

# Curing of Crust Leather by Ultraviolet Radiation with Urethane Acrylate: Role of Pigment

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**ABSTRACT:** Eight different formulations were developed with four diacrylate reactive monomers such as tripropylene glycol diacrylate (TPGDA), 1,4-butanediol diacrylate (BDDA), 1,6-hexanediol diacrylate (HDDA), and 2-ethylene glycol dimethacrylate (EGDMA) and aromatic urethane diacrylate (M1100) in order to modify the crust leather surface. To study the effect of pigment on the performance of ultraviolet (UV)-cured leather surface, 1% pigment (congored) was incorporated in the formulations. Irgacure 369 (2%) was also used in the formulation as photoinitiator. The gel content, tensile strength, elongation at break, and pendulum hardness of UV-cured thin films with and without pigment was

studied. The films without pigment produced better properties. Among all the diluents, BDDA-containing films showed the best performance. Different properties of UV-coated leather surface such as pendulum hardness, tensile strength, elongation, gloss (at 20° and 60°), adhesion, and abrasion were studied. Effect of gloss on simulating weathering was also performed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 692–697, 2002

**Key words:** photopolymerization; thin films; leather; surface; photocuring

## INTRODUCTION

Polymer is a versatile material and can be used for diverse applications from shopping bags to space material. Thus, it is necessary to develop polymers of different textures and characters. Physical and mechanical properties of a polymer very largely depends on the type of formulations from which a polymer (thin film) is prepared. A polymer prepared from urethane oligomer is predominately hard and brittle. Monomers reduce the viscosity of the oligomers in order to conveniently coat a suitable substrate with diverse properties for some specific purpose. Application of these polymers as coatings on substrates depends very much on the rheological properties of the polymers as well as on the substrates. Flexible substrates require flexible polymer to be coated on these substrates in order to match their rheological properties. Urethane coatings are generally applied on flexible substrates like leather.<sup>1</sup> The section of prepolymer (oligomers) most of these materials have high viscosity, making it difficult to manipulate them and therefore, they were diluted largely determine the properties of surface coating with a reactive diluent. Increasing the functionality of the diluent will increase the

crosslinking density in the cured film, and the speed of cure. Many end users require that pigments be present in the curing formulations. For ultraviolet (UV)-cured formulations this presents a problem since the pigments may reduce the amount of light absorbed by the photoinitiator and leather is an important commodity that is widely used in shoes, luggage carriers, bags, belts, tents, purses, etc. Crust leather is an intermediate stage between wet blue leather and finished leather. It is also costly to convert crust leather into finished leather by a number of chemical treatments. Different workers<sup>1, 3–10</sup> have developed different formulations to improve the properties of leather into a wet blue leather. The present article deals with the development for formulations with aromatic urethane diacrylate (M-1100) oligomers using different diacrylate diluents using pigments (dye) or without dye and with the evaluation of the effect of different monomers on the physical and mechanical properties of UV-cured thin polymer films. The formulated solutions were applied on crust leather surfaces in order to improve their physical properties.

## EXPERIMENTAL

### Materials

Aromatic urethanediacrylate (M1100), an Aronix product, was procured from Toagosei Chemical Industry Co. Ltd. (Japan). This oligomer is almost solid

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at 25°C and has two acrylate unites at the two ends of the molecule. Difunctional diluents such as tripropylene glycol diacrylate (TPGDA), 1,4-butanediol diacrylate (BDDA), 1,6-hexane diol diacrylate (HDDA), and 2-ethylene glycol dimethacrylate (EGDMA) were procured from E. Merck (Germany). Photoinitiator Irgacure 369 [2-benzyl-2-dimethylamine-1 (4-morpholino-phenyl)-butanone-1] was procured from Ciba-Geigy, Switzerland. Dye Congored ( $C_{32}H_{22}N_6Na_2O_6S_2$ ) was obtained from Fluka AG-Chem. and methanol (MeOH) from BDH Chemicals Ltd. Crust leather was procured from the local market of Bangladesh.

## Methods

Eight formulations were prepared with a fixed concentration of oligomer (50%) and photoinitiator (2%) with variable concentrations of different monomers and dyes as shown in Table I. The formulated solutions were applied to a clean glass plate (8 × 5 cm) as well as on the leather surface using a draw down bar cotter no. 0.0018 (Abbey Chemical Co., Australia). The coated plates were irradiated by UV radiation through an UV minicure (Me-200 UV, IST Technik, Germany) using an UV lamp (254–313 nm) of 2 kW power at 50 amp current. The cured films and leather surfaces were subjected to various characterization tests.

