globe, mainly due to the globalization of major companies and the need to import into Europe, so that in essence all consolidated manufacturing countries now follow to a greater or lesser extent these or like regulations [10].

European Union sponsored a research program that has been conducted such as FLARETEX in textile industry that has a focus on sustainable flame retardancy for textiles and related materials based on nanoparticles substituting conventional chemicals. The scientific context of this program is concerned with the replacement of existing flame retardants with sustainable and environmentally friendly alternatives for

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textiles and related materials through the development of innovative flame retardants with low fire toxicity and environmental impacts and halogen-free [11].

Non-halogenated flame retardants can be divided into three groups: metal hydroxides, phosphorus-based compounds and nitrogen-based compounds. Each exhibits different mode of actions and very often, a combination of various flame retardants and synergists is necessary to obtain the best performance.

Nitrogen-based flame retardants (NFR) can be divided into two groups with respect to their mode of action. By far the most dominant and well-established group is derived from either ammonia or melamine, although some derivatives of urea and guanidine are known. Molecular structures of common type of resins that are Used in leather manufacturing are shown in figure 1. Their primary mode of action is endothermic decomposition with release of large amounts of non-flammable gases such as nitrogen and ammonia. They are often used as salts which have higher thermal stability and lower volatility. Typical products and applications include melamine in polyurethane flexible foams, melamine phosphates, ammonium polyphosphate-pentaerythritol or ethylene-urea formaldehyde polymers in polyolefins, melamine, melamine phosphates or dicyandiamide in intumescent paints, guanidine phosphates in textiles and guanidine sulfamate in wallpapers

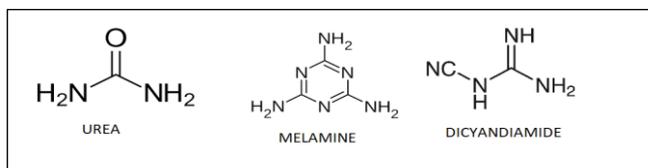


Figure 1. Molecular structures of common type of resins that are used in leather manufacturing.

Açikel et al., investigated the flame retardant effect of tributyl phosphate (TBP) and observed TBP chemical bounded with nitrogen containing resins which are used in leather manufacture and so nitrogen and phosphoric acid interaction prevented flammability of leather [12].

Melamine, its condensation products and salts, are widely used as flame retardants. In most applications they are combined with P-containing flame retardants. Combinations with metal hydrates and halogenated flame retardants are known as well. In all cases melamine undergoes endothermic decomposition leading to cooling of the polymer matrix and the release of non-combustible gases such as water, CO_2 and ammonia. These dilute the combustible decomposition products of the matrix polymer further destabilizing the flame. Since this reaction is independent on the matrix polymer, it can be broadly applied.

Melamine (2, 4, 6-triamino-1, 3, 5 triazine, CAS nr. 106-78-1) is a white crystalline powder with a melting point of approximately 354°C and a density of 1.573 g/cm^3 . At about 200°C , melamine undergoes sublimation and thereby

dilutes the fuel gases and oxygen near the combustion source. The energy of sublimation is about 29 kcal/mole . On the other hand, its decomposition is strongly endothermic in the order of $\sim 470 \text{ kcal/mole}$ and melamine acts as a heat sink in fire situation. Melamine is only slightly soluble in cold water but shows much higher solubility in hot water. Some work has been done on interactions and synergies with other flame retardants. In general, these triazine polymers induce charring and, as such, support other flame retardants such as phosphinates. Interesting results were obtained with a commercial polymer mixture used by loading 20% triazine on polypropylene, it was observed that the LOI value increased from 19% to 31% and thus achieved an UL94 V0 rating. Nitrogen-based flame retardants like melamine cyanurate in polyamide assume a more active role in flame retardancy. They either directly interfere with the decomposition of the polymer or are strong charring agents such as phosphazene or triazine polymers. [13]. When the flame retardancy effects of resins in different materials are examined in the literature; Chen et al, used modified melamine resins on cellulose papers because it is a thermoset resin and they found that LOI values of papers were increased from 32% to 33.5% by the effect of melamine resin [14]. Gaan et al. benefited from nitrogen phosphorus synergistic effect to increase flame retardancy property of TBP in cotton fibers and they used nitrogen containing urea and melamine resins. At the end of their study, LOI values of cotton fibers increased from 25.5% to 27.5% [15]. Gao and Yang synthesized a new flame retardant chemical using melamine, dicyandiamide and formaldehyde resins. They investigated effects of different rates of the flame retardant chemicals on combustion. The chemical with concentrations of 0%, 10%, 20% and 30% had LOI values of 20%, 24.6%, 26.5% and 28.5%, respectively [16]. Zhua and Xu investigated the combustion behavior of rigid polyurethane foams and synthesized the foams using urea, melamine and formaldehyde resins. As a result of this study, they increased the burning resistance of the foams from 18% to 24.4%. Zhang etc. synthesized nitrogen and phosphorus containing polyurethane graphene nanocomposite chemical and they investigated the flame resistance of leather after they used this nanocomposite in retanning process of cattle leathers. They reached that LOI value of cattle leather was increased from 25.3% to 26.3% by this nitrogen-containing nano-composite [17].

