



Modification of Natural leather by Grafting Emulsion Copolymerization Technique

A. S. Badran, H.E. Nasr, N.R.El-Halawany and W.S.Mohamed

Department of Polymers and Pigments, National Research Center, Dokki, Cairo-Egypt

Abstract:-

Grafting emulsion copolymerization of methyl methacrylate (MMA) with butyl acrylate (BuA) of different molar ratios onto natural leather was carried out using developed redox initiation system of potassium persulfate (PPS) as an oxidizing agent and some sodium bisulphite adducts as reducing agents, as well as sodium dodecyl sulphate (SDS) was used as an anionic emulsifier.

The grafted leather was characterized via FTIR, SEM and thermal gravimetric analysis. Moreover, the grafted leather was evaluated through water absorption, tensile strength, dyeing performance and hardness measurements. The obtained results revealed that the physical and mechanical properties of the modified leather were enhanced.

Key words:-

Grafting - emulsion copolymerization- methyl methacrylate - butyl acrylate natural leather

Introduction:-

Graft copolymerization is a well known method for modification of the chemical and physical properties of polymeric materials, various commercial polymers can be used as the grafting substrate ¹⁾. Monomers used for grafting were, for instance, methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BuA), butyl methacrylate (BuMA), styrene (St), and their mixtures²⁾. Best results were obtained by using BuA or its mixture with MMA.³⁾ Mechanical properties of grafted leathers, ⁴⁾ optimum composition of the initiation system,⁵⁾ and kinetics of polymerization,²⁾ were studied. Some investigations reported around the conditions of grafting reactions for optimizing yield ⁶⁾ and also effect on the extent of



grafting of the individual monomer onto the substrate polymer⁷⁾. The grafting reaction can also give more economical graft under the most favorable reaction conditions⁸⁾.

For quite a few years the direct chemical formation of polyvinyl chains bonded with leather tissue has been conducted in order to improve the use properties of leather⁹⁾. But, grafting by free radical polymerization is the most successful method¹⁰⁾. The use properties of leather can improve by chemical grafting with butyl acrylate¹¹⁾.

Leather dyeing is a process of imparting a color to the leather. In dyeing, initially dye penetrates through out the cross section of the leather and is then fixed in the leather fibers by electrostatic attraction.¹²⁾ The substantivity of anionic dyes towards leather accrues from reversible, non specific forces such as Van der Waals and ion-ion interaction¹³⁾. The aim of this work is to improve the leather properties which is a requirement in some industrial uses where, tensile strength, elongation, hardness, water absorption and dyeing properties are improved by grafting process.

Experimental

Leather Samples: -

The experiments were carried out with the commercial chrome-tanned leather. For all experiments the air-dried dumbbell shape leather pieces 5x25 mm cut from the standard part of the skin and kept in a tight glass jar.

Materials:-

Commercial methyl methacrylate (MMA) and butyl acrylate (BuA) were used as received from Merck-Schuchardt Germany and no attempt was made to remove the inhibitor.

The redox initiators potassium persulfate (PPS) and sodium bisulfite (SBS) as well as the emulsifier sodium dodecyl sulphate (SDS) were obtained from El-Nasr pharmaceutical company – Egypt.

Preparation of sodium bisulfite adduct:-

Sodium bisulfite adducts were prepared by using different types of ketones according to the method described previously.¹⁴⁾

Dyestuff:-

- 1- Acid dye: - acidol brown supplied by BASF.



2- Basic dye: - methylene blue supplied by BASF.

Dyeing method:-

Each of ungrafted and grafted leather samples treated with different ratios of MMA and BuA monomers were independently dyed with two classes of dyestuff namely acidic and basic dyes.

The dyeing was carried out by using conventional exhaustion method at dye concentration of 0.25 %, liquor ratio 1:20, pH 4-4.5 for both acidic and basic dyes at 80 °C for one hour. The dyed sample washed by non ionic detergent (Egyptol) for 30 min at 50 °C, and then washed by distilled water.

Impregnation and grafting:-

Pieces of leather about 5 gm in weight were treated with water emulsions of different molar ratios of methyl methacrylate (MMA) and butyl acrylate (BuA) monomers. Then, the redox initiator was added and left for drumming by mechanical stirrer at 500 rpm for 60 min at 60 °C.