## Polymer film characterization

Polymer films prepared from different formulating solutions were characterized after 24 h of curing under UV radiation. Film hardness, an index of crosslinking density at the surface of the film, was measured by using a pendulum hardness tester (model 5458, Byke Labotron). Gel content, amount of crosslink through the entire cured film, was determined by wrapping a known weight of the film in a soxhlet, for extraction with hot benzene for 48 h. The difference of weight of the film before and after extraction determines the gel content. The extracted film was soaked in acetone for 24 h at room temperature (app. 25°C). The difference of weight of the swollen film with that of the dry

extracted film yields the swelling ratio. The cured films were carefully peeled off from the glass plates and these were cut with the help of a dumbbell cutter for tensile property measurement. The tensile properties of films and leathers were measured by using tensile strength machine (Instron, model-1011, UK) maintaining a gauge length of 0.50 in. at a crosshead speed of 0.01 in./min. Tensile strength (TS) and elongation at break (Eb) were directly obtained with the help of a personal computer integrated with the machine.

## Characterization of coated leathers

Crust leather was cut into 4 × 4 in. size and dried at 105°C for 5 h. The formulated solutions were coated on the surface of leather and cured with UV radiation. The coated leather was subjected to various characterization processes. Tensile properties (strength and elongation) were represented as tensile factor ( $T_f$ ) and elongation factor ( $E_f$ ) where  $T_f$  and  $E_f$  are the ratio of TS and Eb of the coated and uncoated leather. Surface gloss both at 60° and 20° angles were measured with the help of a digital micro gloss meter (Sheen-155, Sheen Co., UK). Abrasion property (taber wear index) was determined by the weight loss method using a taber abrader (model 5130, Erichsen GMBH & Co. Germany). The coated leather was abraded between two abradant revolving wheels (CS-10) applying a force of 500 g/cycle with setting 100 vacuum and total 100 cycles in the abrader. Adhesion strength, the force required to pull out coating from the surface of the substrate, was determined by an adhesion tester (model 525, Erichsen, Germany). The coated leather samples were subjected to severe weathering testing by simulating sunshine (4 h) using a UV lamp and condensation (2 h) for 504 h in a accelerated weathering tester (model 26200, Q-U-V, Q-Panel Co., USA). The loss of surface gloss due to accelerated weathering treatment was measured by comparing the gloss of the coated leather before and after weathering treatment.

TABLE I  
Composition of Different Formulations (% w/w)

Formulation	Oligomer M1100	Monomer				Dye	CH <sub>3</sub> OH	Irg 369
		TPGDA	BDDA	HDDA	EGDMA			
A	50	48	—	—	—	—	—	2
B	50	—	48	—	—	—	—	2
C	50	—	—	48	—	—	—	2
D	50	—	—	—	48	—	—	2
A1	50	45	—	—	—	1	2	2
B1	50	—	45	—	—	1	2	2
C1	50	—	—	45	—	1	2	2
D1	50	—	—	—	45	1	2	2

## RESULTS AND DISCUSSION

Table I shows the composition of different ingredients in the formulations Dye (congored) is not soluble in the oligomer and monomer, so before mixing into the formulations, this is dissolved in methanol, and CH<sub>3</sub>OH-dye solution is added to the formulating solutions through constant stirring. For better understanding, the results of the different properties of the films and the coatings are shown in Table II, and from that the effect of dye and diacrylate diluents on the

various physicomechanical properties of the cured film and coatings on leather surface were discussed.

### Characterization of polymer films

#### Pendulum hardness (PH)

The hardness is related to the crosslinking density on the surface of the film. The results of PH of various films are shown in Table II against UV radiation doses represented by number of passes. The hardness in-

TABLE II  
Physicomechanical Properties of UV-Cured Films and Leathers Against Number of Passes