In the light of previous studies, the motivation for this research was to determine the optimum concentration of nitrogen based resins that are commonly used in leather industry. To enhance the durability of retardant properties, concentrations of urea, dicyandiamide and melamine resins were increased gradually. Fire retardant performance and thermal properties of treated leathers were investigated.

2. MATERIAL AND METHOD

2.1 Material

Wet-Blue leathers which are tanned by the chrome tanning agent, are semi-product leathers. After tanning process, leather was finished with recipes of shoes, garment,

upholstery, etc. in the retanning process. Ten wet-blue cattle leathers used in the study were purchased from the Tuzla Leather Industrial Area in İstanbul, Turkey. In retanning process of leathers following commercial chemicals were used, Farben shine forel HT as nonionic tensed, Tan Krom AB %33 as basic chrome sulfate tanning agent, Alpine MX as melamine resin tanning chemical, KR-477 as urea resin tanning chemical, Alpine MD as dicyandiamide resin tanning chemical, Renektan ER (Stahl Company) as polymer tannin, Black ERD (Bur Boya) as acid dyestuff, Farben Retan N as phenolic syntan, Farben Shine Grossöl 55 as synthetic fat liquoring agent, Alpine Soft TK as combine fat liquoring agent with phosphoric ester and Alpine Soft SB as fish oil. The sodium formate and formic acid were supplied by BASF Chemical Company and sodium bicarbonate was supplied by Soda Sanayi A.S. In the finishing recipe; different chemicals were used, Pelle Curtecin PU3234 as polyurethane binder,

Pelle Curial Binder OBN as acrylic binder, Pelle Curtefill CP 5200 as filler, Sarkol K Black (Sarchem b.v.) as black Pigment, Pelle Curtewax 4012N as wax, Selladerm Black (TFL Company) as anilin dye, Pelle Curtebind Lustre TE as protein binder, Melio EW 348B (Clariant b.v.) as hydrolacque, Melio WF 5226 (Clariant b.v.) as feeling agent.

2.2 Method

Recipe of wet blue cattle leathers were prepared for upholstery leather type. Recipe used for processing of leathers is given in Table 1. After the retanning process, mechanical process of leathers and finishing process with a standard recipe were conducted (Table 2). In retanning process; urea, melamine and dicyandiamide resins used at 2%, 3% and 4% rates, and the experimental design is shown in Table 3.

Table 1. Retanning recipe of leathers

Leather Process	Chemical Additives	Rate (%)	Time (min)	Temperature (°C)	Drum Speed (rev/min)	Remarks
Weight Soaking	Water	300		40	12	
	Oxalic Acid	0,3				
	Nonionic Tencid	0,4				
	Formic Acid	0,4	60			Drain
Washing	Water	300	10	30	10	Drain
Chrome Retanning	Water	200		30	12	
	Chrome	4	60			
	Sodium Formate	1,5	30			pH:3.8-4.0
Neutralization	Water	200		35	12	
	Sodium Formate	1				
	Neutral Syntan	1,5	20			
	Sodium Bicarbonate	0,8	60			Ph:5,5 Drain
Washing	Water	300	10	30	10	Drain
Retanning	Water	100		25		
	Polymer Tannin	2	10		14	
	Resin Tannin	%2	10			
		%3				
		%4				
	Phenolic Syntan	2	10			
	Tara Vegetal Tannin	3	10			
Dying	Ammonia	1	5		14	
	Acid Dyestuff	4	60			
	Formic Acid	2	30			pH:4
Fatliquoring +	Water	200		70	14	
	Synthetic Oil	4				
	Combine Fatty Acid Ester	3				
	Fish Oil	2	60			
	Formic Acid	0,5	30			pH:4 Drain
Washing	Water	200	10	30	10	Drain

