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MODIFICATION OF WET BLUE LEATHER SURFACE BY PHOTO-CURING WITH URETHANE ACRYLATE CONTAINING DYE

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ABSTRACT

Wet blue leather was coated with a number of formulated solutions that contained urethane oligomer, acrylated monomers and dye. The coating was cured under UV radiation. Various rheological properties such as hardness, adhesion, tensile properties, water absorption, and gloss were studied. The effect of simulated weathering on these properties was also investigated. The treated leather gained enhanced tensile strength by 70% and elongation by 95%. The adhesion of the coating on leather was high ($2.3\,\mathrm{N/mm^2}$) and the gloss was 75% with minimum abrasion. Water absorption was less than 4% by the coated leather surface. Polymer films were also prepared with the formulated solutions under the UV radiation. These films were characterized.

Key Words: Leather; Photo-curing; UV-radiation; Dye; Urethane acrylate

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INTRODUCTION

Both skins and hides are chemically treated to improve qualities and properties of leather to be useful for making quality products. The quality of leather products thus depends on the extent of the improved properties of the finished leather. This process starts from the very early stage of tanning with chromium salt to the late stage of burnishing and coating with chemicals that are deemed suitable for a particular product and application. The finished leather is a product of the chemical treatment of the wet blue leather. However, many persons treat the finished leather with different chemicals to improve both the surface and the qualitative properties of the leather. Leather contains protein that is carboamide materials. Some researchers[1,2] developed chemical solutions with urethane oligomer in order to improve leather. This treatment also induced abrasion resistance and crack resistance to the leather surface. Attempts[3,4] were also made to modify the leather surface by chemical treatments by incorporating carboamide group containing monomers into the chemical solutions. This improved tensile strength, gloss, flexibility (elongation), abrasion resistance and the surface gloss was not tarnished by simulated weathering test.[5,6] In the previous paper,[7] the wet blue leather was improved under UV radiation by coating its surface with a specially prepared solution of urethane acrylate (without containing any dye in the formulation). The present investigation is an extension of that work involving a dye into the formulations that the leather surface can be coated and cured under UV radiation with different dyes to produce leather products of the desired color.

EXPERIMENTAL

Materials

Urethane acrylate oligomer (Ebecryl 204) was received from UCB, Belgium. It has aromatic backbone. Irgacur-184 was obtained from Ciba-Geigy and was used as the photoinitiator to initiate photochemical reactions under the UV radiation. Two reactive diluents, namely N-vinyl pyrrolidone (NVP), a monofunctional monomer and tripropylene glycol diacrylate (TPGDA), a difunctional monomer were procured from Merck. Three co-additives, namely ethyl hexyl acrylate (EHA), methyl acrylate (MA) and ethyl acrylate (EA) were also products of Merck. An anti-bubbling agent, methyl ethyl ketone (MEK), plasticizer, diallyl phthalate (DP), filler talc and dye Erichrom black T were obtained from BDH Co. Ltd., UK. The substrate (wet blue leather) of bovine skin was collected from the local market of Bangladesh.

Method

Nine different formulations were prepared with the above oligomer, reactive diluents, additives and co-additives in the proportions as shown in Table 1. Thin polymer films were prepared under UV radiation on a glass plate, as well as on wet blue leather, by coating these substrates (8 × 5 cm) with the above formulated solutions with the help of a bar coater (No. 0018 in) of Abbey Chemicals Co. (Australia). The coatings had a thickness of 36 ± 3 μm. The UV radiation was delivered from a Minicure UV source of 1ST-Technik (Me-200-UV), Germany. The UV lamp (254–313 nm) has a 2 KW nominal light intensity. The conveyer speed was 4 m/min. The substrates were irradiated at different UV radiation intensities, represented by the number of passes. The coated wet blue leather and the polymer films obtained from the glass plates were then characterized.

Polymer Films

After 24 hr of UV irradiation of the coating on the glass plate, the hardness of the polymer films (coatings) was measured by a pendulum hardness method using a Pendulum Hardness Tester of Byke Labotron (model 5854). Films peeled off the glass plate were then used to determine gel content and tensile properties.

Gel Content

Gel content, an index of crosslinking density in the polymer films, was determined by wrapping up a known weight of the UV-cured films in a

Table 1. Composition of Formulations (% w/w)

Chemicals	D1	D2	D3	D4	D5	D6	D7	D8	D9
Oligomer	50	50	50	50	50	50	50	50	50
NVP	23	22	11	29	47	16	14	16	16
TPGDA	21	18	29	13		15	17	15	15
MEK			2						
DP	3	3	5	5					
PI	2	2	2	2	2	2	2	2	2
EHA						16	16		
MA								16	
EA									16
Talc		4							
Dye	1	1	1	1	1	1	1	1	1

stainless steel net that was put into a soxhlet for extraction with hot benzene for 48 hr. The weight loss of the cured film after the extraction determines the gel content as % $\text{gel} = 100 - [W_o - W_e/W_o] \times 100$, where W_o is the weight of the cured film and W_e is that of the extracted film.

Tensile Properties

Tensile strength *TS* and elongation at break *Eb* of cured film were determined directly with an INSTRON machine (model 1011, UK) at a crosshead speed of 1.2 m/min with a gauge length 1.2 cm and 200 kg load. The film used had a dumbbell shape.

Wet Blue Leather

Tensile properties *TS* and *Eb* of both treated and untreated leather were measured as above using the INSTRON machine. The changes in the properties were expressed as factors, namely tensile strength factor, T_f that is the ratio of tensile strength of the treated leather TS_t and that of the untreated leather TS_o. This means $T_f = Ts_t/TS_o$, similarly, elongation factor, $E_f = Eb_t/Eb_o$ where Eb_t is the elongation at break of the treated sample and Eb_o is that of the virgin substrate.

Adhesion Test

Adhesion force (N/mm^2) of the UV-cured coating of the leather surface was measured with the help of an Adhesion Tester of Erichen Co., Germany (model ASTM 525). In this process, the metallic knob is firmly glued to the coating, and then the knob is slowly pulled in order to peel off the cured coating from the leather surface. This was calibrated with the standard sample. The force required to pull the coatings off the substrates determines the adhesion force leading to adhesion property of the coating.

Abrasion Test

A Taber Abrasor (model 5130, Erichen Co., Germany) was used to measure the abrasion wear of the cured coating. A hard type calibrated wheel (C5-10) was used with 500 g load at 100 cycles. The weight loss method was adopted and the Taber Index Tl was calculated as the weight in 1000 cycles of the abrasion. The sample that shows the lowest Taber Index is the best in resistance to abrasion wear.

Gloss Measurement

When the leather is coated, its surface shows some gloss, which is normally visible by ordinary eyes; but the gloss is standardized by looking at the surface at certain angles, namely 20° and 60° in order to measure its gloss. The gloss of the cured coating was determined with the help of a Micro gloss Meter (model Sheen 155) of Sheen Co., UK.

Water Uptake

Ability of water absorption by both treated and untreated leather was determined by allowing a drop of water on the leather surface for different periods. At the end of the specific time, the unabsorbed portion of water was smoothly wiped out with tissue paper. The weight gain of the leather sample by soaking water through the surface determines the extent of water absorbed in the particular period during which the water drop was allowed to remain on the surface.

Weathering Test

The coated leather samples were treated by simulated weathering test using the Accelerated Weathering Tester (model Q. U. V. Q-Panel Co., USA) by alternating cycles of sunshine (4 hr) and condensation and dews (2 hr) for a period of 500 hr. During the weathering test, the temperature varied between 45 ± 2°C (sunshine) and 25 ± 2°C (condensation). The quality of coating on the leather surface is mainly determined by the extent of adhesion of the coating and its gloss on the surface. Thus, the loss of adhesive force and of gloss as a result of the weathering treatment was monitored by measuring gloss loss at intervals and the loss of adhesion at the end of the weathering test.

