

Upgrading of Wet Blue Leather Surface by UV Cured Coating

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ABSTRACT: Different formulations were developed with aromatic-based urethane acrylate and reactive diluents. The diluents were *N*-vinyl pyrrolidone and tripropylene glycol diacrylate. Wet blue leather surface was coated with these solutions and cured under UV radiation. Improvement of surface properties such as gloss, abrasion tear, and tensile properties was determined. Effects of different co-additives such as ethylhexyl acrylate, methylacrylate, ethylacrylate, plasticizer, etc. were investigated. Films prepared with these solutions under UV radiation were characterized. It was observed that the best formulation that induced improved properties to the wet blue leather surface was the one that contained the pyrrolidone monomer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 11–18, 1997

INTRODUCTION

Leather is an important commodity that is widely used in shoes, luggage carriers, bags, belts, tents, purses, etc. Thus, leather of different qualities is in demand. Depending on the applications, leather is tanned and treated under different processes starting with the crust variety to the wet blue product, and then finally to the completely finished material. A number of chemical treatments are used to convert the wet blue leather to the finally finished product. This chemical treatment involves various processes that increase the cost of the leather products.

Different workers^{1–4} have developed different chemical methods to improve leather properties keeping the cost to a minimal level. Helmut and Karl⁵ developed some formulations with urethane prepolymer to improve leather through enhancing crack resistance, flexibility, and abrasion resistance. Recently, Uddin, Khan, and Ali^{6–7} used aliphatic backbone-based urethane acrylate oligo-

mer to improve abrasion resistance, gloss, and tensile properties of the finished leather. Incorporation of a carboamide monomer to the formulation of the above urethane oligomer induced the tensile properties of the treated leather to such an extent that the tensile strength was enhanced by 60% and elongation by 75% with improved gloss and abrasion wear. There was a minimal loss of tensile properties as a result of exhaustive weathering treatment. The present article deals with the improvement of wet blue leather (instead of finished leather) by curing the surface coating with ultraviolet radiation. The coating is made with aromatic-based urethane acrylate oligomer combined with other monomer diluents.

EXPERIMENTAL

Materials

Ebecryl 204, a product of Radcure, is a urethane acrylate oligomer with an aromatic backbone. *N*-vinyl pyrrolidone (NVP) is a monofunctional monomer diluent used as a promoter of tensile properties. Tripropylene glycol diacrylate (TPGDA), a difunctional reactive diluent, was procured from

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Table I Composition of Formulations (% w/w)

Chemical	a	b	c	d	e	f	g	h	j
Oligomer	50	50	50	50	50	50	50	50	50
PI	2	2	2	2	2	2	2	2	2
DP	3	3	5	5					
NVP	23	22	11	29	48	16	14	16	16
TPGDA	22	19	30	14		16	18	16	16
EHA						16	16		
MA								16	
EA									16
MEK			2						
Talc		4							

Merck along with NVP and other co-additives such as ethylhexyl acrylate (EHA), methyl acrylate (MA), and ethyl acrylate (EA). Methyl ethyl ketone (MEK) was used as an antibubbling agent, while talc was used to act as a filler in the coating. Diallyl phthalate (DP) was used as a plasticizer. MEK, talc, and DP were procured from BDH Ltd., U.K. Irgacur 184 was used as the photoinitiator during the UV radiation process to initiate the photochemical reactions. Wet blue leather of bovine skin was procured from the local market.

Methods

Nine different formulations were developed with Ebecryl 204 in combination with reactive monomer diluents (NVP and TPGDA) in the presence of other coadditives (EHA, MA, and EA), filler, etc. in the proportions as mentioned in Table I. Thin polymer films were prepared under UV radiation by coating a glass plate (8×5 cm) with these formulated solutions with the help of a bar coater (No. 0.0018) from Abbey Chemicals Co. (Australia). This produced films of 36 ± 3 μm thickness on the plate. A UV-minicure machine (Me-200-UV) from 1ST-Technik (Germany) was used to cure the film on the plate (as well as on the leather) using a UV lamp (254–313 nm, 2 kW). The substrate was run under the lamp at a speed of 4 m/min with the help of a conveyor belt interlocked with the UV radiation process system. The minicure has the efficiency of $\pm 1\%$.

Physical Properties of the Films

Film hardness, an index of crosslinking density at the film surface, was measured with the pendulum method using a pendulum hardness tester (model 5458, Byke Labotron). After 24 h of UV

radiation, the cured film was used for hardness measurement.

