Improving the leather performance via treatment with different adducts and grafting with 1-Vinyl-2- pyrrolidinone

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Abstract: Leather was treated with different aldehyde and ketone sodium bisulphite adducts to improve physical and mechanical properties. Acetaldehyde sodium bisulphite (AcSBS), glutraldehyde sodium bisulphate (GSBS), cyclohexanone sodium bisulphite (ChSBS) and octylaldehyde sodium bisulphate (OSBS) adducts were prepared to be used for treatment of leather. The treatments were carried out at different adduct concentrations (0.5-3.0%). The performance of leather treatment was evaluated in terms of tensile strength (TS) and elongation percent at break (E%), hardness as well as water uptake %. The data obtained showed that all the studied adducts increase the leather performance compared with the untreated one. Moreover, leather treated with octyldehyde sodium bisulphate adduct showed the highest tensile strength with the lowest hardness and water uptake %. The treated leather was grafted with 1-Vinyl-2- pyrrolidinone (VP) monomer using redox initiation system composed of potassium persulphate (KPS) as oxidizing agent and the previously used adduct modifying agent as reducing one. The optimum graft yield was studied by changing type of adducts, liquor ratio, temperature and time of the reaction as well as initiator and monomer concentrations. Higher graft yield of ca. 15.42 % was obtained by using octaldehyde sodium bisulphite adduct at 60°C for 1 hr using 1/20 liquor ratio and KPS and VP concentrations of 0.5 and 4 gm respectively. The grafted leather is characterized with respect to FTIR, SEM and thermal gravimetric analysis. The obtained grafted modified leather samples showed greater dyeing performance with acid dyes and an appropriate improvement in hardness and TS compared with the blank leather sample. [New York Science Journal 2010;3(9):112-119]. (ISSN: 1554-0200).

Keywords: Leather, grafting,1-Vinyl-2- pyrrolidinone, characterization, dyeing,

Introduction

Chemical modification of leather fibers by different methods such as graft copolymerization or finishing treatments was a target of many researchers. Some of these articles oriented to produce new leather products, such as leather boards, with keeping the natural appearance of leather. The researches clarified that observed improvement in the mechanical properties of tanned or untanned leather fibers were obtained using acrylic monomers, such as methyl methacrylate (MMA), butyl acrylate (BA) (1-5). Madera-Santana and Vázquez Moreno prepared the graft polymerization of methyl methacrylate (MMA) monomer onto short leather fibers (SLF) as a function of the monomer/leather fiber ratio. This chemical modification was made by aqueous emulsion polymerization initiated by a redox system. Composites formulated with SLF without chemical modification showed lower tensile and band impact properties in comparison with composites formulated with treated fibers. The micrographs manifested the polymer deposition on both individual fibers and bundles of SLF. The study also revealed that PMMA may interpenetrate the SLF network and deposit in large and coarse aggregates the individual fibers, but without occupation of the voids in the fiber net (6). Abd El-Ghaffar et al., (7) studied the graft copolymerization of ethyl acrylate, butyl acrylate, and 2-ethyl hexyl acrylate onto leather using benzoyl peroxide as an initiator to improve leather mechanical and hydrophobic properties. Optimum conditions for grafting such as monomer and initiator concentrations, as well as temperature and time of grafting beside liquor ratio were extensively investigated. The study concluded that pronounced decrease of water uptake was occurred on using 2-ethyl hexyl acrylate and butyl acrylate monomers.

The kinetics of the grafting polymerization of glycidyl methacrylate (GMA) onto leather was studied using redox initiation systems composed of ammonium persulfate (AmPS), potassium persulfate (PPS) and sodium persulfate (SPS) as oxidizing agent and developed reducing adduct represented as acetone sodium bisulfite (ASBS)(8). The results showed that the rate of grafting of GMA onto leather was highly influenced by initiation system type, emulsifier and monomer concentration. The result demonstrated that the powers were 1.06, 0.48, and 0.43 for AmPS/ASBS, PPS/ASBS and SPS/ASBS respectively, while its values were 1.41, 0.70, and 0.81 using different GMA concentrations for the three initiator types in successive. The apparent activation energy was calculated for each initiation system and was found to be 180.8, 361.63, and

542.45 kcal. Grafting emulsion copolymerization of methyl methacrylate (MMA) with butyl acrylate (BuA) of different molar ratios onto natural leather was carried out using the redox initiation system of potassium persulfate (PPS) developed as an oxidizing agent and some sodium bisulphite adducts as reducing agents (9). 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.