Table 2. Finishing recipe of leathers

Chemical	Rate	Finishing Application
Polyurethane Binder (g)	100	2x Spray
Acrylic Binder (g)	75	Press
Protein Binder (g)	75	(70 atm, 90 oC,1s)
Filler (g)	50	1 x Spray
Wax (g)	75	Press
Pigment Dye (g)	80	(70 atm, 90 oC,1s)
Anilin Dye (g)	20	
Water (g)	500	
Hydrolaque (g)	100	1 x Spray
Feeling Agent (g)	10	Press
Water (g)	150	(70 atm, 90oC, 1 s)

Table 3. Experimental Design

Resin	%Rate		
Melamine	2%	3%	4%
Urea	2%	3%	4%
Disiyandiamide	2%	3%	4%

2.3. Characterization Techniques

10 groups of leather samples, which each group have 15 pieces (140 mm x 60 mm) that were taken from flame-retardant leather were tested in parallel in a limiting oxygen index chamber according to ASTM D 2863-77 LOI test [14]. For SEM analysis the samples were placed on a scanning electron microscope (Fei-Quanta Feg 250) and their images were taken at 500 μm and 100 μm magnifications. FTIR analysis was conducted in order to determine the differences in the chemical properties of leather processed with urea, melamine and dicyandiamide resins and control group (0%). FTIR studies were conducted on Bruker-Vertex70 ATR device with ATR equipment. For this purpose, the leather samples were scanned with IR spectrums at a wavelength of 4000-400 cm^{-1} and the results were evaluated in the FTIR Spectrum Software and compared with the spectrums in the literature. Thermogravimetric analysis (TGA) of the flame retardant leathers were conducted at heating rate of 20 $^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere (flow 60 mL min^{-1}) between 35 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$ temperatures using TGA (Mettler Toledo). Sample mass was approximately 8 mg. TGA curves were mapped by computer automatically.

3. RESULTS AND DISCUSSION

3.1 LOI Results

LOI results of leathers are in Table 4. According to the obtained results, all leather groups that were urea applied had 26.1% LOI values, while control sample had 23.6%. Melamine applied groups at concentration levels of 2%, 3% and 4% had LOI values of 26.1%, 26.8% and 26.1% respectively. While dicyandiamide applied groups with same concentration levels as other resins had LOI values of 24.7%, 24.7% and 21.3%.

Leather is a very different product than other textile materials. A wide variety of factors such as animal race,

breed, age, and climate, can affect the quality of the raw leather, and also structural changes can be seen even in leather samples taken from the same batch. Another factor is determining the chemical ratios of recipe in leather production. The chemical binding capacity of collagen is limited and after leather bounded the optimum chemical, the excess of chemical discharged to the wastewater [19]. Consequently, it has acquired as many chemicals as can get in the leather, and the lack of differences between 3% and 4% has been associated with this. Therefore, the leather consumed maximum resin chemical as it can absorb and the excess of it was not bounded. So in the LOI results, the lack of differences between 3% and 4% has been associated with this.

LOI test results show that 3% melamine applied group had the highest value compared to others. The main reason of this result is the nitrogen containing triazine ring that was found in the molecular structure of melamine resin. LOI results of urea applied groups had same results although concentration levels are increasing. Increasing amount of urea did not provide any negative effect in pyrolysis of the leather. Nitrogen containing resins occurred a protective layer over each fiber to support the resistance of heat transfer, when the material burned. Xu and et al., studied a flame-retardant leather (FR-leather) that was prepared from wet-blue leather treated with tetrakis hydroxymethyl phosphonium-melamine-pentaerythritol diphosphate (THPM). They found that melamine can help to dilute the concentration of O_2 during the thermal degradation of collagen since melamine has released non-combustible gases such as CO_2 and H_2O [20].

