

Development of Polymer Films and Its Application on Leather Surfaces

M. KHABIR UDDIN, MUBARAK A. KHAN, and K. M. IDRIS ALI*

Radiation Chemistry Laboratory, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission, P.O. Box 3787, Dhaka, Bangladesh

SYNOPSIS

Ten different formulations are prepared with a urethane acrylate oligomer in combination with two monofunctional monomers (EHA with low T_g and NVP with a carboamide group) and a difunctional acrylate monomer (TPGDA) in the presence of a plasticizer. Polymer films are prepared with these formulated solutions under UV radiation. Their properties (gel, hardness, tensile characters, etc.) are determined. These solutions are coated on leather substrates and cured under UV radiation. The improvement of quality of leather is manifested through the enhancement of tensile strength and elongation of the coated leather. The coating also imparts high gloss on the leather surface as well as high wear resistance. It also protects the leather from the damage of weathering effect. The best formulation is determined to be the one containing NVP with a carboamide group and a plasticizer. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Development of polymer is a continuous process for achieving polymer in a specific application under certain environmental condition. A polymer used in tropical environment may not necessarily be suitable for application in cold weather. Similarly, a polymer that can be grafted on a carbohydrate cellulose fiber may not be suitably grafted on protein material like silk and leather. Thus, an endeavor is always going on to develop formulation with suitable ingredients of monomers and oligomers in combination with other additives and coadditives capable of inducing relevant characteristic to the developed polymer to be used in certain applications. Applications of these polymers as coatings on substrates depend very much on the rheological properties of the polymers as well as on the substrates. Flexible substrates require flexible/elastic polymer to be coated on these substrates in order to match their rheological properties. Urethane coatings are generally applied on flexible substrates like leather.¹ Some additives and coadditives are incorporated with the urethane pre-

polymer to induce improved abrasion resistance, crack resistance, and flexibility.² High-performance finished leather was developed by adding binders and crosslinking agent. Thus, various workers³⁻⁷ have developed different formulations to improve properties of leather. The present investigation is to develop formulations to characterize their polymeric characters and then to apply these formulations on leather in order to improve its rheological properties.

EXPERIMENTAL

A triacrylated urethane oligomer (EBECRYL 264) with aliphatic chain procured from IAEA was used. Two monofunctional monomers such as EHA (ethyl hexyl acrylate) and NVP (*N*-vinyl pyrrolidone) and a difunctional monomer TPGDA (tripropylene glycol diacrylate) were used for making different formulations. Photoinitiator (Irgacure 184) obtained from IAEA was also used. A plasticizer (diphthalate acrylate) was needed to smooth the polymer film on the leather substrate.

Ten different formulations were prepared by mixing the oligomer with monomers and plasticizer

* To whom correspondence should be addressed.

Table I Composition of Different Formulations

Materials (w/w)	A	B	C	D	E	F	G	H	I	J
Oligomer	50	50	50	50	50	50	50	50	50	50
EHA	48			46			24	24	22	22
NVP		48			46		24		24	
TPGDA			48			46		24		24
Plasticizer				2	2	2			2	2
Initiator	2	2	2	2	2	2	2	2	2	2

at different proportions, as mentioned in Table I. This polymeric films were prepared under UV curing of the coatings made with these formulations on glass plates (5×8 cm) with the help of a bar coater No. 0.018 from Abbey Chemicals Co. (Australia), which gave $36 \pm 3 \mu\text{m}$ thick films. The UV curing was done with an UV-minicure machine of 1ST-Technick (Me-200-UV, Germany, 254–313 nm 2 kW). The speed of the conveyor was 4 m/min. The accuracy margin of the minicure is $\pm 1\%$. The film hardness was measured with a Pendulum Hardness Tester (Labotron BYKE). The cured film was then carefully peeled off the plate for carrying out other property measurements.

Gel and Swelling Property

The gel content of the cured film was determined by wrapping a known weight of the film in a stainless steel net that was put in a soxhlet for extraction with hot benzene for 48 h. The difference of weights of the film before and after the extraction determines the gel content. The extracted film was soaked in acetone for 24 h at 25°C . The difference of weight of the swollen film with that of the dry extracted film yields the swelling ratio.

Tensile Properties

Tensile strength (TS) and elongation at break (Eb) of the UV-cured films were directly measured with tensile strength machine (Instron, model 1011, UK) integrated with a PC (Amstrad) at a crosshead speed of 4 m/min. The load capacity was 500 lbs; the gauge length was 0.5 inch. The Instron has the accuracy margin within $\pm 1\%$. The film (5×3 cm) had a dumbbell shape. Experimental error was less than 2% in the extreme case.

