II

EXPERIMENTAL

II. EXPERIMENTAL

A. ESTERIFIED COTTON

II.1. Esterification of cellulose fibres and fabrics.

1 (a) Preparation of dibasic acid anhydrides

Powdered acid (sebacic, adipic or fumaric) and acetic anhydride , were taken in a round bottom flask fitted with reflux condensor and refluxed on sand bath for about 6 hr. Excess of acetic anhydride was distilled off. The flask was cooled and solid material was taken out. Melting point and infrared spectra of the products were taken and are presented in (table II.1) and (Fig.II.1a) respectively.

Above anhydrides and maleic anhydride were used for esterification reactions with cotton fabrics and fibres.

1 (b) Preparation of acid chlorides

Powdered acid (sebacic, adipic or fumaric) (0.1M) and thionyl chloride (0.3 M) were taken in a round bottom flask fitted with reflux condensor and heated under reflux for 4 hr. Excess thionyl chloride was distilled off. The flask was cooled and the product was taken out.

Its boiling point was measured at 75 mm pressure (table II-2). The products were used for esterification reaction with cotton fabrics and fibres.

Table-II-1

No	Product	Acid used	Melting point of the product (°c)
1	Sbn	Sebacic	52-54
2	Adn	Adipic	145-147
3	Fmn	Fumaric	> 300

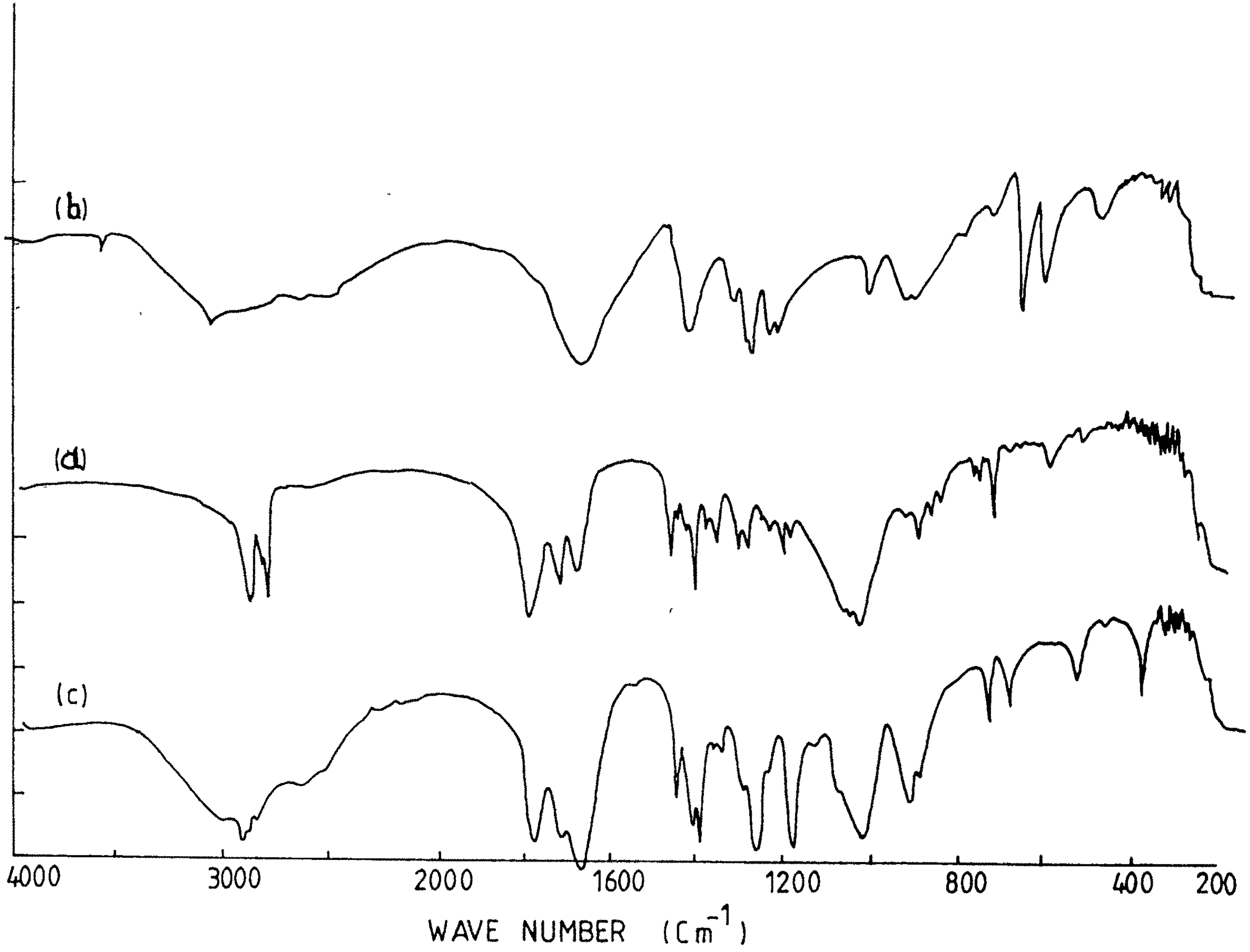


FIG. II.1 (a) IR SPECTRA OF (a) Sbn (b) Adn (c) Fmn

Table-II-2

No	Product	Acid used	Boiling point (at 75 mm) of the product (°c)
1	Sbc	Sebacic	220
2	Adc	Adipic	126
3	Fmc	Fumaric	158-60

1 (c) Preparation of acryloyl chloride and methacryloyl chloride

A mixture of acrylic acid (0.1M), benzoyl chloride (0.3M) and hydroquinone (0.0005M) was distilled at a fairly rapid rate through an efficient distilling column. The distillate was collected in a receiver containing 0.05 g hydroquinone, immersed in ice when the temperature at the top of the column was between 60 and 70°c at 740 mm

Methacryloyl chloride (BP 95 - 96°c) was prepared in the same way using methacrylic acid (0.1M) and benzoyl chloride (0.3M) and collecting the fraction at 95°c.

1 (d) Cotton fabric was first destarched by treating it alternatively with boiling water and cold water several times and drying it at room temperature.

1 (e) Esterification of destarched cotton fabrics using dibasic acid anhydrides

Treatment with sebacic, adipic, fumaric or maleic anhydride

Powdered acid anhydride was dissolved in dimethylformamide and weighed fabric was soaked in it for an hr at room temperature with constant stirring. The fabric was removed from the solution, washed, dried at room temperature and % add -on was determined.

$$\% \text{ add-on} = 100\ (W_2 - W_1) \div W_1$$

where W_1 = weight of the fabric before treatment and

W_2 = weight of the dried fabric after treatment.

1 (f) Esterification of cotton fibres using dibasic acid anhydride

Powdered acid anhydride was dissolved in dimethylformamide. Destarched cotton fibres were soaked in it for an hr at room temperature with constant stirring. The fibres were removed from the solution, dried and extracted with alcohol. Soluble ester was obtained by evaporating alcohol from the extract and insoluble, esterified residue was left after removing the extract. Both soluble and insoluble fractions were studied further.

1 (g) Esterification of cotton fabric with acid chloride

Acid chloride was dissolved in dimethylformamide (or carbon tetrachloride or chloroform). The fabric was placed in it and pyridine was added to it. The reaction was carried out at room temperature or heated at 105°c with constant stirring. The fabric was removed from the solution, washed with water and alcohol, dried and percent add-on was determined. Alcohol soluble ester was obtained as solid after evaporation of alcohol from the extract. Both the soluble and insoluble products were studied further.

1 (h) Esterification of cotton fibres with acid chloride

Acid chloride was dissolved in dimethylformamide. The fibres were soaked in it and pyridine was added to it. The reaction was carried out at room temperature with constant stirring for an hr. The fibres were removed from the solution, washed with water and dried. The dried fibres were extracted with alcohol. Both the soluble and insoluble products were studied further.

1 (i) Polymerization of anhydride treated cotton fabric using benzoyl peroxide (BPO)

The pretreated fabric was placed in toluene. Benzoyl peroxide was added to it. Polymerization was carried out at 90°c for 2 hr with occasional stirring. The fabric was removed from the solution, dried, washed with water and alcohol and again dried.

1 (j) Polymerization of acid chloride treated cotton fabric using benzoyl peroxide (BPO)

Acryloyl chloride (or methacryloyl chloride) treated fabric was placed in toluene and benzoyl peroxide was added to it. Polymerization was carried out at 90°c for 2 hr with occasional stirring. The fabric was removed, washed with water and alcohol and dried.

The amounts of reactants, time and temperature of reaction, etc. are presented in (table II.3).

1 (k) Attempted esterification of cotton fabric with cinnamic anhydride

Cinnamic anhydride was prepared by reacting cinnamic acid with acetic anhydride as presented in II.1(a). The product melts at 115°c and its IR spectrum is presented in fig.II.1 (b). Esterification of cotton fabric with the product was carried out for 4 hr as suggested in II.1(e). No appreciable add-on was found when cotton fibres and fabrics were treated with it, however a sample of the esterified fabric had CRA° of 218.

1 (l) Attempted esterification of cotton fibres with LAB acid chloride

LAB acid chloride was prepared by reacting LAB acid with thionyl chloride [as suggested in II.1 (b)]. The product

Table - II - 3

.3 (a)

No	Product	Fabric wt (g)	Acid Anhydride		Dimethyl-formamide (ml)	time (min)	Temperature (°c)
			Used	wt (g)			
1	CSb-1	1.0	Sebacic	1.0	20.0	120	Room temp
2	CSb-2	1.0	Sebacic	1.0	20.0	90	90-95
3	CSb-3	1.0	Sebacic	1.0	20.0	30	90-95
4	CAd-1	1.0	Adipic	1.0	20.0	90	Room temp
5	CAd-2	1.0	Adipic	1.0	20.0	45	90-95
6	CFm-1	1.0	Fumaric	1.0	20.0	60	Room temp
7	CFm-2	1.0	Fumaric	1.0	20.0	30	90-95
8	CMl-1	1.0	Maleic	1.0	20.0	90	Room temp
9	CMl-2	1.0	Maleic	1.0	20.0	30	90-95

3 (b)

No	Product	Fibres wt (g)	Acid Anhydride		Dimethyl-formamide (ml)	time (min)	temperature (°c)
			Used	wt (g)			
1	CfSb	1.0	Sebacic	1.0	20.0	90	Room temp
2	CfAd	1.0	Adipic	1.0	20.0	90	Room temp
3	CfFm	1.0	Fumaric	1.0	20.0	90	Room temp
4	CfMl	1.0	Maleic	1.0	20.0	90	Room temp

3 (c)

No	Product	Fabric wt (g)	Acid chloride used	Acid chloride(5%)solution			Pyridine	Time (min)	Temperature (°c)
				in dimethyl formamide (ml)	in ccl_4 (ml)	in $CHCl_3$ (ml)			
1	CSbc(D)-1	1.0	Sebacoyl	20.0	-	-	1.0	30	105
2	CSbc(D)-2	1.0	Sebacoyl	20.0	-	-	1.0	90	105
3	CSbc(D)-3	1.0	Sebacoyl	20.0	-	-	1.0	90	Room Temp
4	CSbc(Ct)	1.0	Sebacoyl	-	20.0	-	1.0	90	Room Temp
5	CSbc(Ch)	1.0	Sebacoyl	-	-	20.0	1.0	90	Room Temp
6	CAdc(D)-1	1.0	Adipoyl	20.0	-	-	1.0	30	105
7	CAdc(D)-2	1.0	Adipoyl	20.0	-	-	1.0	90	Room Temp
8	CAdc(Ch)	1.0	Adipoyl	-	-	20.0	1.0	90	Room Temp
9	CFmc(D)	1.0	Fumaroyl	20.0	-	-	1.0	30	105
10	CFmc(Ch)	1.0	Fumaroyl	-	-	20.0	1.0	90	Room Temp

3 (d)

No	Product	Fibres wt (g)	Acid chloride used	Acid chloride(5%) solution in Dimethyl formamide (ml)	Pyridine (ml)	Time (min)
1	CfSbc	1.0	Sebacoyl	20.0	1.0	60
2	CfAdc	1.0	Adipo yl	20.0	1.0	60
3	CfFmc	1.0	Fumaroyl	20.0	1.0	60

3 (e)

No	Product	Fabric esterified with	Toluene (ml)	Benzoyl Peroxide (g)	Temperature (°c)	Time (hr)
1	BCFm	Fumaric anhydride	50.0	0.005	90	2.0
2	BCMl	Maleic anhydride	50.0	0.005	90	2.0

3 (f)

No	Product	Fabric esterified with	Toluene (ml)	Benzoyl peroxide (g)	Temperature (°c)	Time (hr)
1	BCAc	Acryloyl chloride	50.0	0.005	90	2.0
2	BCMac	Methacryloyl chloride	50.0	0.005	90	2.0

3 (g)

No	alcohol soluble product	Melting Point (°c)
1	S-CfSb	112
2	S-CfAd	146
3	S-CfFm	225
4	S-CfMl	70-72
5	S-CfAdc	142
6	S-CfFmc	117

FIG. II. 1 (b). IR SPECTRA OF CINNAMIC ANHYDRIDE was used to esterify cotton fabric as suggested in II.1(h). The product decomposes at 260°c. Its IR spectrum is presented in fig.II.1(c). When the fibres were treated with it and washed with alcohol, alcohol soluble and alcohol insoluble fractions were obtained.

II.2 Measurements : Studies of fabrics and fibres

2 (a) Analysis :

Elemental analysis (% C and % H) of some products was obtained using Carbon-Hydrogen analyzer (model Coleman-29).

2 (b) Thermogravimatric analysis :

The TGA of some samples was performed in nitrogen atmosphere at a heating rate of 10°C/min using Dupont model TGA apparatus. The initial decomposition temperature (IDT) was obtained from the end of the initial straight line portion of the curve from where the actual decomposition is believed to have occured.

2 (c) Infrared spectroscopic measurements :

IR spectra of some samples were obtained using IR spectrophotometers models. Perkin-Elmer-567 and Beckmann-4220. Sample was prepared using KBr disc method.

2 (d) X-Ray diffraction study (XRD) :

X-ray diffractograms of some samples were obtained using X-ray diffractometer model PW 1390 PHILIPS. The parameters maintained were :

2Q (degree) = 5° to 40°, scanning speed = 1°/min.,

chart speed = 1 cm/min., range = 2000 c/s.

