Codiluent Effect on the Properties of UV-Cured Films

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SYNOPSIS

Different formulations were developed with an urethane oligomer combined with a number of reactive diluents with different functionalities such as N-vinylpyrrolidone (monofunctional), butanediol diacrylate (difunctional), tripropylene glycol diacrylate (difunctional), and trimethylolpropane triacrylate (trifunctional). The films were prepared with these formulations and cured under UV radiation in the presence of the photoinitiator Irgacure 184. Their properties were characterized. The effect of codiluents of low glass transition temperatures like ethyl hexyl acrylate and methoxyethyl acrylate on the properties of these films was studied. These formulations were then applied as thin coatings on the leather surface in order to study the improvement of the leather substrate. Both tensile strength and elongation of the treated leather increased. The gloss of the coated leather was also enhanced. Incorporation of a plasticizer into these systems substantially improved the rheological properties of the coated leather. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

A polymer is a versatile material. Its applications are being diversified day by day in different fields. Thus, it is imperative to modify the formulations from which polymers are made in order to match up with the desired applications and utilities. New formulations are being available every now and then according to the requirement of the suitable polymer. Recently,[1] some formulations were developed using urethane acrylate mixed with a number of single-reactive diluent monomers of different functionalities. The characteristic behavior of these monomers on the properties of the UV-cured films was studied. Their tensile properties were correlated with the glass transition temperature (T_g) of the diluent monomers. In the present investigation, codiluent monomers of low T_g were incorporated into the formulations along with a plasticizer in order to study the characteristics of the UV-cured films so that certain potential applications can be derived with a view to using these formulations as coatings on suitable substrates like leather.

EXPERIMENTAL

The oligomer urethane acrylate LR8739 (BASF, Germany) and the photoinitiator Irgacure 184 (Ciba-Geigy) obtained through IAEA were used as received. Four monomers, namely, N-vinylpyrrolidone (NVP), butanediol diacrylate (BDDA), tripropylene glycol diacrylate (TPGDA), and trimethylolpropane triacrylate (TMPTA) procured from E. Merck were used. Two codiluents such as ethyl hexyl acrylate (EHA, $T_g = -50°C$) and methoxyethyl acrylate (MEA, $T_g = -110°C$) were used as procured from E. Merck. Bovine leather was procured from the Dhaka Leather Complex (Bangladesh). It was a finished leather with a traditional base coat and the formula is known only by the supplier.

Formulations were prepared with fixed amounts of the oligomer at 60%, the photoinitiator at 5%, the diluent monomer at 17%, and the codiluent monomer at 18%, w/w. However, when a plasticizer was incorporated into these solutions, the proportions of diluent and codiluent were varied so as to make the formulation oligomer:diluent:codiluent:plasticizer:photoinitiator = 60 : 15 : 15 : 5 : 5, w/w. The formulated solutions were coated on a glass

plate (6 × 10 × 0.5 cm) using a bar coater no. 0.28 in. from Abbey Chemical Co. (Australia), which produces 30 ± 3 μm-thick films. The plates were passed under the UV lamps (2 kW intensity, 254–313 nm wavelength, 9 amp current) of IST-Technik (Germany) to cure the coatings. The cured films were then used for various tests in order to characterize their properties like film hardness, gel content, swelling ratio in acetone, tensile properties, and shape-recovery character. The film hardness was determined by the pendulum method using a digital pendulum hardness tester (Model 5854, BYK Lebtron); the gel content was determined by extracting the cured film with hot acetone for 24 h in a Soxhlet. A known weight of the cured film was wrapped up in a piece of stainless-steel sheet and put into a Soxhlet for the extraction. After the extraction, these were dried at 105°C for 12 h. The difference in weights of the extracted film from that of the cured film determines the gel content, following the equation gel $= 100(w_t - w_0)/w_t$, where w_t = weight of the cured film and w_0 = weight of the extracted film. The tensile properties of the cured film were determined directly from the tensile properties measurement machine (INSTRON, Model 1011, U.K.). The shape-recovery test was carried out by folding the cured film at 180°C; the brittle film cracked easily, while the nonbrittle film folded and it was kept folded for 24 h. The folded film was then heated at 30°C for a period of 1 h and subsequently the temperature was raised by a 5°C step after every 1 h. The shape-recovery temperature was determined by the temperature at which the folding mark on the film disappeared.