Gel content, an index of crosslinking density in the entire film area, was determined by extracting a known weight of the cured film with hot benzene for 48 h in a soxhlet. For this purpose, the film was wrapped in a stainless steel net that was put into the soxhlet. The loss in weight of the cured film due to the extraction process yields the gel content.

Tensile Properties

These properties [strength (TS) and elongation at break (E_b)] were directly measured with an INSTRON testing machine (model 1011, UK) at a cross head speed of 1.2 m/min with a gauge length of 1.2 cm and 220-kg load capacity. The film (5×3 cm) has a dumbbell shape. The INSTRON has an accuracy margin within $\pm 1\%$, and the experimental error was within 2% at the most.

Application on Leather

The wet blue leather sheet (8×5 cm) was dried at 105°C for 24 h before coating the sheet with the formulated solutions using the same bar coater (No. 0.018) as was used for film preparation on the glass plate. The coating was cured with the same UV lamp at the same conveyor speed. Tensile properties were measured with the INSTRON testing machine. Enhancement of tensile properties was expressed as a factor. This means the tensile strength factor T_f was expressed as the ratio of the tensile strength of the treated sample (TS_f) to that of the untreated leather (TS_0), i.e., $T_f = TS_f/TS_0$. Similarly, enhancement of elongation at break for the treated leather was expressed as $E_f = E_{bf}/E_{b0}$.

Abrasion wear of the coated leather was measured by a taber abrasion method using a Taber Abraser (model 5130 of Erichsen Co.), Germany. A hard-type calibrade wheel (CS-10) was used with a 500 g load at 100 cycles of abrasion. The weight loss method was adopted. The taber index is the loss in weight in 1000 cycles. Thus, the lower taber index indicates the better resistance to abrasion by the cured film.

The adhesion ability of the UV-cured film was determined by measuring the force that was applied to peel a certain portion of the cured film with the help of an adhesion tester ASTM (model 525) of Erichsen Co, Germany.

The gloss of the coated leather was measured at two angles, 20° and 60°, using a microgloss meter (sheen-155) of Sheen Co., UK. Water uptake by the leather was determined by putting a drop of water on the surface. This water drop was allowed to stand on the surface for different periods of time in minutes. Then the unabsorbed portion of water drop was smoothly wiped out from the surface of the leather. The increase in weight caused by soaking water in the leather through the surface determines the ability of water uptake.

RESULTS AND DISCUSSION

Pendulum Hardness

Results of pendulum hardness (PH) of different UV-cured polymer films are shown in Figure 1 against UV dose represented by number of passes. As expected, the PH values increase with UV dose with curing of the polymer films, attain maxima, some at the sixth pass, while others at the 10th pass; but mostly at the 8th pass and then decrease. The decrease could be caused by the degradation of the film with higher radiation doses. The highest PH value is imparted by the formulation (h) that contains NVP, TPGDA, and MA. The MA molecule is the smallest among the molecules of other monomer diluents used. The PH represents the film hardness at the surface. The MA molecule possibly floats up at the surface at the time of equilibrium condition during the polymerization process under UV radiation, and then hooks up with the oligomer and other reactive monomers through its vinyl group, enforced by the inductive effect of its $-\text{CH}_3$ part in the MA molecule. The second highest PH value is given by (f) that contains EHA in place of MA (h). EHA is a longer molecule compared to MA; moreover, EHA is a monomer with low glass transition temperature