After the exposure leather samples were rinsed from water and air dried , the homopolymer had to be removed from leather with toluene for 48 hours in the soxhlet apparatus. The amount of polymer in the leather was determined by calculating the grafting yield from the equation:

$$\text{Grafting yield} = [(W_2 - W_1) / W_1] \times 100$$

Where, W_2 = weight of grafted leather

W_1 = weight of ungrafted leather

Testing and analysis:-

Physical , chemical and mechanical analyses were carried out for leather samples as I.R Spectroscopy – Scanning electron microscope (SEM) – Thermal gravimetric analysis (TGA) – Water absorption¹⁵⁾ capacity – Color strength (K/S) – Tensile



strength (T.S) and Elongation at break (E%), as well as the hardness¹⁶⁾ of leather samples were measured.

Results and discussion:-

Grafting of vinyl monomers onto leather samples was carried out by a free radical graft polymerization process. The various parameters affecting the grafting percentage, mechanical properties and water absorption will be discussed as follow:-

Effect of reducing agent molecular weight:-

The role of the molecular weight of reducing agents on the degree of grafting was illustrated in Tables (I&II), where, from the recorded data, it can be concluded that, the degree of grafting increases with increasing the molecular weight of reducing agents from acetone sodium bisulphite, methyl ethyl ketone sodium bisulphite to hexanone sodium bisulphite. This result may be attributed to that, the higher molecular weight of adduct used as reducing agent, the less of free radical formation and consequently decrease the homopolymer formation and then the degree of grafting increased¹⁷⁾

Effect of monomer composition:-

The co-monomer composition has a great influence on the grafting process, it is expected that, one of the binary monomers may enhance the grafting process of the other monomer and vice versa¹⁾. Tables (I& II) show that the degree of grafting increased as the ratio of methyl methacrylate monomer increased in the co monomer composition.

These results suggest that the methyl methacrylate monomer enhances the graft copolymerization of the binary monomer. This may be due to the difference in the diffusion coefficient of both monomers. where the difusibility of the monomer into the polymer matrix has a great influence on the grafting process and also on the grafting yield¹⁾.

Mechanical properties

This part of study was carried out to investigate the effect of grafting percentage of different molar ratios (MMA/BuA) onto leather on the mechanical properties of studied samples. The mechanical properties of treated and untreated samples are recorded in Table (II). As shown from this Table, both the tensile strength and



elongation at break are increased by increasing the reducing agents molecular weight and by increasing the methyl methacrylate monomer in the same reducing agent molecular weight.

On the other hand, the hardness was also measured for grafted and ungrafted leather samples. Table (II) shows that, hardness decrease as the reducing agent molecular weight increased and also as the percentage of methyl methacrylate monomer increased.

From above results, it can be concluded that, both the tensile strength and elongation at break (E%) increased by increasing the grafting percentage, but the hardness decreased by increasing grafting percentage.

Water absorption:-

It is importance for leather to be more resistance to water absorption, so, many methods have been directed to impart increase in the water resistance of leather. Grafting with various synthetic polymers is beneficial for increasing the leather water repellency. From Table (I), it can be concluded that, the grafting of leather by incorporation of monomers onto leather leads to less water absorption by increasing the adduct molecular weight. And also a remarkable decrease in water absorption of leather is observed by increasing the percentages of butyl acrylate monomer in the same adduct. In general, the percentage of water absorption of grafted leather is lower than that of ungrafted leather samples.

Infra-red spectroscopy (IR):

IR spectroscopy has been found to be a valuable tool in the characterization of the grafted substances. This technique has been extensively used to determine the structure of the grafted product. Fig. (1a&1b) show that, the presence of a band in the range 1730-1736 cm^{-1} was attributed to C=O acrylate ester stretching vibration which is not found in ungrafted leather. In the region 2925-2948 cm^{-1} indicated the C-H stretching vibration in leather, the increase in this band intensity is due to methyl and butyl aliphatic acrylate hydrogen. Also, the presence of a band in the region 1300-1250 cm^{-1} indicates the C-O stretching vibration which proof that monomers have been grafted onto leather.



Scanning Electron Microscope (SEM):

Morphological study was carried out for grafted and ungrafted leather samples. Fig. (2) shows the scanning electron microscope of untreated leather sample where it is clear that, the untreated fibers are completely separated from each other, otherwise, in case of grafted leather which present in Fig. (3), full and smooth fibers are noticed. This may be due to the formation of fiber bundles between leather and polymer during the polymerization process and polymer chain the fiber grains.

Color measurement:

Figures (4&5) show the color strength values as a function of methyl methacrylate /butyl acrylate molar ratios (MMA/BuA) for grafted leather dyed with acid and basic dye, respectively. As it evident, the color strength value increased by increasing the methyl methacrylate molar ratio. This was observed regardless of the type of dye used.