The present work is aimed to study the feasibility of using different adducts systems, composed of (AcSBS), (GSBS), (ChSBS) and (OSBS) for modifying the some properties of leather such as mechanical and physical performance. The work is extended to include the application of the best obtained pretreated leather sample in graft emulsion copolymerization using 1-Vinyl-2-pyrrolidinone (VP) monomer. The factors affecting the emulsion graft copolymerization of VP were studied. FTIR, thermal gravemetric analysis, water absorption, hardness, dyeing with an acid dye as well as tensile strength and elongation (%) of the grafted leather, pretreated leather and ungrafted leather were also characterized.

Experimental

Materials

Leather

The chrome-tanned cow leather selected for investigation was supplied from 6-October tanner located at Misr-Elkadima region,Cairo, Egypt. The delivered leather was washed with water, drained and finally neutralized.

Chemicals

1-Vinyl-2- pyrrolidinone was provided by Merck– Schuchardt, Germany, it is redistilled before use and stored at –20°C. Potassium persulphate, cyclohexanone, acetaldehyde, octylaldehyde, glutradehyde, and sodium bisulphite were supplied by BDH Company. The other chemicals were of laboratory grade.

Preparation of acetaldehyde, glutradehyde, hexanone and octylaldehyde adducts

The sodium bisulphite adducts of each of acetaldehyde, glutradehyde cyclohexanone and octylaldehyde were prepared by the addition of sodium bisulphite on the carbonyl of each of acetaldehyde, glutradehyde, octylaldehyde and cyclohexanone respectively(10,11) .

Leather treatment and grafting method

Acetaldehyde, glutraldehyde, cyclohexanone and octylaldehyde sodium bisulphate adducts were prepared to be used for leather treatment. The treatments were carried out at different adduct concentrations of adduct (0.5-3.0%). 1-Vinyl-2-pyrrolidinone monomer was introduced to a conical flask containing water, pretreated leather and potassium prsulphate as oxidizing agent using the recipe given in Table 1.The flask components are mechanically stirred at 200 rpm. The homopolymer is extracted from the grafted leather by washing with water till a constant weight of leather.

The graft yield was calculated according to the following equation

Graft yield $= (W_2 - W_1) / W_1 x100$

Where, W_2 = weight of grafted leather and W_1 = weight of ungrafted leather

Dyeing methods

Each of ungrafted leather and poly 1-Vinyl-2-pyrrolidinone -g- leather was independently dyed with acid dye. The dyeing was carried out using conventional exhaustion method at dye concentration of 0.2%, Liquor ratio of 1:50, and pH of 4-4.5 at 80°C for 1 hr.

Testing and analysis

FT-IR spectroscopy was carried out using Perkin Elmer FTIR (300E, JASCO type– Japan). The Thermogravimetric (TG) was carried out at a temperature range of 30°C to 800°C under nitrogen atmosphere with heating rate of 10°C/min using Shimadzu TGA-50, Japan. The water absorption capacity for the grafted and ungrafted leather samples were measured according to the standard method of testing (12). The tensile strength and elongation at break for the studied samples were measured using Instron Machine (model 1195) according to the standard method of testing (13). The hardness was measured by shore A, Harterpufer apparatus according to standard method of testing (14). The color strength (K/S) values of all examined dyed samples were evaluated using Optimatch 3100 Spectrophotometer.

Table (1): Recipe of graft polymerization of leather by 1-Vinyl-2- pyrrolidinone

Components	**Amount**	**Function**
Pretreated leather	5gm	Substrate and variable type of adducts which act as reducing agents
KPS	Variable	Oxidizing agent
1-Vinyl-2- pyrrolidinone	″	Monomer
Water	Variable	Medium

Results and discussion

The reaction between the aldehydic or ketonic compounds with sodium bisulfite can be summarized as follows:

$R\text{- }CHO + NaHSO_3 \longrightarrow R\text{-}CH(OH)(SO_3Na)$ …… (1)
$R= CH_3$- for acetaldehyde and $R= CH_3\text{-}(CH_2)_6$- for octaldehyde
In case of glutraldehyde the reaction proceed as follows
$CHO\text{-}(CH_2)_4\text{-}CHO+NaHSO \longrightarrow CH(OH)(SO_3Na)\text{-}(CH_2)_4\text{-}CH(OH)(SO_3Na)$....(2)
$R_1\text{-}CO\text{-}R_2 + NaHSO_3 \longrightarrow R_1\text{-}C(OH)(SO_3Na)\text{-}R_2$
R_1 and R_2 = CH3CH2- for cyclohexanone

Leather was pretreated with different aldehydic or ketonic adduct compounds to acquire some desirable properties such as improving tensile strength, elasticity, dyeing availability as well as to minimizing the swelling behavior. On the other hand, the presence of these adducts on the molecular structure of leather will magnify the grafting copolymerization properties with different monomers. Choosing VP monomer in grafting copolymerization of modified leather was of our interest to meet the point of view of increasing the elasticity and dyeing performance. The evidence of leather modification with aldehydic or ketonic adducts as well as grafting with VP is summarized.

Effect of pretreatment of leather with different adduct type and concentration on its performance

Figures 1 and 2 show the effect of different adducts types and concentrations (0.5- 3%) on the performance of treated leather expressed as tensile strength (kg), elongation (%) and hardness (shore). It is evident that, regardless of adduct types increasing the concentration of adducts were accompanied by observed increase in the leather performance up to concentration of 2% after which level off. This could be explained due to the role of the examined adducts as plasticizer. The plasticizing criteria of the adducts could be thought from the coating character initialized via hydrogen bond interaction occurred between the leather amino groups and sulphonic groups bounded with alkyl groups having varied number of carbon atoms (equations 1-3). The plasticizing effect of the studied adducts is confirmed by the graphs of SEM which is seen in figures 10. On the other hand, for the studied treated compounds, octyldehyde sodium bisulphite adducts shows the most significant performance effect and lower water uptake property as shown by Figure 3. The variation in leather performance and water uptake (%) follows the following order: octaldehyde> cyclohexanone> glutradehyde> acetaldehyde. This proves that the compound having higher aliphatic normal long chain groups is the most suitable plasticizing effect and less gain for water molecules.

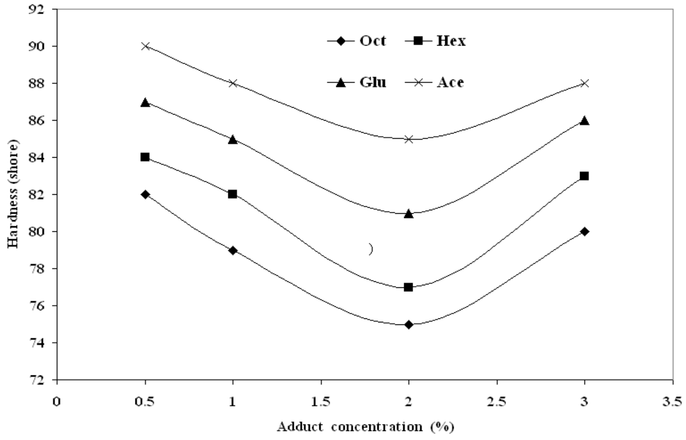

Figure (1): The effect of different type of adducts on the tensile strength and elongation % of treated leather.

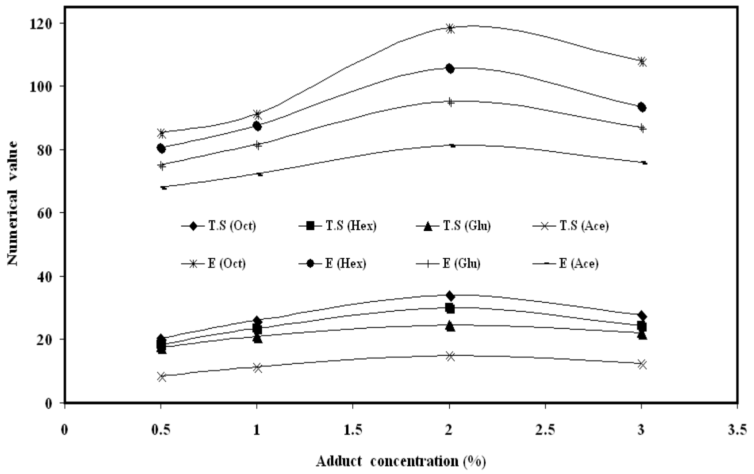

Figure (2): The effect of different type of adducts on the hardness of treated leather.