Application on Leather

A leather sheet (5×8 cm), dried at 105°C for 24 h, was coated with the formulated solutions (Table I)

by the same bar coater (No. 0.018) and was irradiated under the same UV lamp for different passes. The tensile properties of the cured leather were similarly measured. The gloss of the coatings of the leather surface was measured by a microgloss meter (sheen-155) of Sheen Co. (UK). The treated leather substrate was subjected to severe weathering testing by simulating sunlight (4 h) using a UV lamp (313 nm) and condensation (2 h). The accelerated weathering testing was carried out for 493 h with the help of a Tester (Q-UV-26200, Q-Panel Co.). The loss of gloss and tensile properties as a result of the weathering test was determined.

The taber abrasion of the coated leather was measured with a Taber Abraser (model 5130, Erichsen Co.). A hard type calibre wheel (H-18) with 1 kg load was used. The weight loss method was followed. The taber wear index and the wear cycles were measured. The taber wear index is the weight loss in 1000 cycles. This means that the lower wear index indicates the better abrasion resistance of the material.

RESULTS AND DISCUSSION

Table I shows the composition of different ingredients of the formulations. There are four sets of formulations present in this table. Formulations A, B, and C are a single monomer system and D, E, and F contain plasticizer in them, while G and H are a double monomer system and I and J contain a double monomer with a plasticizer. The pendulum hardness of the UV-cured films is plotted against the number of passes (Fig. 1). The hardness increases with dose but decreases after attaining the maxima at the 8th or 10th pass. Among the single monomer system (A, B, C) without the plasticizer, the formulation B that contains the monomer, NVP with a carboamide group has exhibited the highest pendulum hardness (PH). Formulation A contains the monomer, EHA that has glass transition temperature (T_g) far below 0°C , and formulation C

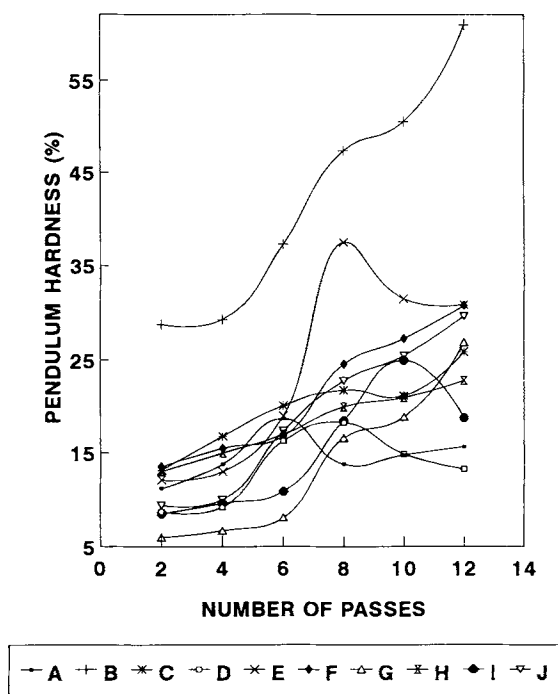


Figure 1 Pendulum hardness of UV-cured films of different formulations is shown against the number of passes.

contains a difunctional monomer, TPGDA. Thus, the PH of C is higher than that of A and should have been also higher than the PH of B because B contains a monofunctional monomer. But this monomer (NVP) has a carboamide group that has the ability of augmenting and crosslinking the monomer unit^{8,9} with the urethane oligomer that also possess a similar carboamide group. Addition of a plasticizer to these (A, B, and C) has substantially reduced the hardness. Films of NVP and TPGDA could not be peeled off, as it is quite brittle.

Gel Content

The gel content is a representation of crosslinking density in the cured film as a whole, while film hardness represents the crosslinking density on the surface of the cured film. The gel contents of the UV-cured films prepared from these formulations were determined by hot benzene extraction over 48 h and are plotted (Fig. 2) against the number of passes under the UV lamp. The gel content initially increases with UV dose, attains the maxima, some at the 6th pass and some at the 8th pass, but the formulation G at the 10th pass. After the maxima, the gel content decreases. This is possibly caused by radiation degradation at higher doses. The formulations B and G have attained the highest gel content,

B at the 8th pass and G at the 10th pass. Both these formulations (B and G) contain the same monofunctional monomer (NVP) with the carboamide group. But G contains another monofunctional monomer (EHA) that has low T_g in addition to NVP. The low T_g monomer (EHA) requires more dose for curing than the high T_g monomer.¹⁰ This is the reason that G needs more radiation to attain the maximum gel. The formulation F has shown reasonably high gel at the 8th pass. F contains the difunctional monomer, TPGDA, which is capable of making crosslinking with two directions because of its difunctional character.