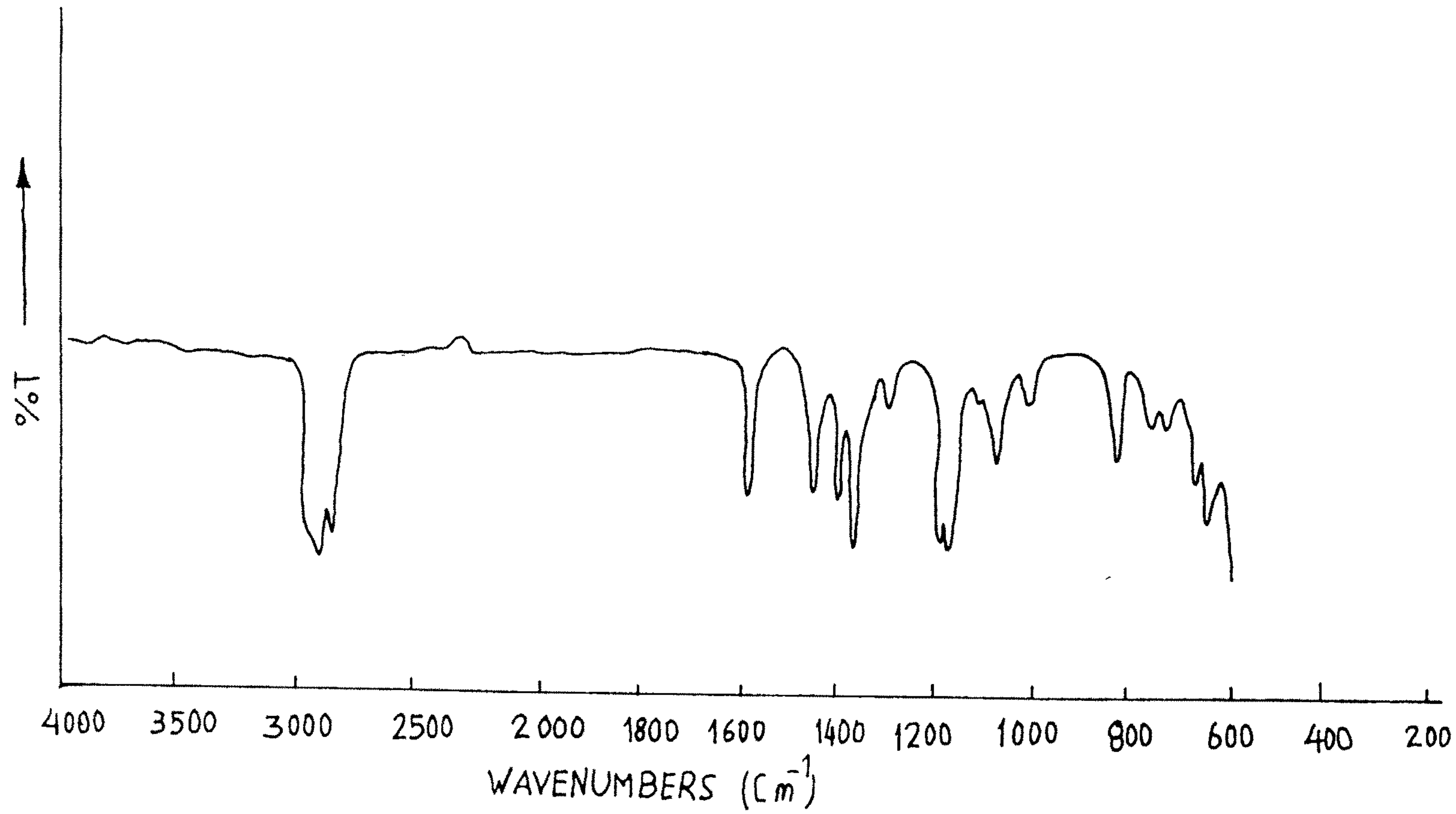


FIG. II.1 (C). IR SPECTRUM OF LAB ACID CHLORIDE

2 (e) Scanning electron microscopic study (SEM) :

SEM study of some samples was done using SEM model JSM 35 c of Joel Japan and sample coating unit model JFC-1100 was used for Gold coating of the sample.

2 (f) Break strength (B.S.) and elongation at break (%El) :

Break strength (B.S.) and elongation (at break) of modified fabrics were obtained using Instron tensile tester. The parameters maintained were :

Full scale load (FSL) = 100 kg;
Cross head speed (CHS) = 100 cm/min.
Chart speed (CS) = 10 cm /min.
Guage length (GL) = 20 cm;
Fabric length = 20 cm;
Fabric width = 2.54 cm;

2 (g) Crease recovery angle :

Conditional (dry) wrinkle recovery angles were determined by an ASTM standard test method. A standard size of fabric was cut and the crease recovery angle was measured using Shasmira crease recovery tester.

2 (h) Diameter measurement :

Diameter of the modified cotton fibre and fabric yarn was measured by using optical microscope having magnification of 500 x and 125 x. Instrument for this measurement used was Carl-Zeiss research microscope model NU-2.

For measurement, fibres or yarns were removed from the fibres or fabrics and sticked on microscope glass slide vertically by double coated adhesive tape. Microscope slide was placed on the platform and readings were taken for 9 samples (average value was recorded).

% Add-on for cotton fabrics and fibres esterified by different methods, crease recovery angle of the treated fabrics, diameter of the treated fabrics and fibres, etc. are presented in table II.4.

Analysis (%C and %H) of some of the samples is presented in table II.5. Thermograms of some of the samples are shown in fig.II.2 and IR spectra of some of the samples are presented in fig.II.3. Scanning electron micrographs of some of the samples are presented in fig.II.4.

B. FORMALIZED COTTON

II.3. Cotton fabrics modified by treatment with polyvinyl alcohol (PVA) and formaldehyde (F)

Cotton fabric was first destarched by treating it alternately with boiling water and cold water several times and drying it at room temperature. Polyvinyl alcohol of SD chem make (S grade) or Koch-Light make (K-grade) was used.

3 (a) Treatment with polyvinyl alcohol, formaldehyde and hydrochloric acid

A cotton fabric piece was placed in 100 ml 1% polyvinyl alcohol in a beaker and left for 24 hr. The piece was taken out of the solution and placed in a flask. 1 ml formaldehyde solution and few drops of HCl in 100 ml water were added to it and the mass was heated under reflux

Table-II-4

4 (a)

No	Product	% Add-on	diameter (mm)	CRA° (W+F)
1	CSb-1	6.5	0.20	169
2	CSb-2	27.0	0.24	170
3	CSb-3	25.0	0.23	169
4	CAd-1	0.3	0.16	179
5	CAd-2	0.9	0.17	177
6	CFm-1	0.6	0.16	180
7	CFm-2	0.9	0.16	176
8	CMl-1	0.2	0.19	170
9	CMl-2	0.4	0.19	160

4 (b)

NO	Product	% Add-on	Diameter (mm)
1	CfSb	6.6	0.029
2	CfAd	4.5	0.026
3	CfFm	3.1	0.027
4	CfMl	5.0	0.018

4 (c)

No	Product	% Add-on	Diameter (mm)	CRA° (W+F)
1	CSbc(D)-1	20.0	0.24	242
2	CSbc(D)-2	21.2	-	247
3	CSbc(D)-3	8.0	0.21	193
4	CSbc(Ct)	2.2	-	200
5	CSbc(Ch)	10.0	-	184
6	CAdc(D)-1	0.4	-	190
7	CAdc(D)-2	0.2	0.21	193
8	CAdc(Ch)	0.6	-	180
9	CFmc(D)	0.2	-	168
10	CFmc(Ch)	0.8	0.23	161

4 (d)

No	Product	% Add-on	Diameter (mm)
1	BCFm	4.4	0.20
2	BCMl	3.0	0.19

4 (e)

No	Product	% Add-on		Diameter (mm)
		Polymerization	After water wash	
1	BCAc	7.9	0.5	0.19
2	BCMac	5.8	1.4	0.21

Table II.5

5 (a)

No.	Alcohol soluble product	Acid anhydride used	Formula	Found % C	Found % H	Calculated % C	Calculated % H
1.	s-CfSb	Sebacic	$(C_{21}H_{31}O_8)_n$	60.0	7.5	61.3	7.5
2.	s-CfAd	Adipic	$(C_{10.5}H_{14.5}O_{6.5})_n$	49.8	6.3	51.5	5.9
3.	s-CfFm	Fumaric	$(C_8H_{10}O_6)$	47.8	4.8	47.5	5.0
4.	s-CfMl	Maleic	$(C_8H_{10}O_6)_n$	46.7	5.3	47.5	5.0

5 (b)

No.	Alcohol-washed product (insol. residue)	Formula	Found		Calculated	
			% C	% H	% C	% H
1.	i-CfSb	$(C_7H_{11.4}O_{5.2})_n$	47.6	6.7	47.0	6.4
2.	i-CfAd	$(C_{6.6}H_{10.6}O_{5.2})_n$	44.6	6.1	45.8	6.1
3.	i-CfFm	$(C_{6.4}H_{10}O_{5.2})_n$	43.2	6.2	45.2	5.9
4.	i-CfMI	$(C_{6.4}H_{10}O_{5.2})_n$	44.3	6.0	45.2	5.9

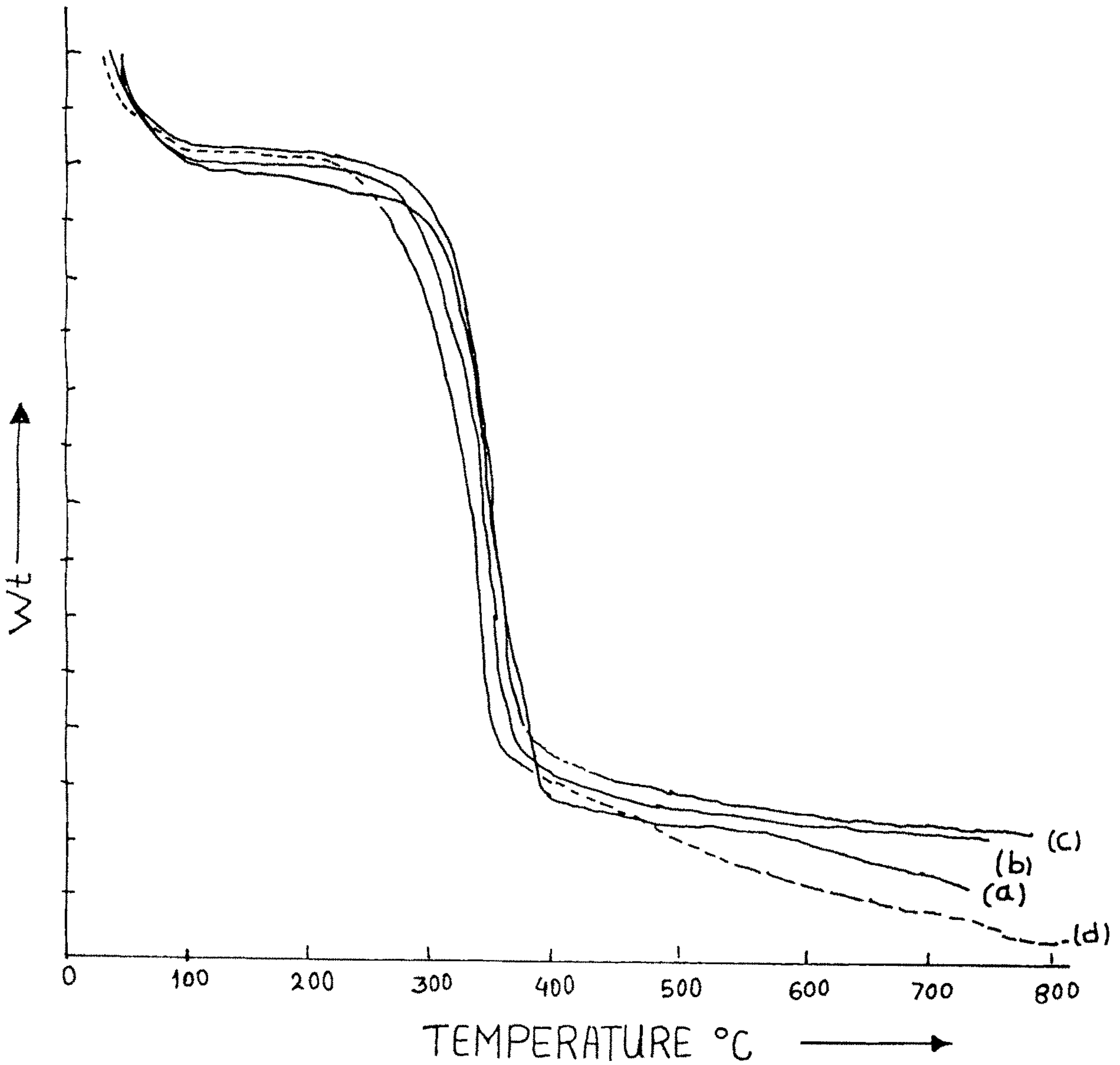


FIG. II.2 (A) THERMOGRAMS OF ESTERIFIED FIBRES
(a) CfSb (b) CfAd (c) CfFm (d) CfML

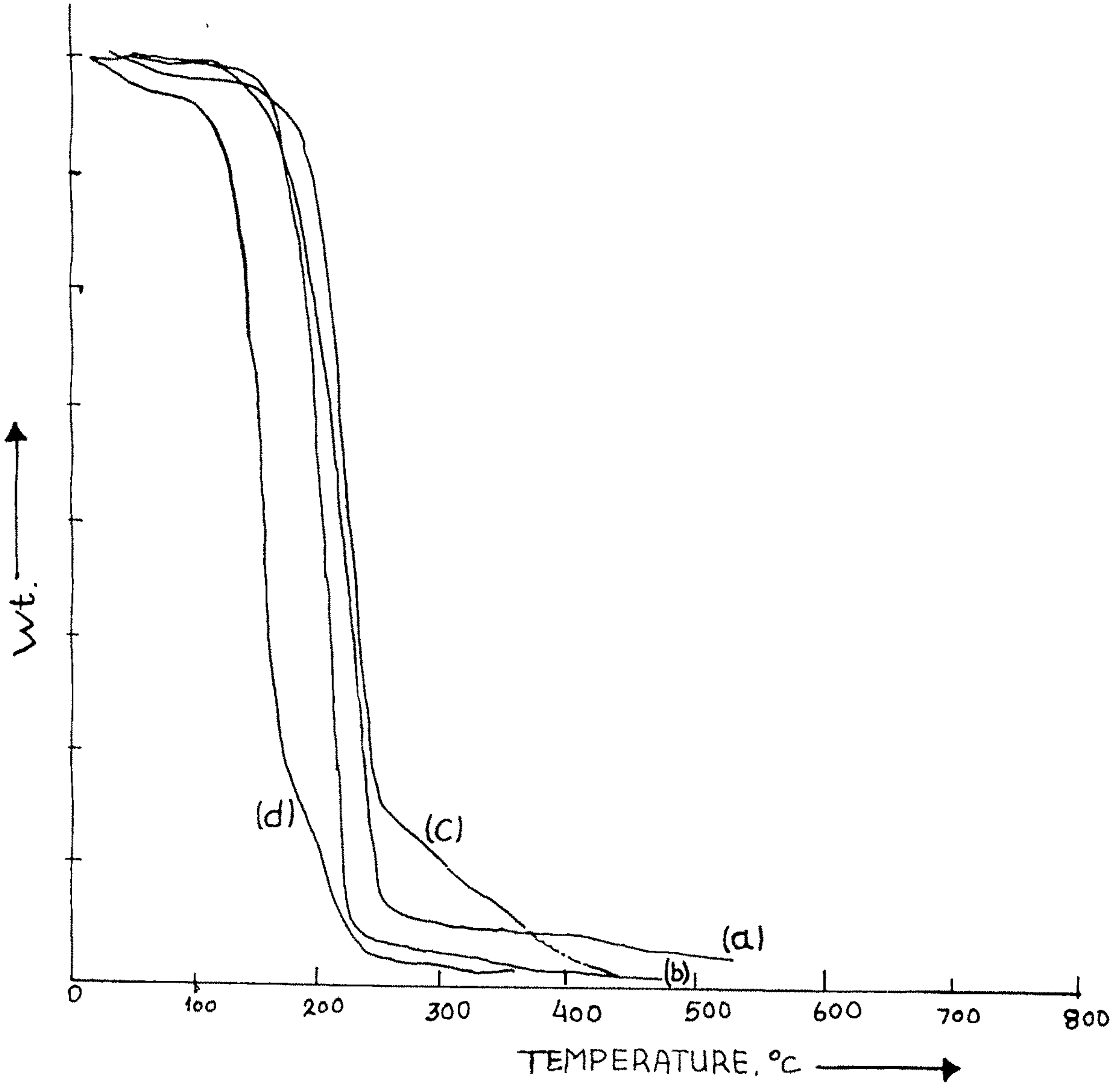


FIG.II.2 (B) THERMOGRAMS OF ALCOHOL SOLUBLE PRODUCTS
(a) S-CfSb (b) S-CfAd (C) S-CfFm (d) S-CfMl
(different initial wts and wt loss / min)