From our previous discussion, it is well known that, increasing the methyl methacrylate molar ratio in the feed composition is accompanied by increasing graft yield. Most probably increasing the methyl methacrylate content ratio with its stereo branched configuration (i.e increasing the amorphous sides) as well as increasing the graft yield percent increase available site for dye aggregation and accumulation. This certainly causes an increasing in the color strength values.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Figure (6) shows the primary thermograms and derivatograms for the ungrafted and leather grafted with three different ratios of BuA/MMA. The thermogram of the ungrafted leather sample shows an initial weight loss of 12.6% around 100°C which could mainly related to the water moisture absorbed by the leather fibers¹⁸⁾. The main decomposition occurs in one step with onset temperature of 309 °C and end set at 362 °C with decomposition temperature of 342 °C. The weight loss at this stage was 35%. The situation was completely different with respect to the grafted leather samples. The thermograms



depict that the initial weight loss were 0, 7 and 8.6% for leather grafted with 0/6, 3/3 and 6/0 of MMA/BuA molar ratios, respectively. The decrease in the initial weight loss compared with the ungrafted one could be related to the decrease in the water moisture contents due to grafting with hydrophobic monomers. The main decomposition for the studied grafted leather samples occur in two steps. Also, the decomposition temperature for the grafted leather samples was increased by increasing the MMA content ratio. On the other hand, the weight loss for the grafted leather with different MMA/BuA molar ratios follows the following sequence: 0/6 > 6/0 > 3/3. The synergetic effect between the two monomers plays the predominant factor for thermal stability variation of the grafted leather samples. Table (III) shows the analyzed onset, end set and the decomposition temperatures of the studied samples.

Conclusion:

Grafting of the vinyl monomers onto leather samples enhanced the mechanical properties and water absorption of the treated samples. The improvement increased with increasing both of methyl methacrylate molar ratio and molecular weight of reducing agent. Color strength of the grafted leather samples was improved by increasing the methyl methacrylate molar ratio for both acid and basic dyes.



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TABLE I: Effect of degree of grafting and molar ratios of MMA/BuA on water absorption of leather

Molar ratio MMA/BuA	Acetone Sodium bisulphite adduct						Methyl Ethyl ketone Sodium bisulphite adduct						Hexanone Sodium bisulphite adduct					
	G%	30 m	60 m	120 m	24 h	48 h	G%	30 m	60 m	120 m	24 h	48 h	G%	30 m	60 m	120 m	24 h	48 h
0/6	2.46	37.1	42.5	44.9	46.7	47.6	3.68	34.5	37.4	39.2	41.6	44.9	3.94	32.5	36.08	38.61	40.1	40.8
1/5	6.36	69.8	73.3	75.4	76.5	76.9	8.47	68.2	70.5	71.2	71.7	72.2	11.5	68.15	69.67	70.08	70.9	71.1
2/4	9.51	72.1	78.7	79.2	80.6	81.3	10.6	72.7	76.3	77.9	78.5	79.0	12.3	69.15	72.33	74.63	74.9	75.0
3/3	10.67	76.4	80.8	81.0	82.3	82.4	12.1	75.2	78.2	79.5	80.1	80.6	14.8	71.7	74.30	76.18	76.9	77.5
4/2	11.33	83.2	87.6	89.0	90.1	91.0	12.6	79.5	82.4	84.6	85.1	85.9	15.6	75.6	79.55	81.88	82.6	83.0
5/1	12.52	87.4	90.9	92.7	93.1	93.9	14.7	83.4	86.5	88.6	89.2	90.2	16.7	77.6	80.41	82.50	83.1	84.0



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6/0	12.56	90.2	93.9	95.2	96.1	96.8	15.0	85.2	87.6	89.0	90.1	90.8	23.4	82.0	85.60	86.05	86.8	87.1
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	30m	60m	120m	24h	48h
Blank	92.16	95.37	100.40	110.21	112.31

TABLE II: Effect of degree of grafting and molar ratios of MMA/BuA on Mechanical properties of leather

Molar ratio MMA/BuA	Acetone Sodium bisulphite adduct				Methyl Ethyl ketone Sodium bisulphite adduct				Hexanone Sodium bisulphite adduct			
	G%	T.S	E%	Hardness	G%	T.S	E%	Hardness	G%	T.S	E%	Hardness
0/6	2.46	7.30	87.61	90	3.68	9.63	101.66	88	3.94	14.38	143.27	83
1/5	6.36	8.24	74.30	87	8.47	12.20	76.25	85	11.51	16.72	107.12	78
2/4	9.51	9.76	68.20	85	10.64	14.15	68.72	82	12.36	18.36	87.10	76
3/3	11.33	11.13	62.46	82	12.13	15.28	67.64	80	14.84	21.56	80.81	75
4/2	10.67	12.62	60.28	80	12.64	15.93	65.57	79	15.63	23.41	73.69	73
5/1	12.52	13.51	58.35	79	14.70	16.37	63.14	78	16.78	25.16	69.34	72
6/0	12.56	14.64	52.97	77	15.02	18.64	54.50	76	23.47	27.56	66.48	70

