Preparation, Characterization, and Performance of Conductive Fabrics: Cotton + PANi

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ABSTRACT

Conductive cotton + PANi fabrics are prepared by *in-situ* chemical oxidative polymerization of aniline using ammonium persulphate as the oxidant by a process of diffusion polymerization in a mixed bath. These fabrics are characterized by elemental analysis, XRF, ATR-FTIR, WAXD, SEM, DSC, and two-probe conductivity. Sorption properties are studied by measuring the weight uptake before and after reaction. The composite fabrics are studied for their performance after repeated washing, and tested for their flame retardancy, EMI shielding, and gas sensing properties.

Recently, electrically conductive fabrics have found uses as filters, de-electrifying coatings, electro-magnetic interference shield materials, and special purpose clothing that is dust- and germ-free. Demand for these products has increased tremendously. Among the manufacturing processes used to produce conductive materials are π-electron conjugate polymers such as polythiophene, polyaniline [19, 10], and polypyrrole [10, 6]. Of the conductive polymers, PANi has the advantage of having the most inexpensive monomer, which is essential for commercial feasibility, and also good stability and attractive colors that can be varied at will. This is due to the presence of the chemically flexible —NH— group in the polymer backbone, which not only takes part in protonation/deprotonation but also contributes to π-band formation [4]. The polymer can be easily prepared by oxidative polymerization with a high yield, and it is stable under ambient conditions [19, 1, 8]. There have been various attempts to use polyaniline with other polymeric materials in the form of films [19, 6, 1] and fabrics [10, 8], but application technology has not yet been adequately perfected [8]. Conductive polymer composites can be produced by *in situ* polymerization, since this method does not require the destruction of the substrate and provides reasonably good conductivity. Aniline monomer can be polymerized on the fabrics from an aqueous solution [8, 5] or a vapor phase [18] using appropriate oxidizing agents.

Genies *et al.* [9] reported the impregnation of PANi into glass textiles. A process to coat each individual fiber in a woven, knitted, or nonwoven textile fabric with a thin layer of conductive polymer, such as polypyrrole or polyaniline, was scaled up to commercial full-width equipment, and over 30,000 linear yards of various substrates had been processed by 1993 [13].

PANi can be obtained either chemically or electrochemically, but care should be taken because of the presence of benzidine in the bath. Although it is easily synthesized in bulk, its use is restricted due to its unprocessability by normal melt or solution techniques. Unlike metallic coatings, PANi is free from corrosion and is very stable in a highly corrosive atmosphere where other conducting coatings fail. It is also lightweight, and a very thin coating is sufficient to give good results for EMI shielding and electrostatic charge dissipation.

Two methods of obtaining conductive fabrics by *in-situ* polymerization of aniline have been reported [17]. Of the two processes for preparing conductive nylon 6 fabrics, the DPMB process is reported to yield better

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conductivity, so in our study, we use this process to prepare conductive cotton + PANi fabrics.

Our recent studies show that fibers of cotton, polyester, silk, etc., can be coated with conducting polymers like PANi and PPy. We have chosen cotton as the substrate because of its highly absorbing nature compared to other synthetic fibers. This paper reports the modification of cotton by polyaniline with a view to developing it as a highly conductive clothing material with improved performance and durability. In this study, we evaluate the stability of the fabrics after multiple washing cycles with distilled water and redoping with HCl, studying their performance as flame retardant materials, EMI shielding materials, and gas sensors.

Experimental

Aniline, concentrated HCl, and ammonium persulfate (APS), all A.R. grade, came from S.D. Fine Chemicals Ltd., India. Aniline was distilled twice before use. Gray cotton fabrics came from the Central Institute for Research in Cotton Technology. Elemental analysis involved the chemical method. The elements sulphur and chlorine were also confirmed by XRF, recorded on a Philips PW 1404 model. The sorption properties of the cotton fabrics were determined by weighing them before and after the reaction. The percent weight gain was calculated from these weights.