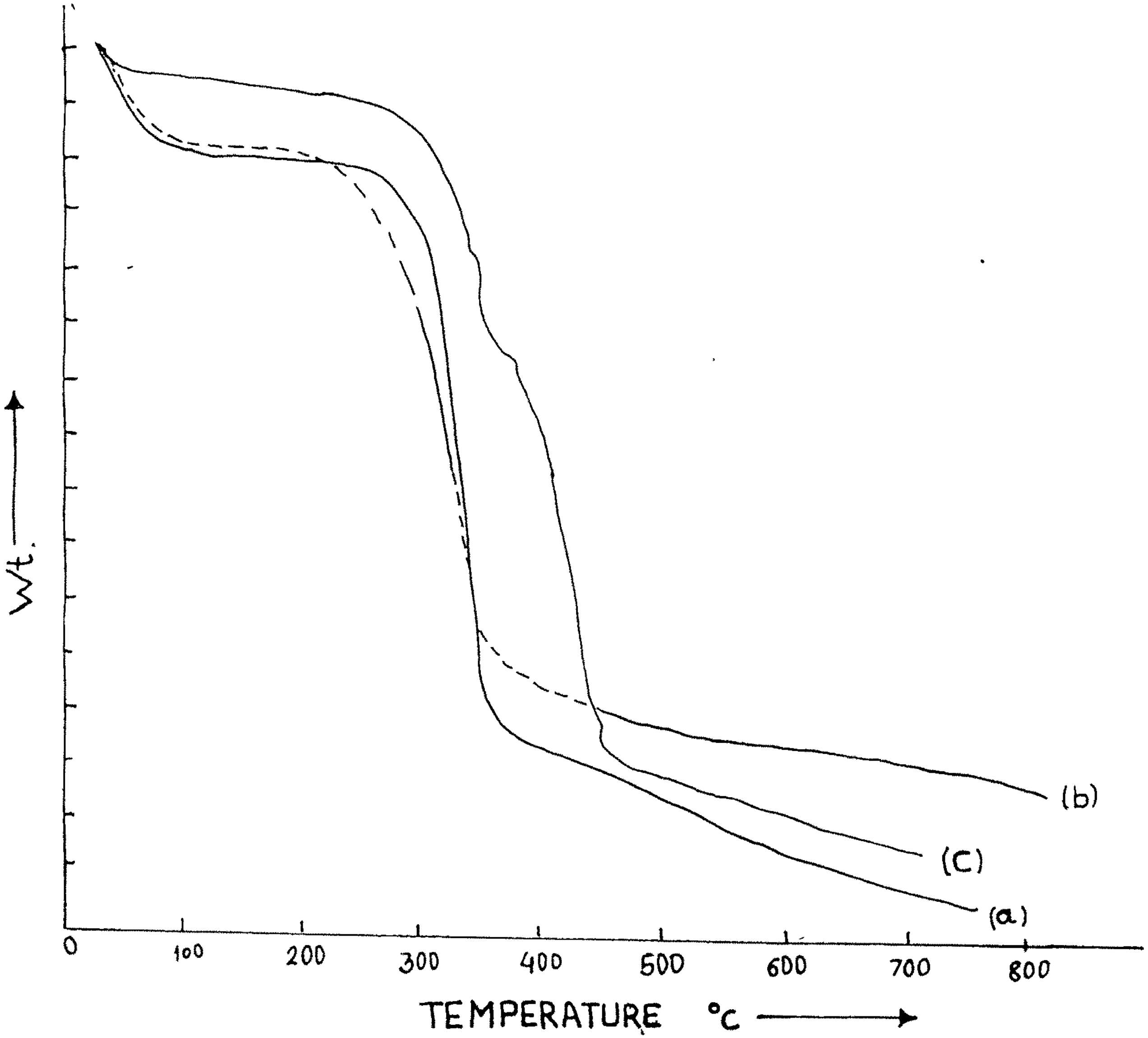


FIG II. 2 (C) THERMOGRAMS OF ESTERIFIED FIBRES
(a) UNTREATED (b) CfAdc (c) CfFmc

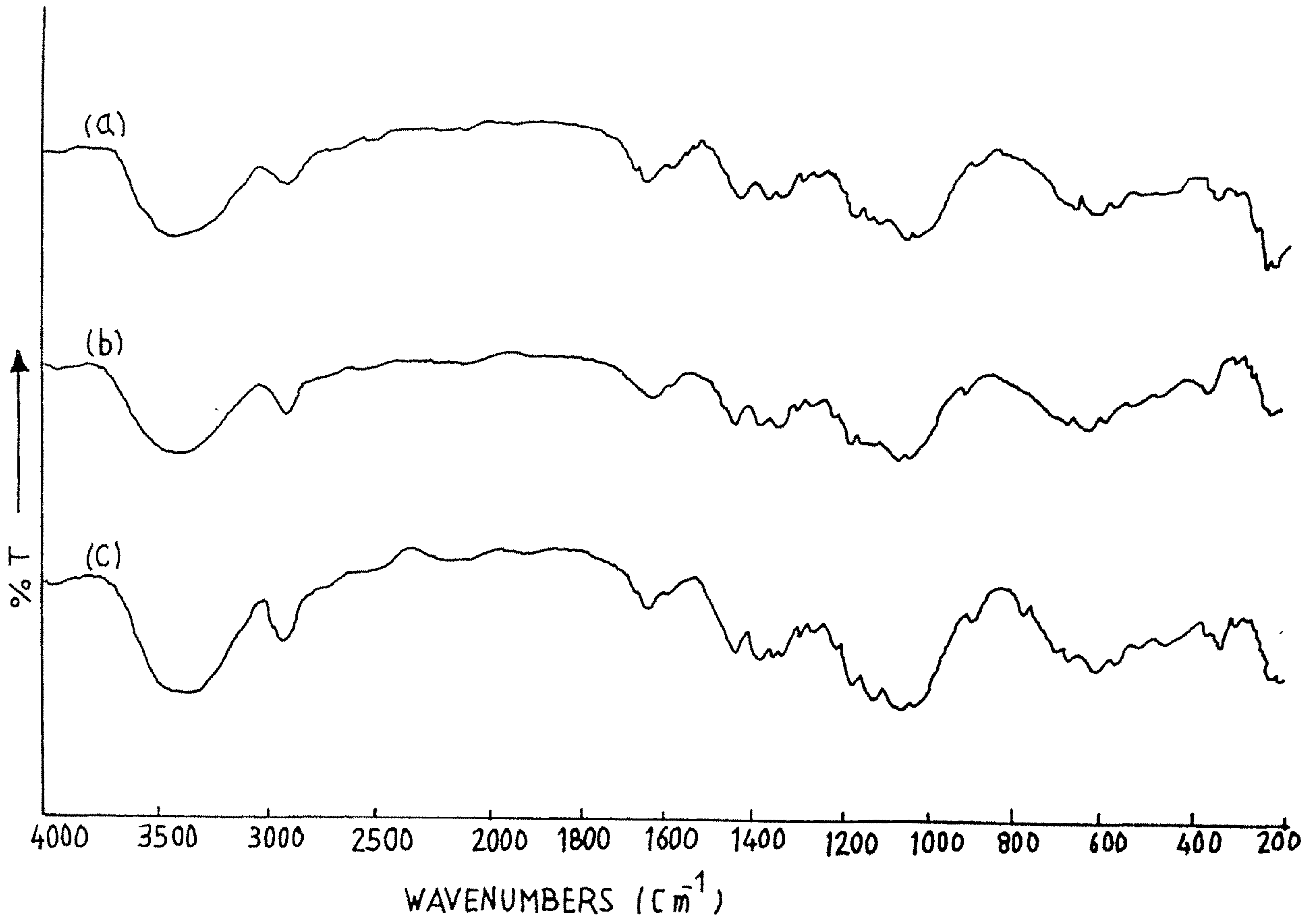


FIG. II.3 (d) IR SPECTRA OF ESTERIFIED FABRICS
(a) CSb (b) CAd (c) CFm

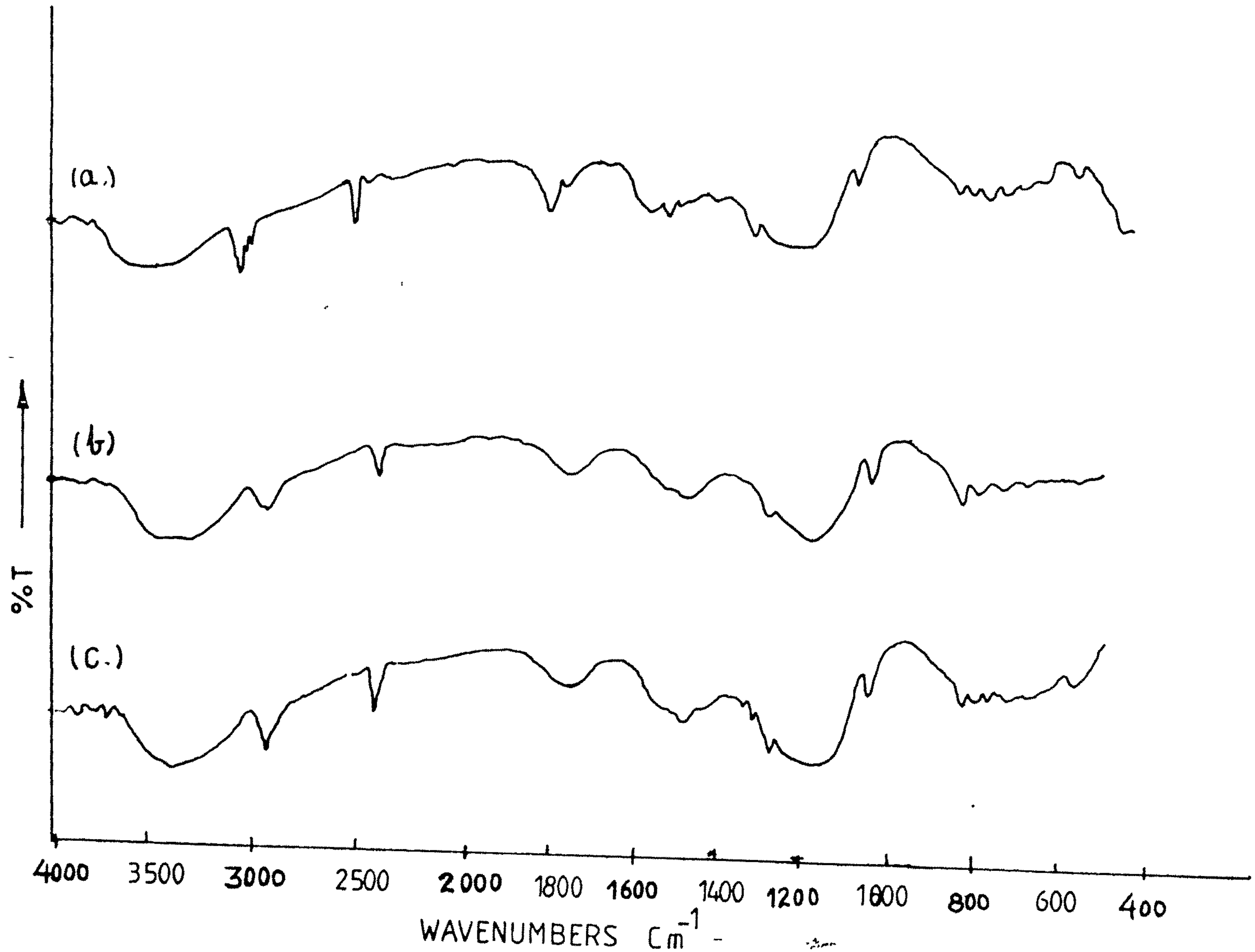


FIG. II.3.(b) IR SPECTRA OF TREATED FIBRES

(a) CfSb (b) CfAd (c) CfFm

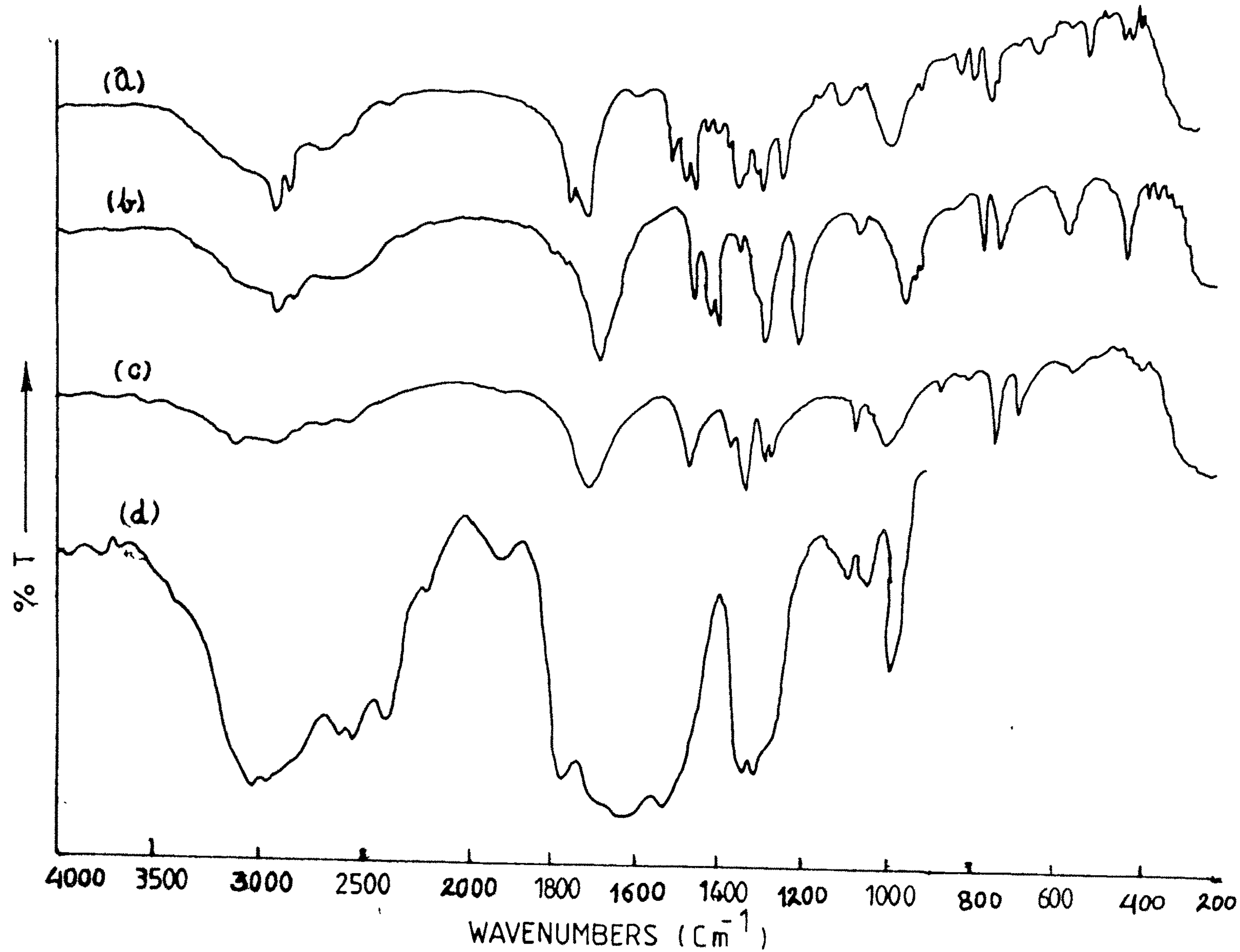


FIG. II. 3 (C) IR SPECTRA OF ALCOHOL SOLUBLE PRODUCTS