RESULTS AND DISCUSSION

Polymer Films

Pendulum Hardness

The hardness of the UV-cured polymer films obtained at different radiation doses was measured by pendulum hardness method and is shown in Fig. 1 where pendulum hardness of each film is plotted against a number of passes under the UV lamp. The hardness increases with the UV dose, attains a maximum value, mostly at the eighth pass. All the films have registered decreased hardness after the maximum. The decrease in hardness could be caused by the damage at the film surface at higher radiation doses. However, the highest hardness is achieved by the D4 film, followed by D3. Both these

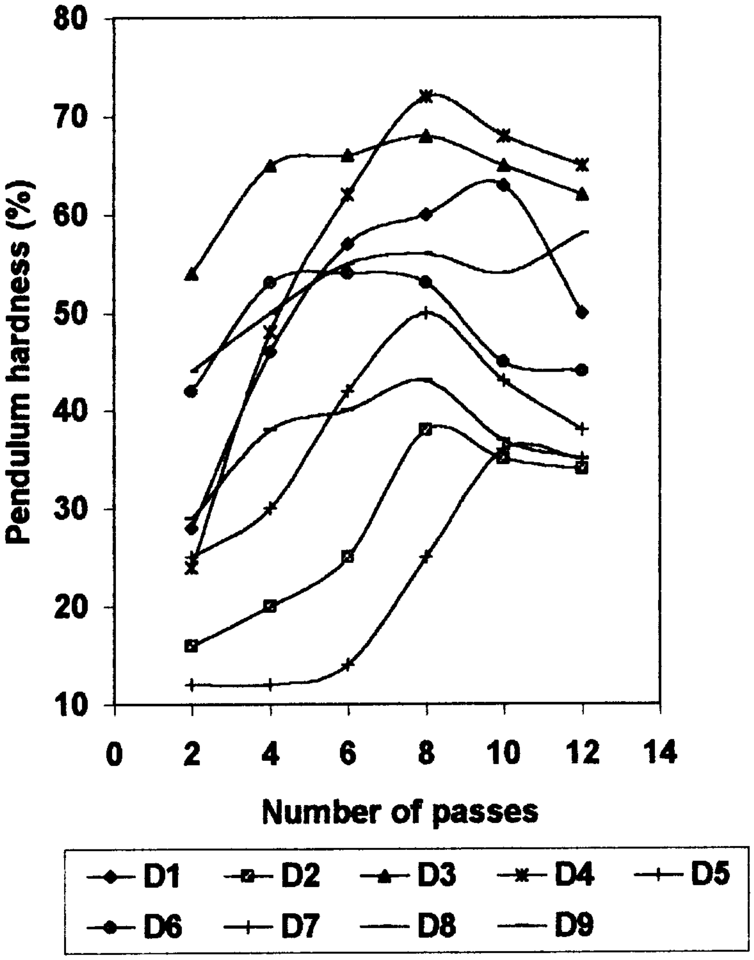

Figure 1. Pendulum hardness of the UV-cured films containing different additives against number of passes under the UV lamp.

films contain NVP and TPGDA at different proportions. The higher amount (29%) of NVP is with D4 while D3 contains 11% NVP and 29% TPGDA and D4 contains 13% TPGDA. This shows that NVP is playing some important role in combination with TPGDA pertaining to the highest hardness to the UV-cured films. NVP alone is not responsible for inducing the highest hardness. If it so, then D5 which contains 47% NVP without any TPGDA, should have given the highest hardness. NVP has also played a similar augmentation role in other systems with wood[8] and jute.[9] The lowest hardness is exhibited by D7 which contains EHA and has a low glass transition temperature ($T_g = -50°C$).

Gel Content

The results of gel contents of the UV-cured films are represented in Fig. 2 against a number of passes under the UV lamp. The gel value increases with an increase in UV radiation and attains a maximum value, mostly at the eighth pass except D6 and D7 films, which obtain maximum gel values at the tenth pass. After the maxima, the gel values decrease; it is consistent to the values of film hardness that this decrease could be associated with the damage caused by higher radiation. The highest gel value is obtained by the D6 film, followed by D7. Both D6 and D7 contain EHA. Both gel and hardness represent crosslinking density in the polymer film. Film hardness is

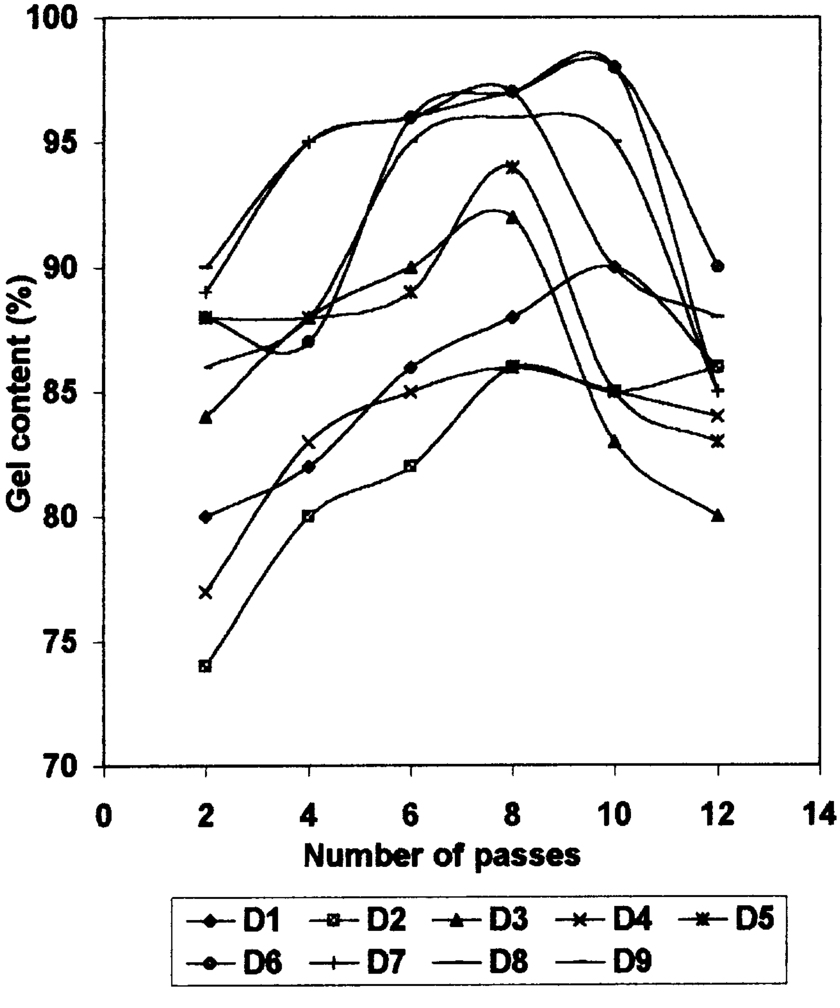

Figure 2. Gel content of the UV-cured films containing different additives against number of passes under the UV lamp.