Formulation	No pass	% PH	% Gel content	Swelling ratio	TS (kPSi)	% Eb	$T_f$	$E_f$
A	3	13.0	88.0	1.12	2.05	10	1.10	1.12
	5	17.0	92.5	1.09	3.60	12	1.20	1.30
	7	21.5	95.5	1.07	4.10	14	1.26	1.44
	9	29.5	97.0	1.05	4.95	18	1.42	1.58
	11	26.5	94.0	1.07	3.30	13	1.20	1.40
	13	27.0	93.0	1.08	2.30	11	1.10	1.28
B	3	32.0	89.0	1.14	4.63	13	1.09	1.10
	5	35.5	92.0	1.12	4.20	17	1.15	1.26
	7	45.0	93.0	1.09	4.05	22	1.20	1.38
	9	58.0	94.5	1.08	4.20	24	1.24	1.54
	11	65.5	97.5	1.07	3.50	20	1.38	1.32
	13	56.0	93.0	1.09	3.30	18	1.18	1.24
C	3	22.5	91.0	1.23	2.15	18	1.05	1.19
	5	27.0	98.0	1.19	2.60	23	1.10	1.34
	7	38.0	97.0	1.13	3.32	26	1.26	1.50
	9	46.5	94.0	1.11	3.85	23	1.36	1.31
	11	49.0	93.5	1.12	4.63	21	1.20	1.24
	13	39.0	90.0	1.15	3.10	16	1.16	1.11
D	3	15.0	82.0	1.07	1.90	11	1.16	1.24
	5	17.5	87.0	1.05	2.28	14	1.22	1.37
	7	21.0	89.0	1.03	2.95	17	1.26	1.44
	9	27.0	93.0	1.01	3.55	21	1.32	1.63
	11	36.0	90.0	1.02	4.20	15	1.46	1.30
	13	24.0	87.0	1.04	3.80	12	1.24	1.18
A1	3	9.0	89.0	1.14	2.20	9	1.04	1.12
	5	12.5	91.5	1.12	2.90	10	1.06	1.30
	7	20.0	92.0	1.09	3.80	12	1.20	1.40
	9	27.2	92.6	1.07	4.08	14	1.24	1.50
	11	24.1	91.4	1.08	3.30	22	1.37	1.34
	13	22.0	90.2	1.10	3.00	10	1.18	1.20
B1	3	24.0	90.0	1.15	1.90	11	1.15	1.10
	5	25.5	91.9	1.13	2.45	14	1.18	1.20
	7	32.4	93.7	1.12	3.15	19	1.29	1.30
	9	38.0	96.0	1.10	3.75	22	1.43	1.54
	11	47.2	94.8	1.09	4.40	17	1.39	1.30
	13	41.0	92.3	1.10	3.30	13	1.14	1.22
C1	3	18.0	88.0	1.22	2.40	16	1.04	1.20
	5	21.2	90.0	1.17	3.10	21	1.07	1.28
	7	27.0	85.0	1.14	3.50	24	1.20	1.32
	9	34.0	94.3	1.12	4.50	22	1.38	1.44
	11	30.0	92.2	1.13	3.45	18	1.24	1.20
	13	26.3	89.1	1.15	2.60	16	1.14	1.16
D1	3	12.0	83.0	1.10	1.75	10	1.04	1.16
	5	14.1	84.9	1.07	2.10	13	1.12	1.32
	7	18.3	88.4	1.05	2.80	16	1.19	1.40
	9	24.0	87.0	1.03	3.85	20	1.28	1.60
	11	28.1	89.0	1.06	4.20	15	1.44	1.28
	13	17.9	95.0	1.08	3.85	11	1.20	1.10

creases with UV doses but decreases after attaining a maximum. The decrease of PH at higher radiation doses could be caused by the degradation of polymer at higher UV intensities.<sup>11</sup> Almost all the formulations reach maximum hardness at the eleventh pass except for A and A1, where maximum values are obtained at the ninth pass. This shows that the diacrylate monomer TPGDA needs less radiation to attain maximum hardness. The highest PH values for two cases, without dye (65.5%) and with dye (47.2%), are imparted by the formulations B and B1 containing BDDA. So among the difunctional diluents used in this work (TPGDA, BDDA, HDDA, EGDMA), BDDA possess the highest pendulum hardness, indicating maximum crosslinking density on the film surface. These four molecules have different molecular volumes associated with different molecular shapes and geometry. Diffusion of these molecules into an aromatic urethane diacrylate chain at the time of equilibrium needed for the crosslinking reactivity is different. BDDA has the smallest molecular volume among the used difunctional diluents and can be easily diffused into the prepolymer chain within the time of equilibrium condition needed for producing higher surface hardness. It is also observed that formulations containing dye yields less hardness than those without dye. This may happen due to the fact that dye (congored) reduces the amount of light absorbed by the photoinitiator. The lowest PH is given by A and A1; both of these contain TPGDA, which is the bulkiest molecule and is thus the slowest in reactivity compared to other diluents.