(a) s- CfSb (b) s-CfAd (c) s-CfFm (d) s-CfMl

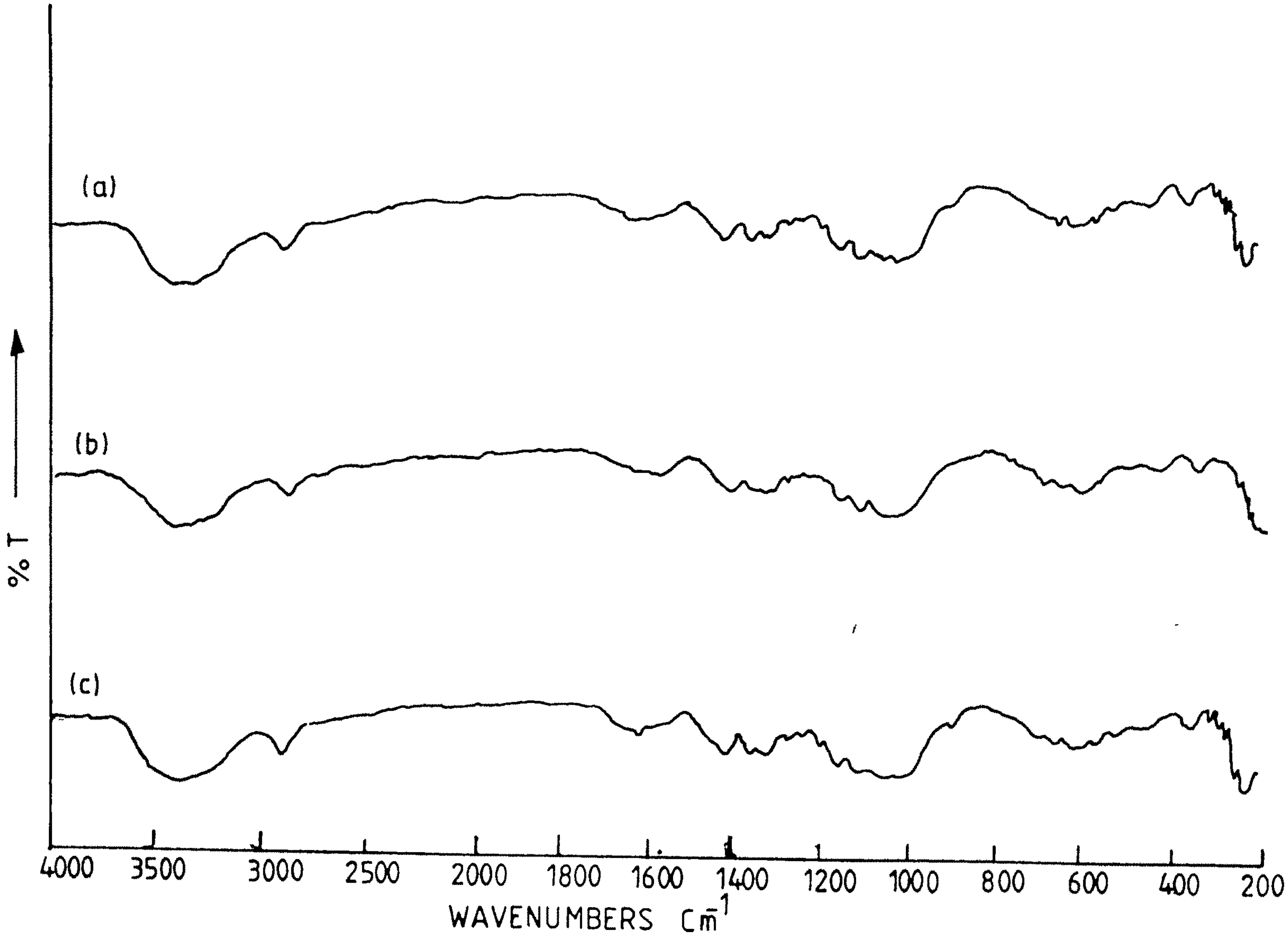


FIG. II. 3. (d) IR SPECTRA OF ESTERIFIED FABRICS
(a) CSbc (b) CAdc (c) CFmc

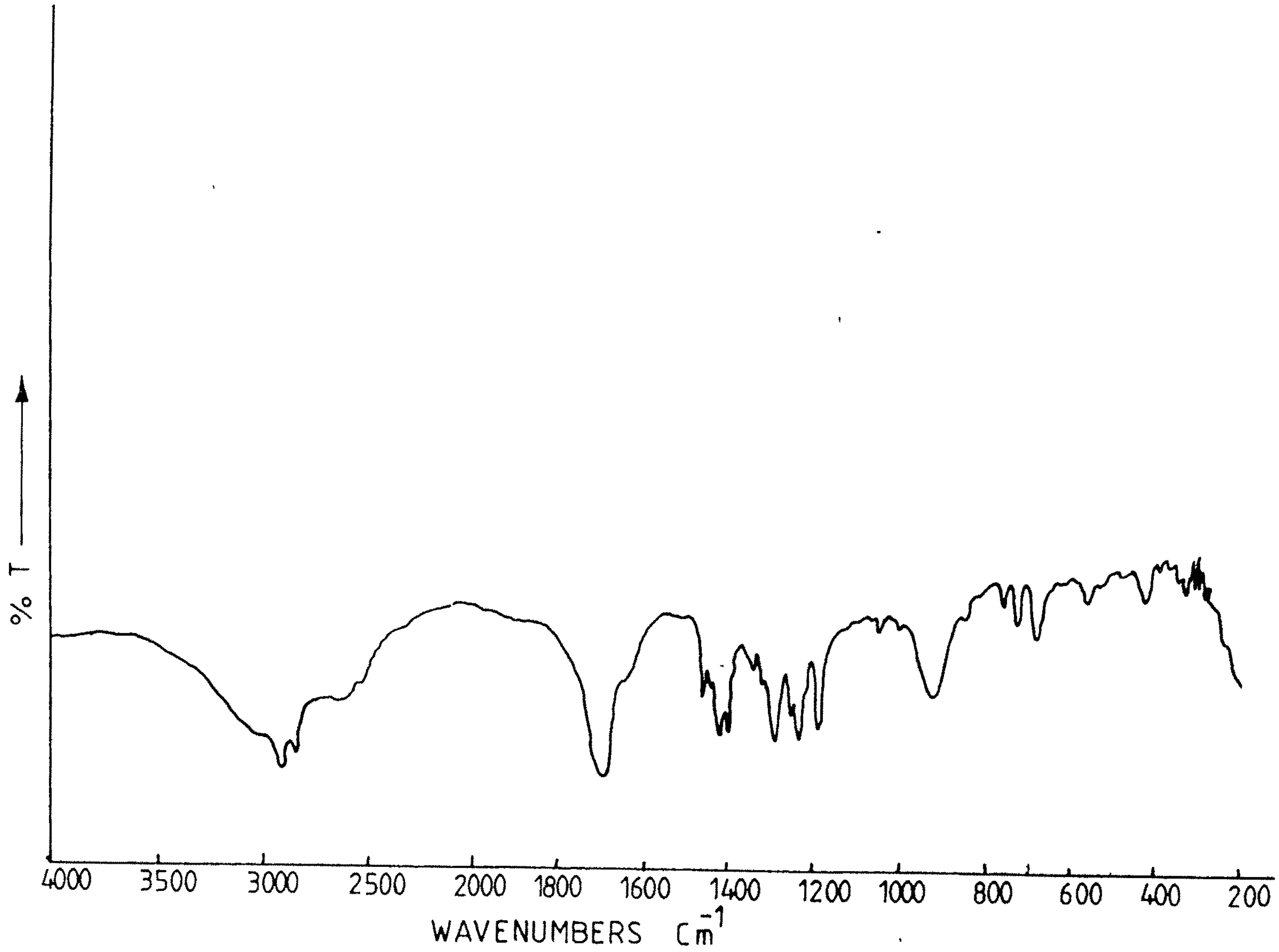


FIG II.3.(e) IR SPECTRA OF ALCOHOL SOLUBLE PRODUCTS

(a) s - CfFmc

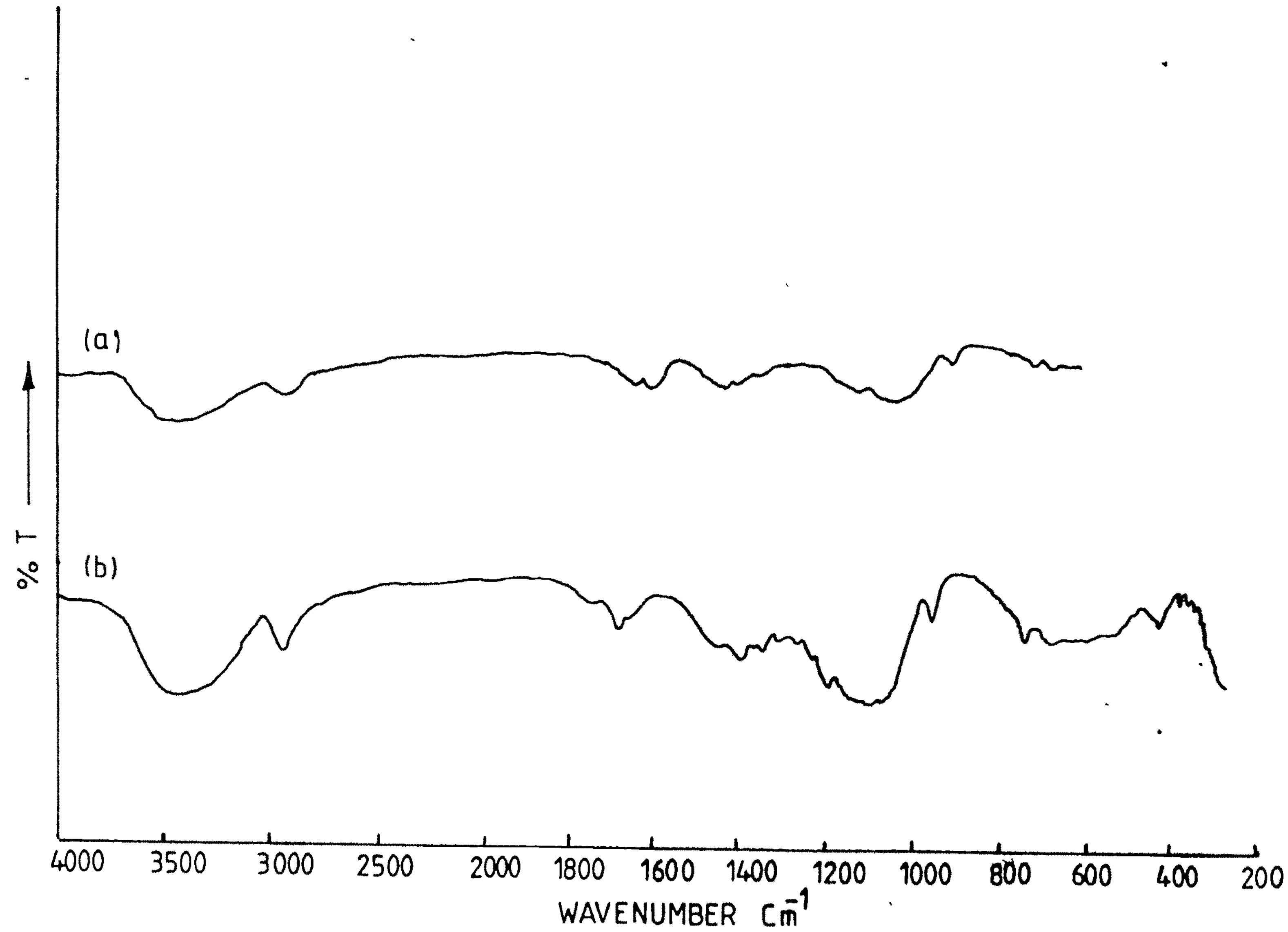


FIG. II 3 (f) IR SPECTRA OF ESTERIFIED FIBRES (INSOLUBLE RESIDUE)
(a) *i*-Cf Adc (b) *i*-Cf Fmc.