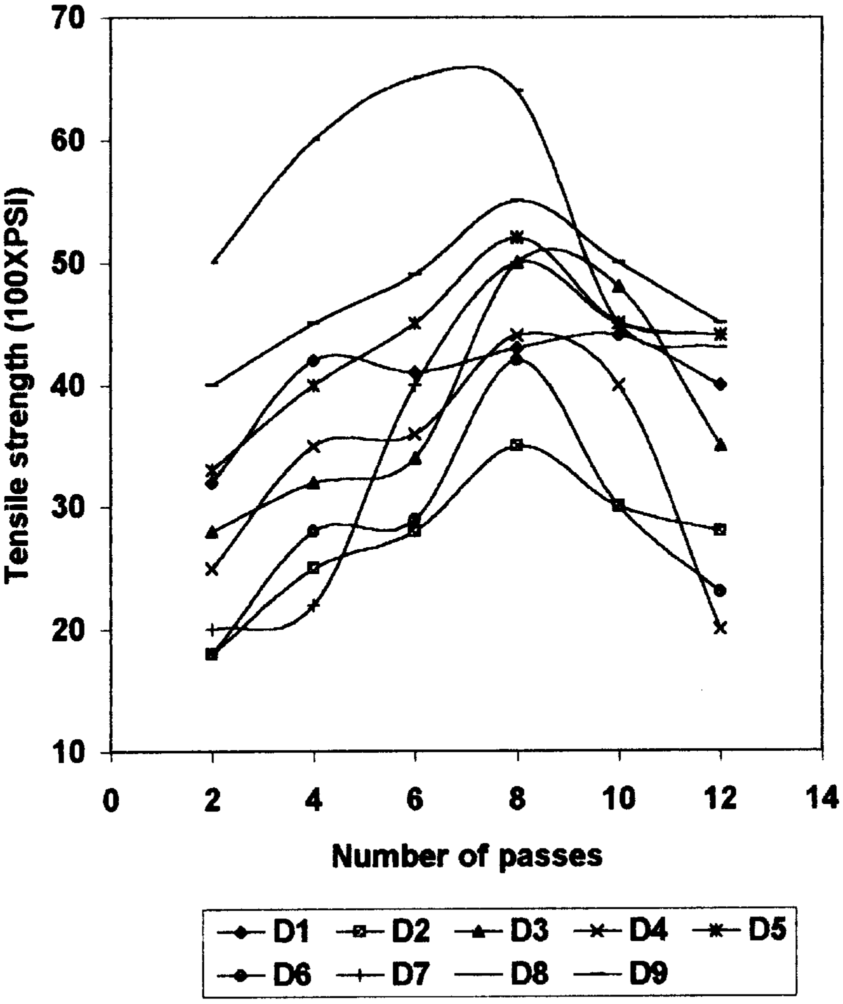

Figure 3. Tensile strength of the UV-cured films containing different additives against number of passes under the UV lamp.

measured on the surface of the film and as such, it represents the crosslinking density at the surface of the film, the gel is the crosslinking density of the entire film. This is the reason that although D6 and D7 films yield the highest gel contents, they do not give the highest hardness, film D4 yields the highest film hardness. In fact, D4 film produces the second lowest gel among all the films and the lowest gel is given by the D2 film.

Tensile Properties

Results of both tensile strength *TS* and elongation at break *Eb* of the UV-cured polymer films are shown in Figs. 3 and 4, respectively. Both *TS*

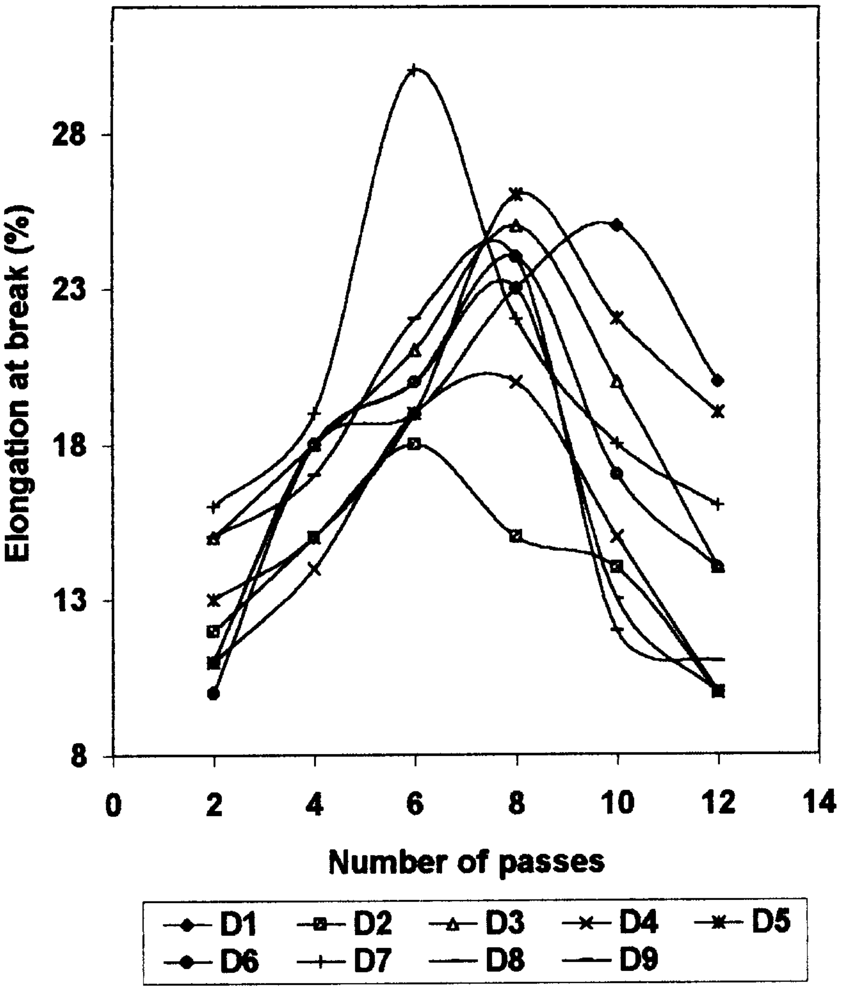

Figure 4. Elongation at break of the UV-cured films containing different additives against number of passes under the UV lamp.

and *Eb* values increase initially with an increase of UV radiation represented by a number of passes. All the films, except D8, show the maximum *TS* values at the eighth pass, while most of the films exhibit *Eb* maxima at the eighth pass except D2 and D7 that have *Eb* maximum at the sixth pass and D1 that shows maximum *Eb* value at the tenth pass. After the attainment of the maximum *TS* and *Eb* values, these properties decrease with UV radiation. The highest *TS* value is obtained with D8 film that contains MA as a co-additive, along with NVP and TPGDA additives. The reason for the high *TS* value may be that MA has a smaller molecular volume compared to molecular volumes NVP and TPGDA. Thus, the MA molecule may have easily diffused into the polymerization reaction zone, thereby creating favorable

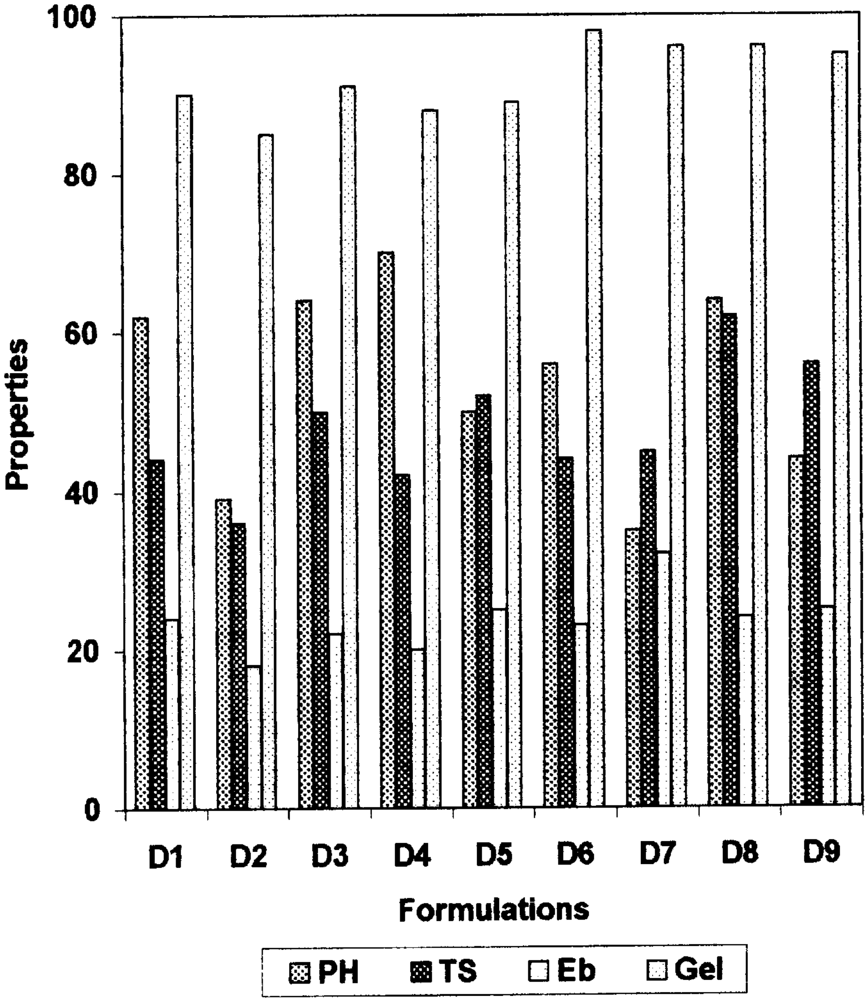

Figure 5. Different properties of the UV-cured films against different formulations.