The thickness of the fabric samples was measured with a Baker-Mercer C-17 thickness meter with a least count of 10^{-6} meters. The infrared absorption spectra of the various samples were recorded in the range of 500–4000 cm^{-1} using a Perkin Elmer FTIR spectrophotometer, model Paragon 500, at a resolution of 4 cm^{-1} with background correction for 350 scans in the ATR mode using a KRS-5 crystal at an incident angle of 45°. The XRD patterns were recorded by a Philips x-ray generator PW 1729 and automatic x-ray diffractometer model PW 1710 unit. A nickel-filtered Cu K_α line ($\lambda = 1.542$ Å) served as a source of radiation. From the x-ray diffractogram, the lateral order or crystallinity index was determined with Manjunath's formula [14]. Crystallite size was determined from the strongest peaks of the fabric samples using Scherrer's equation [2].

The SEM images were recorded by a Philips SEM model 515 to study the surface morphology of these samples in both the longitudinal and cross-sectional views. Thermal studies of the samples were made with a Perkin Elmer differential scanning calorimeter model DSC 7. The bulk conductivity of the samples was measured using a standard two-probe conductivity apparatus in a sandwiched configuration. The I–V characteristics of all samples were studied in air as well as in a vacuum over a temperature range of 30 to 90°C.

The gas sensing experiments for ammonia involved cotton + PANi fabric samples. The flow rate was adjusted such that only one bubble passed at a time. The apparatus was designed and fabricated in the laboratory, and housed six sensor heads.

Since fabrics are normally subjected to washing in daily life, it is essential for them to perform well after washing so as to be useful in actual applications. The washability of cotton + PANi fabric samples was studied by washing these samples with distilled water for fifteen cycles, fresh distilled water being used for each cycle. The samples were dried under ambient conditions for 24 hours and then tested again for their conducting properties.

The EMI shielding experiments involved an HP-E-4411B, ESA-L series spectrum analyzer and a signal generator, Aplab 2000, using the coaxial cable method. The shielding efficiency (*SE*) was calculated by taking 45 decibels as the maximum amplitude of the unattenuated frequencies, kept constant for all experiments over the frequency range of 0–60 MHz when no sample was inserted in the sample holder. The shielding efficiency was calculated by

$$SE = (S_{AS}/S_{BS}) \times 100 \quad , \qquad (1)$$

where SE is shielding efficiency in percent, S_{AS} is shielding or attenuation of the signal amplitude after inserting the sample in the path of the signal generator and signal recorder in the sample holder, and S_{BS} is shielding or attenuation of the signal amplitude without any sample in the path, *i.e.*, unattenuated signal amplitude. An important point to note is that since fabrics have gaps between the fibers because of the weaving process, shielding values are low and hence were folded to block out the gaps statistically.

Flame retardancy was measured by noting the time required to burn a yarn 20 cm long.

Preparing Conductive Cotton + PANi Fabrics

Polyaniline was prepared by the standard chemical method [7], and the conductive fabrics were prepared as follows: Washed and dried cotton fabric samples were allowed to soak in an aniline solution (0.1 *M*, 1.0 *M*) in 1 *M* HCl for various times (1 hour, 4 hours). The bath containing the fabric was then cooled to 0–5°C and a precooled (0–5°C) solution of ammonium persulphate in 1 *M* HCl was added gradually to polymerize the aniline. The oxidant-to-aniline ratio was maintained at 1:1. Polymerization occurred with continuous mild stirring, and after the addition of all the oxidant solution, it was further stirred for different times (1 hour, 4 hours) so as to complete the polymerization. These samples were then thoroughly washed with a sufficient quantity of 1 *M* HCl in many portions so as to remove any unreacted monomer and excess ammonium persulphate, and then with an equal volume of distilled water to remove excess HCl molecules. The fabric samples were various shades of emeraldine green, resembling polyaniline, thus proving polyaniline deposition had indeed occurred.

The final substrate-to-bath ratio in both cases was maintained at 1:100, and the final concentration of aniline and oxidant was 0.05 *M* or 0.5 *M*. Normally about 2 g of fabric samples were used initially, with dimensions of about 25 × 5 cm. The different conditions used for polymerization are given in Table I.