The formulation solutions were then applied as thin coatings on the leather surface pretreated with the traditional base coat applied by the supplier. The gloss of the leather surface was measured at 60° and 20° angles with the help of a glossmeter of Sheen Co. (Model 155). The change in tensile properties (T_f and E_f) of the coated leather was also determined.

RESULTS AND DISCUSSION

Four diluent monomers such as NVP (monofunctional), BDDA and TPGDA (difunctional), and TMPTA (trifunctional) were selected from the earlier[1] single-monomer diluent system in order to investigate the effect of a codiluent monomer of low glass transition temperature (T_g), such as EHA and MEA, on the rheological properties of the UV-cured films. The films were prepared from a solution com-
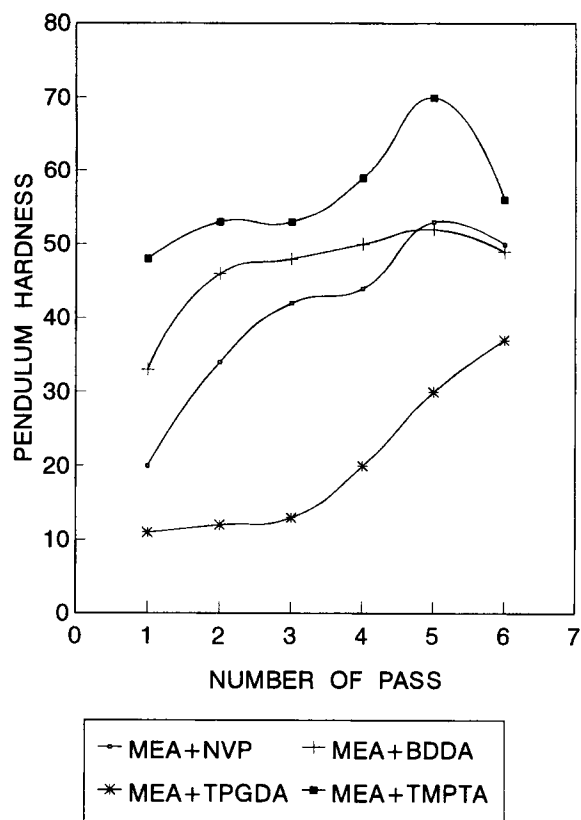
posed of an urethane acrylate oligomer and a monomer diluent (NVP, TPGDA, or TMPTA) in the presence of a codiluent (EHA or MEA) with the view to develop formulations which could be suitable for applications as coatings on flexible substrates like leather.

Film Hardness

The hardness of the cured film was determined by the pendulum method. Pendulum hardness (PH) is plotted against the number of the pass under the UV lamp. The results of the EHA series are shown in Figure 1, while those of the MEA series are given in Figure 2. The PH increases with UV radiation, attains a maximum, usually at the fifth pass, except for the EHA + TMPTA system where the maximum is at the third pass and then decreases. The decrease is probably caused by the radiation degradation. The highest PH is obtained in both series by TMPTA, followed by BDDA and NVP. The lowest PH value is exhibited by TPGDA. The TMPTA molecule has three acrylate groups which act as branches and can easily provide more crosslinking networks with the
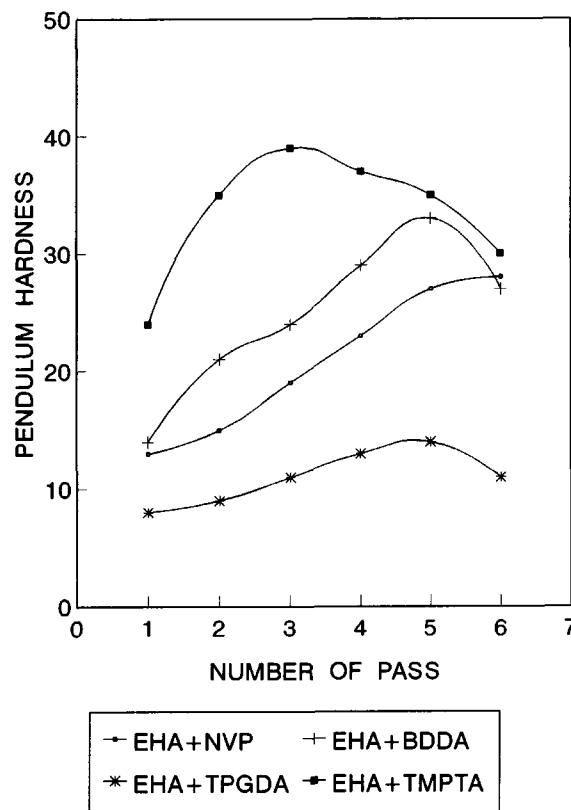
Figure 1 Pendulum hardness of the EHA series against number of pass.