Swelling Ratio

The more a film is cured and crosslinked, the less ability it has to swell, because the swelling molecule, in that case, can hardly find enough functional group and space to swell the cured polymer through loose bonding or so. Thus, as the crosslinking density (curing) increases, the swelling ratio is expected to decrease. This is actually found in Figure 3, where the swelling ratio is plotted against the number of passes. In most of the cases, the lowest swelling is observed at the 8th pass where the films attained the highest gel. The swelling ratio increases after the 8th pass except formulation G, which shows in-

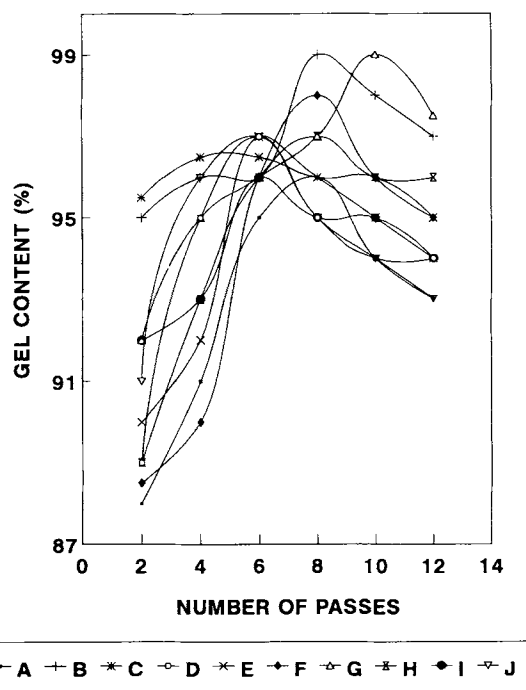


Figure 2 Gel content of UV-cured films of different formulations is shown against the number of passes.

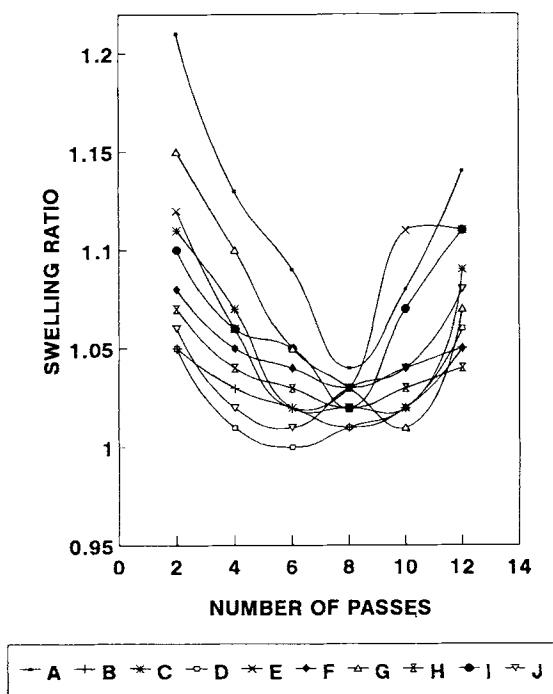


Figure 3 Swelling ratio of UV-cured films of different formulations is shown against the number of passes.

crement after the 10th pass consistent with the highest gel obtained with G at the 10th pass (Fig. 2). After attaining the lowest swelling, it increases again at high doses. This is also in conformity with the low gel obtained (Fig. 2) at high doses. As the gel is degraded at higher doses, the broken molecules possess some specific sites where the molecules of the swelling solvent can form loose bonding to swell the degraded polymers.

Tensile Properties

Tensile properties are very important in selecting diverse applications of polymer and polymer-grafted substrates. Tensile strength (TS) values determined with the cured films are plotted against number of passes (Fig. 4). Film (C) with the difunctional monomer TPGDA has shown the highest TS values at the 8th pass. Incorporation of a plasticizer into the formulation (C), the TS values is drastically reduced to half its original strength. The second highest TS values is obtained by film (B) that contains a carboamide group in the monomer (NVP). The lowest TS values are exhibited by the formulations (I and G) that are composed of EHA and NVP (I contains EHA, NVP, and plasticizer). The film of formulations A and D could not be peeled off the plates, because these were very soft and sticky