Blank	T.S	E%	Hardness
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	6.72	45.30	95
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TABLE III: Thermogravimetric analysis of ungrafted leather and poly (MMA/BuA) g- leather with three different molar ratios.

Sample Type	1 st stage degradation				2 nd stage degradation				Residue at 600 ^o C
	T _i	T _m	T _f	W _L	T _i	T _m	T _f	W _L	
Ungrafted leather	44.2	77.8	101.2	12.6	309	342	362	35	27
MMA/BuA (6/0)	50.8	85.34	108.15	8.6	311.7	344.7	361.2	32	11
					368.3	414.2	424.7	24.6	
MMA/BuA (3/3)	44.9	74.8	98.8	7	311.2	341.24	357.8	28.3	25
					338.9	409	422.7	22	
MMA/BuA					316.2	338.9	345.9	25.74	4.7



(0/6)					393.0	404.6	413.3	33.42	
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T_i , T_m and T_f : onset temperature, temperature corresponding to the maximum rate of weight loss (W_L) and final temperature, respectively.

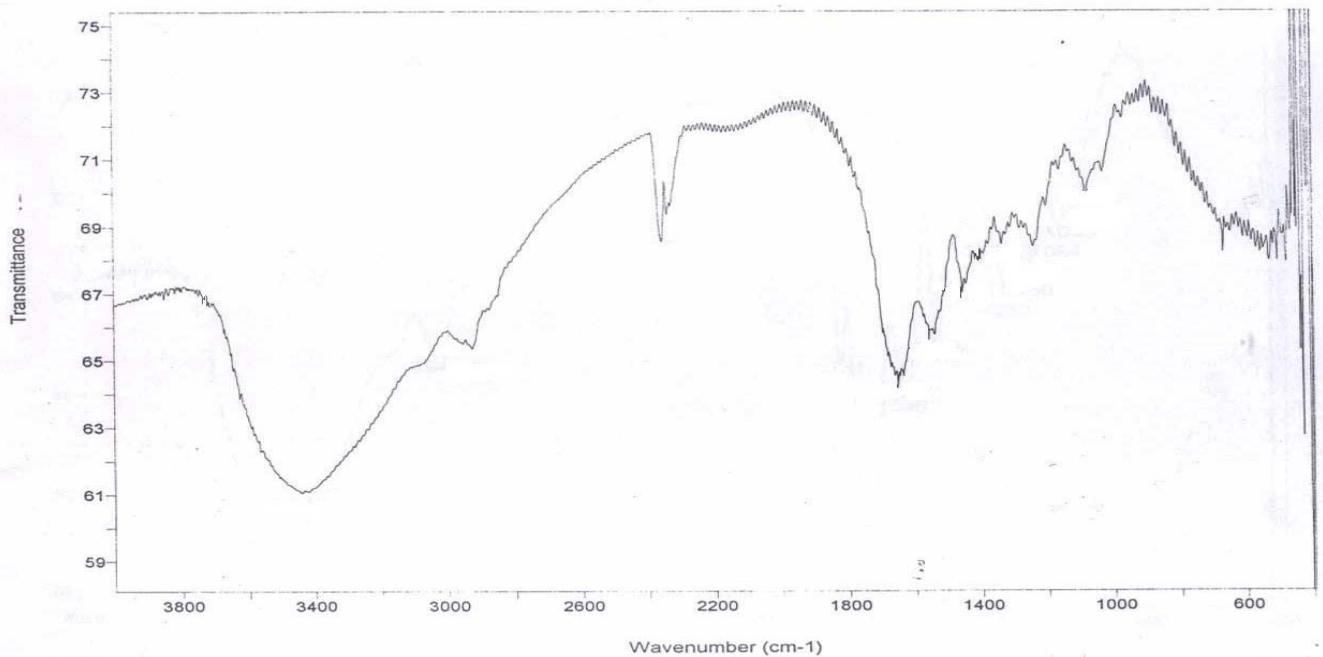


Fig. (1-a): Infra-red spectra of ungrafted leather sample

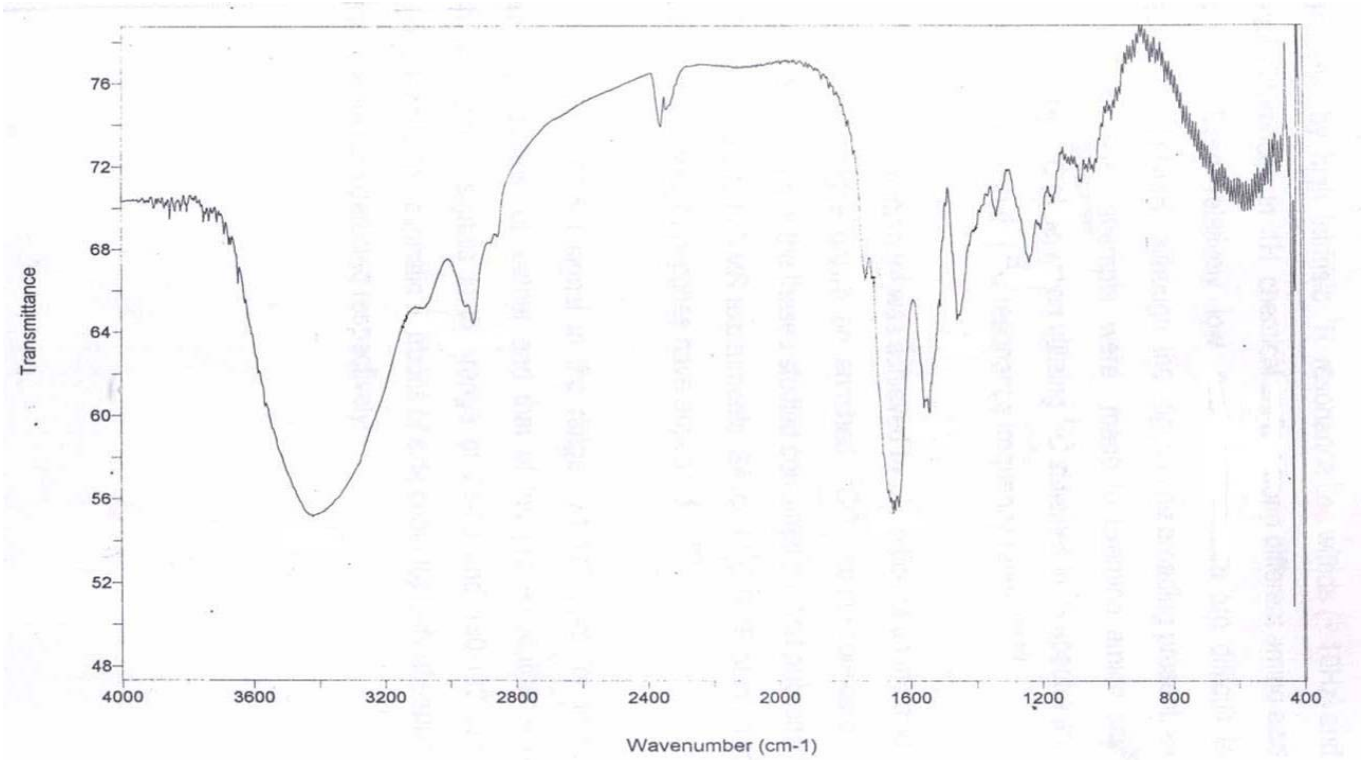


Fig. (1-b): Infra-red spectra of poly (MMA/BuA)-g-leather

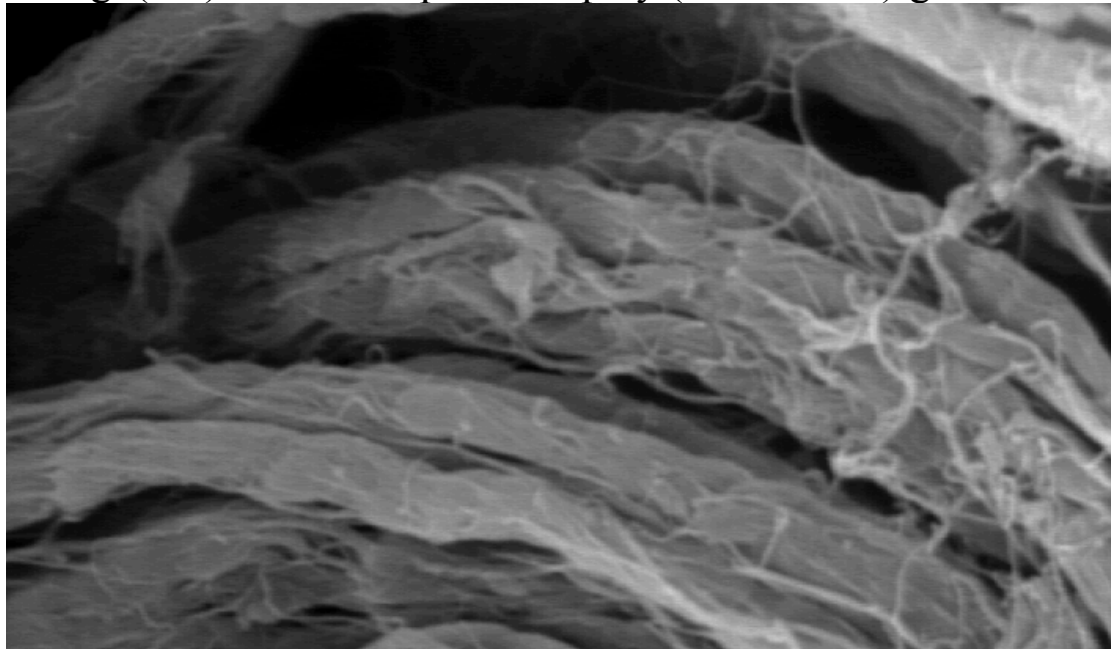


Fig.(2): SEM of ungrafted Leather Sample (X=1500)

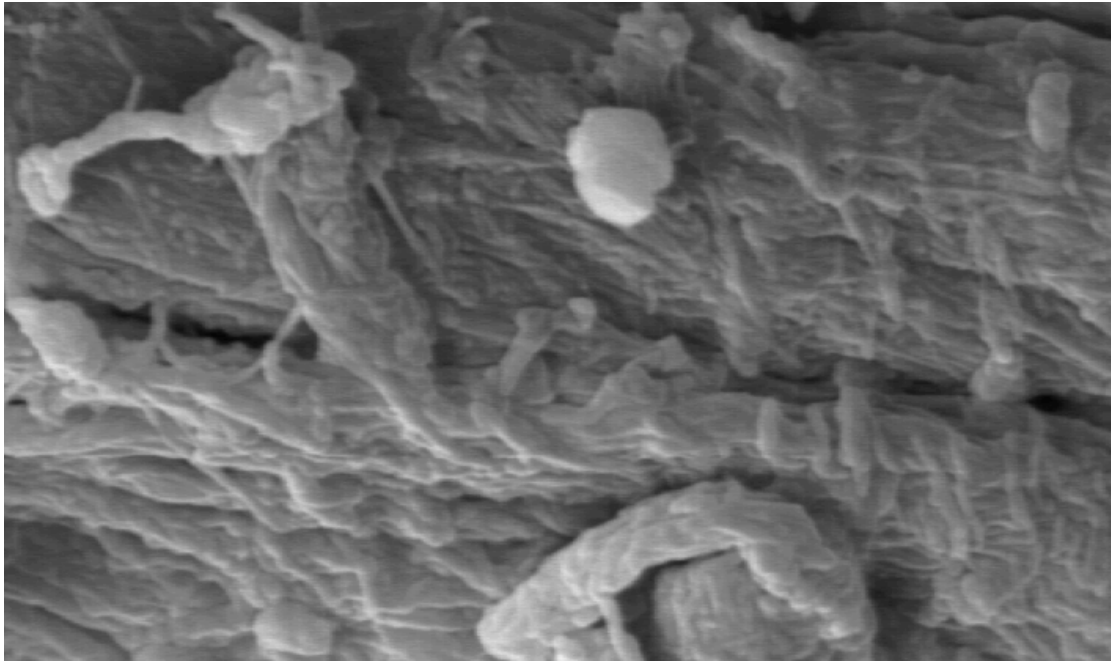


Fig.(3): SEM of grafted Leather Sample using MMA/BuA molar ratio 3/3 and hexanone sodium bisulphite adduct as reducing agent (X=1500)