Figure 2   Pendulum hardness of the MEA series against number of pass.

smaller molecule compared to EHA. Moreover, the $-OCH_3$ group plays a significant role in providing favorable electron density around the reaction site of the vinyl double bound through an inductive effect of the CH_3 group. The methoxy group can also form some hydrogen bonding with the chain of the oligomer skeleton to create more hardness.

Effect of Plasticizer

When a plasticizer is incorporated into these systems, it is observed that the pendulum hardness increases with the EHA series (Figs. 1 and 3), but decreases with the MEA series (Figs. 2 and 4). This indicates a different mode of interactions of the plasticizer with the oligomer and diluent monomers in the presence of these two codiluents (EHA and MEA). This information is important during selecting their applications on suitable substrates. It is known that a plasticizer has improved properties on a leather surface when coated with formulations containing a plasticizer and cured under UV radiation.[6] Thus, a plasticizer is incorporated into the present formulated solutions along with the co-
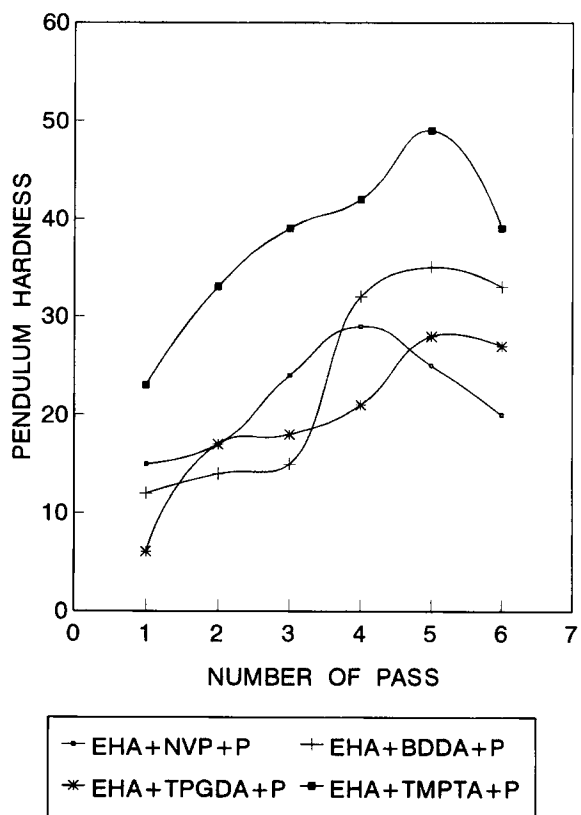
prepolymer unit. Thus, difunctional molecules have less crosslinking density, yielding less hardness than that of TMPTA. Between the two difunctional diluents (BDDA and TPGDA), BDDA has shown higher PH than has TPGDA. The molecular volume of BDDA is smaller than that of TPGDA. BDDA can, therefore, diffuse easily into the prepolymer chain at the time of equilibrium conditions needed for the overall polymerization process. Although NVP is a monofunctional monomer, it has exhibited more hardness than has TPGDA, a difunctional diluent. It is because NVP has a carboamide $(=N-CO)$ group, and the lone pair of an electron associated with a N atom of this group can make conditions favorable for easily augmenting the molecule with the prepolymer unit at the time of the polymerization process. A similar observation has also been noticed with NVP in other polymeric systems[2-4] and in a wood–plastic composite system.[5]