due to the presence of the monomer EHA, which has very low T_g (-50°C).¹¹

Application on Leather

Tensile Properties

Finished leather is coated with these formulated solutions and cured under the same UV lamp and its tensile strength values are determined. The enhancement of tensile strength (TS) of the treated leather is represented by TS factor (T_f), which can be described as the ratio of TS values of the treated and the untreated samples, i.e., $T_f = \text{TS treated} / \text{TS untreated}$. The T_f values are plotted against number of passes (Fig. 5). It is observed that T_f increases with UV radiation and attains the maxima mostly at the 8th pass. All the coated leather samples have attained the enhanced strength. The highest strength (about 60%) has been obtained by the leather grafted with the formulation E that contains the monomer (NVP) with the carboamide group capable of strong augmentation between the leather cell backbone and the monomer (NVP) unit. The plasticizer (P) present in E has also helped to plasticize the leather material to gain more strength than the sample coated with the monomer (NVP) without the plasticizer. Thus, the formulation B (with NVP

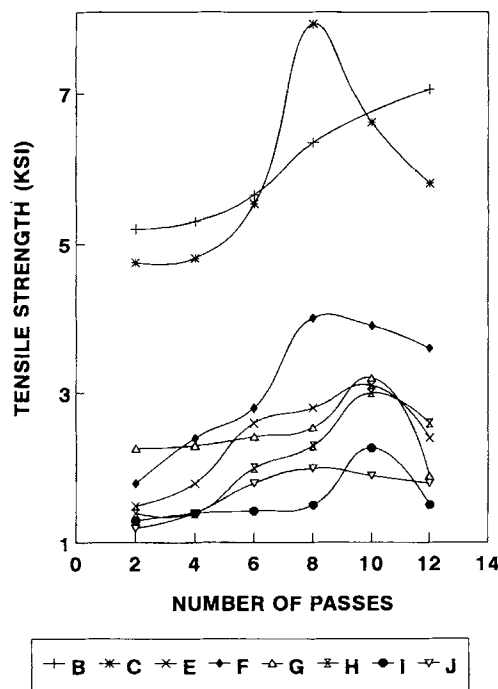


Figure 4 Tensile strength (TS) of UV-cured films of different formulations is shown against the number of passes.

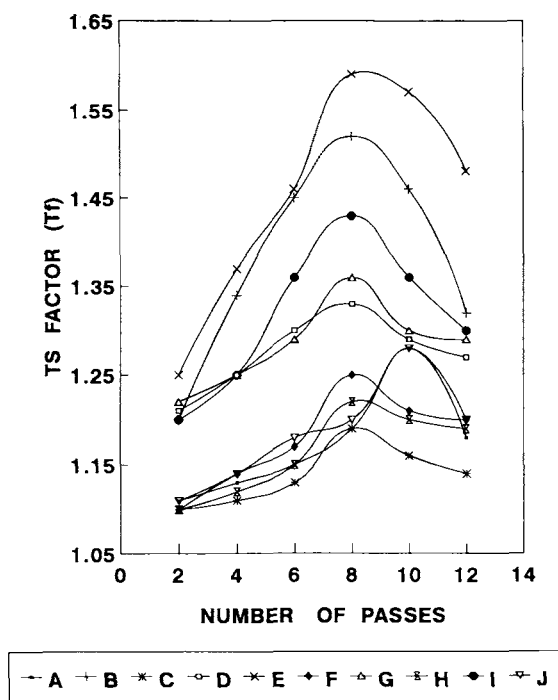


Figure 5 Enhancement of tensile strength (TS) of leather coated with different formulations and cured under UV radiation is shown as tensile strength factor (T_f) against the number of passes.

without plasticizer) has induced the second highest tensile strength to the leather materials. The lowest tensile strength is achieved by the samples coated with the formulation (C) of difunctional monomer (TPGDA). The difunctional monomer has a larger molecule than that of the monofunctional monomers (EHA and NVP). Thus, it has become difficult for the large molecule to diffuse into the leather cell chain at the time of the equilibrium conditions needed for the copolymerization reactions.