Results and Discussion

SORPTION PROPERTIES (WEIGHT UPTAKE)

The sorption property of cotton is well known—about 7–11% moisture [12]. Because of this property, we chose cotton as the substrate so that a sufficient quantity of PANi could be taken up to produce good conductive fabrics. We measured the weight uptake of PANi in the fabrics and calculated the percent uptake or percent weight gain. The results are shown in Table I. We can clearly see that the maximum weight uptake is about 8%, but there seems to be little correlation between the period of diffusion and polymerization with weight uptake, especially when higher concentrations of monomer and oxidant are used. However, with reduced concentrations of monomer and oxidant, the weight uptake decreases drastically from 8% to about 2%.

THICKNESS MEASUREMENTS

Cotton fibers swelled due to polyaniline impregnation. The average thickness of the control fabrics was 312 μm, which increased to 338 μm for a lower concentration and then to 341 μm for a higher concentration (Table I).

ELEMENTAL ANALYSIS RESULTS

From the elemental analysis results (Table II), we see that there is a definite uptake of PANi, which can be recognized by the nitrogen content and is otherwise absent in the control cotton samples.

The percentage of nitrogen decreases from the sample with the composition of 0.5/0.5/4+4 to 0.5/0.5/1+1, though the percentage becomes somewhat steady for the compositions of 0.5/0.5/1+4 and 0.5/0.5/1+1. We observed the same trend of decreasing nitrogen content for the samples with compositions having lower concentrations of monomer and oxidant. It seems the percent nitrogen does not change much with respect to time of diffusion and polymerization, rather it seems to be greater in the samples with lower concentrations of monomer and oxidant. This is in contrast to our expectation that as the amount of PANi increases, the nitrogen content should increase. The presence of sulphur in the samples prepared with low concentrations of monomer and oxidant, which was not detected in the samples prepared with higher concentrations of monomer and

TABLE I. Various reaction conditions for preparation of cotton + PANi fabrics and some properties.[a]

Sr. no.	Reaction conditions MC/OC/DT/PT	Weight gain, %	Thickness, μ	Crystallinity, %	Crystallite size, Å	Time taken to burn, seconds	EMI shielding efficiency					
							0–20 MHz, %		20–40 MHz, %		40–60 MHz, %	
							B	A	B	A	B	A
	Control cotton	—	312	79.49	59.7	2	not applicable					
Group I												
1	0.5/0.5/4/4	7.93	345	77.45	64.8	5	100	100	78	89	67	82
2	0.5/0.5/4/1	7.06	343	77.83	56.2	5	78	100	67	93	49	82
3	0.5/0.5/1/4	8.32	—	76.40	60.5	5	60	89	49	71	38	60
4	0.5/0.5/1/1	9.25	334	76.57	64.7	5	71	89	60	67	49	60
	Average	8.14	341	—	—	5	not applicable					
Group II												
5	0.05/0.05/4/4	2.00	337	72.40	59.8	3	38	78	27	67	22	60
6	0.05/0.05/4/1	1.72	340	75.82	60.4	3	38	38	27	27	16	16
7	0.05/0.05/1/4	—	334	76.86	59.9	3	27	49	16	33	7	27
8	0.05/0.05/1/1	1.93	341	76.92	64.4	3	27	44	13	33	6	22
	Average	1.88	338	—	—	3	not applicable					

[a] MC = monomer concentration, OC = oxidant concentration, DT = diffusion time, and PT = polymerization time. Oxidant is ammonium persulphate (APS). Length of fiber taken is 20 cms. Percent efficiency is relative to time taken for the control cotton sample to burn. Note: the shielding efficiency is calculated by taking 45 decibels as the maximum amplitude of the frequencies, and is kept constant for all experiments over the entire frequency range studied. B = before redoping or as-prepared sample, A = after redoping with 1*M* HCl for 2 hours.

TABLE II. Elemental analysis results showing the weight percentages and the atomic fractions of the control cotton and the cotton + PANi samples.