#### Gel content and swelling ratio

The film that gives the highest PH does not necessarily yield maximum gel value as gel content reflects the crosslinking density in the cured film as a whole, while film hardness represents the crosslinking density on the surface. Gel content of UV-cured films obtained for all the formulations are plotted in Table II, where percent gel content is shown against number of passes. Gel content increases with UV dose, reaches the maximum, and reduces after the fifth pass for C, sixth for A and D, and ninth for formulation B, whereas a decrease in PH values occurred after the eleventh pass. The reduction of gel value after attaining the maxima is probably caused by radiation degradation by longer exposure of UV. Of all formulations, the highest gel value (98%) is imparted by B containing BDDA without dye and B1 (96%) with dye, which also contain the same diluent. D and D1 containing diluent monomer EGDMA gave the lowest gel content in both cases.

The more a film is crosslinked, the less ability it has to swell because the swelling molecule in that case hardly finds enough functional group and space to swell the cured film through loose bonding or so.<sup>12</sup>

Thus, as crosslinking density increases the swelling ratio is expected to decrease. These are actually found in Table II, where the swelling ratio is plotted against UV doses. Swelling ratio decreases with UV doses and in most cases it increases after nine passes. As the film is degraded at higher doses, the broken molecule passes some specific sites where the molecules of the swelling solvent can form loose bonding to swell the degraded polymers. B exhibits the lowest swelling ratio and B1 having BDDA and the minimum in two cases are observed by D and D1 having diluent EGDMA, as compared with PH and gel, the swelling ability of the film containing dye is quite higher.

#### Tensile strength (TS)

Tensile property is very important in selecting diverse applications of polymer and polymer-coated flexible substrates. Results of tensile strength (kPSi) of UV-cured polymer films are represented in Table II against the intensity of UV radiation. It is found that TS increases with radiation intensities and after maximum strength is achieved the TS then decreases. The maximum TS is obtained mostly after nine passes and after that TS reduces. This may be caused by radiation deterioration of the polymer at higher doses.<sup>10</sup> However, the highest TS in two cases without dye and with dye (4.81 and 4.47 kPSi) are attained by the formulations C and C1 having diluent HDDA followed by the sample B and B1 containing BDDA. It is also found that the TS value of the formulations containing dye are quite less than those that have no dye, which is probably due to the reduction of light absorption by the photoinitiation and dye pigments absorbed some of the UV light. The lowest maximum TS (4.20 and 4.03 kPSi) was achieved by A and A1 with the diacrylate monomer TPGDA.

#### Elongation at break (Eb)

Flexibility of a polymer is an essential parameter that is very actively considered during the application of a polymer in a certain area. The extent of elongation of these UV-cured films at the breaking point is shown in Table II. The elongation property (Eb) increases with UV radiation and attains maximum mostly after nine passes; after that Eb decreases gradually with UV radiation. The highest elongation is C (26%) and C1 (24%) obtain both cases at the seventh pass with diacrylate monomer HDDA followed by B and B1 containing BDDA. The formulations A and A1 that contain TPGDA exhibit the maximum elongation (18 and 14%) at the ninth pass of UV radiation, but these are the lowest values among all the formulations used.

#### Application on crust leather surface

All of the formulations without dye (A–D) and with dye (A1 and D1) were coated on the crust leather



surface and cured under the same UV lamp as on the polymer film. After 24 h of curing, different properties of coated leather were measured in respect to uncoated leather. The effect of different diacrylate diluents and dye (congored) on coated crust leather surface was evaluated.