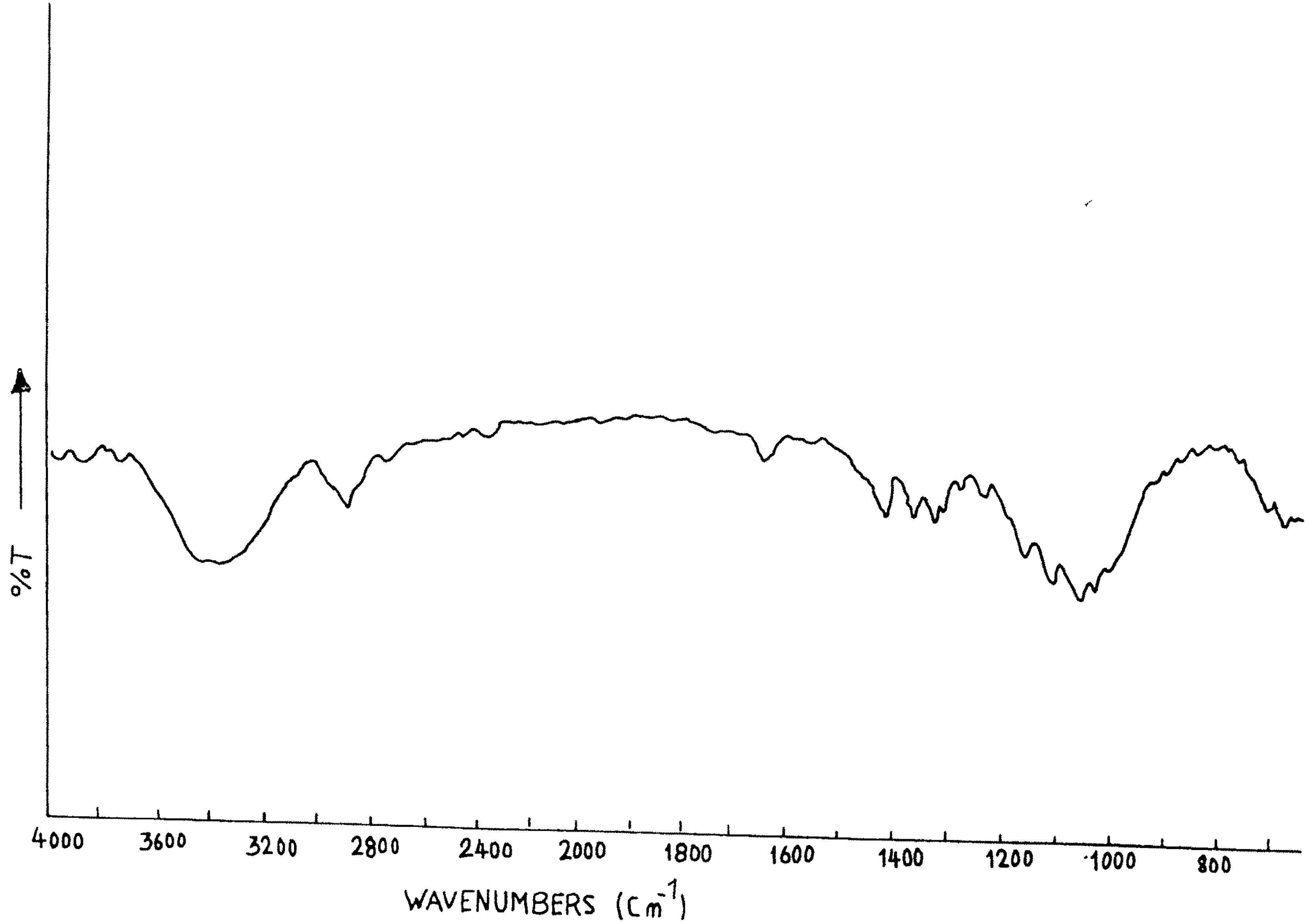
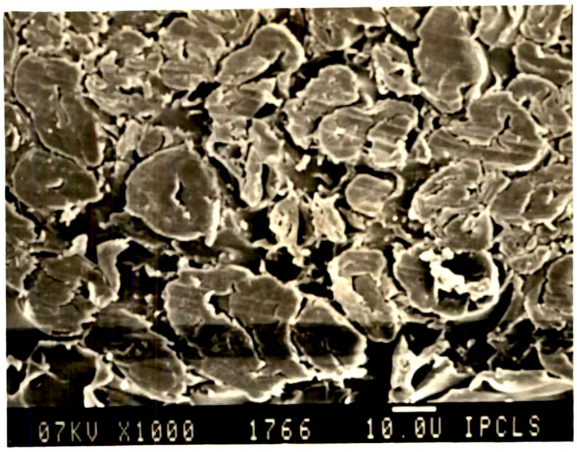
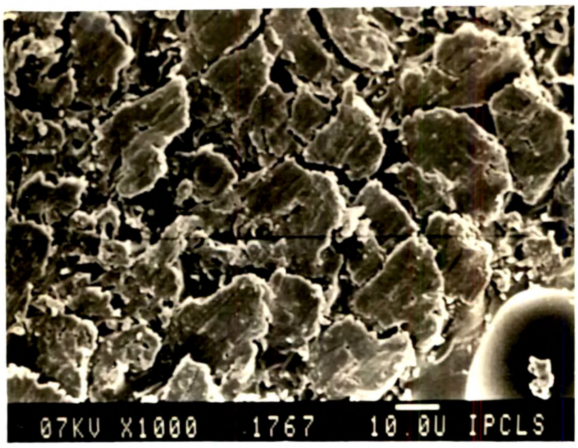


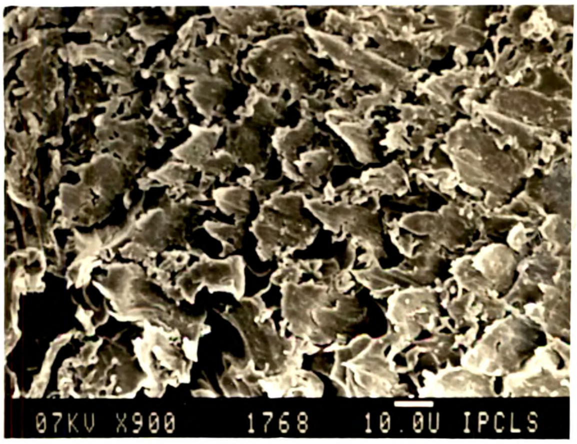
FIG. II.3.(9). IR SPECTRUM OF LAB CHLORIDE TREATED FIBRES (ALCOHOL WASHED).



(a) Yarn cross-section from cotton fabrics (untreated)



(b) Fibre cross-section from cotton fibres CfMl



(c) Fibre cross-section from cotton fibres CfAd

FIG.II.4 (a, b and c) SEM PHOTOGRAPHS OF ESTERIFIED COTTON FIBRES for 2 hr with occasional stirring. The mixture was made acidic with hydrochloric acid during reflux such that gelation took place. The fabric was removed from the flask, washed with water and dried at room temperature (product = CVF).

3 (b) Treatment with polyvinyl alcohol, formaldehyde and acid/alkali

(i) Acidic Condition

A mixture of formaldehyde solution, acetic acid and hydrochloric acid was taken in a flask and cooled to 25°c in ice bath. The weighed fabric was placed in the above mixture for about an hr. The fabric was removed from the solution and semidried.

Basic Condition

The above fabric sample was placed in a solution of polyvinyl alcohol containing Na_2CO_3 at room temperature for an hr. The fabric was taken out, dried and percentage add-on was determined (The fabric lost tear strength). (product = CVFa-1)

(ii) Acidic Condition

The mixture of acetic acid and formaldehyde solution was cooled to 20 to 25°c in ice bath. The fabric was placed in the above mixture for an hr. The fabric was removed from the solution and semidried.

Basic Condition

Semidried sample was placed in the solution of polyvinyl alcohol containing Na_2CO_3 at room temperature for an hr. The fabric was removed, washed with water, dried and percentage add-on was determined. (product = CVFa-2)

(iii) Acidic Condition

The mixture of acetic acid, formaldehyde solution and hydrochloric acid was cooled to 20 to 25°c in ice bath. Fabric was soaked in it for 1 hr. The fabric was removed from the solution and semidried.

Basic Condition

Above semidried fabric was placed in the solution of polyvinyl alcohol containing caustic soda for an hr at room temperature. The fabric was removed, washed with water and dried. Percentage add-on was determined. (product = CVFa-3)

The data regarding the amounts of the reactants used, percentage add-on, etc., are presented in table-II.6.

II.4. Cotton fabric modified by treatment with polyvinyl alcohol and paraformaldehyde

Cotton fabric was destarched as suggested in II.1.

4 (a) Treatment with polyvinyl alcohol, paraformaldehyde and acid/alkali

Paraformaldehyde dissolved in acetic acid was mixed with hydrochloric acid and cotton fabric was soaked in it for an hr at room temperature with occassional stirring. The fabric was removed from the solution and semidried.

Semidried sample was placed in 100 ml solution of polyvinyl alcohol (1%) and Na_2CO_3 (1%) at room temperature for an hr. The fabric was taken out of the solution, washed with water, dried and percentage add-on was determined. (product - CVP)

Table-II.6

No	Product	Fabric wt (g)	Polyvinyl alcohol		Acetic Acid (ml)	Formaldehyde (37%) (ml)	Hydrochloric Acid (ml)	Na_2CO_3 (g)	NaOH (g)	% add-on
			Grade	wt (g)						
1	CVF	1.0	S	1.0	-	1.0	-	-	-	1.0
2	CVFa-1	1.0	S	1.0	100	10.0	10.0	1.0	-	0.1
3	CVFa-2	1.0	S	1.0	100	10.0	-	1.0	-	0.4
4	CVFa-3(i)	1.0	S	1.0	100	10.0	5.0	-	1.0	0.1
5	CVFa-3(ii)	1.0	S	1.0	100	10.0	2.0	-	1.0	0.2

4 (b) Treatment with polyvinyl alcohol, paraformaldehyde and acid/alkali/Acetic anhydride

The fabric was placed in 100 ml polyvinyl alcohol (2%) in a beaker and left for an hr at room temperature. The fabric was removed from the solution and semidried.

Semidried sample was placed in 100 ml solution of paraformaldehyde (2%) containing Na_2CO_3 (1%). The mass was heated under reflux for half an hr with occassional stirring. The mixture was then neutralized with hydrochloric acid and heating under reflux was continued further for half an hr. The fabric was removed from the flask and dried at room temperature. Dried sample was placed in 50 ml acetic anhydride and heated under reflux for an hr. The fabric was taken out of the flask, washed with water, dried and percent add-on was determined for warp and weft. (product : CVPn (wp) - CVPn (wf)).

4 (c) Treatment with polyvinyl alcohol, paraformaldehyde and Acetic acid/Acetic anhydride

The fabric was placed in a solution of polyvinyl alcohol in a beaker and left for an hr at room temperature. The fabric was removed from the solution and semidried.

Semidried sample was placed in a solution of acetic acid and paraformaldehyde and cooled to 20 to 25°c in ice bath for an hr with occassional stirring. The fabric was taken out of the solution and dried.

Dried fabric was placed in 50 ml of acetic anhydride and mass was heated under reflux for an hr. The fabric was removed from the flask, washed with water, dried and add-on was determined. (product : CVPan)

4 (d) Treatment with polyvinyl alcohol, paraformaldehyde, resorcinol and alkali

The fabric was placed in 100 ml solution of polyvinyl alcohol (2%) in a beaker and left for an hr at room temperature. The fabric was removed from the solution and semidried.

Semidried sample was placed in a solution of paraformaldehyde containing Na_2CO_3 (1%) in water. The mass was heated under reflux for an hr with occassional stirring.

Above treated fabric was placed in a solution of resorcinol containing sodium hydroxide (1%). The mass was heated under reflux for an hr. The fabric was taken out of the solution, washed with water, dried and % add-on was determined. (product : CVPR(wp)-CVPR(wf))

4 (e) Treatment with polyvinyl alcohol, paraformaldehyde, resorcinol and acid/alkali

The fabric was placed in a solution of polyvinyl alcohol in beaker and treated as in 4 (d). The fabric was removed from the solution and semidried.

Semidried sample was placed in a solution of acetic acid and paraformaldehyde (cooled to 20 to 25°c in ice bath) for an hr. The fabric was removed from the solution and dried.

Above dried fabric was soaked in a solution of resorcinol containing NaOH and the mass was heated under reflux for an hr. The fabric was taken out of the flask, washed with water, dried and % add-on was determined. (product : CVPR-1)

4 (f) Treatment with polyvinyl alcohol, paraformaldehyde, resorcinol and alkali/acid

The fabric was soaked in a solution of polyvinyl alcohol in beaker and kept for an hr at room temperature. The fabric was removed from the beaker and semidried.

Semidried sample was placed in a solution of paraformaldehyde containing NaOH. The mass was heated under reflux for an hr. Resorcinol was added and heated under reflux for half an hr. Hydrochloric acid was added after reflux and agian heated for half an hr under reflux with occassional stirring. The fabric was taken out of the flask, washed with water, dried and % add-on was determined. (product CVPR-2)

4 (g) Treatment with polyvinyl alcohol, paraformaldehyde, acetic acid and resorcinol

The fabric was soaked in a solution of polyvinyl alcohol for half an hr at room temperature. The fabric was removed and semidried.

Semidried sample was placed in a mixture of acetic acid and paraformaldehyde and the mass was cooled to 20 to 25°c in ice bath for an hr with occassional stirring. Resorcinol was added to above mixture and mass was heated under reflux for half an hr. The fabric was removed from the flask, washed with water, dried and % add-on was determined. (product : CVPR-3)

The data regarding the amounts of the reactants used, % add-on, etc. are presented in table II.7.

II.5. Cotton fabrics modified by treatment with polyvinyl alcohol, paraformaldehyde and melamine

5 (a) Treatment with alcohol, paraformaldehyde, melamine and acid/alkali

The fabric was soaked in a solution of polyvinyl alcohol in a beaker and left for an hr at room temperature. The fabric was removed from the beaker and dried. Dried sample was placed in a mixture of acetic acid and paraformaldehyde (cooled to 20 to 25°c in ice bath) for an hr. The fabric was taken out.

Above fabric was placed in acetic acid solution and sodium hydroxide was added to it to make pH $\simeq$ 8. Malamine was added to the mixture and the mass was heated under reflux for half an hr with occassional stirring. The fabric was taken out of the flask, washed with water, dried and % add-on was determined. (product : CVPM-1)

5 (b) Treatment with polyvinyl alcohol, paraformaldehyde, acetic acid and melamine

The fabric was soaked in asolution of polyvinyl alcohol for one hr at room temperature. The fabric was then removed from the solution and dried.