Samples	Percentages of elements							
	C	H	N	Cl	S	O (by difference)	Total	Cl/N
Cont. cotton	41.25	6.79	0	0	0	51.96	100	—
0.5/0.5/4+4	42.16	7.27	1.04	2.33	0	47.20	100	0.88
0.5/0.5/4+1	41.90	7.67	0.89	2.00	0	47.54	100	0.89
0.5/0.5/1+4	41.8	7.67	0.8	1.84	0	47.89	100	0.91
0.5/0.5/1+1	41.78	7.16	0.87	2.08	0	48.11	100	0.94
0.05/0.05/4+4	42.31	7.38	7.2	0	5.9	37.21	100	—
0.05/0.05/4+1	41.08	7.45	6.2	0	4.7	40.57	100	—
0.05/0.05/1+4	41.46	6.85	7.0	0	6.6	38.09	100	—
0.05/0.05/1+1	38.16	7.33	6.1	0	8.9	39.51	100	—

oxidant, suggests that the oxidant or the byproducts are trapped inside.

This is also confirmed by x-ray fluorescence (XRF) studies, which we conducted for two representative samples from each group. For the first group, the sample 0.5/0.5/4+4 showed a chlorine percentage of 2.78 (sulphur negligible), while for the second group, the sample 0.05/0.05/1+1 showed a sulphur percentage of 6.15 (chlorine negligible). From the x-ray diffraction studies, we established that there is greater penetration of the monomer molecules from a dilute solution compared with a relatively concentrated solution. Because of this, when polymerization occurs at 0–5°C, the fibers shrink and penetration of the oxidant molecules becomes difficult. Moreover, polymerization naturally starts at the first layer of contact with the monomer on the surface of the fibers, which further hinders penetration of the oxidant molecules, thereby reducing the polymerized product. This is probably because of the excess unreacted persulphate ions trapped in the interstices, which is supported by observation of the lower conversion of the monomer into the polymer when the polymerization time is lowered from 4 hours to only 1 hour.

The Cl/N ratio also increases from 0.88 to 0.91 and further to 0.94 from 0.5/0.5/4+4 to 0.5/0.5/1+4 to 0.5/0.5/1+1. The values of these Cl/N ratios are quite high compared to the normal Cl/N ratios for PANi prepared by the standard method. The hydrogen content also increases because the Cl/N ratio is increasing, which might be due to moisture or remaining HCl.

The important observation is that a higher percentage of (0.5 + 0.5) aniline and oxidant always yields a greater degree of polymerization, weight uptake, etc., than with a second group with a lower percentage of aniline and oxidant. In the subsequent discussion, therefore, we have decided to discuss one sample from each of these two groups as the illustrative one, although all samples (four in each group) were fully characterized.

ATR-FTIR ANALYSIS

Figure 1 shows the ATR-FTIR spectra of the control cotton, the PANi prepared by the standard method, and the cotton + PANi fabric. The broad band centered at 3323.5 cm^{-1} in the ATR spectra of the control cotton is due to the stretching vibrations of the OH groups, combined to form inter- and intra-molecular hydrogen bonds [20].

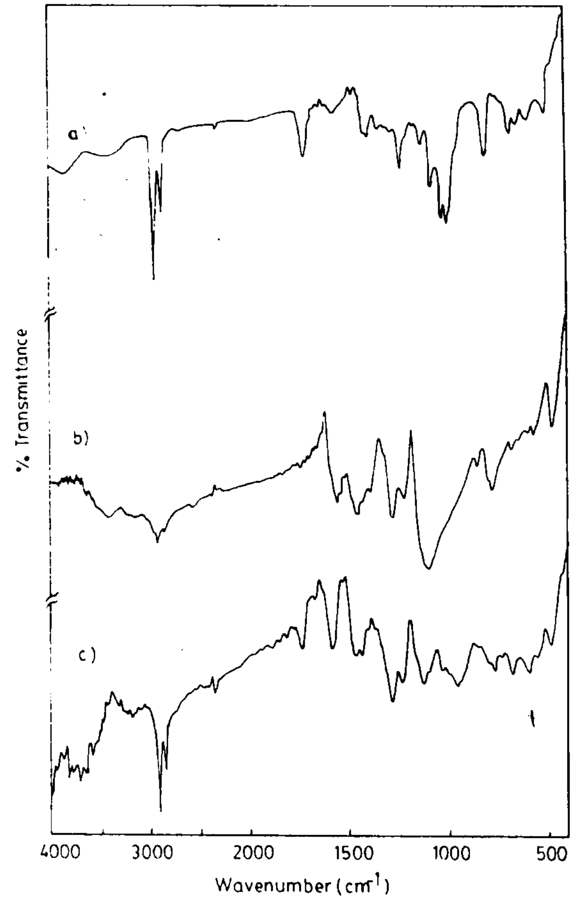
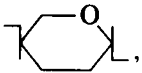