Application of dicyandiamide contributed less to the incombustibility of the leather than other groups. Dicyandiamide has a lower combustion resistance compared to melamine and urea. It is thought that it may be due to fact that it has only one amine group in molecular structure. Also we are in the opinion that there is a deviation in the test result of 4% dicyandiamide due to the fact that leather material is a non-homogeneous material. According to LOI test results; melamine or urea-containing resins should be used instead of dicyandiamide when preparing retanning recipe in flame resistance leather manufacturing.

Table 4. LOI results of treated leathers

Resin Tannin	Group (%)	LOI (%)
0	0	23.6
Urea	2	26.1
Urea	3	26.1
Urea	4	26.1
Melamine	2	26.1
Melamine	3	26.8
Melamine	4	26.1
Dicyandiamide	2	24.7
Dicyandiamide	3	24.7
Dicyandiamide	4	21.3

3.2 SEM Results

SEM images of the leather samples are shown in Figure 2 and Figure 3. In all SEM photographs it is seen that, resin types and ratios used in the retanning process did not cause any deformation on the leather surface. These chemicals are compatible with the leather since they are often used in leather retanning. On the other hand, images from SEM analysis verify that these chemicals, which contribute to the flame retardancy of the leathers, provided fullness and

smoothness as expected from the retanning process. There is a slight fullness effect in 2% melanine resin used leather, when compared to 3% and 4% melanine-resin respectively. Pore diameters are narrower, but swell by volume on the surface, indicating that 3% and 4% melanin resin is absorbed by the material with increased saturation. Although not at the level of effect observed in melanin and dicyandiamide resin applied leathers, fullness effect was observed also in the urea resin applied leather material.