conditions for NVP and TPGDA molecules to reach the oligomer backbone chain easily through the MA augmentation process. The highest *Eb* value is given by D7 that contains EHA as a co-additive. EHA molecule renders soft polymer film because of its low glass transition temperature. Between D6 and D7, the only difference is the amount of NVP and TPGDA used in them. D7 has more TPGDA than D6. TPGDA has two acrylate branches compared to a ring present in NVP. It is, therefore, the TPGDA that helps make the films elastic in comparison to NVP. Thus, the D7 film is more elastic than the D6 film, though both D6 and D7 contain the same ingredients, but in different proportions. In conclusion, the maximum values of *PH*, *TS*, *Eb* and gel properties obtained for each film (D1–D9) are shown by bars in Fig. 5 against

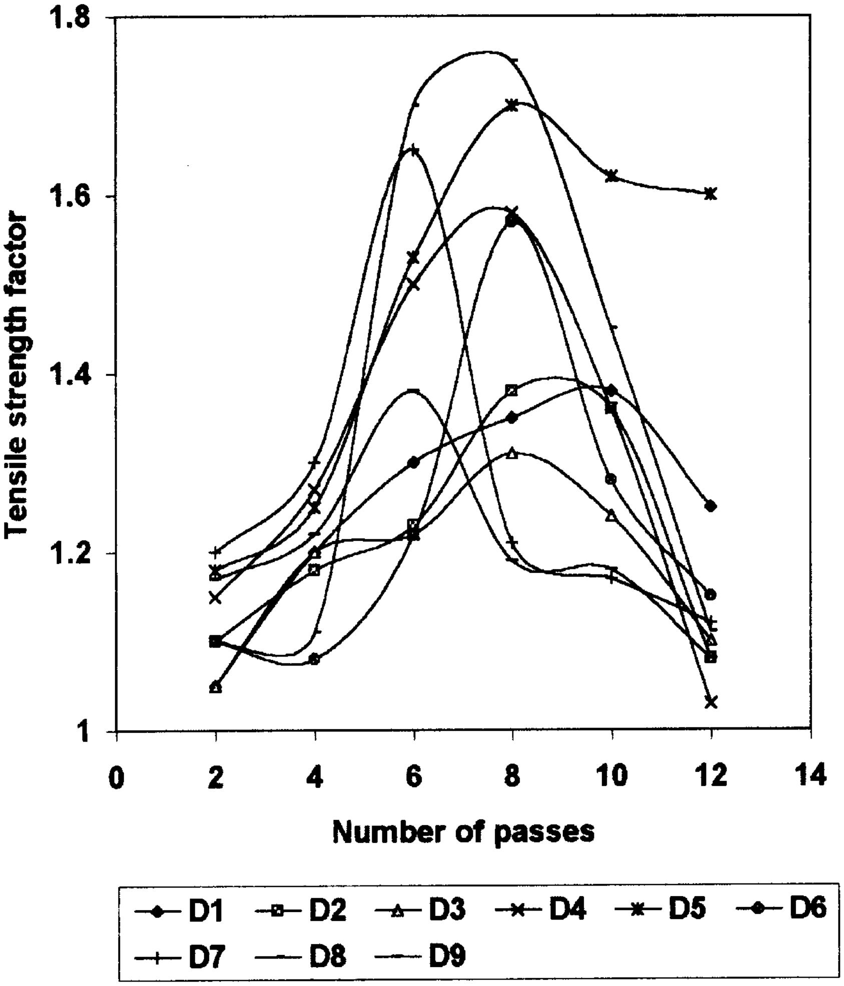

Figure 6. Tensile strength factor of the UV-cured leather against number of passes under the UV lamp.

each formulation in order to have a comparative look at a glance. It is observed that D4 has the highest *PH*; D8 has the highest *TS*; D7 has the highest *Eb* and D6 has the highest gel values.

Application on Leather

Tensile Properties

The enhancement of tensile strength as a result of the UV-cured coating on the leather surface is represented by the tensile strength factor T_f. This means $T_f = TS_{treated}/TS_{untreated}$. The results are shown in Fig. 6, where T_f is

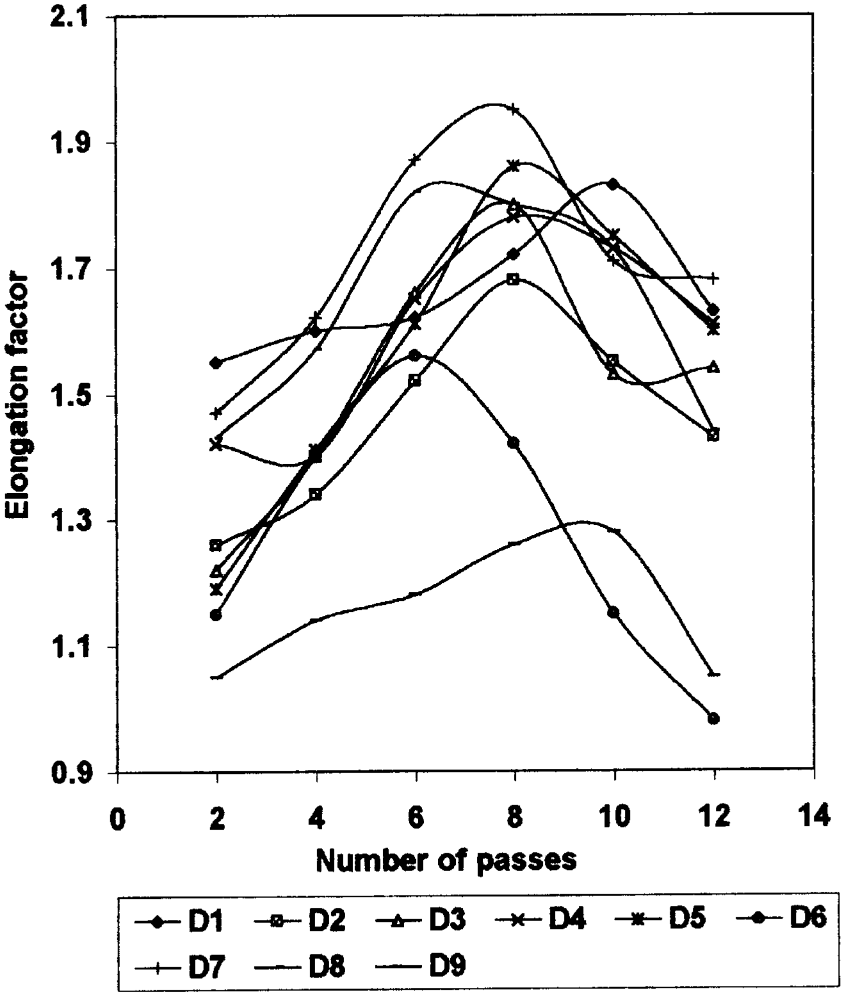

Figure 7. Elongation factor of the UV-coated leather against number of passes under the UV lamp.

plotted against the number of passes under UV radiation. All the formulations have registered enhanced tensile properties when these are coated on the leather surface and cured under UV radiation. The enhancement increases with an increase in curing of the coating with higher UV radiation than 1 pass. The increase of *TS* values attain maxima, mostly at the eighth pass except for formulations D8 and D9 that yield the *TS* maxima at the sixth pass. It is observed that the enhancement of *TS* values induced by different formulations varies between 30% and 70%. The lowest enhancement is by formulation D3, while formulation D8 gives the highest increment in the *TS* value. However, formulations D5 yield about 60% enhanced *TS* values.