Table-II.7

7 (a)

No	Product	Fabric wt (g)	Paraform-aldehyde (g)	Acetic acid (ml)	Dist. water (ml)	Hydro-chloric acid (ml)	Polyvinyl alcohol		Na_2CO_3 (g)	% Add-on
							grade	wt (g)		
1	CVP	4.0	4.0	100.00	20	2.0	K	1.0	1.0	8.5

7 (b)

No	Product	Fabric (g)	Polyvinyl alcohol		Distilled Water (ml)	Para-formaldehyde (g)	Na_2CO_3 (g)	Hydrochloric acid (ml)	Acetic anhydride (ml)	% Add-on
			grade	wt (g)						
2(i)	CVPn(Wp)	1.0	K	2.0	100	2.0	1.0	2.0	50	10.9
(ii)	CVPn(Wf)	1.0	K	2.0	100	2.0	1.0	2.0	50	15.1

7 (c)

No	Product	Fabric wt (g)	Polyvinyl alcohol		Acetic acid (ml)	Acetic anhy-dride (ml)	Paraform-aldehyde (g)	Distilled water (ml)	% Add-on
			grade	wt (g)					
3	CVPan	1.0	K	2.0	50.0	50.0	2.0	20.0	6.5

7 (d)

No	Product	Fabric wt (g)	Polyvinyl alcohol		Distilled water (ml)	Paraformal dehyde (g)	Na_2CO_3 (g)	NaOH (g)	Resor-cinol (g)	% Add-on
			grade	wt (g)						
4(i)	CVPR(Wp)	1.0	K	2.0	100	2.0	1.0	0.1	0.1	2.2
(ii)	CVPR(Wf)	1.0	K	2.0	100	2.0	1.0	0.1	0.1	3.4

7 (e)

No	Product	Fabric wt (g)	Polyvinyl alcohol		Paraformal-dehyde (g)	Acetic acid (ml)	Disti-lled (ml)	Resor-cinol (g)	NaOH (g)	HCl (ml)	% Add-on
			grade	wt (g)							
5	CVPR-1	1.0	K	2.0	2.0	50.0	20.0	0.1	1.0	-	-
6	CVPR-2	1.0	K	2.0	2.0	-	-	0.1	2.0	2.0	2.0
7	CVPR-3	1.0	K	2.0	2.0	50.0	-	0.05	-	-	3.2

Dried sample was placed in a mixture of acetic acid and paraformaldehyde (cooled to 20 to 25°c in ince bath) for an hr. Melamine was added and the mass was treated under reflux for half an hr. The fabric was removed and semidried. Semidried sample was soaked in a solution of NaOH (1%) and heated under reflux for half an hr. The fabric was removed from the flask, washed with water, dried and % add-on was determined. (product: CVPM-2)

The data regarding the amounts of reactants used, % add-on, etc. are presented in table II.8.

II.6. Cotton fabrics modified by treatment with polyvinyl alcohol butraldehyde, melamine and formaldehyde

The fabric was soaked in 100 ml solution of polyvinyl alcohol (2%) in a beaker and left for 1 hr at room temperature. The fabric was removed from the solution and dried.

The dried fabric was placed in a mixture of acetic acid and butraldehyde at room temperaure for an hr with occassional stirring. Formaldehyde and melamine were added and the mass was heated under reflux for half an hr. The fabric was removed from the flask, washed with water, dried and % add-on was determined. (product : CVBFM)

The amounts of reactants used, percentage add-on, etc, are presented in table II.9.

Break strength (B.S.) and % elongation at break of some treated fabrics are presented in table II.10 and crease recovery angle (CRA) of some treated fabrics is presented in table II.11.

Table II.8

No	Product	Fabric wt (g)	Polyvinyl alcohol		Paraformaldehyde (g)	Acetic acid (ml)	Melamine (g)	NaOH (g)	% Add-on
			Grade	wt(g)					
8	CVPM-1	1.0	K	2.0	2.0	50.0	0.1	33.0	3.1
9	CVPM-2	1.0	K	2.0	2.0	50.0	0.1	1.0	3.7

Table II.9

No	Product	Fabric (wt) (g)	Polyvinyl alcohol		Butraldehyde (ml)	Formal-dehyde (ml)	Acetic acid (ml)	Melamine (g)	% Add-on
			grade	wt(g)					
1	CVBFM	1.0	K	2.0	2.5	5.0	50.0	0.1	5.1

Table II . 10

10 (a)

No	Product	B.S. (Kg)	% elongation
1	C (untreated)	5.2	12
2	CVF	3.4	6.5
3	CVP (Wp)	9.5	12
4	CVP (Wf)	5.7	13.3
5	CVPR (Wp)	3.5	9.9
6	CVPR (Wf)	4.2	6.5
7	CVPR-1	27.2	18.8

10 (b)

NO	Product	B.S. (Kg)	% elongation
1	C (untreated)	24.1	13.7
2	CVPM (Wp)	26.3	16.3
	(Wf)	12.0	6.3
3	CVBFM (Wp)	23.7	18.2
	(Wf)	17.3	14.1

Table II.11

No	Product	CRA (°) (W+F)
1	CVF	174
2	CVPan	194
3	CVPM-1	174
4	CVPM-2	148
5	CVBFM	220

Scanning elecron micrographs (SEM) of some of the samples are shown in fig.II.5 and X-ray diffractograms (XRD) of some of the samples are presented in fig.II.6.

C. GRAFTED COTTON

II.7. Acrylografted cotton fabrics (without pretreatment)

7 (a) Grafting of acrylonitrile on cotton fabric using pottasium persulfate and sodium bisulphite(KPS + SBS)

The fabric was placed in aqueous solution of acrylonitrile in three necked round bottom flask. The acid was added to maintain pH between 2 to 3. Pottasium persulfate and sodium bisulphite were added and the mixture was heated to reflux for an hr with constant stirring.

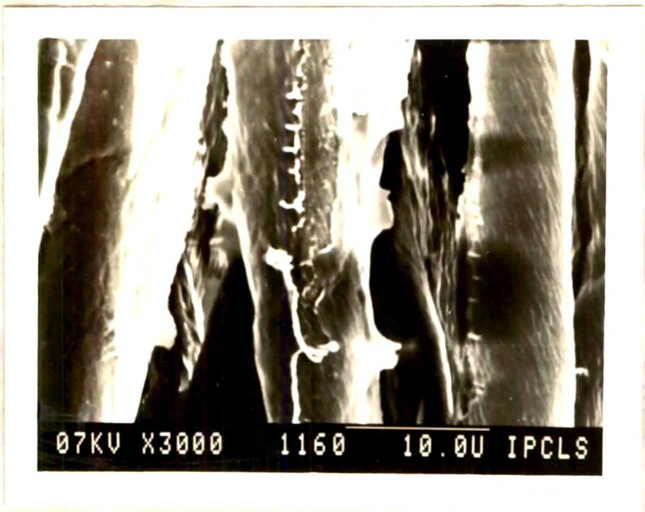
The grafted product so obtained was washed thoroughly with water and dried at room temperature. The homopolymer was removed from the graft copolymer by repeated extractions with dimethyl formamide. The grafted fabric was dried till constant weight.

7 (b) Grafting of acrylonitrile on fabric using ferrous ammonium sulfate and hydrogen peroxide (FAS + HP)

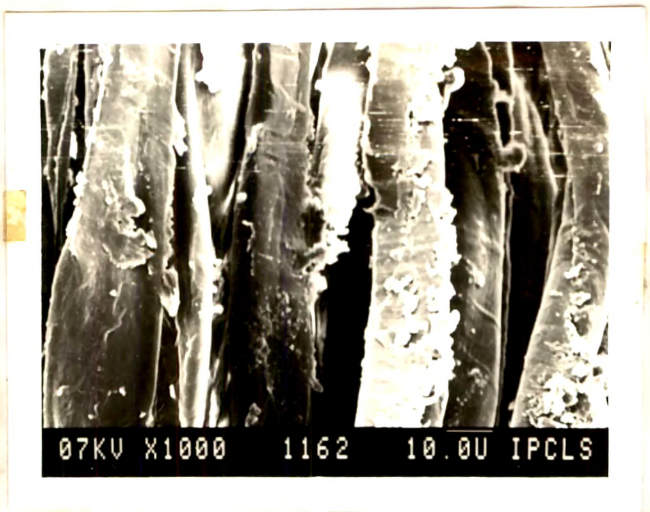
The fabric was treated as in 7(a) using ferrous ammonium sulfate and hydrogen peroxide in place of KPS + SBS.

7 (c) Grafting of cotton fabric with acrylamide using potassium persulfate and sodium bisulphite(KPS + SBS)

Acrylamide was dissolved in distilled water and fabric was placed in it. Mixture of pottasium persulfate and sodium bisulphitewas added in parts during the reaction. The mixture

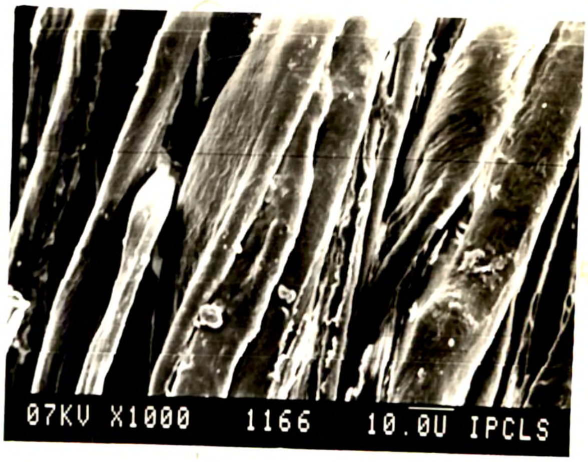


(a) Cotton yarn (untreated warp)

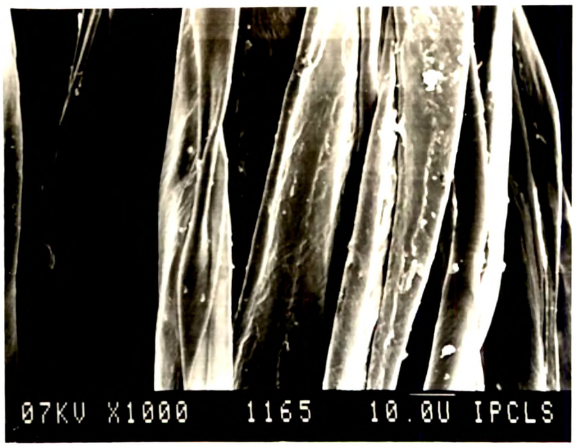


(b) Cotton yarn (untreated weft)

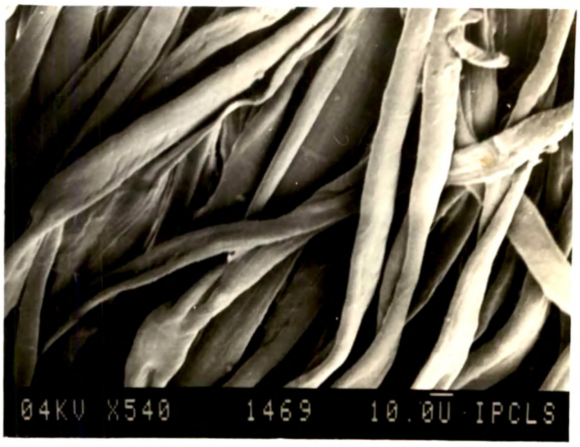
FIG.II.5 (a and b) SEM PHOTOGRAPHS OF COTTON YARN