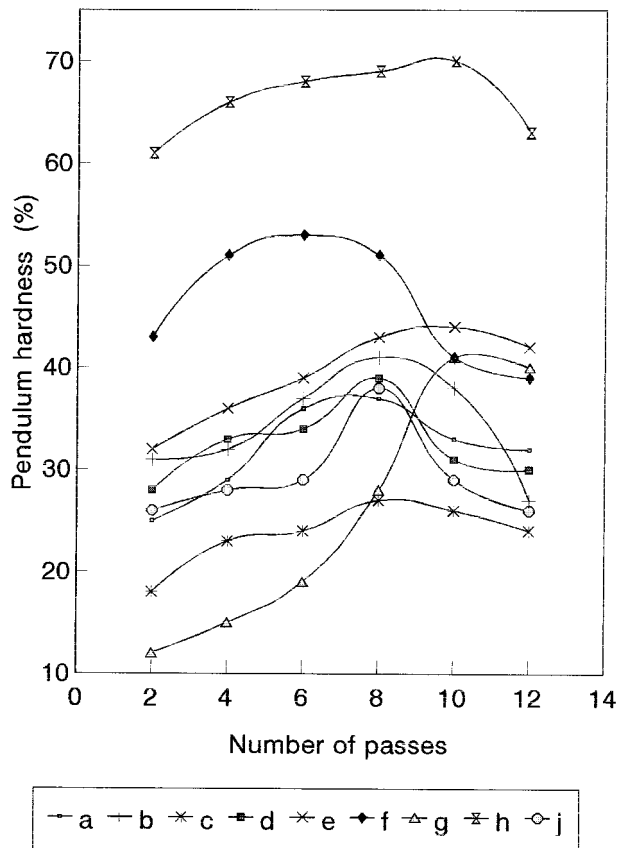


Figure 1 Pendulum hardness of UV-cured films of different formulations against number of passes.

(T_g). The lowest PH value is induced by the formulation (c) that contains the lowest amount of NVP. The NVP molecule is known to create better augmentation⁸ with other neighboring molecules of monomer, oligomer, and cellulose. This is more clearly manifested in the gel contents described below.

Gel Content

The gel values determined through hot benzene extraction of the UV-cured films prepared from different formulations developed with Ebcryl 204 and other materials are plotted in Figure 2 against the number of passes under the UV lamp. The gel content, an index of crosslinking density present in the entire film area, increases nicely as the UV dose increases. Each film attains a maximum gel content, some at the sixth pass (h), while others at the eighth pass (a, c, d, e, f, and g); films (b and j) have the maxima at the 10th pass. All the films have decreased gel contents after the maxima. As mentioned above, the decrease could be caused by the higher radiation.

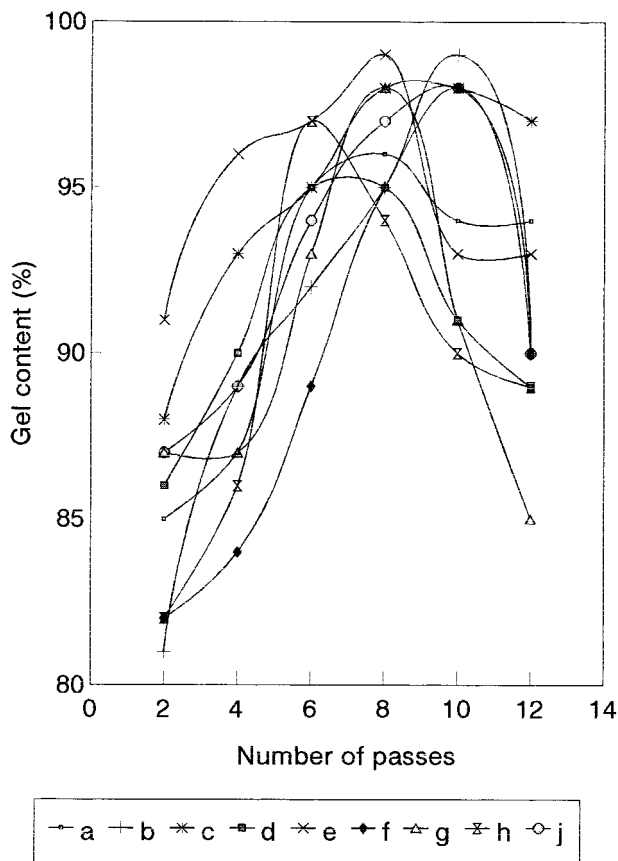


Figure 2 Gel content of UV-cured films of different formulations against number of passes.

The highest gel value is achieved by the (e) film that contains only NVP (48%) along with the oligomer. The NVP molecule has attained maximum facility for augmenting crosslinking with the oligomer without any interference by other reactive monomers. The second highest gel content is given by (h) that contains both MA and TPGDA besides NVP. TPGDA is a difunctional monomer and is capable of making crosslinking through two of its branches. On the other hand, MA is already mentioned to play a good role in creating better crosslinking density at the surface, manifested by the highest pendulum hardness (Fig. 1). It is observed in Figure 2 that the gel values of all these films vary from 94% to 99%. This indicates that these formulations possess high crosslinking ability under the UV radiation.

Tensile Properties

Results of tensile strength (*TS*) of the UV-cured polymer films are plotted in Figure 3 against the number of passes under the UV lamp. The *TS*

values increase with curing of the films. The maximum *TS* values are mostly obtained at the eighth pass except the film (h) that attains the maximum *TS* value at the sixth pass. In fact, the film (h) has registered the highest *TS* value among all the films. The film (h) contains MA besides NVP and TPGDA, which are also present in the films (j and f) in the same proportions as in (h). The only difference is the presence of MA in (h), EHA is (f) and MEK is (j). It is, therefore, the MA molecule that has been able to impart the highest tensile strength to the (h) film. NVP has also contributed much toward inducing tensile properties to the film that contains NVP. The second highest *TS* value is given by the film (e). The lowest *TS* value is produced by the film (j) that contains EHA, which has T_g (-50°C) lower than 0°C .