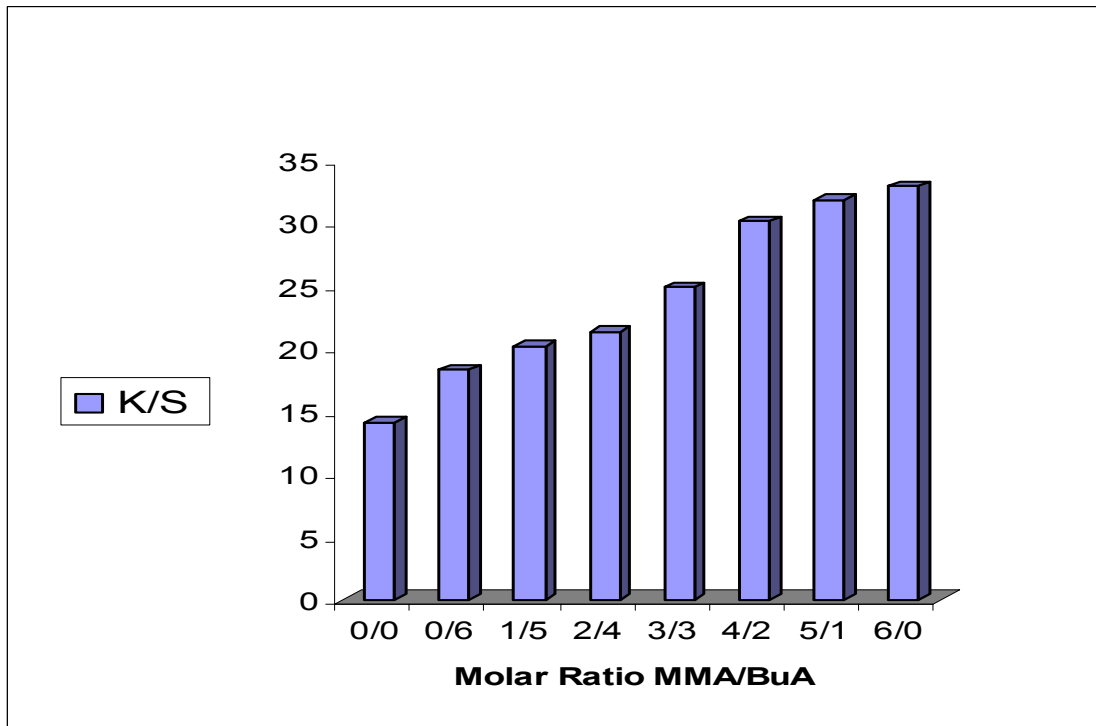
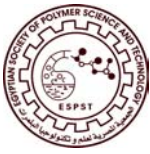


Fig. (4): Effect of molar ratios of MMA/BuA on color strength (K/S) of acid dye.

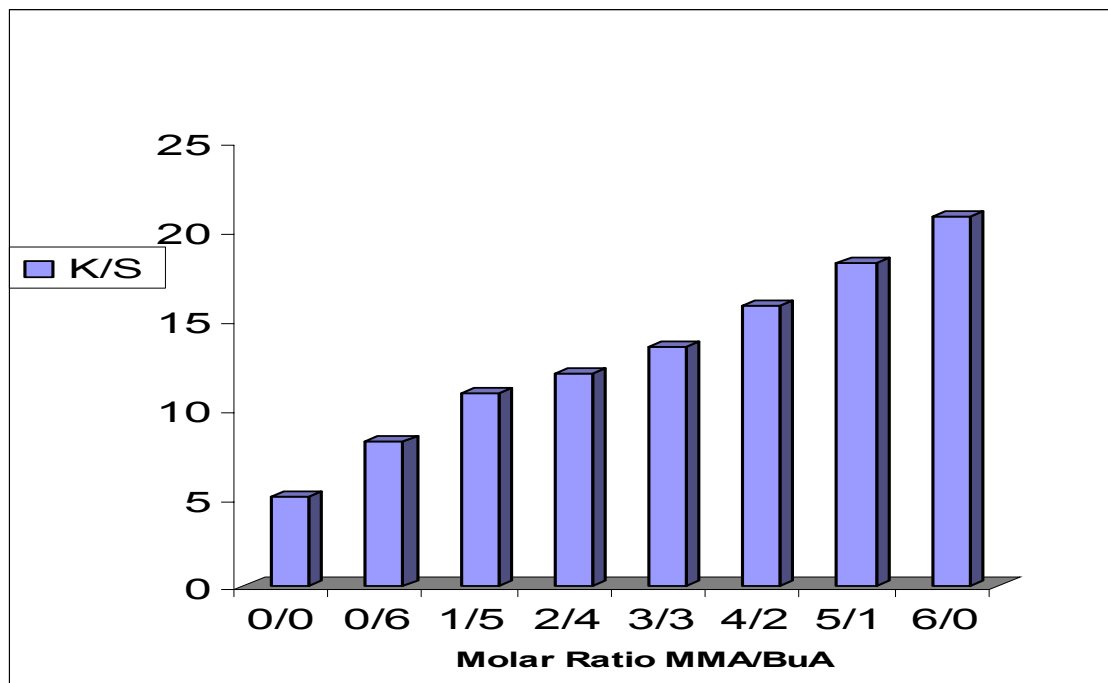


Fig. (5): Effect of molar ratios of MMA/BuA on color strength (K/S) of basic dye.



