STUDIES ON THE BLENDS OF n-BUTYL METHACRYLATE-ETHYL ACRYLATE COPOLYMERS WITH CHLORINATED RUBBER AS TOP COAT*

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The copolymers of n-butylmethacrylate-ethylacrylate were blended with chlorinated rubber in solution. The lacquers were formulated based on each blends and their utility as top coats on leather substrates were assessed. It was concluded that the blends resulted out of the above two polymer systems serve as the source for the formulation of top coats on leather substrate.

Introduction

In the recent past, demand has increased dramatically for the development of polymer with an increasing variety of complex compositions. The goal has been to develop polymers for newer areas of application with the limitation of number of monomers, due to cost. Studies were thus initiated with the purpose of changing the properties of combining different polymers in a variety of ways.[1] This technique has been used to facilitate processing and impart flexibility, tensile and impact strength, chemical resistance, weatherability and various other properties.[1-4] In our earlier communication, we have reported that the blends of n-butyl methacrylate ethyl acrylate copolymers with chlorinated rubber serves as good film-forming materials.[5] In this paper, their utility as top coats on leather substrate is assessed.

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Experimental

(i) *Purification of materials*

Ethylacrylate (EA) (Mitsubishi Chemicals, Japan) and n-butyl methacrylate (n-BMA) (Riedel, LR) were washed successively with 5 per cent NaOH and distilled water, dried over an anhydrous sodium sulphate and finally distilled under vacuum. The middle fraction of the monomers was used for the copolymerisation. The solvents, ethyl methyl ketone (E-Merck) and xylene (BDH, LR), were purified and distilled as per the standard procedure.[6] Benzoyl peroxide was recrystallised from chloroform-methanol system and used as initiator for copolymerisation.

Commercially obtained chlorinated rubber (M/s. Rishiroop Polymers Pvt. Ltd., Bombay) was purified by dissolving it in MEK and precipitated by methanol. The process of dissolution in MEK and precipitation by methanol were repeated a number of times to get pure chlorinated rubber.

(ii) *Copolimerisation of ethylacrylate and n-butyl methacrylate*

A mixture of EA, nBMA and BPO of calculated quantities were fed into a 3-necked flask fitted with a condenser and a nitrogen inlet. A fixed volume of MEK was added to the above mixture and the polymerisation carried out at 60°C to achieve 100 per cent conversion of the monomers. The co-polymers were isolated by precipitating the reaction medium into water-methanol mixture.

(iii) *Solution blending with chlorinated rubber*

Purified chlorinated rubber and the copolymer of given composition of nBMA/EA were weighed accurately, dissolved in xylene and blended by stirring. The resulting solution was clear and homogeneous. To some of the blends, a small amount of chlorinated paraffin (plasticizer) was added.

(iv) *Preparation of upper leather*

The preparation of upper leather consisted of the following operation. Wet salted cow hides were soaked in water and then liming, deliming, pickling, chrome tanning, neutralisation, retanning, fatliquoring and impregnation were carried out successively as per the standard procedure followed in this Institute. The final operation was the finishing of leather. This consisted of (a) clearing coat, (b) season coat and (c) top coat.

(a) *clearing coat :* The composition given below was used for this coat.

Liquor ammonia	—	10 cc
Isopropyl alcohol	—	30 cc
Water to make	—	1 litre

This was applied with a brush on the grain side and dried.

(b) *season coat* : The season coat consisted of.

Pigment (Crown)	—	100 g
Primal B41 (Indofil)	—	150 g
Naxol P.A. (DCI)	—	10 g
Liquor ammonia	—	5 ml
Water to make	—	1 litre

These were mixed throughly and two pad coats were applied in between drying the leather. Then the season coat was sprayed as two cross coats and dried. (Primal B41 is an acrylic based binder. Naxol PA is a wax emulsion.)

(c) *Top coat :* This consisted of blends of chlorinated rubber and n-butyl methacrylate-ethylacrylate copolymers in solution. A number of samples of the size 20 × 20 cm were cut from the finished upper leather and used for the study. The lacquers based on each blend were sprayed as one full cross coat at 5 kg/sq. cm. pressure. While spraying the lacquers, the spray was held close to the leather to get more gloss. The samples were allowed to dry and plated.

Testing of leathers

The finished leather samples were conditioned and tested for flexibility and colour fastness as per the standard procedure.[7]

Results and discussion

It is already reported that the blends of the nBMA/EA copolymer and chlorinated rubber yield good film forming materials. In the present investigation, these film forming materials were assessed as top coat for leather surface. The aim of giving a top coat on finished leather is to impart desired physical properties such as flexural endurance, dry, and wet rub fastness etc. To meet these requirements, flexible film formation material of the above blends were chosen

and the method of solution blending was employed as it permits rapid and thorough blending with low power requirement ; causes no colour degradation or premature curing reactions and produces a fluid product that can be applied directly in most end uses.[8] Table I describes the various types of copolymers employed in blending for the formulation of top coats.