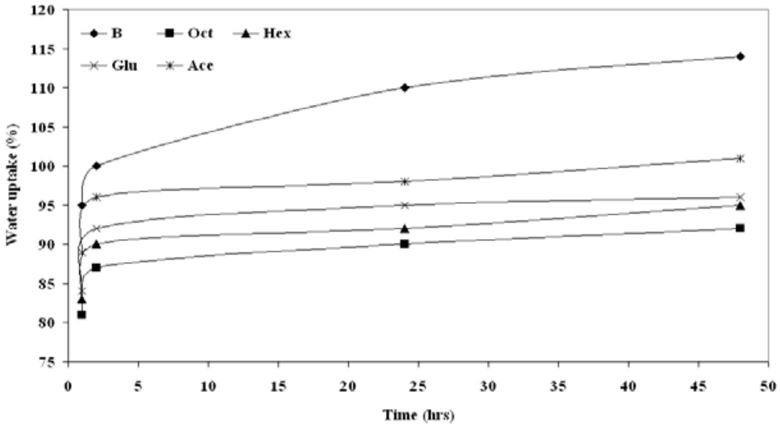

Figure (3): The effect of different type of adducts on the water up take %. of treated leather.

Graft copolymerization of VP onto pretreated leather

Effect of different adduct types and concentrations

The data illustrated in Figure (4) shows the effect KPS concentration (2.5-20mmol/l) on the grafting yield of VP onto pretreatment leather with different concentrations of AcSBS, GSBS, ChSBS, OSBS. It is evident, regardless of the adduct type used, that the grafting yield increases as the initiator concentration increases up to certain level 10 mmol/l after which the grafting level off. This could be recognized to the increase in number of free radical species on the leather backbone as well as in the polymerization medium, which act in favor of grafting and homopolymerization thereby enhancing the polymer yield (15). Moreover, the magnitude of the grafting obtained by using the initiation system composed of KPS as oxidizing agent and OSBS adduct as pretreatment reagent was the higher and ASBS the lower while each of HSBS and GSBS was intermediate. The obtained data reflect the availability of OSBS adduct to enhance initiator decomposition i.e free radicals and faster forming leather macroradical. The latter has tendency to capture the double bond of VP molecule to initiate grafting as well as creating best favorable conditions for polymer propagation in the proximity of leather molecule. For the examined adducts the sequence of the graft yield % follows the following order: OSBS> HSBS> GSBS>ASBS.

Effect of time and temperature

Figure (5&6) shows the effect of time and temperature on the degree of grafting of VP (400 mmol/l) onto pretreatment leather with OSBS in the presence of KPS as aoxidizing agent. It is clear that the grafting % of VP onto pretreatment leather increases gradually with time up to 1 hrs, extra time leads to constant degree of grafting % due to the depletion in monomer by time. Moreover, rising the polymerization temperature from 50°C to 60°C brings about significant increase in the grafting % and further increase in temperature leads to level off. Increasing the polymerization temperature is expected to cause: (a) faster rate of persulphate decomposition, giving rise to more free radicals, (b) increasing the swellability of leather and mobility of VP molecules, creating a suitable environment for monomer diffusion from aqueous phase to the leather phase (5), and (c) increasing the rate of termination. Factors (a) and (b) are expected to cause higher grafting yield while factor (c) leads to lower grafting.

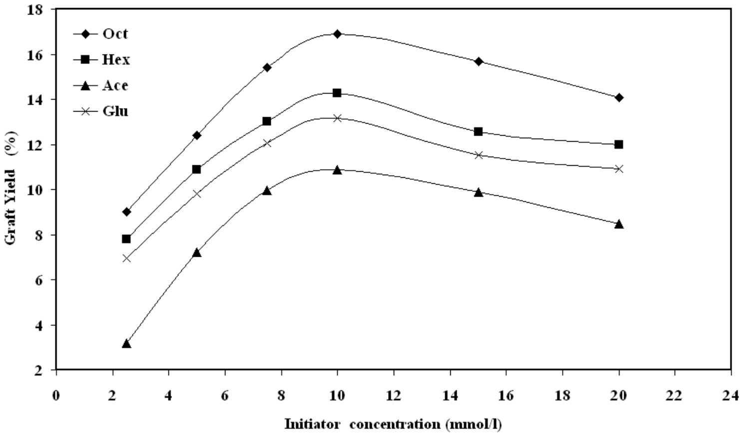

Figure (4): The effect of initiatior concentration on the GY % of grafted leather.