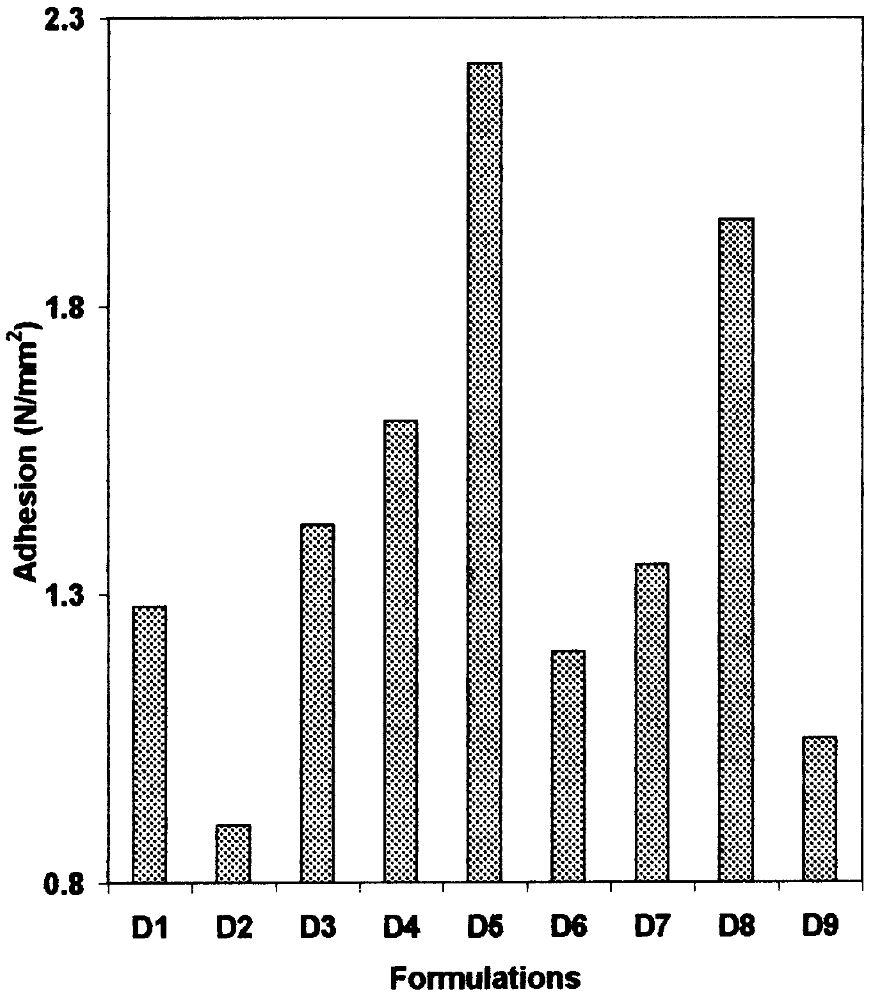

Figure 8. Adhesion of the UV-cured coating on the leather surface against different formulations.

All the formulations (D1–D9) have induced enhanced stretching ability (elongation at break, *Eb*) to the coated leather. This can be demonstrated by plotting elongation factor *Ef* of the treated leather against the number of passes in Fig. 7. The highest stretching ability is to the leather by the formulation D7, followed by D5. The lowest is by D9. About 100% enhanced ability gained by the coated wet blue leather is an important achievement for anticipating diverse applications of leather. It appears that the eighth pass under the UV lamp induces the maximum stretching ability for the coated leather as well. As mentioned earlier, the higher UV doses (represented by 8 passes) required to obtain the maximum outputs of *TS* and *Eb* could be due to the diminished efficiency of the lamp. Moreover, incorporation of different

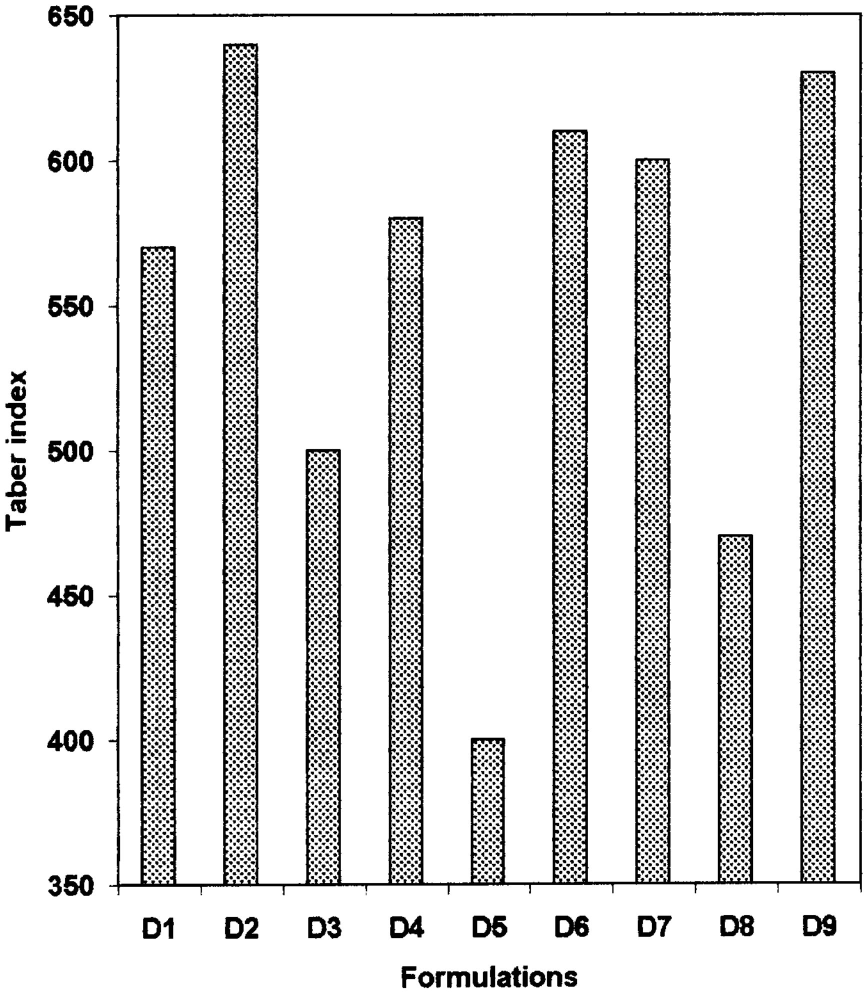

Figure 9. Abrasion represented by Taber Index of the UV-cured coating on the leather surface against different formulations.

additives, co-additives and fillers may have necessitated for higher UV doses to obtain the full curing of the coating.