FIGURE 1. ATR-FTIR spectra of (a) control cotton, (b) PANi prepared by standard method, and (c) cotton + PANi.

The shoulder peak at 2953.9 cm^{-1} in the spectrum of the control cotton, which is just discernible, is due to CH_2 antisymmetric stretching vibrations [16] of the secondary CH_2OH groups present in the glucose units of cellulose. A careful look at this region in the composite spectrum shows that it appears to be missing in the spectrum of the PANi-incorporated composite fabrics, which might be due to the relatively low number of secondary CH_2OH groups present after the inclusion of PANi. The most intense peak in the spectrum of the control cotton sample is the peak at 2922.8 cm^{-1}, which is the CH stretching band of the glucose units of cellulose, its major constituent. The CH_2 symmetric stretching band of the control cotton appears at 2853.1 cm^{-1}.

The C—O linkage of the lactone ring is observed at 1740.5 cm^{-1} in the spectra of cotton fabrics. The adsorbed water molecule is seen as a small peak at 1652.4 and 1637.8 cm^{-1}, while the absorbed water molecule is seen as a weak shoulder at 1623.1 cm^{-1}. The aromatic rings of the impurities present as lignin are observed by the bands at 1597.1 and 1523.9 cm^{-1} of the respective C═C stretching vibrations of the ring [20]. OH in-plane bending vibrations are observed at 1470.6 cm^{-1} as a shoulder, and CH_2 symmetric bending vibrations are observed at 1452.9 cm^{-1}. The external deformations (wagging) present in cellulose and its derivatives are found at 1260.3 cm^{-1}.

The three characteristic peaks at 1164.7, 1105.9, and 1058.9 cm^{-1} are due to the stretching vibrations of , —C—O—H, and —C—O—C groups present in cellulose. The shoulder peak at 985.3 cm^{-1} has been reported but not assigned in the literature [16]. External deformations, rocking vibrations of cotton, which are normally found within the range of 950 to 800 cm^{-1}, are seen at 918.0 and 874.0 cm^{-1} in the control cotton fabric spectrum. The ring-breathing mode of vibration is doubtful as reported in the literature [16] and is found at 799.6 cm^{-1}.

OH out-of-plane deformations or out-of-plane bending vibrations, which normally occur over a broad range in the region from 700 to 400 cm^{-1}, are seen at 699.3, 664.7, 617.5, 558.2, 517.6, 488.2, and 450.0 cm^{-1} as small peaks with diminishing absorbances.

Characteristic PANi peaks are observed in the spectra of the PANi-incorporated cotton fabrics. The very intense, broad peak at 1589.1 cm^{-1} is due to the salt form of the quinoid form of PANi, which merges with the broad C═C ring breathing mode of the impurities present as lignin. The characteristic benzenoid repeat units of PANi are also observed as peaks at 1482.4 cm^{-1}. The shoulder peak at 1405.9 cm^{-1} is due to the benzene ring breathing mode of PANi molecules. The characteristic C—N and $(C—N)^+$ stretching vibrations of PANi are observed at 1298.8 cm^{-1}, and the N═Q═N stretching of the quinoid units of PANi, which is due to electron delocalization, is seen at 1147.1 cm^{-1}. The C—H out-of-plane bending vibrations characteristic of 1,4 disubstituted compounds are observed at ~ 823 cm^{-1}. This shows that the aniline molecules polymerize only at the *para*-positions. The C—H stretching vibrations of the terminal phenyl rings of PANi are observed at 752.9 cm^{-1}.