Among the two series of codiluents (EHA and MEA), MEA has exhibited relatively more film hardness, indicating formation of more crosslinking density with the MEA than with the EHA series. EHA is a long-chain molecule, whereas MEA is a

Figure 3   Pendulum hardness of the EHA series against number of pass in the presence of plasticizer.
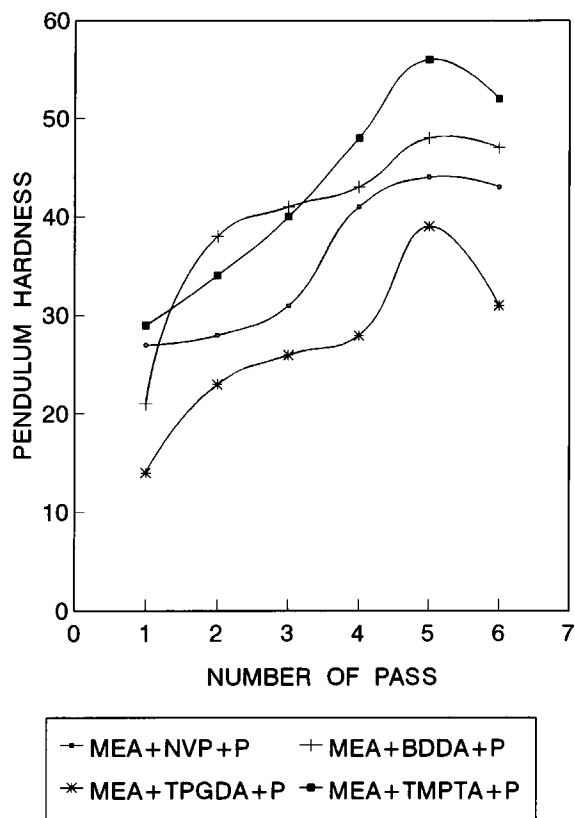
Figure 4 Pendulum hardness of the MEA series against number of pass in the presence of plasticizer.

diluents in order to study further the surface properties of the substrates, particularly leather. The film hardness results of the EHA and MEA series, both in the presence and absence of a plasticizer, are summarized in Table I.
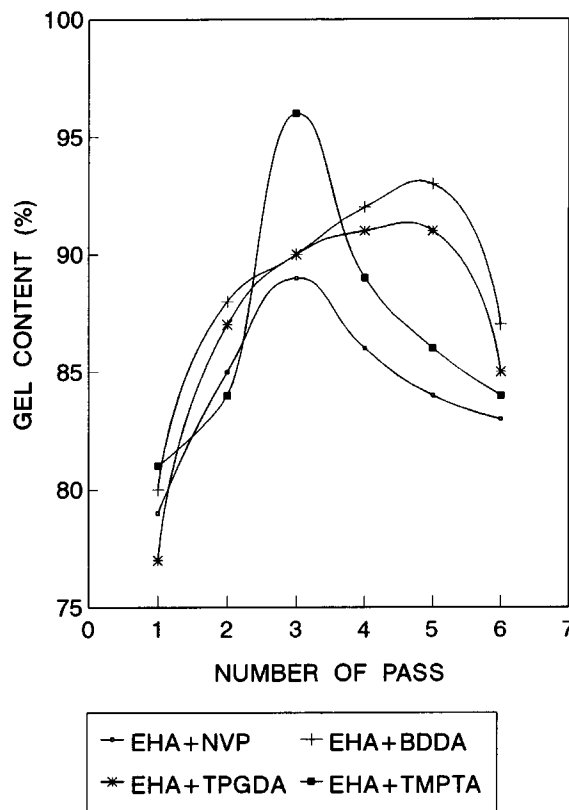
Gel Content