Elongation at Break

Flexibility of a polymer is an essential parameter that is very actively considered during the applications of the polymer. Flexibility and elasticity are two related phenomena that are associated with the suitability of the application of a polymer in a certain area. Rigid (plastic) and flexible (elastic) polymers have different applications. All these properties are related to the structural shape and geometry of the molecule. Thus, a polymer formed with a monomer of highly low T_g value is very soft. On the contrary, a high T_g monomer will mostly produce brittle film. The polymeric films prepared under UV radiation with these formulations are elongated to such an extent that the films break. The extent of elongation

of these UV-cured films at the breaking point are plotted against number of passes (Fig. 6). The elongation (Eb) increases with radiation and attains maxima; some at the 6th pass and others at the 8th pass. This variation is caused in order to attain the properly cured film. Some formulated solutions need more radiation dose than the other to achieve the full curing. Films A and D are so soft that these films could not be taken off the coated plates. The highest Eb is shown by the film (I) that contains both EHA and NVP and a plasticizer. Both plasticizer and the monomer EHA have helped to enhance the elastic property of the film. The lowest Eb is exhibited by film C, which contains a difunctional monomer (D). Incorporation of a plasticizer to C has enhanced the elasticity to some extent as it is shown with film F. The monomer EHA is playing some important role to induce elasticity to the film, as evidenced by the fact that all the films that contain EHA have enhanced elasticity denoted by elongation of the film. This is more clearly demonstrated in that film C has higher elongation when EHA is added to it to give the formulation H. The idea of enhanced elongation of the film containing EHA, a low T_g monomer, is completely changed when these formulations are coated on leather surface and cured under UV radiation. Leather is not known to have

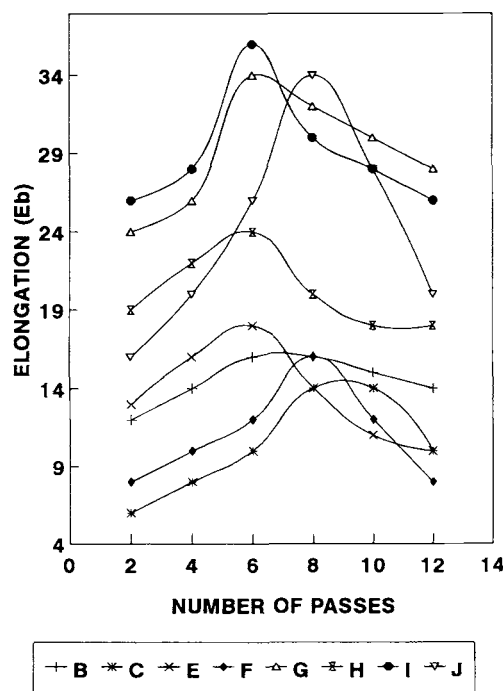


Figure 6 Elongation at break (Eb) of UV-cured films of different formulations is shown against the number of passes.

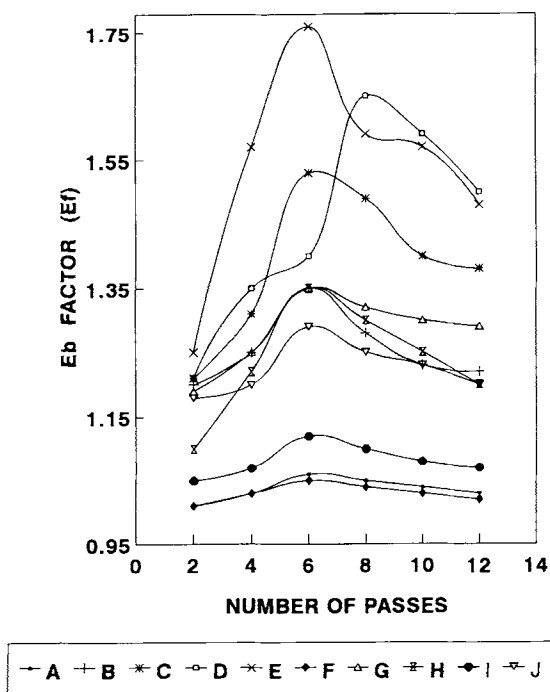


Figure 7 Enhancement of elongation (E_b) of leather coated with different formulations and cured under UV radiation is shown as elongation factor (E_f) against the number of passes.

high elongation like the elastic polymer; but it has been possible to elongate the coated leather up to 75% more than the uncoated leather through stretching. This is shown in Figure 7 when elongation factor, E_f is plotted against number of passes under the UV lamp. The E_f is the ratio of the elongation (E_b) of the treated leather to that (E_b) of untreated leather, i.e., $E_f = E_{b\text{-treated}}/E_{b\text{-untreated}}$. The formulations B, E, G, and I contain the same monomer NVP that has a carboamide group present in them. The UV-cured films of G and I (Fig. 6) have high E_b values because these films (G and I) contain a plasticizer (formulation I) and EHA, a low T_g monomer (formulation G); but the leather samples coated with formulations B and E exhibit 35 and 75% enhancements in E_b , respectively. This increment (35 to 75%) is due to the presence of the plasticizer. The plasticizer present in E has been of great help to stretch the coated leather. The carboamide group present in NVP is also helpful to make linkage between the protein moiety of leather and the monomer. However, the low T_g monomer (EHA) in combination with the plasticizer (formulation D) and the difunctional monomer (formulation C) have also registered elastic property to the leather coated with these for-

mulations (C and D) and the E_f remains above 50%. This is a good achievement. Addition of a plasticizer with the difunctional monomer to formulation F has reduced the elastic property of the coated leather to a minimum (Fig. 7).