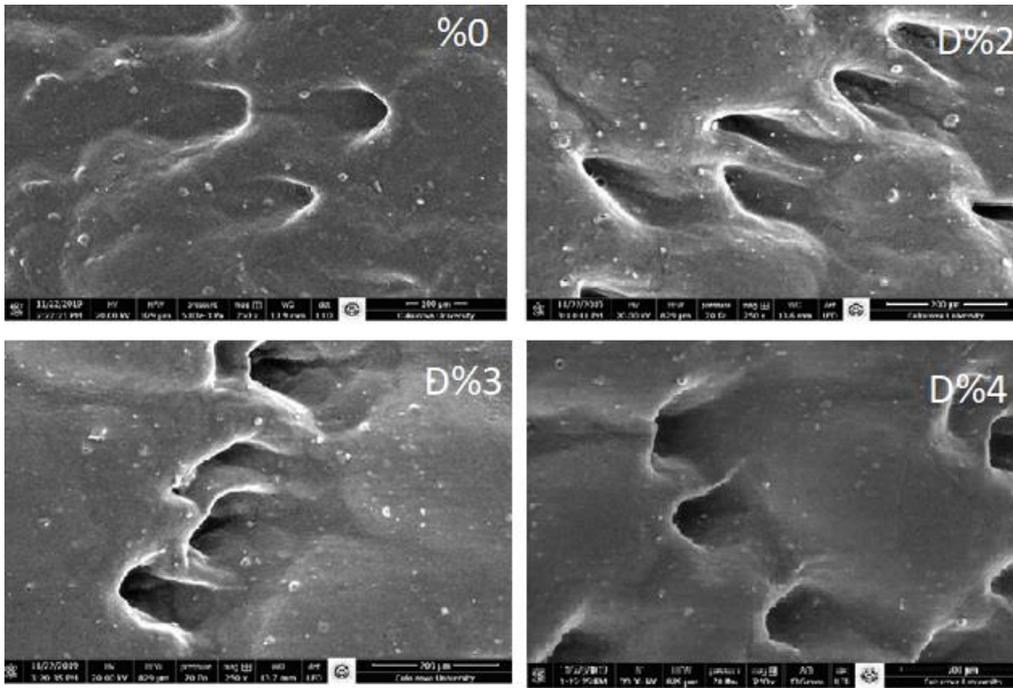


Figure 2. SEM Results of %0 and dicyandiamide used leathers

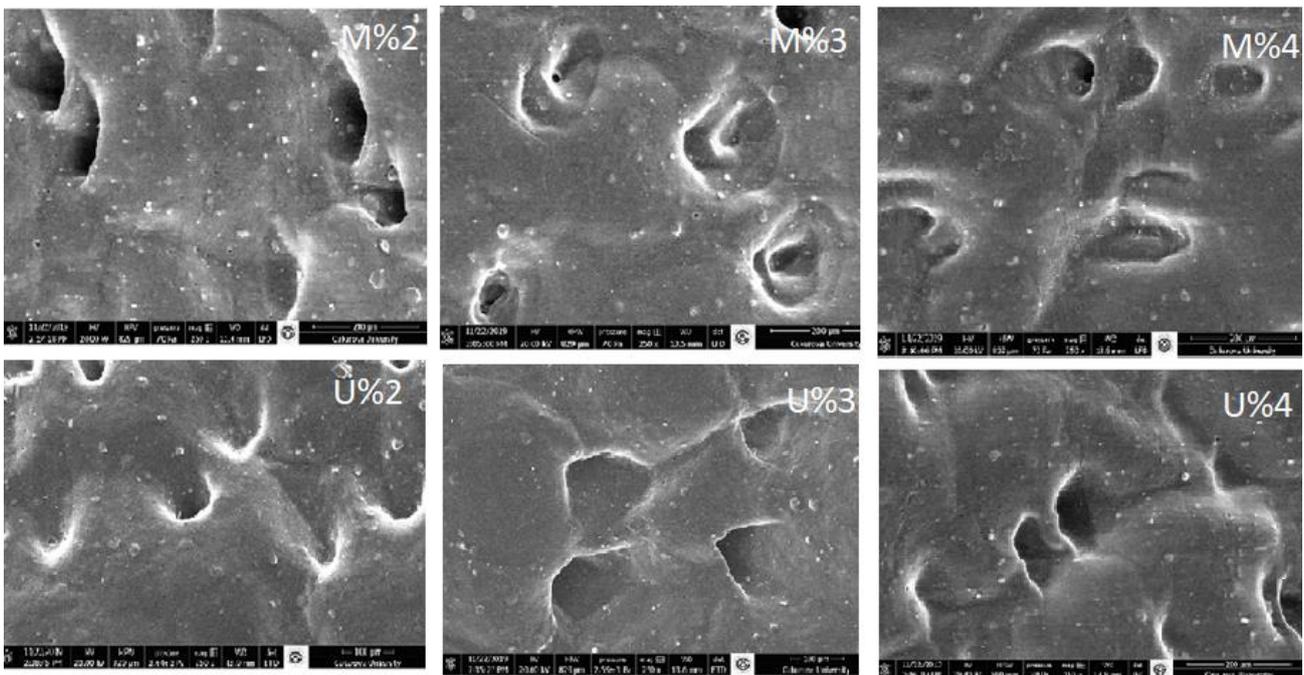


Figure 3. SEM Results of melamine and urea used leathers

3.3 ATR-FTIR Results

FTIR results of resin applied leathers are shown in Figure 4, Figure 5 and Figure 6. According to results, FTIR curves have some characteristic peaks because of collagen structure. These are 3282 cm⁻¹(Amide A), 2921 cm⁻¹(Amide B), 2856 cm⁻¹ (C-H Stretch of C=O), 1644 cm⁻¹(C=O, Amide I) and 1277 cm⁻¹(Amide III) [20].

Urea, melamine and dicyandiamide resins used in the retanning process of leather manufacturing are products of the condensation reaction with formaldehyde. Urea and dicyandiamide resins contain primary amines in molecular structure while melamine has the triazine ring. So in Figures. 4, 5 and 6 two characteristic peaks at 798 cm⁻¹ and

1373 cm⁻¹ that corresponds to C-N stretching vibration, were occurred because of nitrogen containing resins [21].

The peak at 1373 cm⁻¹ was assigned to -CH₂OH, this illustrates the typical reaction between resin and formaldehyde and also belonged to the stretching vibration of triazine ring or amine group. The two peaks at 1442 cm⁻¹ and 1537 cm⁻¹ which were attributed to CN and CN stretching vibrations, were occurred because of molecular structure of resins and amino groups of collagen inside leather. Another characteristic peak of 1256 cm⁻¹ was attributed to the stretching of C-N and N-H of amines. [22]