The gel content of the UV-cured film was determined through hot acetone extraction and was found to increase with UV radiation represented by the number of passes under the UV lamps. A typical plot of the gel vs. the number of passes is shown in Figure 5 for the EHA series. This increment of gel content (Table I) becomes maximum between the number of passes of three to five, after which the gel formation falls. This may be due to the radiation degradation process. However, in both the series of EHA and MEA, the most gel is achieved by the presence of TMPTA, a trifunctional monomer, followed by the difunctional monomers BDDA and TPGDA. The least gel is obtained by the NVP series. Between BDDA and TPGDA, BDDA has produced more gel than has TPGDA. It has already been ex-

plained that BDDA has a smaller molecular volume compared to that of TPGDA and, as such, has the advantage of easy diffusion into the reaction zone during the polymerization process. The EHA series has exhibited relatively more gel than has the MEA series; moreover, the MEA series requires more radiation (number of passes) to obtain the maximum gel (except TMPTA) compared to the EHA series.

The difference in the ability of producing more gel by EHA than by MEA can be explained by the fact that EHA has a simple long-chain molecule that is easy to penetrate and diffuse into the zone of reactivity compared to MEA whose methoxy group ($-OCH_3$) remains outside the plane of the MEA molecule and thus creates some sort of steric hindrance. This phenomenon may create an advantageous position for EHA to yield more crosslinking, which means more gel. However, incorporation of a plasticizer into these series slightly decreases the overall gel content.

Tensile Strength

Tensile strengths (TS) of the UV-cured films of both the EHA and MEA series are presented against the

Figure 5 Gel content of the EHA series against number of pass.

Table I   Pendulum Hardness and Gel Content of UV-cured Films

Formulation	No. Passes						No. Passes					
	1	2	3	4	5	6	1	2	3	4	5	6
	Pendulum Hardness (%)						Gel Content (%)					
EHA + NV	13	15	19	23	27	28	79	85	89	86	84	83
EHA + BD	14	21	24	29	33	27	80	88	90	92	93	87
EHA + TP	8	9	11	13	14	11	77	87	90	91	91	85
EHA + TM	24	35	39	37	35	30	81	84	96	89	86	84
MEA + NV	20	34	42	44	53	50	76	78	79	82	85	83
MEA + BD	33	46	48	50	52	49	77	81	89	93	88	84
MEA + TP	11	12	13	20	30	37	78	81	88	90	90	89
MEA + TM	48	53	53	59	70	56	80	85	94	88	87	85
EHA + NV + P	15	17	24	29	25	20	75	83	84	82	81	78
EHA + BD + P	12	14	15	32	35	33	79	81	86	88	84	81
EHA + TP + P	6	17	18	21	28	27	73	76	77	80	79	77
EHA + TM + P	23	33	39	42	49	39	83	87	91	87	85	80
MEA + NV + P	27	28	31	41	44	43	68	72	79	82	86	86
MEA + BD + P	21	38	41	43	48	47	76	80	86	86	84	83
MEA + TP + P	14	23	26	28	39	31	81	86	87	89	90	87
MEA + TM + P	29	34	40	48	65	52	86	88	93	90	84	80

[a] TP = TPGDA; TM = TMPTA; BD = BDDA; NV = NVP.

number of passes in Table II. The TS increases with the number of passes up to a certain UV radiation after which the film strength decreases. In the case of the EHA series, NVP has produced the highest TS at three passes, followed by TMPTA. The diluent TPGDA shows the lowest TS among all. However, in the MEA series, the highest TS is observed with TMPTA at two passes, but a similar high TS