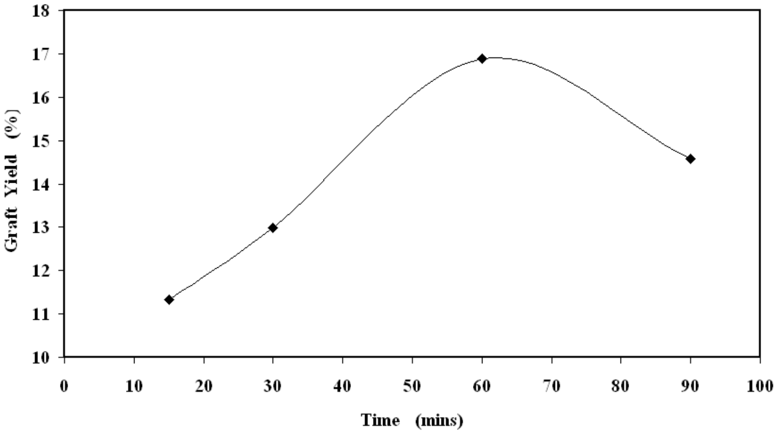

Figure (5): The effect of reaction time on the GY % of grafted leather.

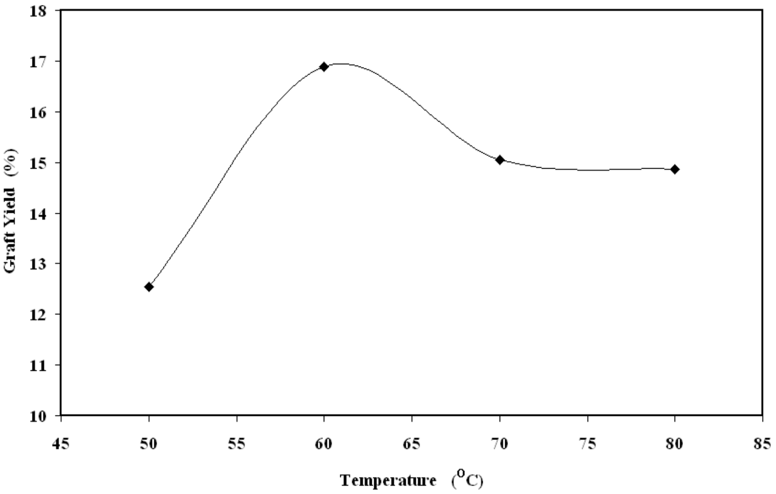

Figure (6): The effect of reaction temperature on the GY % of grafted leather.

Effect of monomer concentration

Figure (7) shows the effect of VP monomer concentration (200-500mmol/l) on the graft yield of the pretreated leather with OSBS. It is obvious that the grafting yield increases with monomer concentration within the range studied. This may be due to the fact that (5, 16), at higher monomer concentration more number of growing polymer chains are available near collagen matrix which are mainly utilized for grafting polymerization.

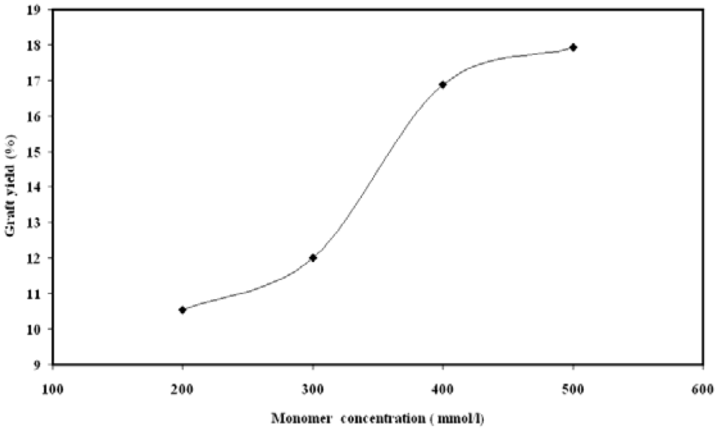

Figure (7): The effect of VP concentration on the GY % of grafted leather.