The stretching ability of a polymer film is related to the elastic behavior of the film. A film may have a high tensile strength, but may not have high elastic character, and vice versa. Elastic behavior is determined by the elongation of the film up to the film breaking point, i.e., elongation at break (E_b). All these UV-cured films have dif-

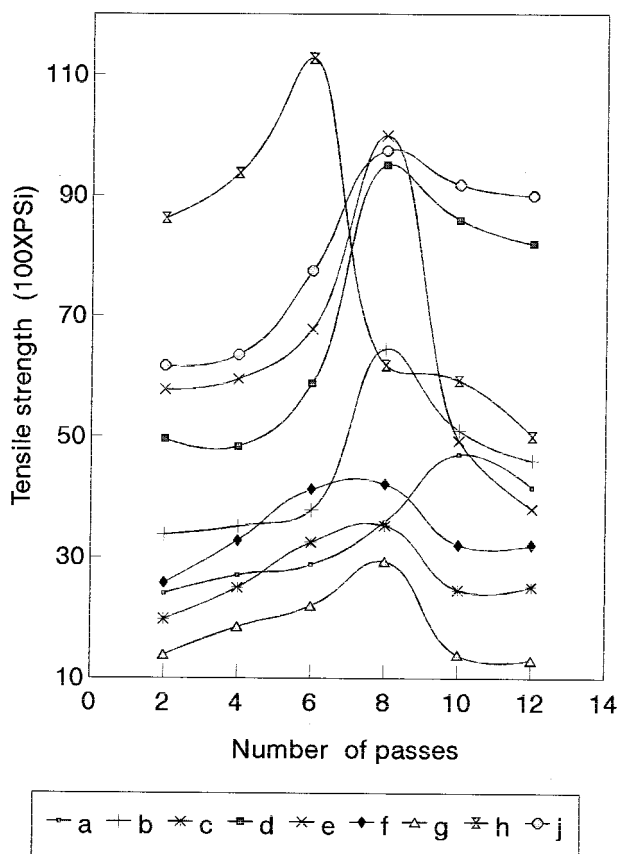


Figure 3 Tensile strength (*TS*) of UV-cured films of different formulations against number of passes.

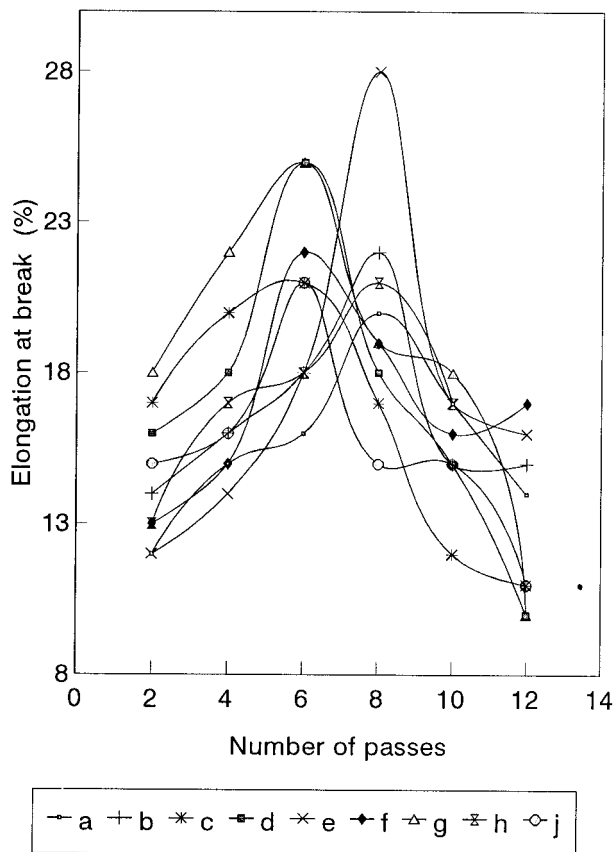


Figure 4 Elongation at break (E_b) of UV-cured films of different formulations against number of passes.

ferent E_b values, as shown in Figure 4 where E_b values are plotted against number of passes. Some films have shown the maximum elongation at the sixth pass, while others are at the eighth pass. The highest E_b value is produced by the film (e) that contains NVP, which is known to impart high tensile strength with moderate elongation.⁹ The lowest E_b value is imparted by the film (a). The films (f and g) contain EHA and yield moderately high E_b values.