Table II   Tensile Properties of UV-cured Films

Formulation	No. Passes						No. Passes					
	1	2	3	4	5	6	1	2	3	4	5	6
	Tensile Strength (psi × 1000)						Elongation at Break (%)					
EHA + NV	2.65	3.55	4.41	3.25	2.85	2.75	40	50	76	66	56	54
EHA + BD	1.70	1.80	2.80		2.60	2.4	24	26	34		26	18
EHA + TP	1.80	1.84		1.87	2.00	2.65	50	52	55	57	60	68
EHA + TM	3.80		3.97	3.9	3.62	3.00	27	28	14	13	10	9
MEA + NV	2.20	2.79	5.35	5.40	5.00	4.30	19	22	28	24	23	24
MEA + BD	4.3	6.00	6.30	6.60	7.90	6.90	15	21	23	28	70	44
MEA + TP	2.50	2.65		2.80	3.60	3.50	16	20	33	64	56	38
MEA + TM	6.60	7.90	7.10	6.30	6.30	5.40	12	16	23	24	18	13
EHA + NV + P	1.80	2.30	4.30	4.80	3.40	3.10	28	42	54	78	70	50
EHA + BD + P	3.00	3.20	3.30	3.60	3.30	3.00	25	28	34	44	26	16
EHA + TP + P	1.40	1.50	2.00	2.30	2.50	2.10	30	34	57	59	64	56
EHA + TM + P	2.60	3.30	3.60	4.20	4.00	3.50	17	21	22	24	17	14
MEA + NV + P	3.00	3.40	3.80	4.20	4.91	4.10	48	71	71	30	25	13
MEA + BD + P	2.60	3.10	3.60	3.80	4.10	4.90	15	22	54	30	20	19
MEA + TP + P	3.20	4.30	4.40	4.50	5.20	4.70	27	36	58	36	24	20
MEA + TM + P	3.60	4.00	4.40		6.40	5.10	14	15	21	19	18	16

TP = TPGDA; TM = TMPTA; BD = BDDA; NV = NVP.

value is also produced with BDDA with higher UV radiation at five passes. TPGDA has shown the lowest TS value, similar to that of the EHA series. The TS values are almost double with the MEA series compared to those of EHA. This is because of the —OCH$_3$ group which plays some role through hydrogen bonding in the augmentation process among different reacting units of oligomers and monomers. When a plasticizer is incorporated into the EHA series, the TS values slightly enhance and the maxima of the curves are obtained at higher UV radiation. The effect of the plasticizer in the MEA series is different. The overall TS values have decreased. However, the maximum TS is obtained at relatively high radiation.

Film Elongation

Results of elongation at break (Eb) for both EHA and MEA series are also shown in Table II against the number of passes, both in the presence and absence of the plasticizer. It is observed that the film containing NVP has the highest elongation. This means that the NVP-containing film is more stretchable compared to the others. The TMPTA film has the least stretching ability. It is because of its highly crosslinkable nature and the presence of a netlike molecular structure. Among the two difunctional diluents (TPGDA and BDDA), film containing TPGDA is more flexible/stretchable than is the BDDA film. The presence of a plasticizer has made the film more stretchable as well. In general, the MEA series has more elongation than has the EHA series.

Shape Recovery

The cured films of different formulations were folded at 180°. Most of the films of both the EHA and MEA series showed positive tests except those with TMPTA. The TMPTA films were brittle and cracked easily during the 180° folding. Most of the folded films of other systems could not keep their folding at less than 90° for 24 h. However, these folded films were heated over a period of 1 h at temperatures above 25°C and it was observed that the EHA + NVP film regained its initial shape at 60°C, and that of MEA + TPGDA, at 50°C, and the folding of rest of the folded films disappeared at room temperature. The presence of a plasticizer in these films destroyed the shape-recovery nature.

Application on Leather

On having characterized the properties of the UV-cured films prepared with different formulated solutions containing an urethane acrylate oligomer in combination with various diluents (NVP, TPGDA, BDDA, and TMPTA) and codiluents (EHA and MEA) in the presence and absence of a plasticizer, these solutions were then applied on a leather surface as a thin coating with the help of a bar coater and finally cured under UV radiation. The treated leather was then examined to study its gloss and change in tensile strength and elongation.