The peak at 2853.1 cm^{-1} in the spectrum of the control cotton is quite sharp, with the base of the peak at both ends following the baseline properly. But when PANi is incorporated, the base toward the lower wavenumber side becomes broad, indicating that hydrogen bonding is taking place. In the literature, the region identified for hydrogen bonding in cotton is from 2500–3000 cm^{-1}. The other peak affected after polymerization of aniline inside the cotton matrix by *in-situ* chemical polymerization is the C—O stretching vibration of the lactone ring being shifted to the lower wavenumber side, thereby suggesting that there is some interaction occurring at this site. The peak corresponding to the absorbed water is shifted to the higher wavenumber side, which shows that the water molecules are more tightly bound. This can be due to the presence of chloride ions, which might be solvated by the water molecules, also reflected in the peak corresponding to the adsorbed water molecules. CH_2 symmetric bending vibrations are also observed at lower wavenumbers because of the possible interaction of the chloride ions in the PANi with the hydrogen of the OH in CH_2OH to form hydrogen bonds. Also, the ring stretching vibration of the glucose units of cellulose becomes more difficult, which might be due to some steric hindrance after the inclusion of PANi molecules. The peaks due to the O—H out-of-plane bending vibrations at 500 cm^{-1} are being shifted to the lower wavenumber side. This suggests that the interaction of the PANi molecules with the cellulose molecules occurs at the hydrogen of the OH in CH_2OH. Also, the C—H stretching vibration of the CH_2OH is affected more compared to the other C—H stretching vibrations present in the ring.

WAXD ANALYSIS

The WAXD patterns for the control cotton, the PANi prepared by the standard method, and the cotton + PANi fabrics are shown in Figure 2. It is interesting to determine how the diffusion of PANi in cellulose affects the structure of the cotton fibers. Therefore, we have determined percent crystallinities for all the impregnated samples, and their values are shown in Table I. Note that the percent crystallinity decreases to a small extent in all the PANi-impregnated fabrics. The maximum decrease is in

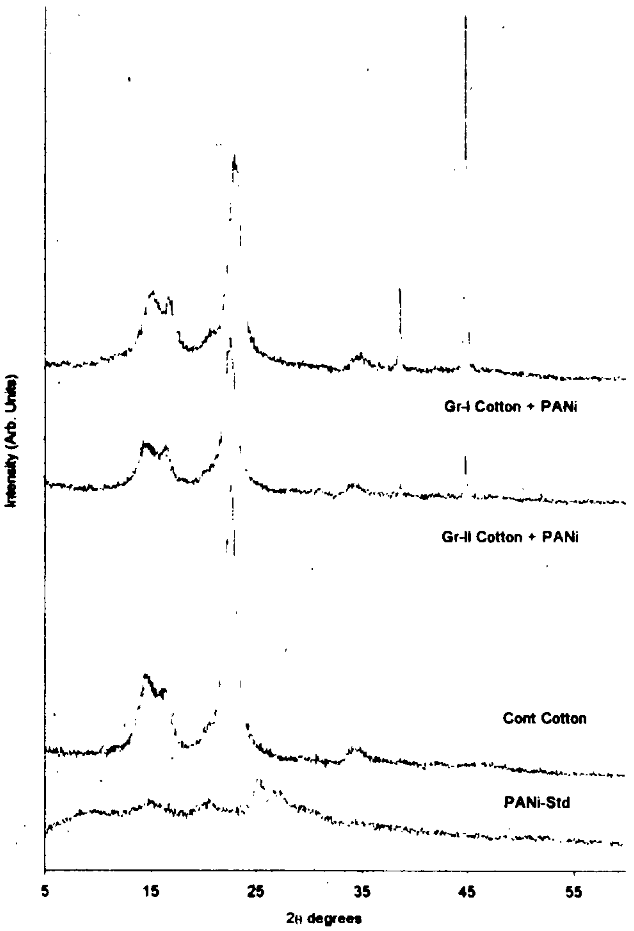


FIGURE 2. WAXD patterns of (a) PANi-std., (b) control cotton, (c) cotton + PANi (Group II), (d) cotton + PANi (Group I).