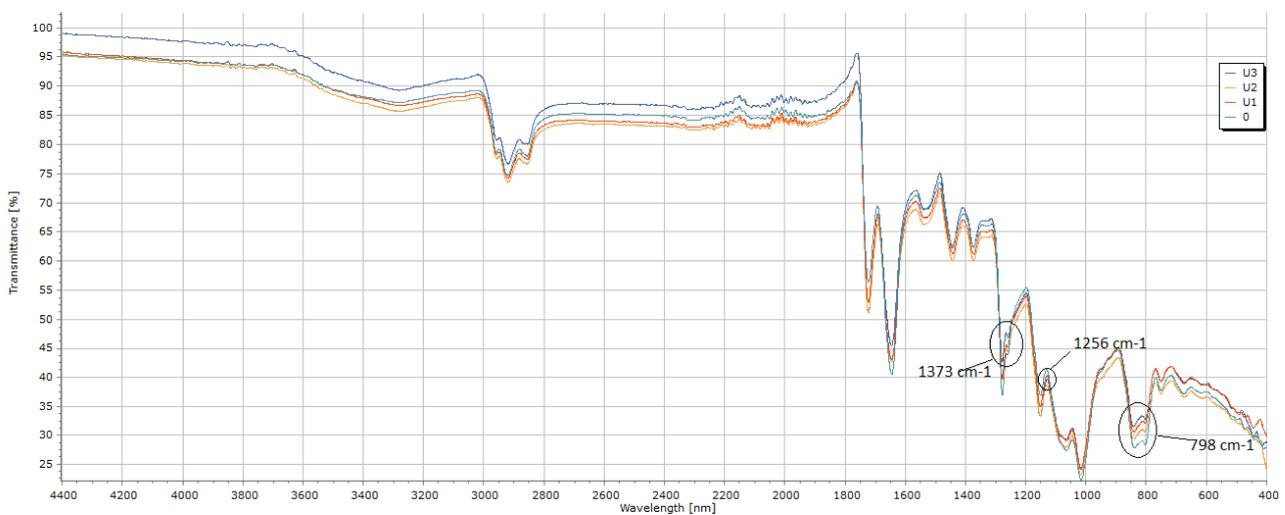


Figure 4. ATR-FTIR result of urea applied leathers

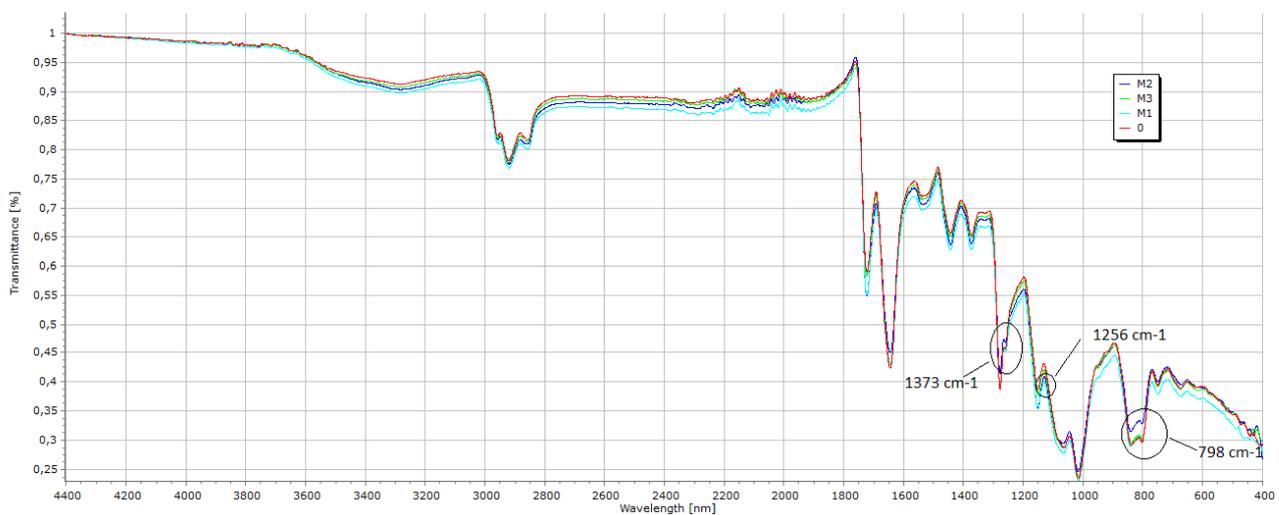


Figure 5. ATR-FTIR result of melamine applied leathers

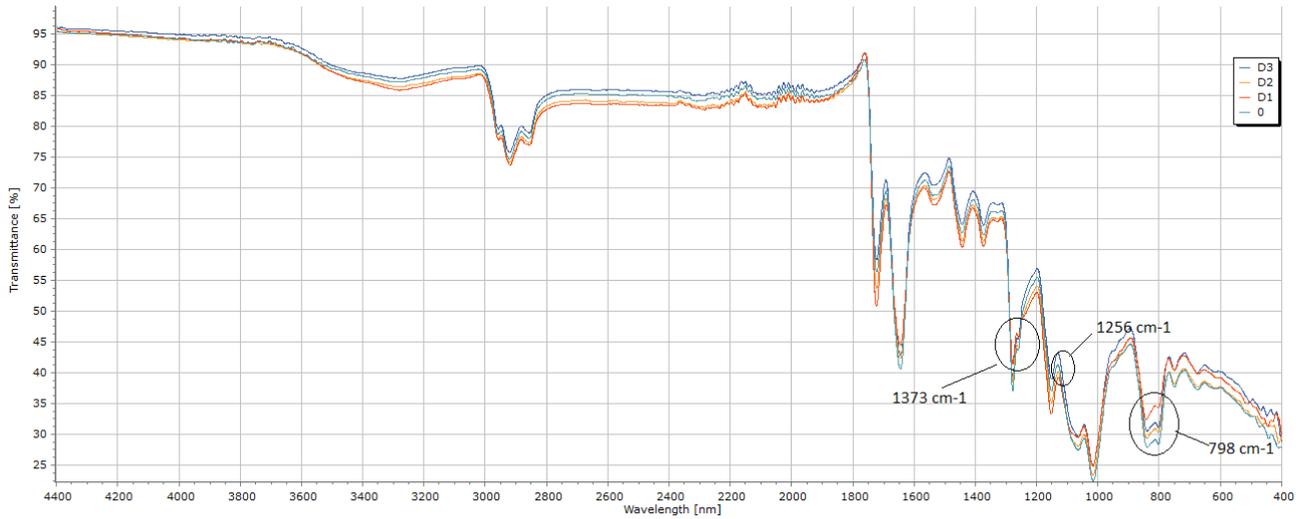


Figure 6. ATR-FTIR result of dicyandiamide applied leathers

3.4 TGA Results

The thermal stability of leather was evaluated by TGA analysis in nitrogen (N_2) atmosphere, and the corresponding results are presented in Figure 7, Figure 8 and Figure 9. Each TGA graph can be divided into two stages: initial stage between 25 °C and 150 °C, which can be related with the evaporation of water content of the material, and the second mass loss stage between 150 °C and 500 °C, namely the main thermal decomposition stage. [20]

According to TGA results, 3% melamine resin degraded at highest temperature value giving maximum weight loss. The temperature at which 15% weight loss and maximum weight loss rates were occurred defined as initial degradation temperature ($T_{initial}$) and maximum degradation temperature (T_{max}). Moreover, a three step degradation

profile is exhibited in Table 5. The char yields at 650 °C - 700 °C range were 29.35% for 2% urea and 27.12% for 3% melamine applied leathers while 0% group had a char yield of 26.98%. As observed in the results of LOI tests, there is a deviation also in the TGA test result of 4% dicyandiamide resin due to the fact that leather material is a non-homogeneous material.