Adhesion

The coating cured on the leather surface may have different adhesion properties depending on the type of the formulations containing various constituents. The adhesive force calculated for different UV-cured coatings are shown by bars in Fig. 8 against formulations. The coating D5 has the highest adhesion. The coating D5 contains NVP and the urethane oligomer, plus dye and photoinitiator. Both NVP and the oligomer possess carboamide

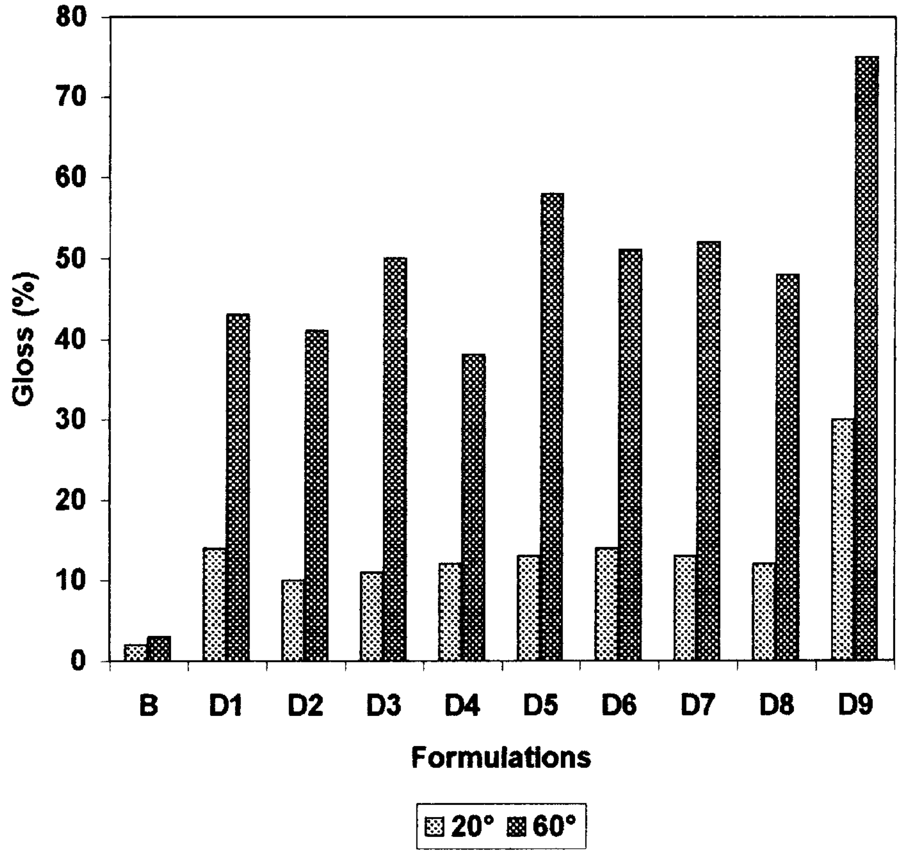

Figure 10. Gloss of the UV-cured coating on the leather surface against different formulations.

group (=N-CO-) which is very congenial to make augmentation with the protein moiety of the leather. The second highest adhesion is given by D8 that contains MA (16%) and TPGDA (15%) in addition to NVP (16%) and oligomer (50%). The presence of MA and TPGDA and the lower amount of NVP present in D8 (NVP 16%) may be the cause of smaller adhesion than D5 (NVP 47%). The lowest adhesion is obtained by the D2 coating.

Abrasion

The abrasion test to wear out coated films by rubbing the coating of the leather surface with a certain load determines the quality of the coating on the surface. The adhesion index represented by Taber Index (amount of coating in gm lost by every 1000 cycles of rubbing the coated surface) is shown by bars in Fig. 9 against each coating formulation. The best coating that has the highest adhesion to the surface should have the lowest Taber

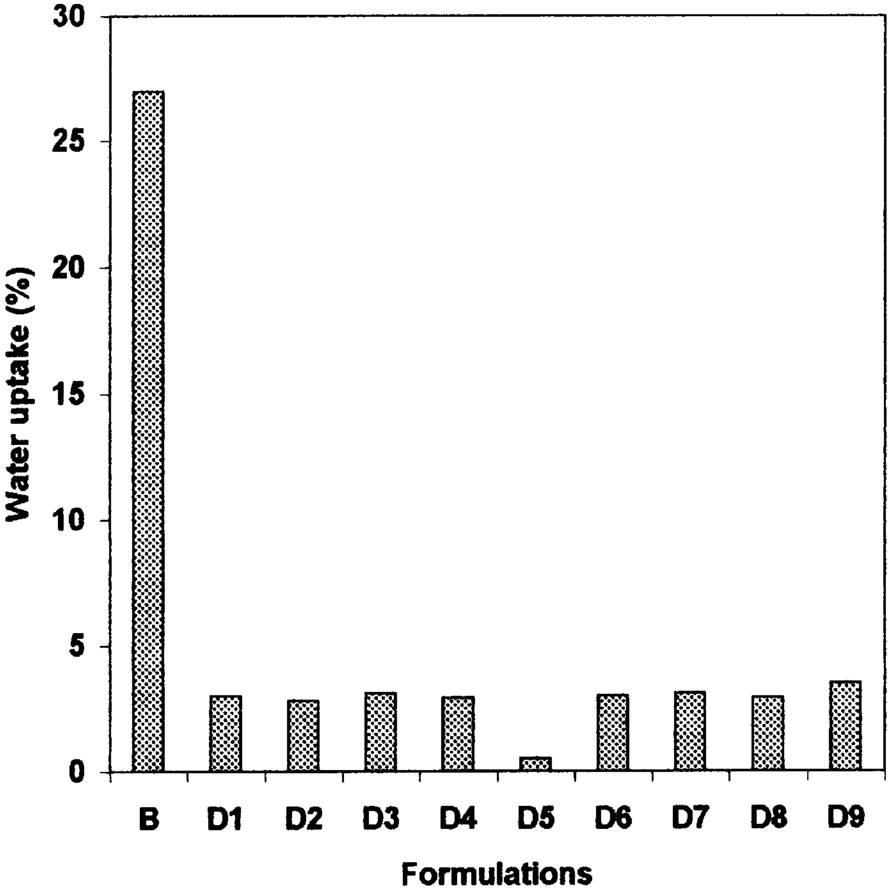

Figure 11. The maximum water absorption made in 5 min by both treated and untreated leather against different formulations.

Index. It is observed in Fig. 9 that the D5 coating has the lowest Taber Index, however, the highest Taber Index is given by the D2 film. The D9 coating has an unusually high Taber Index; the reason is not known at this stage.

Micro Gloss

The gloss of a coating, particularly on leather, is very important. Usually gloss property is measured at 20°C and 60° angles to the coated surface. The results of gloss properties measured at these angles are given in Fig. 10 by bars against the coating. The gloss property measured at 60° is always higher than the same measured at 20°. The coating perturbs the highest gloss (70%) at both these angles. All these coatings have undoubtedly enhanced the gloss property of the wet blue leather. It appears that EA has

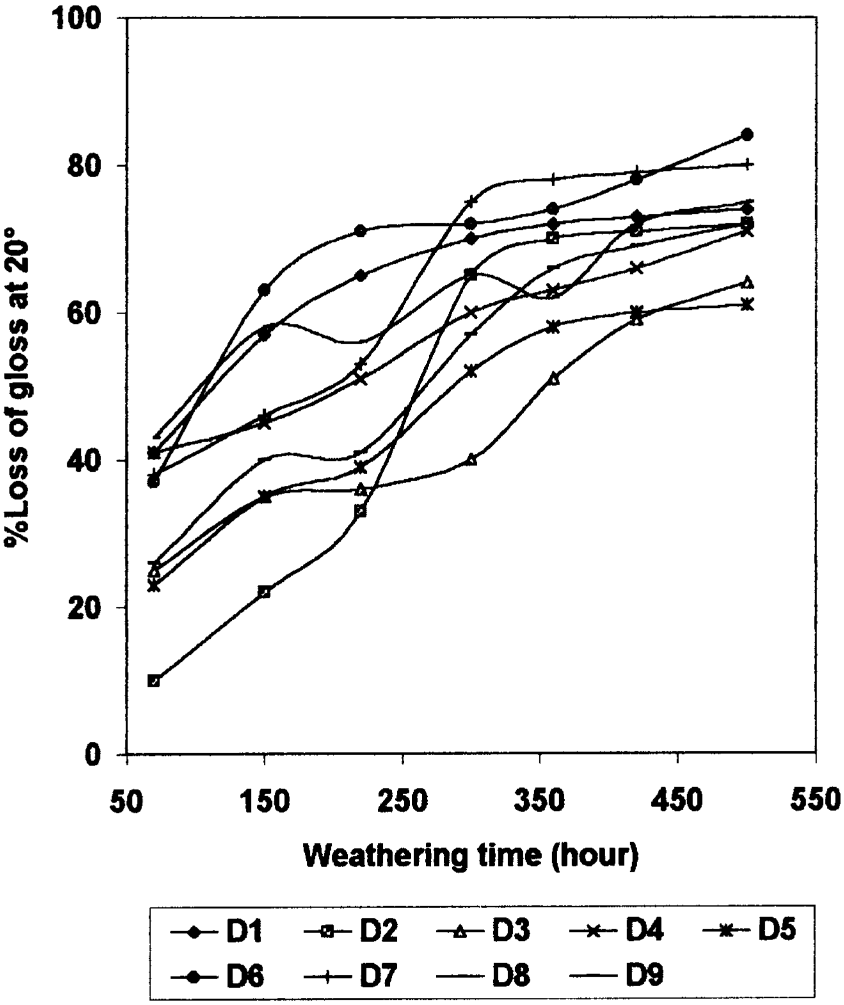

Figure 12. Loss of surface gloss at 20 caused by weathering treatment as a function of different formulations.