Leather Characterization

FTIR

Figure (8 a&b) shows the IR spectra of the native leather (BL) and VP grafted pretreated leather. It is evident that both spectra have similar peaks such as a wide band at 3410 cm^{-1} which is corresponding to the hydroxyl group. The presence of short peaks around 3070 cm^{-1} and 2930 cm^{-1} are due to the asymmetrical stretching bands of -CH3 and =NH bonds, respectively. The C=O group in native leather (Figure 8a) is characteristic at 1642 cm^{-1}, while it observed with higher intensity in PVP-g-leather at 1665 cm^{-1} (Figure 8b), which may be consider as proof for leather grafting (17,18). For the two spectrums the presence of characteristic band at 1548 is related to carboxyl groups.

Thermogravemetric analysis (TG/ DTG)

Thermogravemetric analysis TGA is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Figure 9 (a&b) shows the primary thermograms and derivatograms for the native (BL), leather treated with OSBS (L-t-OSBS) and VP grafted pretreated leather (L-t-OSBS-g-poly-VP) having graft yield of 14.6%. As is evident the native leather sample has an initial weight loss of 14.1% around 100^{O}C, which is mainly due to the evaporation of absorbed moisture $^{(5)}$. The main decomposition proceeds in two steps (RF), the first one with weight loss of 36.7 occur at decomposition temperature (T_d) of 320 ^{o}C and the second with weight loss of 14.5% occur at T_d of 455^{O}C. The leather treated with OSBS show a behavior similar to the native leather. On the other hand, for the L-t-OSBS-g-poly-VP the first degradation occurs due to the absorbed moisture has weight loss of 10.2%. Also, the main decomposition process started at a relatively lower temperature than that of ungrafted leather. This could be explained due to the degradation effect caused by either the action of grafting bath, including persulphate free radicals and pH medium, or opening up the leather chains structure with the deposited grafted chains. The DTG curve (Fig. 9b) shows two inflections with T_d of 210^{O}C and 320^{O}C, and weight losses of 9.2% and 45.4%, respectively. The first inflection could be recognized to the degradation of poly-VP grafted chains while the second inflection with the sharp peak records the same T_d of native leather. Our finding in accordance with previous work in which TGA thermograms for leather grafted with poly methyl methacrylate (PMMA) showed two inflections for each of leather and PMMA, respectively$^{(6)}$.

Morphological study

A morphological studies were carried out for some selected samples : (a) untreated leather; (b) leather treated with CSBS ; (c) leather treated with OSBS; (d) leather treated with CBSB and grafted with VP monomer; and (e) leather treated with OBSB and grafted with VP monomer and the graphs are shown in Figure (10). It is seen that the ungrafted leather (Figure 9a) is characterized by opening up structure i.e the surface seems smooth and completely separated. The graphs of the leather treated with the suggested adducts showed more uniform and blocking of the leather pores. This criteria manifest the role of adducts as sizing agent with proper film forming properties to the leather inter-chains. More blocking and film forming properties for OBSB than CBSB (Figure 10 b & c) can be recognized due the effect of long chain alkyl groups of octyl groups as plasticizing agent for leather. So, it could be consider that the adducts act as coating material for leather fibers. When the pretreated leather samples grafted with VP monomer the surface become more uniform film coating as well as disappearance of pores and separation of leather chains was the predominate (Figure 10 d & e).