Gloss

Gloss of the treated leather surface was studied at two angles (60° and 20°). These are shown in Figure 6 for the oligomer and diluent system only. It is observed that a 60° angle gloss is maximum for each case and TPGDA has been able to produce more gloss on the leather surface compared to other three monomer diluents (NVP, EHA, and MEA). EHA exhibited the lowest gloss. The gloss of the TPGDA film can be slightly enhanced by adding EHA or
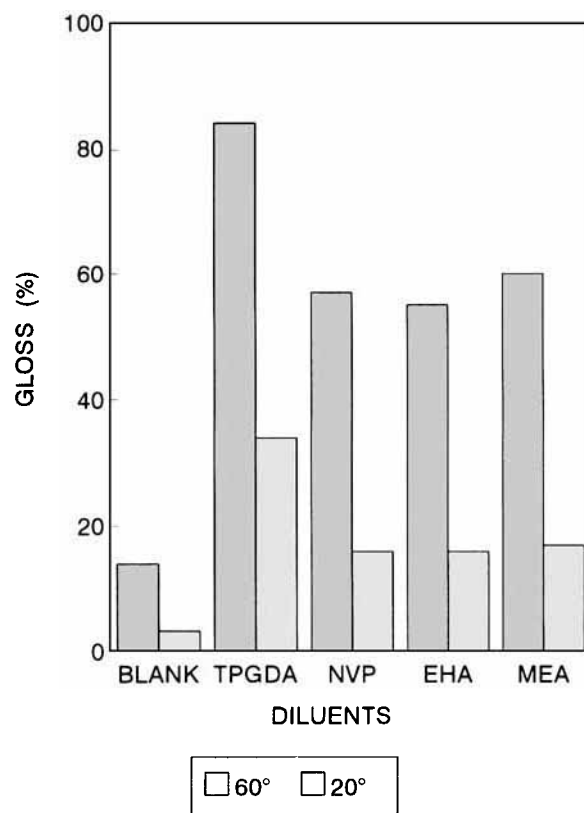
Figure 6   Gloss of the leather surface coated with different diluents at 60° and 20°.
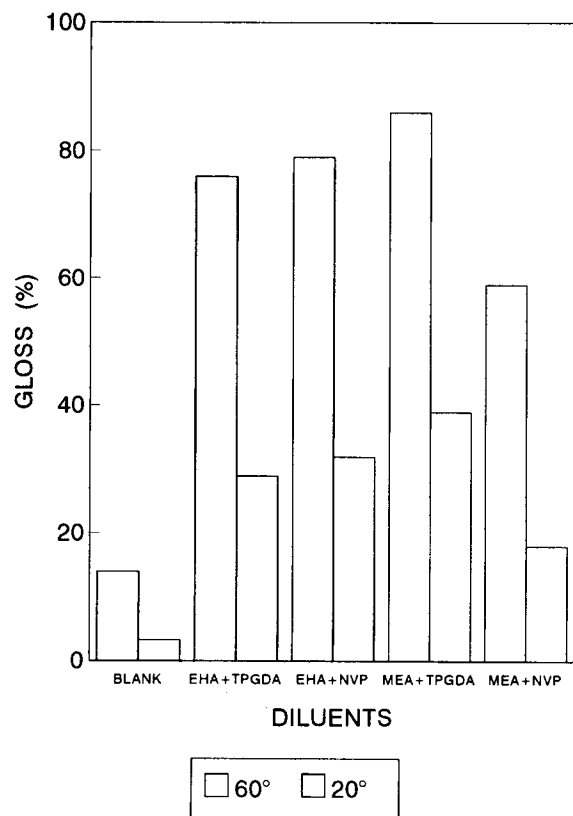
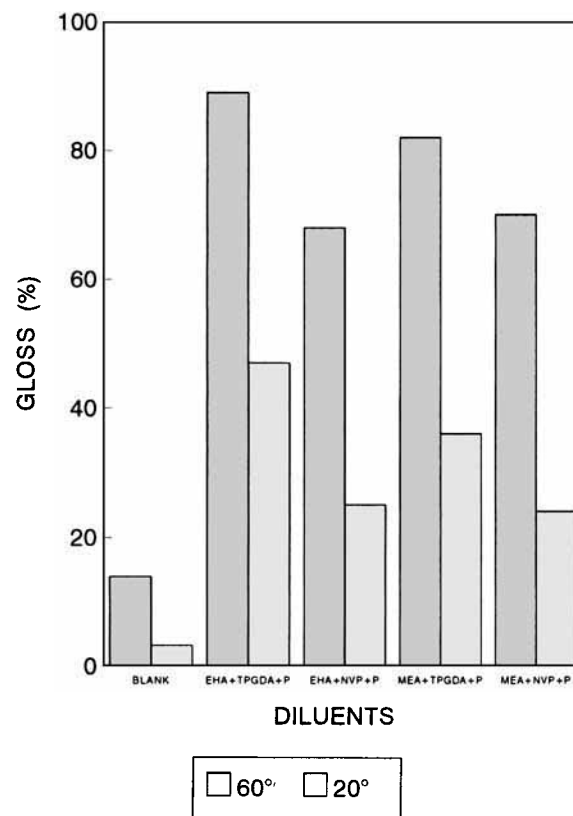**Figure 7**   Gloss of the leather surface coated with EHA and MEA series.