Application on Leather

Tensile Properties

Wet blue leather is coated with these formulated solutions and cured under UV radiation. Enhancement of tensile strength of the coated leather surface is manifested by the tensile strength factor $T_f = TS_f/TS_0$. The T_f values are plotted in Figure 5 against the number of passes. It is observed that there is enhancement of tensile strength of the coated leather irrespective of whether the coating is fully cured or not. How-

ever, the strength of the leather increases with the increase of UV dose represented by the number of passes. Most of the coatings induce maximum strength at the eighth pass except the formulation (g) that yields the maximum TS value at the 10th pass. The highest strength (70%) is imparted by the formulation (e) that contains NVP, which is easily augmentable with the protein moiety of the leather material. The lowest TS is $\sim 30\%$, and that is attained by both (a and b) coatings. This is a significant improvement of wet blue leather in that it attains 30–70% enhancement in the tensile strength property as a result of UV-cured coating.

Elongation at Break

Since leather is mainly used as shoes, bags, tents, carrier materials, etc., it is good to have leather that possesses extra stretching ability. The values of elongation factors E_f are plotted in Figure 6 against number of passes. E_f is the ratio of E_b of

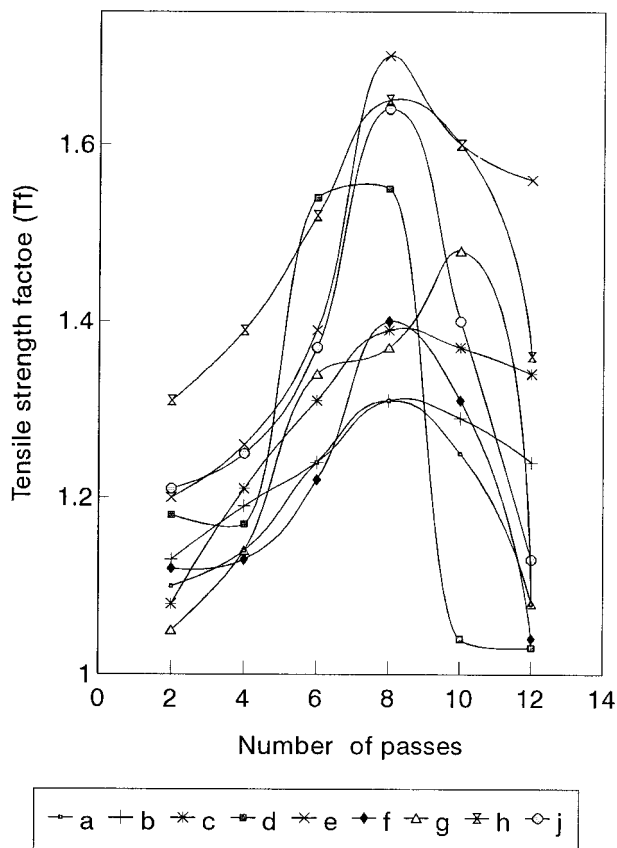


Figure 5 Enhancement of tensile strength (TS) of wet blue leather coated with different formulations and cured under UV radiation is shown as tensile strength factor (T_f) against number of passes.

the coated leather to that of the uncoated virgin leather, i.e., $E_f = E_{b,f}/E_{b,0}$. It is observed that stretching ability of the wet blue leather has been increased between 60% and 95% as a result of the UV-cured coatings. The highest elongation is obtained by the coating (e), followed by (b and h). The lowest E_b is given by (f) coating. The wet blue leather has gained more strength and elongation compared to the finished leather^{6,7} as a result of the UV-cured coatings. The finished leather attained tensile strength enhanced up to 60% and elongation by 35–75%, whereas the wet blue leather gained E_b enhanced up to 95% and TS up to 70%. This is also an important achievement that the wet blue leather has gained significantly enhanced TS and E_b values.