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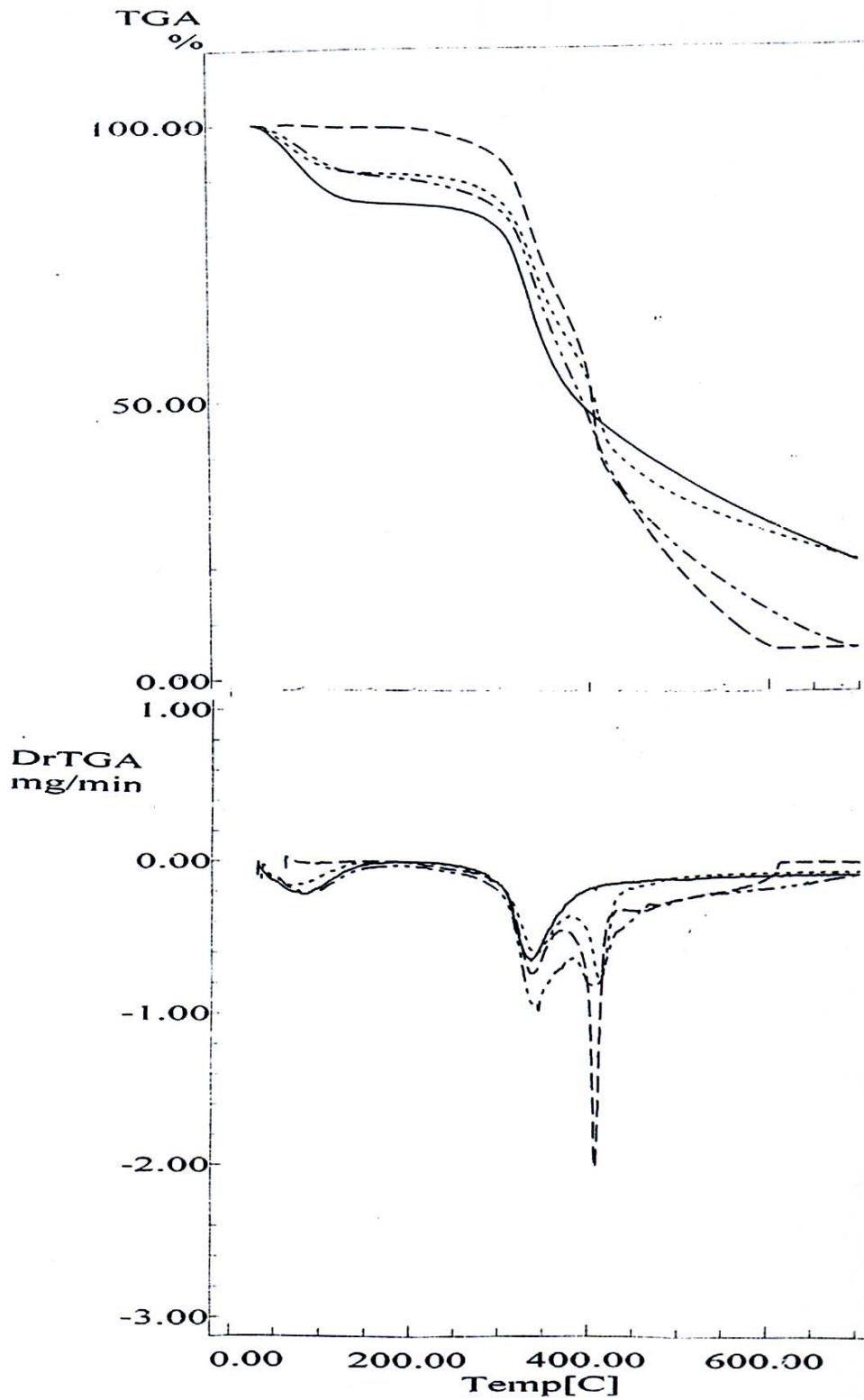


Fig.(6): The TG/DTG curves for the ungrafted and grafted leather samples having different molar ratios of MMA/BuA (—) ungrafted, (.....) 3/3, (---) 0/6 (— .. — ..) 6/0 molar ratio.



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