the samples prepared with maximum diffusion and polymerization times in both sets of concentrations. Further, the samples in which a dilute solution of the monomer is involved show maximum changes in percent crystallinity, which suggests that the monomer is able to penetrate more deeply into the interstices of the cotton fibers in the latter case. Though there is no fixed trend for the changes in percent crystallinity for the samples with greater concentrations of monomer and oxidant, the trend is clearer in the samples with lower concentrations of monomer and oxidant. In the latter case, as the polymerization time increases from 1 hour to 4 hours, the percent crystallinity decreases, and as the diffusion time increases again, the percent crystallinity decreases further. This suggests that the crystalline areas of cotton are not easily penetrated at lower diffusion times and in the concentrated solution of the monomer, but are more easily attacked when the solution is dilute and allowed to swell for longer duration, *i.e.*, 4 hours. But because the percent crystallinity is affected slightly, we can conclude that the PANi molecules are able to diffuse only into amorphous and *para*-crystalline regions. This is further supported by the fact that the change in crystallite size is not significant and has no correlation with processing parameters (Table I).

The increase in the relative intensity values of the first two peaks corresponding to the (101) and ($10\bar{1}$) planes is quite significant with respect to the (002) plane. This shows that the (101) and ($10\bar{1}$) planes are growing at the expense of the (002) plane because the relative intensity directly suggests the relative number of such planes being present in the material. As we see from Table III, the major peak for cotton corresponding to the (002) plane is slightly displaced toward a higher diffraction angle. Also note that the other two peaks corresponding to (101) and ($10\bar{1}$) planes are similarly shifted. The trend within a group of the same molar concentrations of both monomer and oxidant is that as the diffusion time and polymerization time increase, the decrease in the percent crystallinity is greater and, similarly, the shift in the 2θ positions is also greater, *i.e.*, there is a decrease in the interplanar spacings. The shift in the values of the d spacings can be understood by considering the monoclinic lattice structure of cotton, which suggests that the (101) and ($10\bar{1}$) planes are coming closer to each other, also reducing the β angle in the process.

TABLE III. WAXD peak tables showing the 2θ positions, d values, and relative intensities (RI) of the three peaks obtained in the diffractograms of the fabric samples.

Sample composition	2θ	d, Å (101)	RI	2θ	d, Å ($10\bar{1}$)	RI	2θ	d, Å (002)	RI
Control cotton	14.78	3.022	29.8	15.12	2.959	25.2	22.67	3.993	100
0.5/0.5/4/4	15.11	2.958	24.0	15.78	2.835	26.5	23.22	3.831	100
0.5/0.5/4/1	14.89	3.000	31.5	16.43	2.835	26.0	22.80	3.901	100
0.5/0.5/1/4	14.66	3.05	28.7	17.25	2.600	26.7	22.86	3.891	100
0.5/0.5/1/1	14.83	3.012	33.6	16.33	2.742	26.8	22.94	3.877	100
0.05/0.05/4/4	15.17	2.946	36.0	16.61	2.697	30.7	23.91	3.804	100
0.05/0.05/4/1	15.27	2.928	33.3	16.75	2.675	31.2	22.71	3.916	100
0.05/0.05/1/4	15.11	2.958	33.6	16.56	2.705	28.9	23.22	3.831	100
0.05/0.05/1/1	15.00	2.979	35.8	16.46	2.721	27.8	22.86	3.891	100