Taber Abrasion

The coated wet blue leather was abraded between two abradent revolving wheels applying a load of 500 g/cycle. The weight loss obtained by the sam-

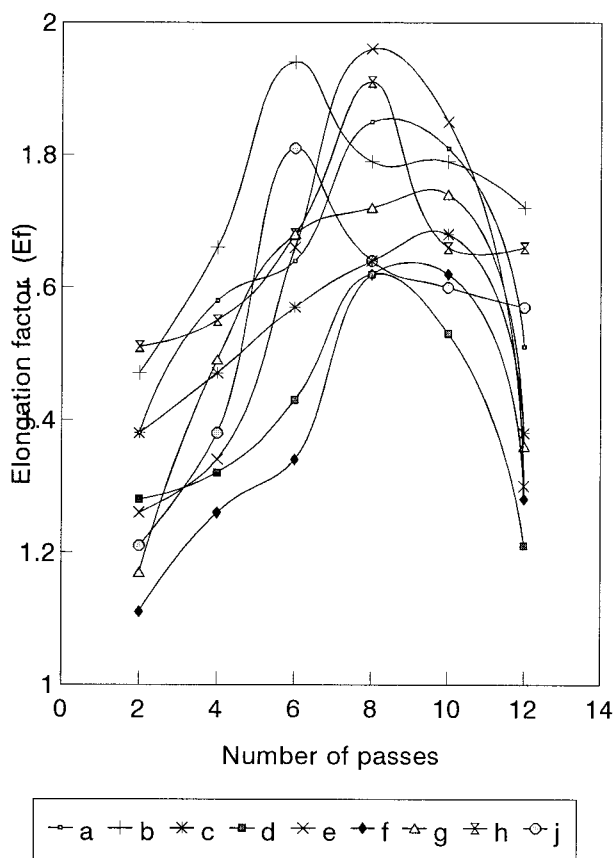


Figure 6 Enhancement of elongation at break (E_b) of wet blue leather coated with different formulations and cured under UV radiation is shown as elongation factor (E_f) against number of passes.

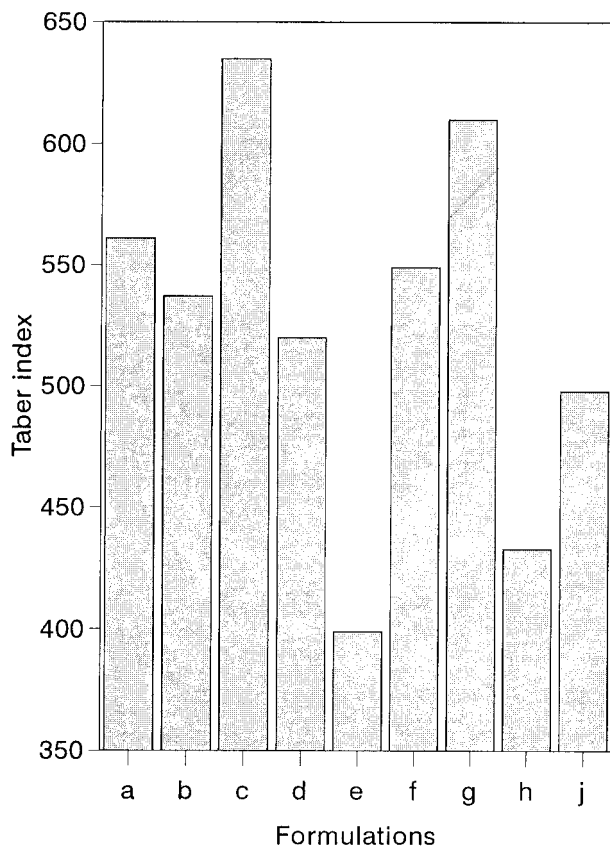


Figure 7 Taber index property of the UV-coated wet blue leather.

ple due to such abrasion between the wheels in 100 cycles is related to the taber wear index. This means that the abrasion resistance is high when the wear index is low. The values of the taber index thus determined are shown in Figure 7 against each coating. It is observed that the coating of formulation (e) shows the minimum taber index, and (c) yields the maximum index. This means that the coating (e) has the highest resistance to wear abrasion pertained by 100 cycles in the revolving wheels, compared to other coatings applied on the leather surface. The formulation (e) contains the lone monomer diluent NVP that contains carboamide ($=N-CO-$) group which is prone to make better augmentation with the protein moiety of the leather material. The same formulation (e) has also imparted the highest strength to the coated leather (Fig. 5).