Nitrogen containing resins provided a two-unit increase in char yield. However, the use of resins caused an increase 10 to 15 units in the thermal decomposition temperatures compared to the control group in the initial stage, that is the most important stage in the development of flame behavior of a leather material. According to TGA results, the leather recipe with % 3 melamine resin which has triazine rings can be used in the retanning process in order to obtain better flame retardancy effect.

Table 5. Temperature of maximum weight loss in TGA analysis of resin applied leathers

Group	Stage 1		W_1 (%)	Stage 2		Stage 3 Char Residue At 650 °C - 700 °C Range (%)
	$T_{initial}$ (°C)	T_{max} (°C)		T_{max} (°C)	W_2 (%)	
%0	110	210	84.66	410	42,30	26.98
%2 Urea	125	216	84.54	409	44.81	29.35
%3 Urea	125	215	83.92	410	43,86	27.79
%4 Urea	125	211	84.74	427	43,37	28.12
%2 Melamine	125	212	84.40	414	42,61	27.02
%3 Melamine	125	221	84.44	414	42,68	27.12
%4 Melamine	120	212	83.52	410	43,55	27.07
%2 Dicyandiamide	121	223	84.31	417	43.13	27.43
%3 Dicyandiamide	120	212	85.61	423	42.03	27.63
%4 Dicyandiamide	125	228	83.74	410	44.50	28.25