#### Tensile properties (tensile factor $T_f$ )

Enhancement of tensile strength of the coated leather is manifested by tensile strength factor or tenacity factor ( $T_f$ ), where  $T_f$  is the ratio of tensile strength of the coated leather to that of the uncoated leather. The values of  $T_f$  are represented in Table II against the number of passes under UV. It is observed that there is enhancement of tensile strength of the coated leather irrespective whether the coating is fully cured or not.  $T_f$  increases with UV radiation, and B,B1 and D,D1 passes maximum  $T_f$  at the eleventh pass, whereas A,A1 and C,C1 yields after nine passes. The TS enhancements in two cases (without dye and with dye) were given by D (46%) and D1 (44%) containing EGDMA followed by A and A1 having diluent TPGDA. C and C1 imparted the lowest maximum  $T_f$  of the coated leather without dye and dye bearing formulations with diluent BDDA, which passes maximum TS on UV-cured film. It is also found that tensile strength of the formulations that do not have dye is always higher than that containing dye, and the reason for this is probably due to the reduction of light absorption by the initiator.

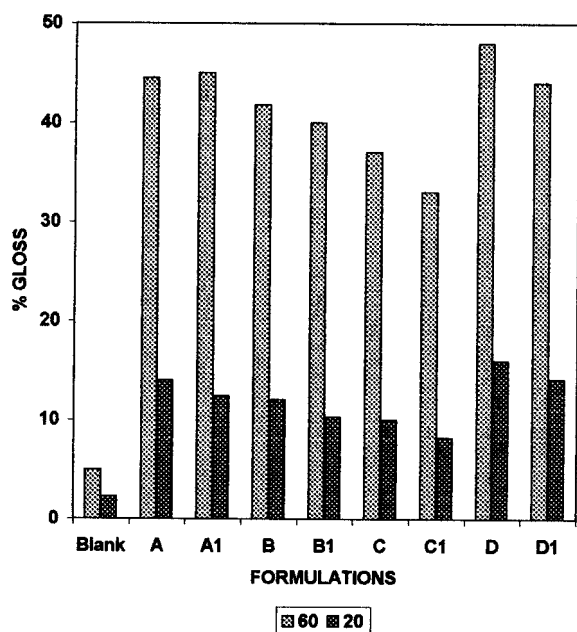


Figure 1 Micro gloss properties both at 60° and 20° of UV-cured leather surface without dye and containing dye.

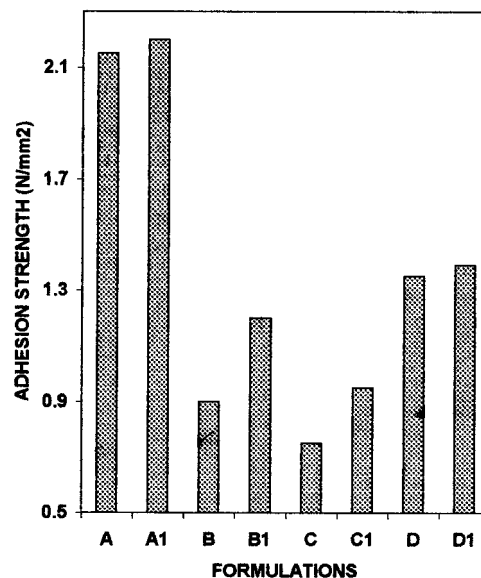


Figure 2 Adhesion strength in  $N/mm^2$  of UV-cured leather surface without dye and containing dye.

#### Elongation property ( $E_f$ )

Enhancement of elongation or elongation factor ( $E_f$ ) is shown in Table II.  $E_f$  is the ratio of elongation at break of the coated and untreated crust leather. It is observed that the stretching ability of the crust leather has been increased between 50 to 63% (without dye) and 45 to 60% (containing) for various coatings. The highest elongation enhancements, 63 and 60%, were produced by D and D1 respectively after 9 passes, having diacrylate EGDMA, followed by B and B1 containing BDDA. The C and C1 that contain HDDA achieve the lowest  $E_f$  value.

#### Surface gloss of the coated leather

Surface gloss is an important property of leather goods, and a shiny surface is normally desired for better goods. Gloss is related to the extent of crosslinking and it is generally determined at 60° and 20° angles on the plane of the coated and uncoated crust leather surface. Gloss determined at 60° angle is higher than 20°. Results of gloss both at 60° and 20° angles are shown in Figure 1 against the coatings or formulations. For better comparison, the gloss of the untreated leather surface is also shown in the same figure. D and D1 exhibit the highest surface gloss both at 60° and 20° angles; both of these coatings contain EGDMA. The trend of gloss value is  $C < B < A < D$ . Similar trend is also observed for the coatings with pigment (congored).