(c) Cotton yarn from cotton fabrics CVPan



(d) Cotton yarn from cotton fabrics CVPR



(e) Cotton yarn from cotton fabrics CVPM

FIG.II.5 (c, d and e)
SEM PHOTOGRAPHS OF FORMALIZED
COTTON FABRICS

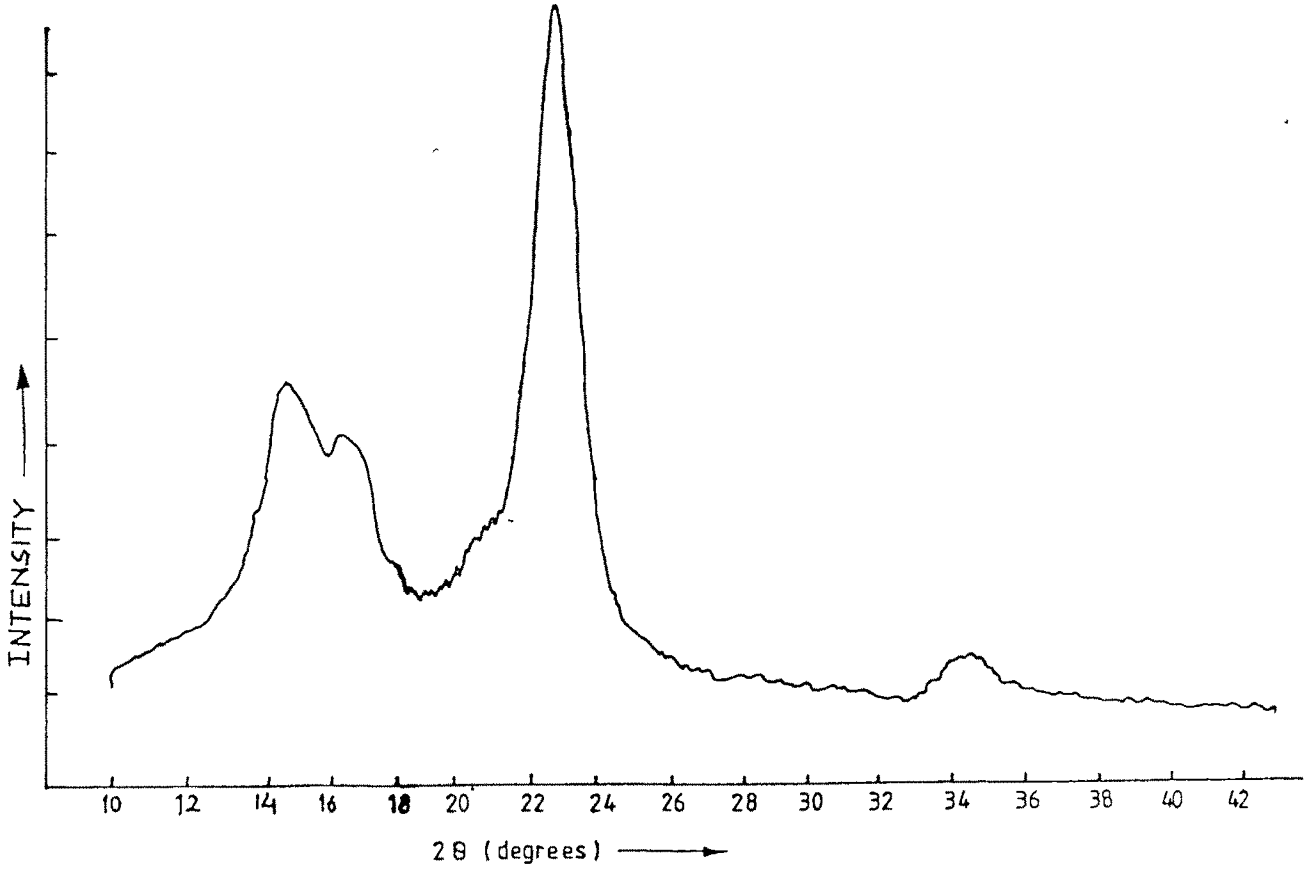


FIG. II 6(a) XRD OF UNTREATED COTTON FABRICS

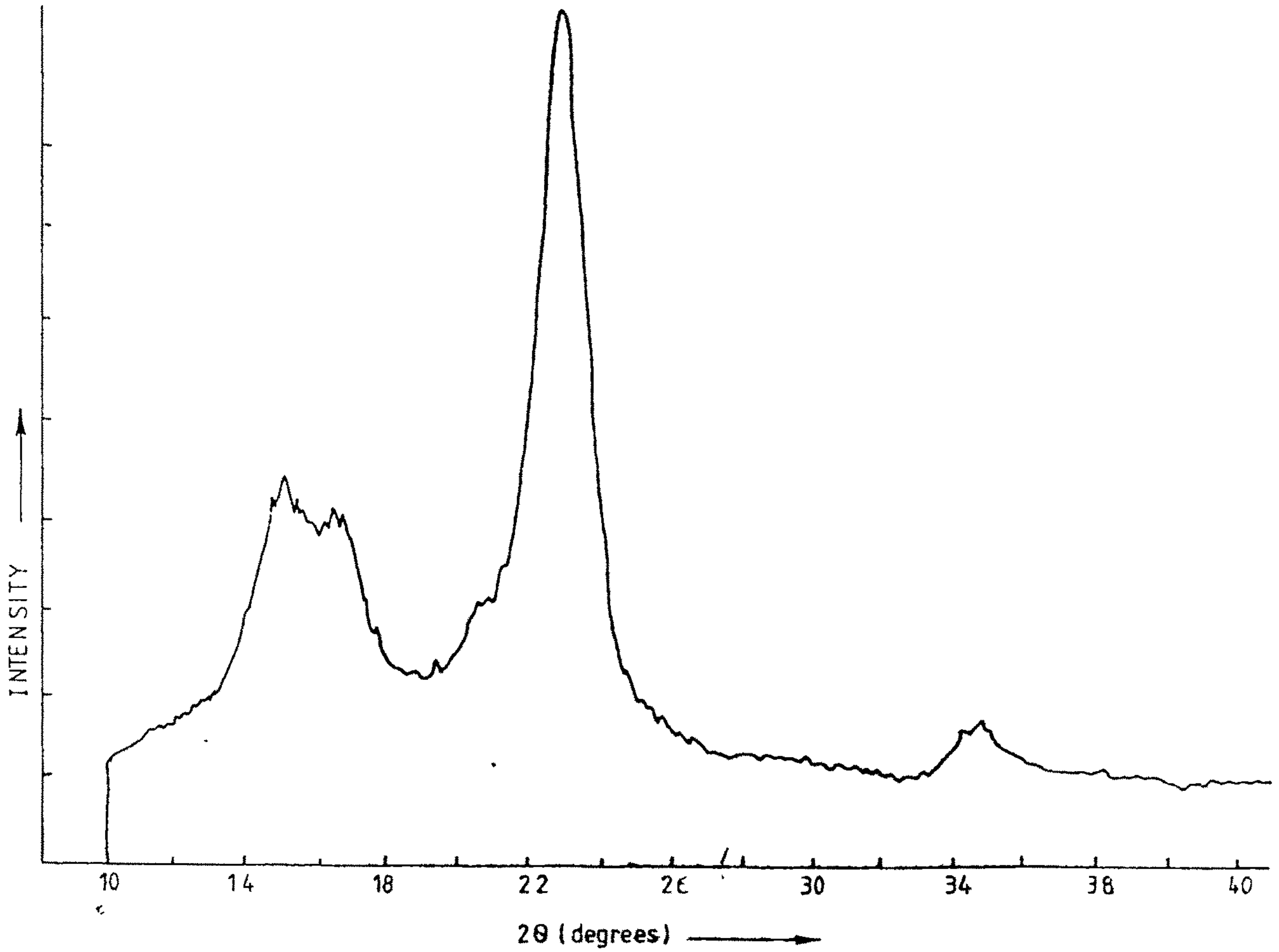


FIG II.6(b)XRD OF TREATED COTTON FABRICS(CVPM).

was heated to reflux for different time intervals with constant stirring. (Polyacrylamide gel being soluble in water will remain in solution). The grafted fabric was removed from the solution, washed with water and dried.

7 (d) Grafting of cotton fabric with acrylamide using ferrous ammonium sulfate and hydrogen peroxide (FAS + HP)

The fabric was treated as in 7(c) above, using ferrous ammonium sulfate and hydrogen peroxide in place of (KPS + SBS).

7 (e) Grafting of cotton fabric with acrylonitrile using benzoyl peroxide (BP)

The fabric was placed in water-methanol mixture, and acrylonitrile and benzoyl peroxide were added to it. The mixture was heated to reflux for different time intervals using different water-methanol mixtures. The homopolymer formed was extracted with dimethylformamide and fabric was washed and dried.

7 (f) Grafting of cotton fabric with acrylamide using benzoyl peroxide (BP)

The fabric was treated with acrylamide in place of acrylonitrile as in 7(e).

The amounts of reactants used, time and temperature of reaction, etc.,are presented in table II.12.

II.8. Acrylografted cotton fabrics and fibres (with pre-treatment)

8 (a) Pretreatment of cotton fabrics and fibres

Cotton fabrics and fibres were first purified by extraction with alcohol for 3 hrs. The fabric or fibre was removed

Table II.12

12 (a)

No	Product	Fabric wt (g)	Acrylo-nitrile (ml)	Pottasium persulfate (%)	Sodium bisulphite (%)	Water (ml)	Time (hr)	Temperature (°c)
1	K-An-g-C-1	1.0	6.0	0.6	0.4	50	1.0	(i)50, (ii)60, (iii)80
2	K-An-g-C-2	1.0	6.0	0.6	0.4	50	3.0	(i)50, (ii)60, (iii)80

12 (b)

No	Product	Fabric wt (g)	Acrylo-nitrile (ml)	Ferrous ammonium sulphate (g)	Hydrogen peroxide (ml)	Water (ml)	Time (hr)	Temperature (°c)
1	F-An-g-C -1	1.0	6.2	0.025	0.25	50	1	(i)50, (ii)60, (iii)80
2	F-An-g-C -2	1.0	6.2	0.025	0.25	50	3	(i)50, (ii)60, (iii)80

12 (c)

No	Product	Fabric wt (g)	Acryl-amide (g)	Pottasium persulfate (%)	Sodium bisulphite (%)	Water (ml)	Time (hr)	Temperature (°c)
1	K-Aa-g-C-1	1.0	5.0	0.6	0.4	50	1.0	(i)50, (ii)60, (iii)80
2	K-Aa-g-C-2	1.0	5.0	0.6	0.4	50	3.0	(i)50, (ii)60, (iii)80

12 (d)

No	Product	Fabric wt (g)	Acryl-amide (g)	Ferrous ammonium .sulphate (g)	Hydrogen peroxide (ml)	Water (ml)	Time (hr)	Temperature (°c)
1	F-Aa-g-C-1	1.0	5.0	0.025	0.25	50	1.0	(i)50, (ii)60, (iii)80
2	F-Aa-g-C-2	1.0	5.0	0.025	0.25	50	3.0	(i)50, (ii)60, (iii)80

12 (e)

No	Product	Fabric wt (g)	Acrylo-nitrile (ml)	Benzoyl peroxide (%)	Water + Methanol (ml)	Time (hr)	Temperature (°c)
1	B-An-g-C-1	1.0	6.0	1.0	100+00	3.0	60
2	B-An-g-C-2	1.0	6.0	1.0	60+40	3.0	73
3	B-An-g-C-3	1.0	6.0	1.0	50+50	3.0	80

12 (f)

No	Product	Fabric wt (g)	Acrylamide (g)	Benzoyl peroxide (%)	Water+ methanol (ml)	Time (hr)	Temperature (°c)
1	B-Aa-g-C-1	1.0	5.0	1.0	100+00	1.0	50
2	B-Aa-g-C-2	1.0	5.0	1.0	100+00	1.0	60
3	B-Aa-g-C-3	1.0	5.0	1.0	70+30	1.0	80
4	B-Aa-g-C-4	1.0	5.0	1.0	40+20	1.0	60
5	B-Aa-g-C-5	1.0	5.0	1.0	50+00	1.0	65
6	B-Aa-g-C-6	1.0	5.0	1.0	40+20	1.0	80
7	B-Aa-g-C-7	1.0	5.0	1.0	*70+30	1.0	75

* No Acidic medium was used. Other experiments were carried out in acidic media. pH = 2 to 3.

from solvent and squeezed in order to remove alcohol. The dried fabric (or fibre) was placed in 1% solution of sodium hydroxide and boiled for 10 minutes. The fabric (or fibre) was washed thoroughly with water to remove sodium hydroxide and neutralized with dilute acetic acid. The fabric (or fibre) was washed again with distilled water and dried.

8 (b) Grafting of acrylonitrile on cotton fabric (or fibre) (pretreated) using potassium persulfate and sodium bisulphite (KPS + SBS)

Pretreated cotton fabric (or fibre) was placed in aqueous solution of acrylonitrile in three necked round bottom flask. The acid was added to maintain pH 2 to 3. Potassium persulfate and sodium bisulphite were added in parts during the reaction as the mixture was heated to reflux with constant stirring. The homopolymer formed was extracted with dimethylformamide. The grafted fabric (or fibre) was washed with water and dried.

8 (c) Grafting of acrylamide on cotton fabric using benzoyl peroxide (BP)

Acrylamide was dissolved in water-methanool mixture. Pretreated fabric was placed in it and benzoyl perooxide was added. The mixture was heated to reflux with continuous stirring. The fabric was removed from the solution, washed with water and dried.

8 (d) Grafting of methyl methacrylate on cotton fabric or fibres

(i) Purification of methyl methacrylate (MMA).

Free acid was removed from methyl methacrylate by washing it with 5% sodium hydroxide solution. It was then washed thoroughly with water till washing showed neutral pH and dried over anhydrous calcium chloride. Dried material was vacuum distilled.

(ii) Grafting of cotton fabrics or fibres with methyl methacrylate using benzoyl peroxide (BP)

Methyl methacrylate was dissolved in water-methanol mixture. Pretreated fabrics or fibres were placed in it and benzoyl peroxide was added to it. The mass was heated under reflux at constant temperature with continuous stirring. The grafted fabrics or fibres were removed from the solution, washed with water and methanol and dried.

8 (e) Grafting of methacrylic acid on cotton fabric using ferrous ammonium sulfate and hydrogen peroxide (FAS + HP)

Pretreated cotton fabric was placed in aqueous ferrous ammonium sulfate (0.1%) for 15 minutes at room temperature in a beaker. The fabric was then squeezed to 75% wet pick up and dried at ambient condition.

Methacrylic acid was dissolved in distilled water and hydrogen peroxide was added to it. Pretreated fabric was placed in it and the mixture was heated under reflux at constant temperature for an hr with continuous stirring. The grafted fabric was removed and repeatedly extracted with boiling water and dried.

8 (f) Grafting of vinyl acetate on cotton fabric using, benzoyl peroxide (BP)

Pretreated fabric was placed in a mixture of benzene and vinyl acetate and benzoyl peroxide was added to it. The mass was heated under reflux at constant temperature with continuous stirring till gel formation took place. The fabric was removed, washed and dried.

The amounts of reactants used, temperature and time of reaction, etc are presented in table-II.13.

Percentage add-on of treated cotton fabrics, crease recovery angle, diameter of some of the treated fabrics, etc are presented in table-II.14. IR spectra of some of the samples are presented in fig. II.7 and scanning electron micrographs of some of the samples are presented in fig.II.8.

II.9 SORPTION STUDIES

9 (a) Moisture content

Cotton fabrics were cut into small pieces (wt = 1.0 to 2.0 g). The fabric sample was exactly weighed and placed in an oven for 24 hr at 80 to 90° C and again weighed. Moisture content percentage was calculated as suggested,

$$\% \text{ moisture content } (Q) = \frac{w - w_1}{w} \times 100$$

where w and w_1 are weights of the sample before and after oven drying respectively.

9 (b) Water sorption

The fabric sample was soaked in 100 ml water for 24 hr. It was taken out and surface dried. The sample was weighed (W_{AS}) and was then kept in the oven at 80 to 90°C for 24 hr and weighed (W_{DS}). The experiement was repeated three times and mean value was recorded. Water sorption

Table II.13

13 (a)

No	Product	Fabric/ Fibre wt (g)	Acrylo-nitrile (ml)	Potassium persulfate (%)	Sodium bisulfite (%)	Water (ml)	Time (hr)	Temperature (°c)
1	K-An-g-Ct	Fabric 1.0	4.8	0.75	0.25	50	1.0	60
2	K-An-g-Ct-f	Fibres 1.0	4.8	0.75	0.25	50	3.0	60

13 (b)

No	Product	Fabric wt (g)	Acrylamide (g)	Benzoyl peroxide (%)	Water+ Methanol (ml)	Time (hr)	Temperature (°c)
1	B-Aa-g-Ct	1.0	5.0	1.0	25+25	3.0	80

13 (c)

No	Product	Fabric or Fibres wt (g)	Methyl methacrylate (g)	Benzoyl peroxide (%)	Water+ Methanol (ml)	Time (hr)	Temperature (°c)
1	B-MM-g-Ct	1.0	1.0	1.0	15+35	3.0	80
2.	B-MM-g-Ct-f	1.0	1.0	1.0	70 + 30	2.0	80

13 (d)

No	Product	Fabric wt (g)	Methacrylic acid (ml)	Hydrogen peroxide (ml)	Ferrous ammonium sulfate (g)	Water (ml)	Time (hr)	Temperature (°c)
1	F-Ma-g-Ct-1	1.0	1.0	0.5	0.1	18.5	1.5	85
2	F-Ma-g-Ct-2	1.0	1.0	0.5	0.1	18.5	1.0	90

1. Methacrylic acid contain inhibitor.
2. Methacrylic acid free of inhibitor.

13 (e)

No	Product	Fabric wt (g)	Vinyl acetate (ml)	Benzene (ml)	Benzoyl peroxide (g)	Time (hr)	Temperature (°c)
1	B-V-g-Ct	0.5	2.2	20.0	0.04	4.0	90

Table II.14

14 (a)

No.	Product	Temperature (°C)	% Add-on
1.	K-An-g-C-1	(i) 50	2.0
		(ii) 60	10.8
		(iii) 80	8.7
2.	K-An-g-C-2	(i) 50	7.0
		(ii) 60	5.8
		(iii) 80	7.2

14 (b)

No.	Product	Temperature (°C)	% Add-on
1.	F-An-g-C-1	(i) 50	27.5
		(ii) 60	39.8
		(iii) 80	33.5
2.	F-An-g-C-2	(i) 50	31.4
		(ii) 60	29.7
		(iii) 80	19.9

14 (c)

No.	Product		Temperature (°C)	% Add-on
1.	K-Aa-g-C-1	(i)	50	3.4
		(ii)	60	3.7
		(iii)	80	1.7
2.	K-Aa-g-C-2	(i)	50	6.1
		(ii)	60	14.9
		(iii)	80	5.7

14 (d)

No.	Product	Temperature (°C)	% add-on
1.	F-Aa-g-C-1	(i) 50	23.1
		(ii) 60	20.3
		(iii) 80	18.2
2.	F-Aa-g-C-2	(i) 50	27.3
		(ii) 60	17.7
		(iii) 80	15.2

14 (e)

No.	Product	% Add-on
1.	B-An-g-C-1	-
2.	B-An-g-C-2	3.1
3.	B-An-g-C-3	3.2
4.	B-Aa-g-C-1	-
5.	-2	-
6.	-3	6.8
7.	B-Aa-g-C-4	-
8.	-5	1.5
9.	-6	2.5
10.	-7	15.1