Abrasion Property

Abrasion property is important in the sense that leather is normally used in making shoes, bags, luggage, coats, jackets, etc. If the wearing resistance is high, the leather products are considered to be more durable and can last longer. Thus, the wearing resistance of the coated leather is determined by the application of Taber Abrasion Test through weight loss method. The coated leather was abraded between two abrader revolving wheels applying a force of 1 kg per cycle. The Taber wear cycle is considered to be the number of cycles at which the product (substrate) starts wearing, determined by the loss of weight of the substrate caused by the abrasion between the wheels. Figure 8 represents the number of Taber wear cycles at which the leather substrate treated with different formulations starts showing the abrasion wear. The leather coated with formulation C shows the lowest number of wear cycles, indicating the minimum abrasion resistance, while E exhibits the maximum number of wear cycles, projecting the highest abrasion resistance. E contains the monomer NVP (with carboamide group) and the plasticizer. The next highest resistance is induced by the formulation B that contains the same monomer NVP but without the plasticizer. It is to be noted here that the formulation E imparts

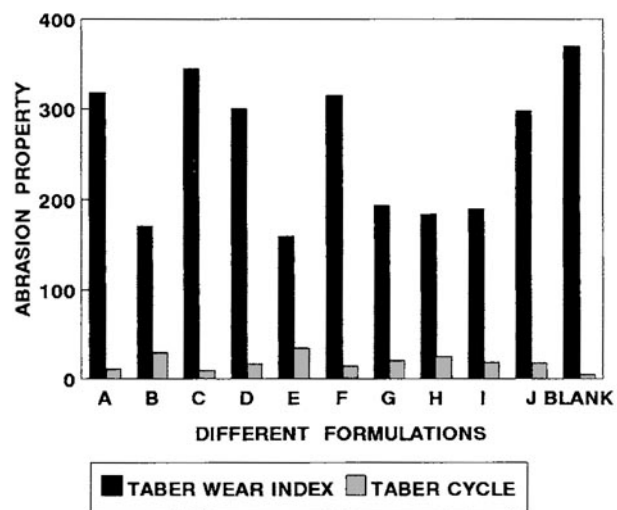


Figure 8 Abrasion properties of treated and untreated leather substrates.

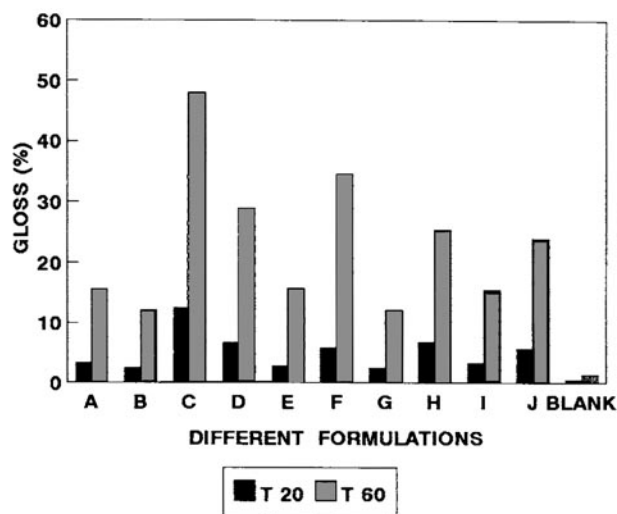


Figure 9 Gloss of treated and untreated leather substrates at 20° and 60°.

the highest TS (Fig. 5) and Eb (Fig. 7) values along with the highest abrasion resistance (Fig. 8). The Taber wear index is the weight of the substrate after every 1000 cycles of abrasion between the two wheels. This means that if the wear index is low, the abrasion resistance is high. Figure 8 represents the Taber wear index of the leather substrates coated with different formulations. It is observed that the formulation E-coated leather shows the highest abrasion resistance indicated by the lowest wear index. Similarly, C shows the lowest abrasion resistance.