possibly been responsible for inducing the highest gloss on the leather surface. The D9 coating contains EA among all the coatings used in this study.

Water Uptake

The extent of water absorption made from a drop of water put on the coated surface is determined up to 5 min. The water absorption increases with the time of allowing the water drop to stand on the surface of both treated and untreated leather. There is a sharp increase of water absorption by the untreated wet blue leather after 4 min, whereas such absorption of water is

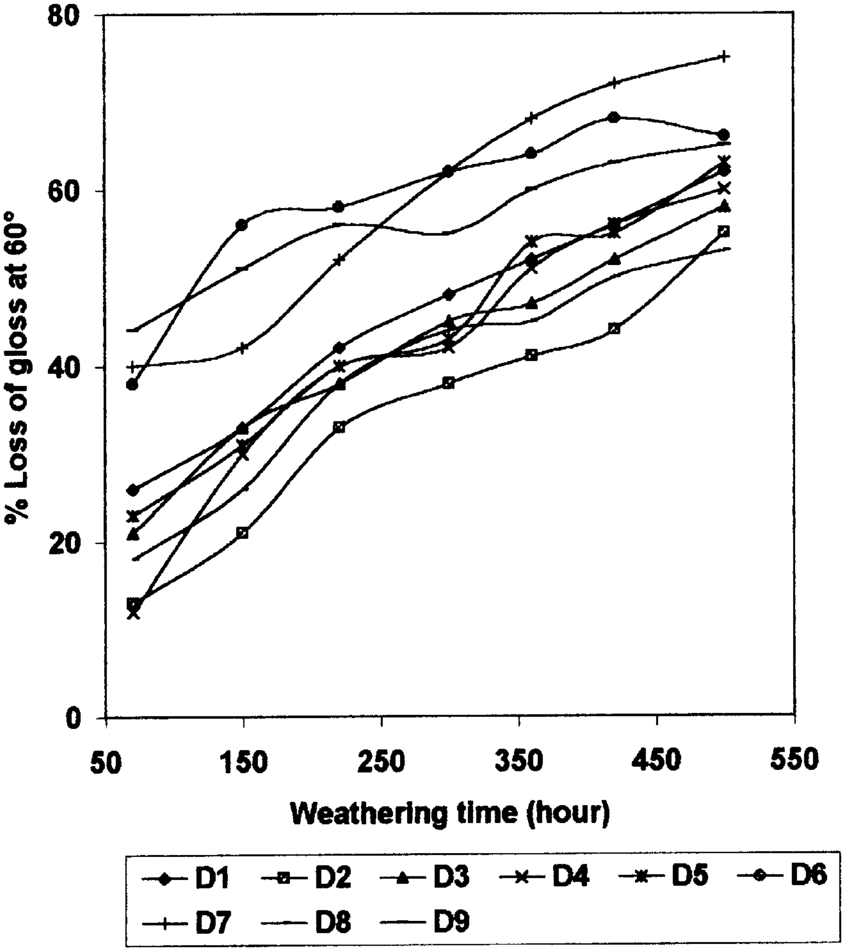

Figure 13. Loss of surface gloss at 60 caused by weathering treatment as a function of different formulations.

very low with the coated leather. This can be clearly demonstrated by plotting the water uptake at 5 min against formulations in Fig. 11. The blank (untreated leather) has about 27% water absorption in 5 min, while all the coated leather surfaces show less than 3% water absorption. In fact, D5 coating has less than 1% water absorption in 5 min. The formulation D5 contains only NVP monomers; carboamide group (-N=CO-) of NVP may be reacted or augmented with leather and crosslinked with oligomer with the help of photoinitiator. As a result the highest adhesion (Fig. 8) and the lowest abrasion as well as moderate tensile properties (Figs. 6 and 7) produced by D5 coated leather. So, the leather coated with D5 formulation preformed the lowest water uptake.

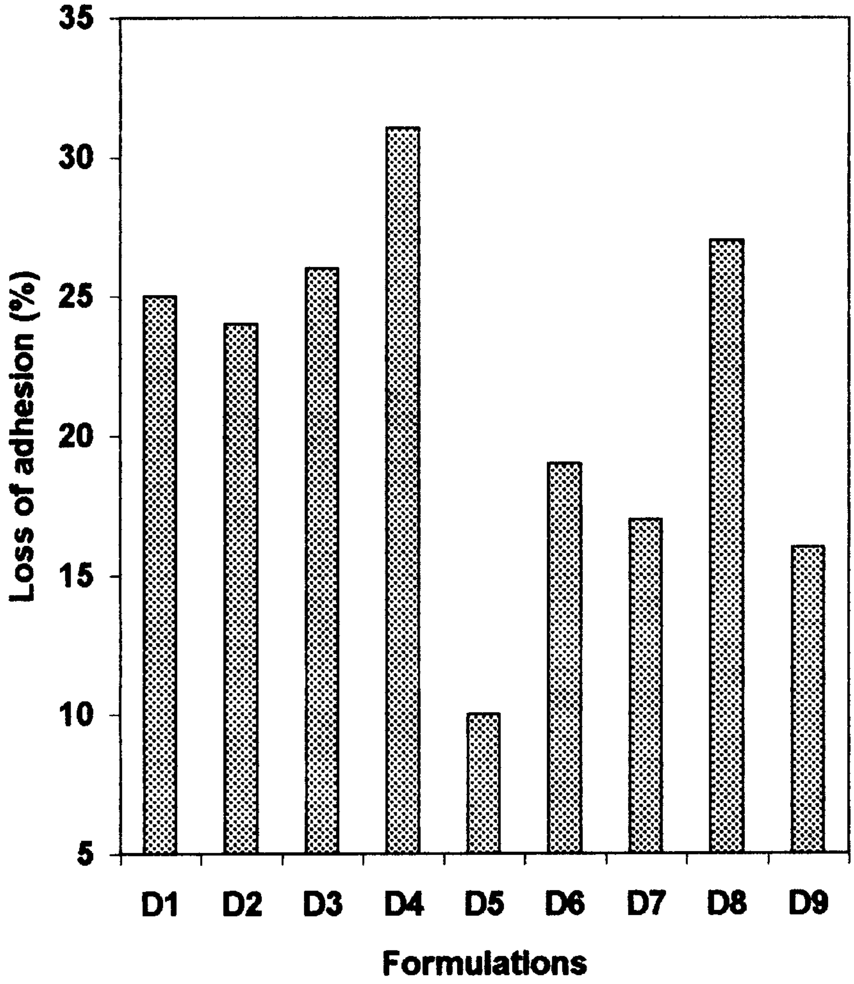

Figure 14. Loss of adhesion of the UV-cured coatings on leather as a result of weathering against different formulations.