TABLE 1

Copolymers employed in blending

Code No	*Amount of n-BMA wt. per cent*	*Amount of EA wt. per cent*
A	67	33
B	60	40
C	55	45
D	50	50

TABLE 2

Visual evaluation of the finish by an experienced tanner

Code No.	*General appearance*	*Adhesion*	*Finish crackiness*		*Resistance to*		*Gloss*	*Tackiness*	*Cold test*
			On single fold	*On double fold*	*Dry rub*	*Wet rub*			
A_1	Good	Poor	Does not crack	Does not crack	Good	Good	Good	No	Does not crack
A_2	-do-	-do-	-do-	-do-	-do-	-do-	-do-	No	-do-
A_3	-do-	Good	-do-	-do-	-do-	-do-	-do-	No	-do-
A_4	-do-	-do-	-do-	-do-	-do-	-do-	-do-	No	-do-
B_1	-do-	Poor	-do-	-do-	-do-	-do-	Fair	No	-do-
B_2	-do-	-do-	-do-	-do-	-do-	-do-	Fair	No	-do-
B_3	-do-	Good	-do-	-do-	-do-	-do-	Fair	No	-do-
B_4	-do-	-do-	-do-	-do-	-do-	-do-	Fair	No	-do-
C_1	-do-	Better	-do-	-do-	-do-	-do-	Fair	No	-do-
C_2	-do-	-do-	-do-	-do-	-do-	-do-	Fair	Yes	-do-
C_3	-do-	-do-	-do-	-do-	-do-	-do-	Fair	No	-do-
C_4	-do-	-do	-do-	do	do-	-do	Dull	Yes	-do
D_1	-do-	-do-	-do-	-do-	-do-	-do-	Fair	Yes	-do-
D_2	-do-	-do-	-do-	-do-	-do-	-do-	Fair	Yes	-do-
D_3	-do-	-do-	-do-	-do-	-do-	-do-	Fair	Yes	-do-
D_4	-do-	-do-	-do-	-do-	-do-	-do-	Fair	Yes	-do-

Tables 2,3 and 4 describe the results obtained on leathers treated with the blends. The subscripts 1,2,3 and 4 of code numbers A,B,C,D in the above tables indicate the following amounts of blended material.

1. 40 wt. per cent of Chlorub 40
   60 wt. per cent of nBMA/EA copolymer.
2. 40 wt. per cent of Chlorub 40 ; 60 wt. per cent of nBMA/EA copolymer and 5 wt. per cent of chlorinated paraffin.

3. 33.3 wt. per cent of Chlorub 40 and 66.7 wt. per cent of nBMA / EA copolymer.

4. 33.3 wt. per cent of Chlorub 40 and 66.7 wt. per cent of nBMA / EA copolymer and 5 wt. per cent of chlorinated paraffin.

TABLE 3

Bally's flexometer reading for the finished upper leather treated with lacquer based on the blends of Chlorub 40 and nBMA+EA copolymer

Code No.	*No. of flexing at which grain cracked*
A_1	After 10,000
A_2	After 20,000
A_3	After 15,000
A_4	No crack after 80,000
B_1	After 15,000
B_2	After 40,000
B_3	After 25,000
B_4	No crack after 80,000
C_1	After 50,000
C_2	No crack even after 90,000
C_3	-do-
C_4	-do-
D_1	-do-
D_2	-do-
D_3	-do-
D_4	-do-

Table 2 indicates the visual observation of the finish made by an experienced tanner. From the observation, D_1–D_4 and C_1–C_4 show a better adhesion to the substrates than that of the code numbers A_1–A_4 and B_1–B_4. The better adhesion of D and C groups may be due to the increased flexibility of films, formed on the substrate. The finish crackiness on single and double fold has not occurred on any of the formulations. The flexibility of the finishes has been tested in flexometer and the results are given in Table 3. This indicates that the code numbers C and D are able to withstand 90,000 flexes (more than the normal flexes required for a top coat). The code numbers of B_2 and A_4 are also able to withstand flexes around 80,000. The formulations of A_1 and A_2 showed a crack after 10,000 flexes, which may be attributed to poor elongation.[5]

The formulations based on D and C showed some tackiness on plating due to higher amount of EA in the copolymer feed. The formulations based on A and B showed no tackiness when plated. The gloss of the finishes seemed to be better for the formulations based on blends containing higher methacrylate polymer content in the blend (A and B) than that of the formulation containing more amount of EA (C and D). The cold test was found to yield no crack for all the finishes indicating that these systems are suitable even at low temperature. The resistance to wet and dry rub was found to be good for all the finishes and the results obtained by colour fastness tests are given in Table 4.

It can be seen that all the finishes were able to withstand more than 1024 revolutions attaining grade 4 for both wet and dry rubbing. Only in few cases, grade 1 and grade 3 were obtained. These results indicate that the top coat based on blends of nBMA/EA copolymer with chlorinated rubber provide good colour fastness to the finish.

From the foregoing discussions, it can be seen that the blends of nBMA/EA copolymers with chlorinated rubber serve as a source for the formulation of top coats on leather substrate. In addition, chlorinated rubber provides resistance to acid and alkali and oxidation.

TABLE 4

Colour fastness

Code No.	Dry rubbing			Wet rubbing		
	Number of revolutions to cause contrast grade 4 (grey scale)	*Number of revolutions to cause contrast grade 1 (grey scale)*	*Contrast grading after 1024 revolutions*	*Number of revolutions to cause contrast grade 4 (grey scale)*	*Number of revolutions to cause contrast grade 1 (grey scale)*	*Contrast grading after 1024 revolutions*
A_1	1024	1024	4	1024	1024	4
A_2	1024	1024	4	1024	1024	4
A_3	1024	1024	4	512	1024	3
A_4	1024	1024	4	1024	1024	4
B_1	1024	1024	4	1024	1024	4
B_2	128	256	1	128	256	3
B_3	1024	1024	4	512	1024	1
B_4	1024	1024	4	512	1024	1
C_1	1024	1024	4	1024	1024	4
C_2	1024	1024	4	512	1024	3
C_3	1024	1024	4	1024	1024	4
C_4	1024	1024	4	1024	1024	4
D_1	1024	1024	4	1024	1024	4
D_2	1024	1024	4	1024	1024	4
D_3	1024	1024	4	1024	1024	4
D_4	1024	1024	4	1024	1024	4

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