Surface Gloss

Surface gloss is another important property for leather products. The gloss is generally determined at two angles (20° and 60°) of the plane of the surface. The extent of the gloss, determined by the gloss meter at these angles, is depicted in Figure 9. The highest gloss is exhibited at 60° angle and with those substrates coated with the difunctional monomer (TPGDA). Incorporation of plasticizer and/or monomer EHA into formulation C has reduced the extent of gloss. Gloss of the untreated leather is the minimum at both the angles.

Weathering Effect

On Gloss

When the treated leather substrates are weathered for a period of about 500 h at different cycles of simulating sun, dews, and condensation, the loss in gloss is observed to be different. Although the high-

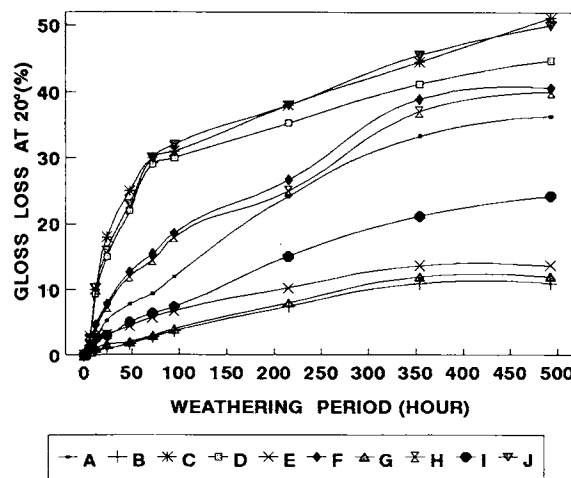


Figure 10 Loss of gloss of treated leather substrates at 20° due to the weathering effect.

est gloss is found to be with samples treated with the difunctional monomer, TPGDA, the gloss loss is also the maximum with these samples by the weathering treatment. This is obvious from Figures 10 (20°) and 11 (60°). The gloss loss is the minimum with the leather samples treated with the monomer (NVP) that contains the carboamide group. This means that formulations B, G, and E induce the lowest gloss loss of the samples after the severe weathering tests.

On Tensile Properties

The coated leather substrates cured by UV radiation with eight passes are treated under simulating weathering tests at alternating cycles of sunshine,

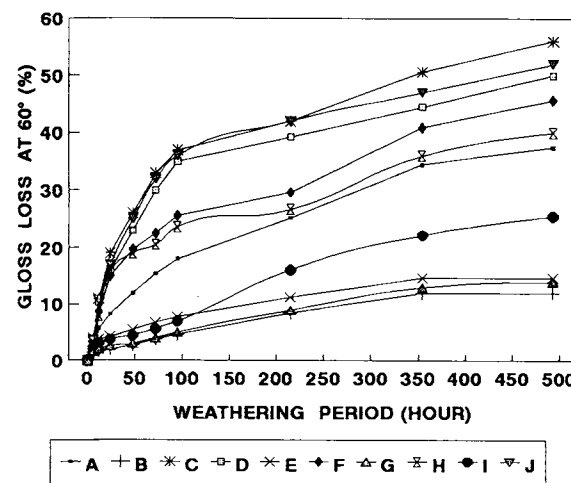


Figure 11 Loss of gloss of treated leather substrates at 60° due to the weathering effect.

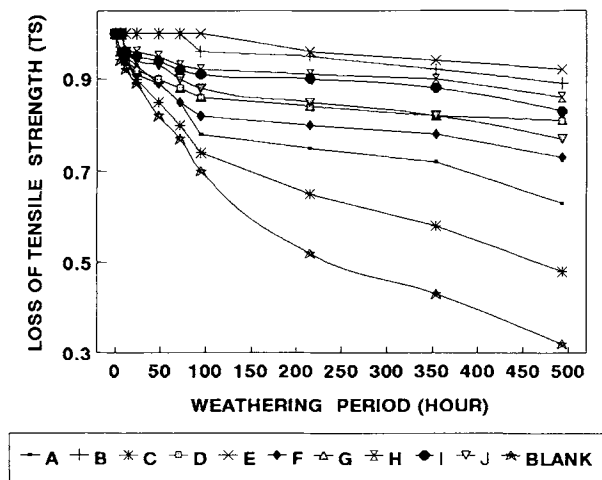


Figure 12 Loss of tensile strength (TS) of the treated and untreated leather substrates due to the weathering effect.