Figure 8   Gloss of the leather surface coated with EHA and MEA series in the presence of plasticizer.

MEA to the TPGDA system. This is shown in Figure 7 and the increase of the gloss at a 20° angle is more dominant than that at a 60° angle. On the other hand, the gloss of the MEA + TPGDA film is more than that of the EHA + TPGDA film. The case of NVP is different: The gloss of MEA + NVP is less than that of EHA + NVP. In fact, the gloss of EHA + NVP has substantially increased (Fig. 7). This increment of gloss is further enhanced when a plasticizer is incorporated into the system, as shown in Figure 8. The plasticizer is added to the system in order to increase the flexible character of the leather.

Tensile Properties

Tensile strength (TS) of the treated leather is measured and compared with that of the untreated leather; it is found that the TS values of the treated leather have increased as shown in Table III. The change of the tensile strength is expressed as T_f, which is the ratio of the TS values of the treated leather (TS_t) to that of the untreated leather (TS_0). This means that $T_f = TS_t/TS_0$. Among the single-monomer diluent systems (TPGDA, NVP, EHA,

and MEA), MEA and NVP have produced the maximum TS to the leather compared to TPGDA, a difunctional monomer. EHA has a low T_g and can be expected to produce soft film on the leather surface, thereby yielding a small increase in TS. However,

Table III   Change of the Tensile Properties of the Treated Leather

Formulation	T_f	E_f
TPGDA	1.76	1.13
NVP	2.05	1.11
EHA	1.62	0.88
MEA	2.07	0.94
EHA + TPGDA	2.27	1.04
EHA + NVP	2.23	0.90
MEA + TPGDA	1.78	0.97
MEA + NVP	1.81	1.01
EHA + TPGDA + P	1.65	1.12
EHA + NVP + P	1.40	1.14
MEA + TPGDA + P	2.03	1.14
MEA + NVP + P	1.43	1.19

$T_f = TS_{treated}/TS_{untreated}$; $E_f = E_{b_{treated}}/E_{b_{untreated}}$.

when EHA is mixed with NVP or TPGDA, there is about 20% increment of TS values of the leather. On the other hand, mixing of MEA with NVP or TPGDA decreased the TS values. Incorporation of a plasticizer into the systems has little effect on the TS values of the leather, but it has made the treated leather more flexible and has increased the elongation (E_b) capacity of the leather. The change of elongation caused by treating the leather with these formulations is represented by E_f, where $E_f = E_b$ treated/E_b untreated leather, and the results are shown in Table III. A single-monomer diluent and double-monomer diluents have, in fact, slightly decreased the elongation of the substrate except for the NVP and TPGDA systems, where elongation has slightly increased.

This means that the coating has influenced both the TS and E_b of the leather substrate. Incorporation of the plasticizer into the formulation has enhanced the stretching ability of the leather to some extent. It is very likely that the UV curing of this coating on the leather surface may have caused some sort of chemical phenomena leading to these changes. This needs further investigation which is beyond the scope of this report. However, a similar observation has also been made[6] with the leather substrate treated under UV radiation in the presence

of a set of formulations. It was indicated that same sort of interaction between the leather substrate and the ingredients of the formulated solution had occurred.

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