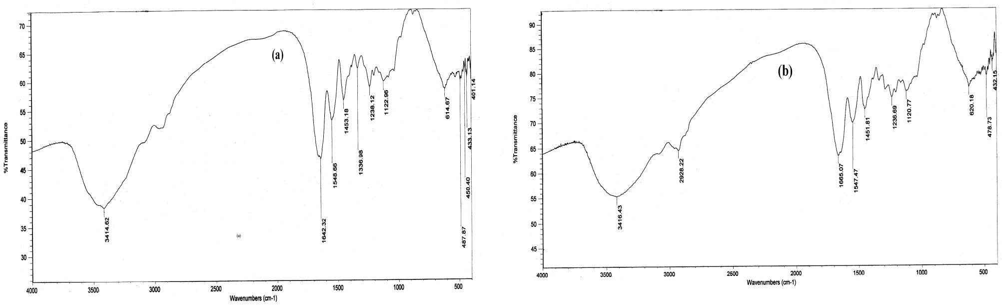

Figure (8): The FTIR spectra of a)- ungrafted leather and b)- L-t- OBSB-g-poly-VP

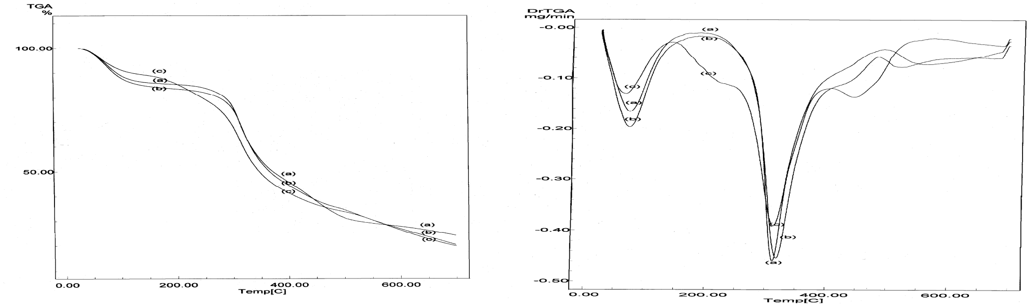

Figure (9): Thermogravimetric analysis (TGA) and differential thermogravimetric of: a)- ungrafted leather; b)- L-t-OBSB ; and c) L-t- OBSB -g-poly-VP