dews, and condensation for a period of about 500 h. The change in tensile strength due to this weathering treatment is noted and plotted against the weathering period (Fig. 12). It is observed that the tensile strength of leather decreases with the weathering. There is a sharp decrease of strength within the first few hours with most of the samples except formulation E. After this, the decreases is relatively slow. However, the difunctional monomer, TPGDA-treated leather, has the maximum loss in tensile strength due to the weathering treatment. On the other hand, there is very little impact on the tensile property of the substrates coated with formulation E that contains the monomer NVP and a plasticizer. It is clear from the plots (Fig. 12) that the monomer NVP has the strongest augmentation (grafting) with the leather fiber. The severe simulating weathering treatment of about 500 h could decrease the tensile strength to a value of 8% (formulation E) and 11% (formulation B), as shown in Table II. Similar behavior is also observed with the elongation property of the leather substrates by the weathering treatment. This is shown in Figure 13, where Eb values obtained after the weathering test are plotted against time of weathering. The minimum loss of Eb is obtained by the samples treated with fomulation E. The relative Eb loss is also given in Table II.

CONCLUSION

Formulations prepared with monofunctional monomers EHA (low T_g) and NVP (high T_g and with the carboamide group) as well as with difunctional

Table II Loss of Tensile Properties of Leather by Weathering

Formulations	Eb Loss (%)	TS Loss (%)
A	35	37
B	10	11
C	50	52
D	20	19
E	9	8
F	25	27
G	20	19
H	12	14
I	16	17
J	22	23
Blank	52	68

monomer (TPGDA) seem to behave differently when these formulations are used in making polymer films under UV radiation as well as in coating on leather substrates. Films with the carboamide functional group possess high film hardness (Fig. 1) with enhanced tensile property (Fig. 4). Incorporation of a plasticizer with the carboamide group containing monomer (NVP) increases the T_f by 60% (Fig. 5) and E_f by 75% (Fig. 7) for the leather substrates. The same formulation E also imparts the highest Taber resistance (wear resistance) to the leather surface (Fig. 8). The minimum loss in wear, tensile strength, elongation, and gloss by weathering treatment is also observed with the leather substrates treated with formulation E. Thus, it can be concluded hat the formulation containing a monofunctional monomer NVP with $-N=CO-$ group and a second solute plasticizer (diphthalate) is consid-

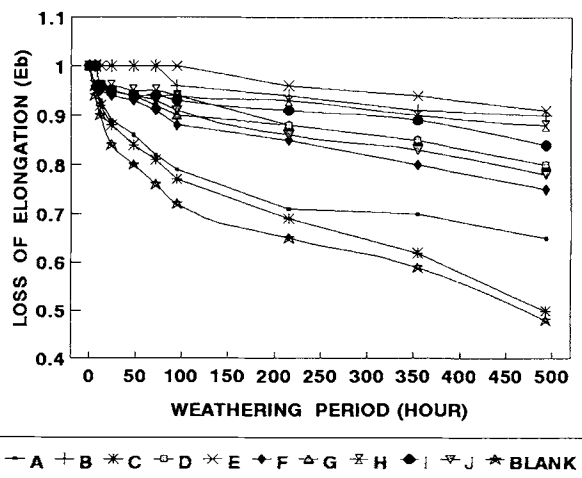


Figure 13 Loss of elongation (Eb) of the treated and untreated leather substrates due to the weathering effect.

ered to be of much value to improve the quality of leather.

REFERENCES

1. M. K. Uddin, M. A Khan, and K. M. Idriss Ali, *Polym. Plast. Technol. Eng.*, **34**(3), 447 (1995).
2. W. Helmut and F. Karl, *J. Am. Leather Chem. Assoc.*, **86**(2), 49 (1991).
3. G. Kumar, C. Sai, S. Rajadwai, and M. Santappa, *Bull. Mater. Sci.*, **4**(5), 583 (1982).
4. F. Scholnick, P. R. Buechler, and E. J. Difendorf, *J. Am. Leather Chem. Assoc.*, **83**(8), 262 (1988).
5. A. W. Bateman, U.S. Pat. 2,801,949 (to Du Pont).
6. M. Nehar and V. Vely, U.S. Pat. 3,066,997 (to Titecoat Copp.).
7. M. Mills, *Drying Oil Technology*, Pergamon Press Ltd, London, 1952.
8. M. A. Hossain, T. Hasan, M. A. Khan, and K. M. Idriss Ali, *Polym. Plast. Technol. Eng.*, **33**(1), 1 (1994).
9. K. M. Idriss Ali, M. A. Khan, and M. Husain, *Radiat. Phys. Chem.*, **44**(4), 427 (1994).
10. K. M. Idriss Ali and T. Sasaki, *Radiat. Phys. Chem.*, **43**(4), 371 (1994).
11. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 3rd ed., Wiley, New York, 1974.

Received May 22, 1995

Accepted October 22, 1995