Weathering Test

The coated leather was exclusively treated with a simulated weathering test up to 500 hr. The loss of gloss to this weathering treatment through alternating sunshine (4 hr) and condensation (2 hr) is shown in Figs. 12 and 13, respectively for 20° and 60°. Initially, the loss of gloss is high (up to about 300 hr of treatment) and then slows down. The overall loss of gloss is low at 60 than 20. The loss of coatings adhesion with the leather as a result of the weathering test is shown by bars in Fig. 14 against each formulation. The loss is minimum with the D5 coating and maximum with D4 coating.

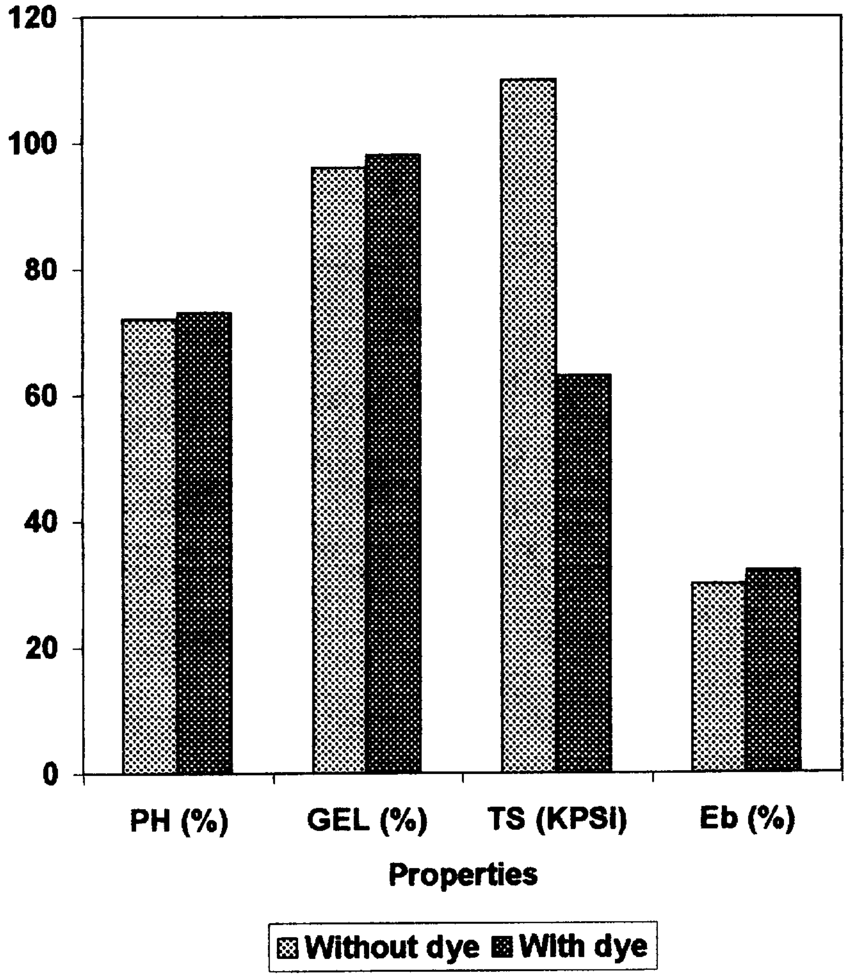

Figure 15. Effect of dye (1%) on the various properties of UV-cured films.

CONCLUSION

The D5 coating is good for the wet blue leather in respect to the attaining high adhesion, low abrasion, minimum water absorption, good tensile properties, and better gloss. This clearly demonstrates that the reactive diluents monomer that contains carboamide group (-N=CO-) viz. NVP induces the maximum improvement of the leather surface. However, EA, MA, TPGDA, and EHA play some positive roles in the improvement of the leather surface. Both urethane and NVP possess carboamide groups and these groups are also present in the leather. Thus, these are assumed to be compatible to each other. The presence of the dye in both thin films at leather coating causes some slight changes in their physical properties. There have

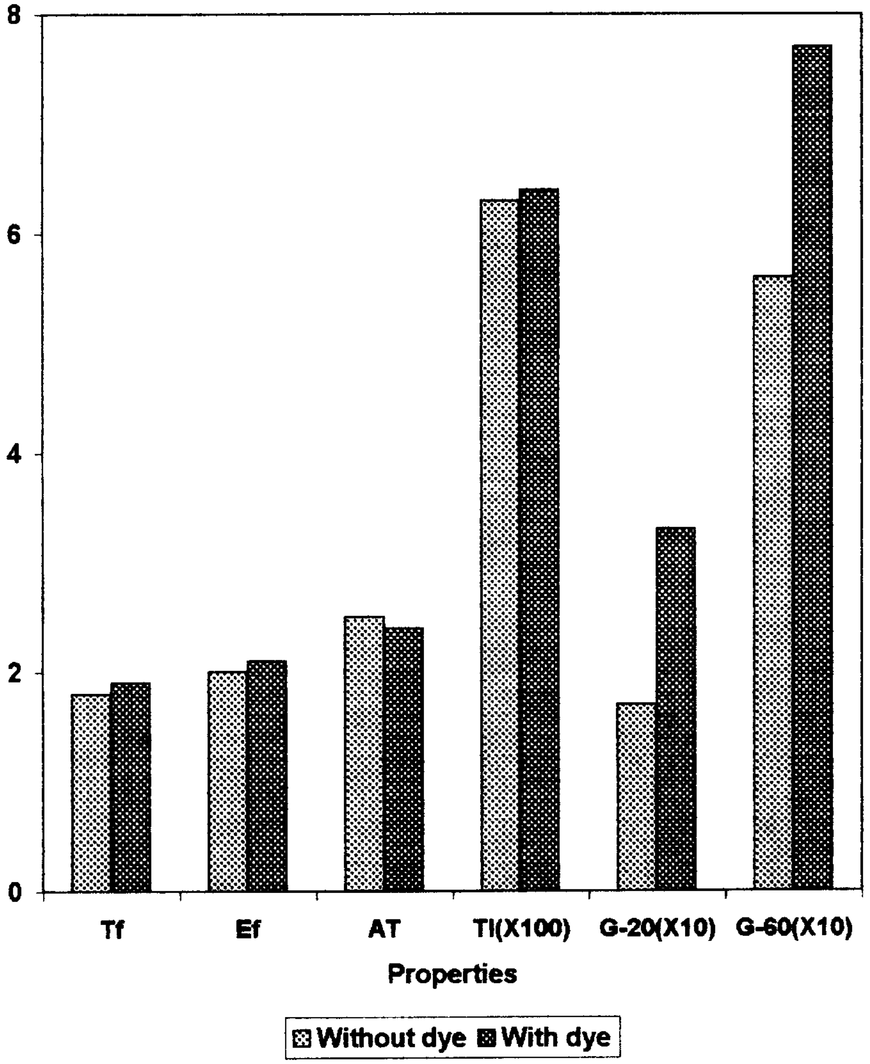

Figure 16. Effect of dye (1%) on the different physical properties of UV-cured leather surface; AT = Adhesion Test (N/mm^2); TI = Taber Index (gm/1000 cycles); G-20 = Gloss at 20° and G-60 = Gloss at 60°.

been some changes with physical properties of both thin films and leather surface coating when 1% dye is incorporated into each of the formulations. Film hardness (*PH*), gel content and film elongation are slightly enhanced but tensile strength (*TS*) is hardly reduced when dye is present in the film (Fig. 15). The dye possibly hampers the augmentation/crosslinking among the different monomers, additives and oligomers during the polymerization process. The case is slightly different with leather surface coating containing the dye. Tensile strength, elongation, and Taber index are slightly increased when dye is present in the coating. However, the adhesion of the coating on the leather surface is slightly reduced (Fig. 16) for the obvious reasons. Gloss of the coating at both the angles (20° and 60°) are quite enhanced by the presence of the dye in the coating. The dye molecules present in the coating play additional reflection of the incident light in forward of the gloss.

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