Adhesion Property

Adhesion is a test that applies a certain force to pull out the coating from the surface of the leather. It is a pulling out mechanism. If a coating is loosely bound with the substrates surface, then

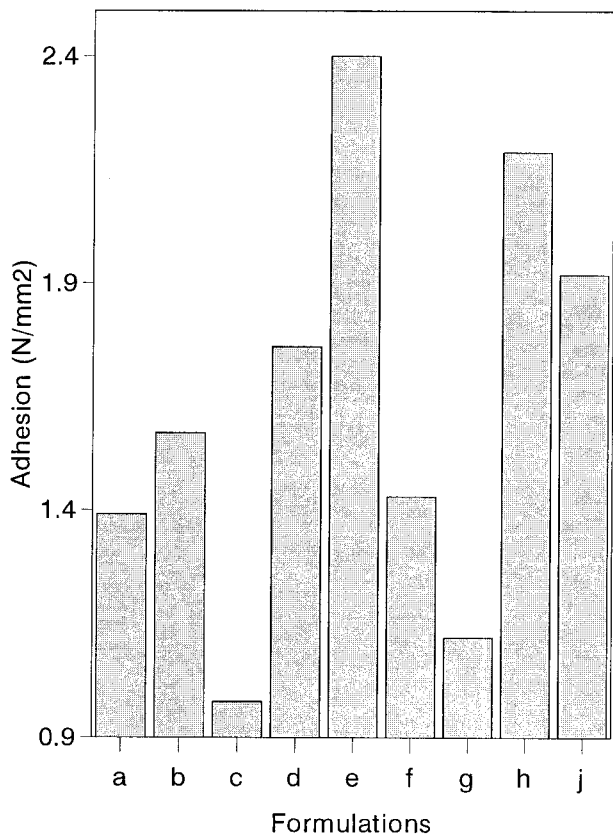


Figure 8 Adhesion property of the UV-coated wet blue leather.

it can be easily peeled off by applying a small peeling force, and vice versa. The results of adhesion force required to pull out the coating from the coated wet blue leather are given in Figure 8 against each coating. As expected, the coating (e) has required the highest force to pull out the coating from the leather surface. This is again demonstrated that the coating (e) is the best among all the formulations developed in this investigation. The minimum force has been required by the coating (c) that contains the minimum amount of NVP among all these formulations. This again proves that NVP (containing a carboamide group) is a better monomer diluent for coating leather.

Surface Gloss

Surface gloss is an important property of leather that is used in making shoes, bags, purses, and articles like these. Gloss is generally determined at two angles (20° and 60°), of the plane of the coated surface. Gloss determined at a 60° angle is generally higher than that at a 20° angle. Results of gloss determined at 20° and 60° are shown

against each coating in Figure 9. The highest gloss is produced by the coating (e) at both angles. The gloss of the coating (e) is >50 times higher than the gloss of the uncoated blank sample mentioned in Figure 9. It is clearly observed that each coating has increased the extent of gloss of the coated leather, but the extent of gloss is variable depending on the types of the formulations of the coatings made on the leather surface. The coatings (b and c) have registered the minimum gloss among all the coatings made on the leather surface.

Water Uptake

The extent of water uptake by putting a drop of water on the leather surface is determined by increased weight of the leather due to water absorption during the period the water drop was allowed to stay on the surface. The wet time period of the water drop is up to 5 min. The results are depicted as water uptake (%) against coating in Figure 10. It is observed that there is very little uptake of water by each coated leather, whereas the un-

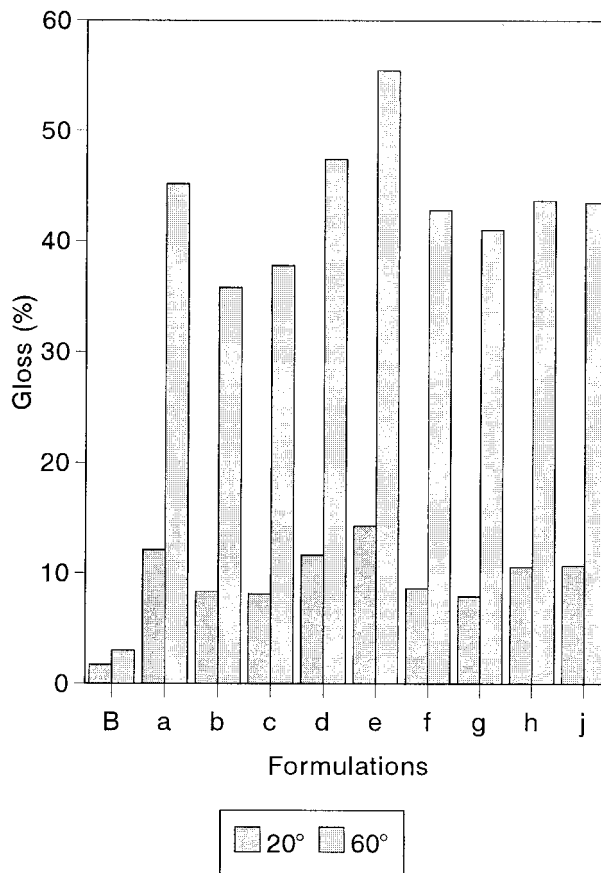


Figure 9 Gloss of the treated and untreated wet blue leather at 20° and 60° angles.

coated virgin wet blue leather has soared in water absorption up to $\sim 28\%$ in 5 min, compared to $< 3\%$ by the coated leather. The difference of water uptake is very little among the coated leather materials possessing coatings of different formulations.