14 (f)

No.	Product	% Add-on	Diameter (mm)
1.	K-An-g-Ct	21.2	0.23
2.	K-An-g-Ct-f	14.4	0.028

14 (g)

No.	Product	% Add-on	Diameter (mm)	**C**RA(°) (W+F)
1	B-Aa-g-Ct	10.5	0.**18**	191

14 (h)

No.	Product	% Add-on	Diameter (mm)	DCRA(°) (W+F)
1.	B-MM-g-Ct	12.5	0.22	182
2.	B-MM-g-Ct-f	12.8	0.016	–

14 (i)

No.	Product	% Add-on	Diameter (mm)	CRA(°) (W+F)
1.	F-Ma-g-Ct	1.3	0.21	171
2.	F-Ma-g-Ct-f	21.7	-	-

14 (j)

No.	Product	% Add-on
1.	B-v-g-Ct	7.2

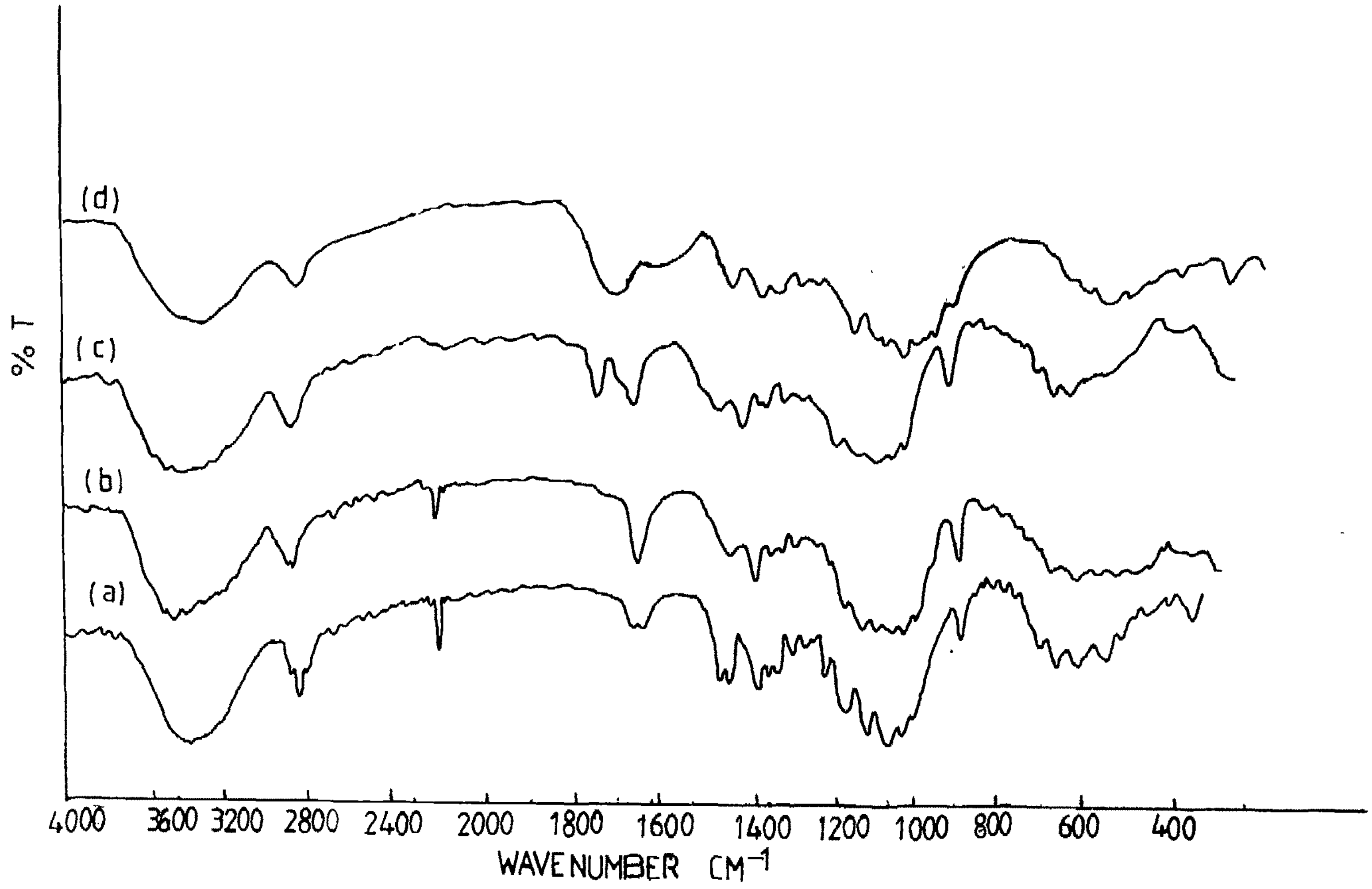
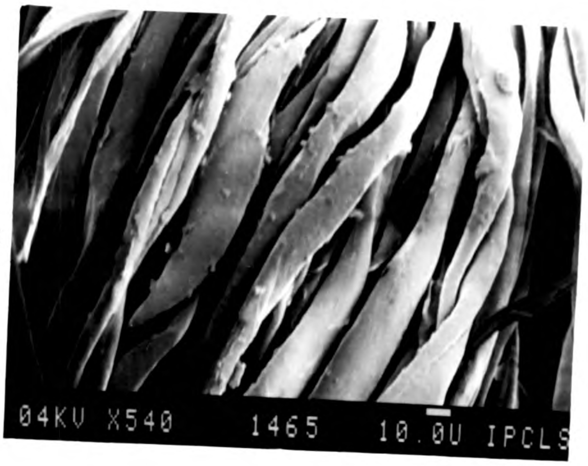
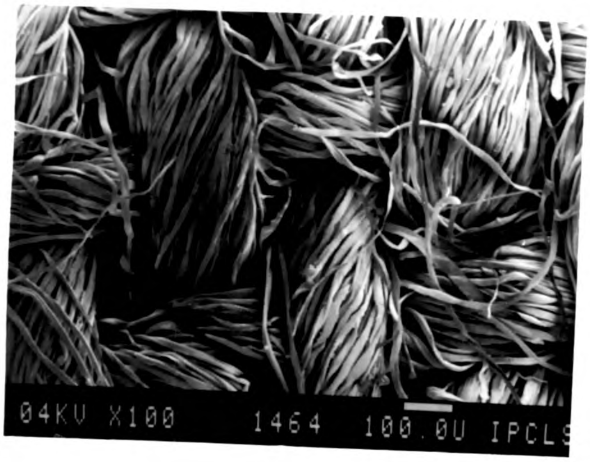


FIG II.7 IR SPECTRA OF GRAFTED FABRICS AND FIBRES

(a) K-An-g-Ct (b) K-An-g-Ct-f (c) B-MM-g-Ct-f (d) F-Ma-g-Ct

(a) Surface of cotton fabrics (untreated)





(b) Surface of cotton fabrics (untreated)

(c) Surface of cotton fabrics B-Aa-g-Ct

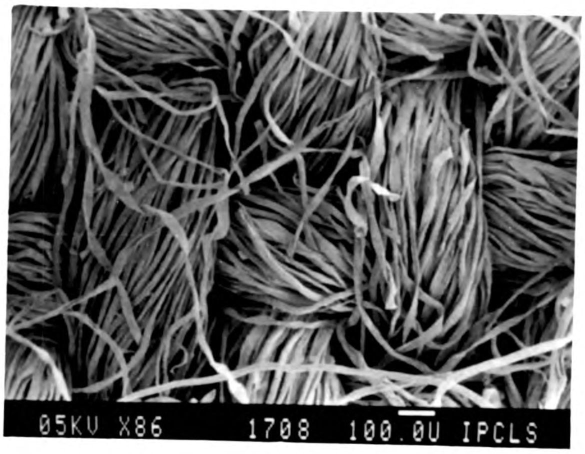
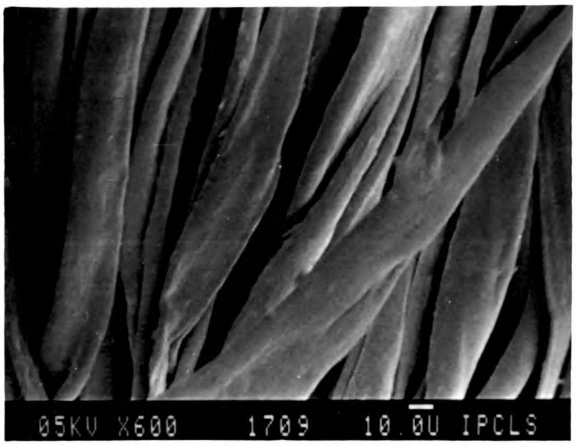
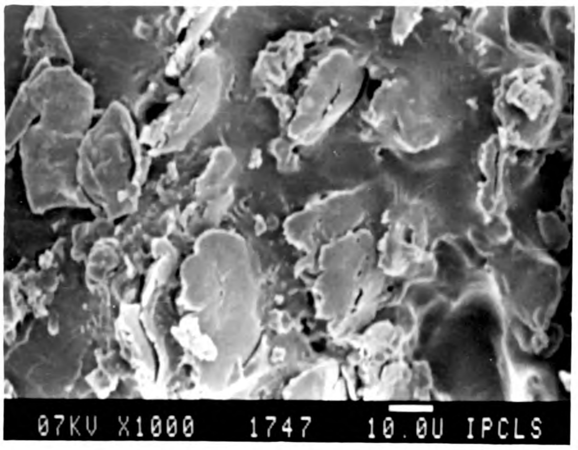


Fig.II.8 (a, b & c) SEM PHOTOGRAPHS OF GRAFTED COTTON FABRICS

(d) Surface of cotton fabrics B-Aa-g-Ct





(e) Yarn cross section from cotton fabrics B-Aa-g-Ct

(f) Surface of cotton fabrics B-MM-g-Ct

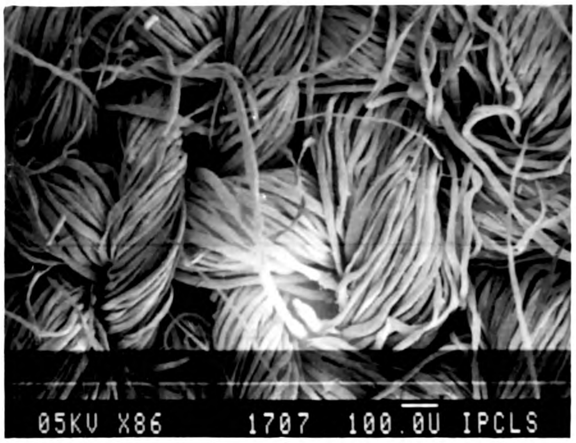
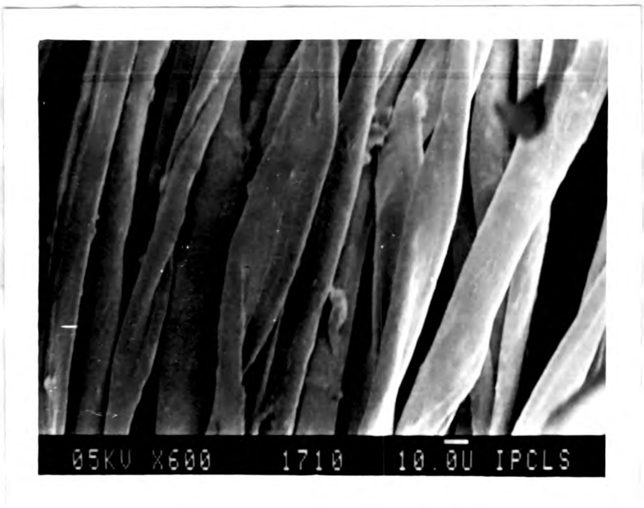
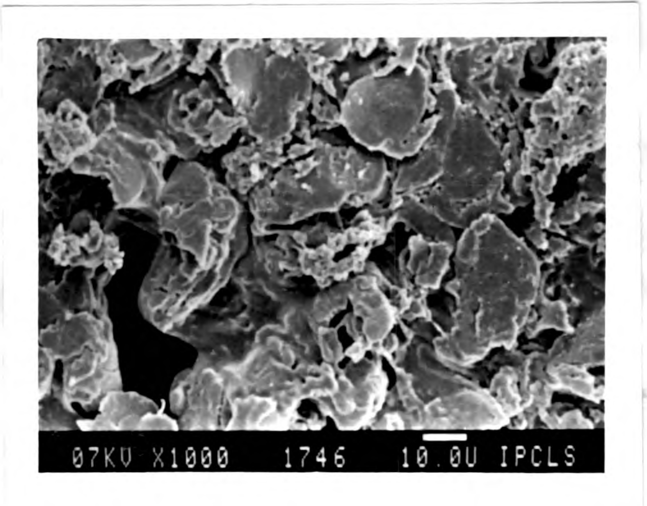


Fig.II.8 (d, e and f) SEM PHOTOGRAPHS OF GRAFTED COTTON FABRICS



(g) Surface of cotton fabrics B-MM-g-Ct



(h) Cross-section from cotton fabrics B-MM-g-Ct

Fig.II.8 (g and h) SEM PHOTOGRAPHS OF GRAFTED COTTON FABRICS was calculated as weight gain per g of dried fabric.

$$\text{water sorption} = \frac{W_{AS} - W_{DS}}{W_{DS}}$$

9 (c) Sorption from salt solution

Cotton fabrics were cut into small pieces (wt = 1.0 to 2.0 g). The fabric sample was kept in an oven for 24 hr at 95°C and weighed. The dried fabric was soaked in 1% or 10% aqueous solution of sodium chloride for 24 hr, then surface dried under vaccum at room temperature and swollen fabric was weighed (W_{AS}). Swollen fabric was put in an oven for drying at 90°C for 24 hr. The fabric was weighed (W_{DS}), then washed with water, dried at 95°C and weighed again (W_{WD}).

Moisture content percent, and weights (W_{AS}, W_{DS} and W_{WD}) are presented in table II.15.

The results of all these investigations are discussed in the following chapter.

Table II.15

Sorption

No	Product		Moisture content (%)	NaCl in solution (%)	Weights (g)		
					W_{AS}	W_{DS}	W_{WD}
1	Untreated fabric	(a)	6.6	0	2.610	1.060	-
		(b)	7.0	1	2.633	1.011	0.945
		(c)	6.7	10	2.925	1.178	0.965
2	CVPn	(a)	7.7	0	1.053	0.437	-
		(b)	7.4	1	3.630	1.370	1.337
		(c)	7.6	10	2.928	1.171	0.978
3	Csb-2		4.4	10	1.870	0.907	0.765
4	CSbc		5.0	10	1.909	0.870	0.719
5	K-An-g-c-1		7.9	10	2.758	1.105	0.937
6	F-An-g-C-1		7.3	10	2.601	1.162	0.992
7	K-Aa-g-C-2		9.1	10	2.665	1.143	0.977
8	F-Aa-g-C-2		10.5	10	2.788	1.177	0.989