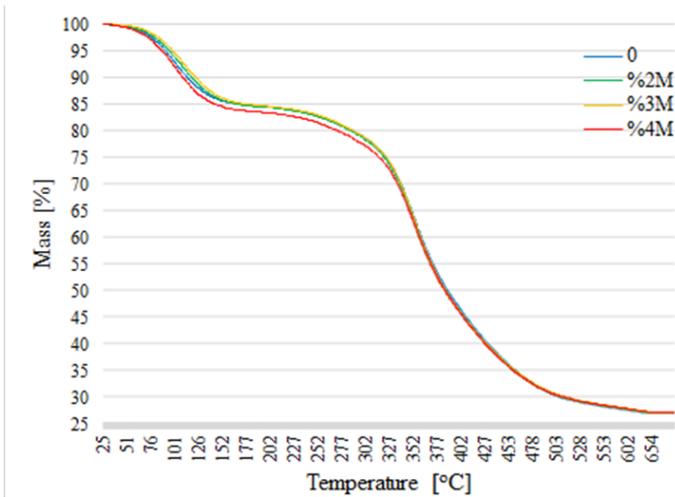


Figure 7. TGA results of melamine applied leathers

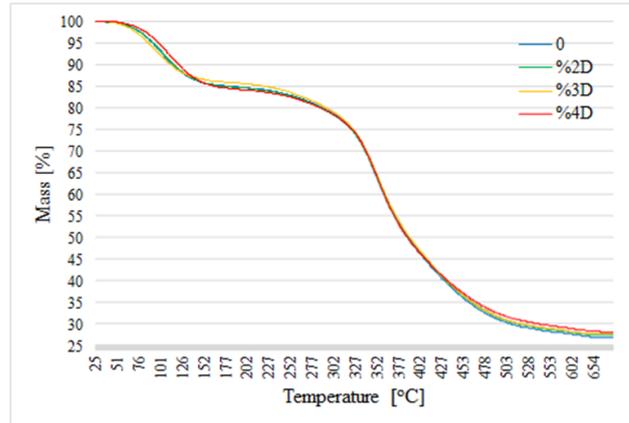


Figure 8. TGA results of dicyandiamide applied leathers

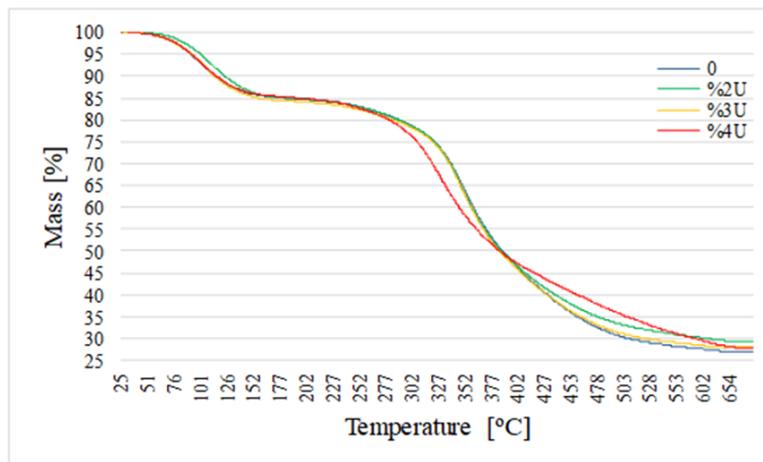


Figure 9. TGA results of urea applied leathers

4. CONCLUSION

In this study, different ratios of urea, melamine and dicyandiamide resins were investigated on the effect of flammability of leather. All of the resins contributed to the flame retardancy of cattle leather and the LOI of leather was increased from 23.6% to 26.8%. In leather production, it was concluded that 3% melamine resin is the most effective ratio in retanning process in order to increase the flame retardant effect of leather. The presence of nitrogen

containing triazine ring in the molecular structure of melamine resin showed better flame resistance than other resins. Thus, it is recommended to increase amount of melamine resin in the retanning process in order to achieve a more effective flame retardant leather.

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