CONCLUSION

In order to have a comparative look at a glance among the various investigated properties such as adhesion test (AT), enhancement of tensile properties (T_f and E_f), and taber index (T_1) obtained as a result of UV-cured coatings with different formulations on the wet blue leather surface, the results of these investigated properties are depicted against each coating in Figure 11. It is observed that the coating (e) is the best compared to other coatings. It induces the highest adhesion to the leather surface, maximum strength, and minimum wear due to abrasion. The

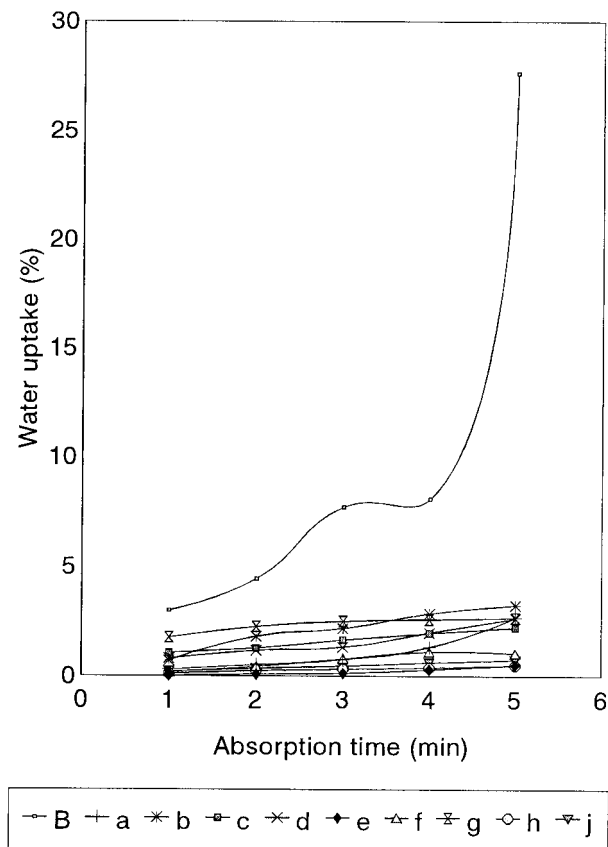


Figure 10 Water uptake of the treated and untreated wet blue leather.

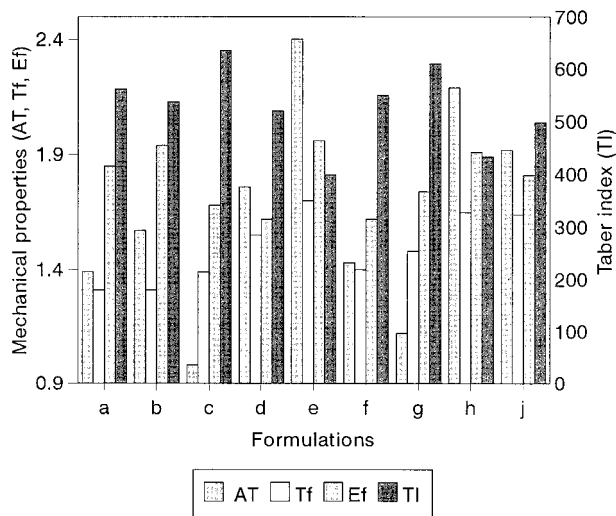


Figure 11 Mechanical properties such as adhesion test AT, tensile strength factor T_f , elongation factor E_f (Y 1 axis), and Taber index T1 (Y 2 axis), of the treated wet blue leather.

coating (e) contains NVP that contains a carbamide ($=N-CO-$) group, which is known to create better coating on the finished leather^{6,7} as well.

The use of plasticizer has not influenced the coating properties of the wet blue leather as it has done with the finished leather^{6,7} by increasing its tensile properties (TS and E_b) by the incorporation of plasticizer into the formulation containing the NVP. It can be concluded that the coating containing the NVP is considered to be the best coating for both wet blue and finished leather.

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