#### Adhesion property

The force ( $N/mm^2$ ) that is required to pull out the coatings of the polymer from the leather surface is

adhesion strength. If a coating is loosely bound with the substrate surface, then it can be easily peeled off by applying a small peeling force and vice versa. Results of adhesion strength (N/mm<sup>2</sup>) are shown in Figure 2. It is clear from the figure that adhesion strength of the colored coatings is slightly higher than that having no dye. Formulations containing TPGDA shows maximum adhesion value, 2.15 N/mm<sup>2</sup> for A and 2.20 N/mm<sup>2</sup> for A1. The formulations that contain diacrylate HDDA yield minimum adhesion strength (C = 0.75 N/mm<sup>2</sup> and C1 = 0.95 N/mm<sup>2</sup>).

**Abrasion resistance**

Abrasion is another important property of leather goods. If the wearing resistance is high, the leather products are considered to be more durable and can last longer. The wearing resistance of the polymer-coated leather surface was determined by the application of taber abrasion test through weight loss method. The weight obtained by the sample 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 taber index is low. The values of taber index thus determined are show in Figure 3. It is observed that the coating of formulation B shows the highest taber index followed by C, A, and D. So formulation or coatings D containing can resists more toward abrasion wear. In the case of colored coatings, the trend of abrasion resistance is A1 > D1 > B1 > C1.

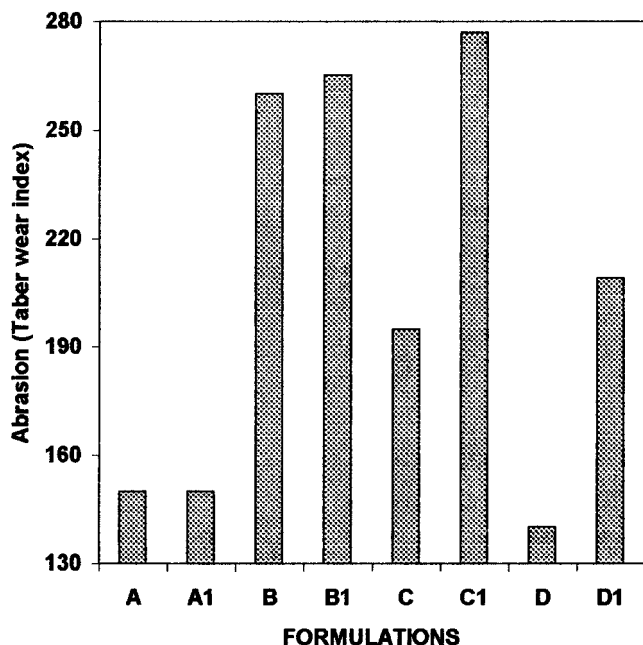


Figure 3 Abrasion resistance or taber wear index of UV-cured leather surface without dye and containing dye.

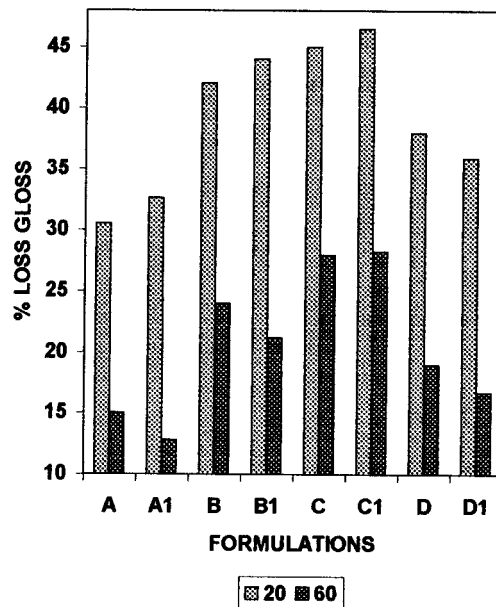


Figure 4 Effect of simulating weathering on gloss both at 60° and 20° of UV-cured leather surface without dye and containing dye.

**Weathering effect**

The loss of micro gloss properties of the coated samples was measured after 504 h of weathering treatment in the accelerated weathering tester. The values of gloss loss is plotted in Figure 4 against weathering time. It is observed that gloss loss at 60° is lower than C and C1 containing HDDA observe 20° and maximum loss of gloss both 60° and 20°. The minimum losses were achieved by A and A1 with diacrylate TPGDA. The loss of gloss of the formulations with dye is highest in most cases except for D and D1 containing EGDMA, where gloss loss is lower for colored coatings.

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