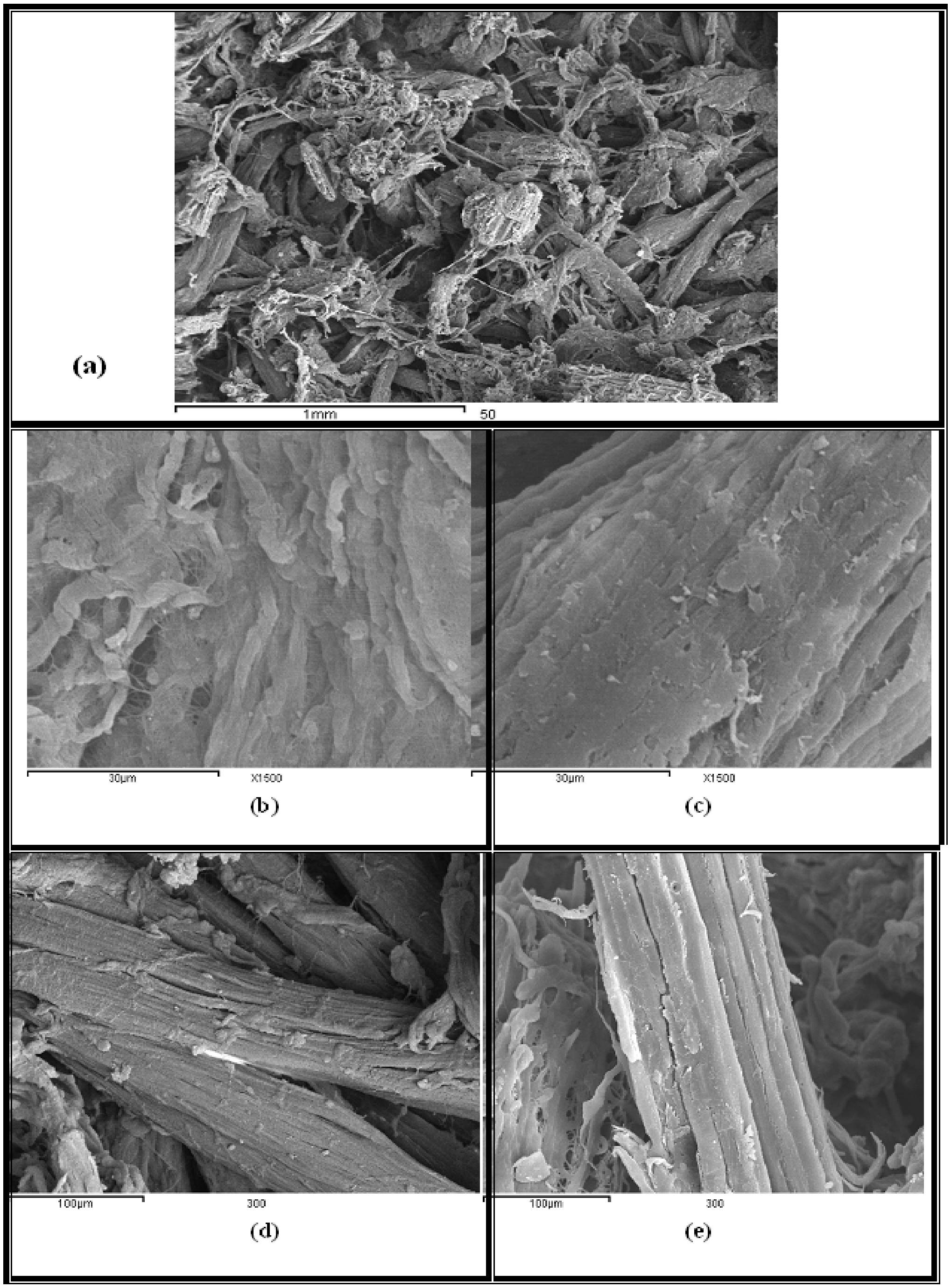

Figure (10): SEM photographs for a) untreated leather; b) L-t-CSBS; c) L-t- OSBS; d) L-t- CSBS-g-poly-VP; and e) L-t- OBSB -g-poly-VP

Table (2): Effect of grafting % of polyvinyl pyrrolidinone on color strength (k/s), tensile strength, elongation and hardness of leather.

Graft %	K/S	Tensile strength (kg force)	Elongation (%)	Hardness (shore)
Blank leather	15	9.1 (± 0.4)	64.4 (± 3.4)	95 (± 3)
(L-t-OSBS)	11	23.7 (± 0.3)	91.6 (± 5.0)	74 (± 2)
4.8	17	17.6 (± 0.8)	80.7 (± 2.3)	83 (± 4)
7.9	21	19.9 (± 0.6)	85.1 (± 3.1)	85 (± 2)
10.1	24	22.6 (± 0.9)	89.2 (± 1.7)	84 (± 4)
12.4	25	24.9 (± 1.1)	93.0 (± 2.7)	88 (± 3)
17.7	27	18.5 (± 1.4)	84.6 (± 1.9)	91(± 2)

Evaluation of grafted leather via dyeing property and mechanical performances

The effect of grafting % of polyvinyl pyrrolidinone on the acid dyeing property and mechanical performance of grafted leather is shown in table (1). The data represents many interesting points: (i) chemical modification of leather with OSBS brings about substantial improvement in the mechanical performance expressed as tensile strength (TS), elongation percent (E%) and hardness (shor) while there is a decrease in the acid dyeing property, the latter is due to repulsion interaction between the acid dye and the sulfite groups incorporated in the leather structure; (ii) when the pretreated leather is subjected to graft copolymerization the mechanical properties firstly decreased due to the degradation action of grafting bath condition represented by pH and initiator free radicals, on the contrary the acid dyeing increased due to deposition of PVP in the leather structure (18) , (iii) increasing the grafting % up to 12.4 % results in gradual improvement in each of mechanical and dyeing properties due the role of PVP as film forming and plasticizing effect as seen in figure 10; (iv) further increase beyond 12.4% cause leather opening structure which in turn initiate decreasing the mechanical properties, meanwhile the k/s still rising due to the favorable effect of PVP on acid dyeing.

Conclusion

Treatment of leather with different aldehydic and ketonic adducts represented as AcSBS, GSBS, ChSBS and OSBS improve the mechanical properties expressed as TS, E%, hardness and decrease the water uptake. OSBS adduct is more effective in its performance due to the effect of plasticizing effect of the long chain normal alkyl group. The presence of these adducts in the molecular structure of leather play an important role in enhancing the leather grafting by VP monomer. Increasing graft % is directly proportional to the improvement of dyeing property and the mechanical performance but up to certain value (12.4%) after which level off.

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