Thus, the diffusion of the aniline molecules is facilitated more by a dilute solution, and subsequent polymerization seems to push the cellulose molecules closer to each other. In this process, polymerization of the aniline monomers occurs on the surface of the cellulose lattice, rupturing the tie molecules, and the crystal becomes strain-free. This leads not only to a small decrease in crystallinity but also to changes in the lattice parameters. Figure 2 shows typical diffractograms for PANi powder prepared by the standard method, the control cotton fabric, the cotton + PANi composite from a higher concentration group, and the cotton + PANi composite from a lower concentration group. The PANi prepared by the standard method is semicrystalline (curve a), and there are definite peaks. In the cotton + PANi composite, the peak of the cotton at 22.67° has a hump-like shape, probably due to the presence of PANi in the composite. Further additional sharp peaks appear at 38.55° and 44.80° corresponding to pure PANi crystals as reported earlier [3]. This reveals the presence of PANi in the composite. Note the increased intensity of the peak at 44.8° for the lower concentration sample as compared to the higher one, again confirming that a lower concentration solution has a stronger effect.

SEM STUDIES

The surface views and cross-sectional views of SEM micrographs of the control cotton and cotton + PANi are shown in Figures 3 and 4. Just a glance at the fabrics with the naked eye shows a uniform color (in this case, green), suggesting that PANi has penetrated into the cotton fabrics. However, the SEM studies reveal how evenly the surface has been coated and the depth of penetration.

From these SEM studies, it is clear that the PANi particles are very evenly deposited on the fabric, and are seen as small globules. The diameter of the globules varies from 0.21 to 1.4 μm, the average being 0.64 μm. The surface studies clearly reveal uniform distribution even at the microscopic level, which is necessary for the reproducibility and reliability of applications. The average diameter of the treated fiber is 24 μm (it varies from 16 to 30 μm), which is quite a bit higher than that for the control cotton (10–15 μm). This evidently shows that diffusion and polymerization of aniline in the fiber has swollen it significantly [15]. This trend was also evident at the macroscopic level in terms of the increased thickness of the fabric (from 312 to 340 μm), and is further confirmed by the studies of the cross sections of fibers and clearly shown by the micrographs.

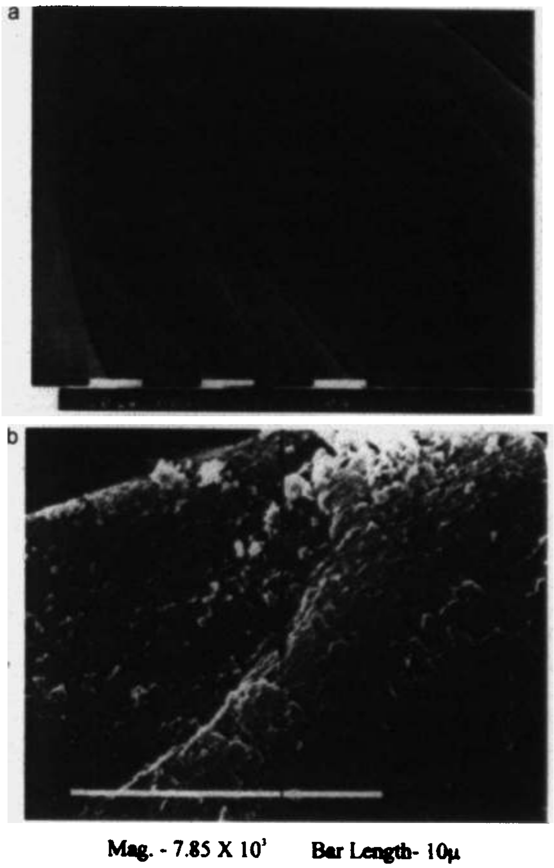


FIGURE 3. SEM micrographs of (a) surface of control cotton fiber, (b) surface of cotton + PANi fiber.

THERMAL STUDIES (DSC)

The DSC thermograms for the control cotton, the PANi prepared by the standard method, and the cotton + PANi are compared in Figure 5. The DSC thermograms of the control cotton and the optimized sample with maximum concentrations of monomer and oxidant and maximum periods of diffusion and polymerization are considered here. The thermogram of PANi prepared by the standard method is also used for comparison.

From the thermograms, we see that there is lot of moisture present in the control cotton and the PANi prepared by the standard method, whereas the fabric impregnated with PANi shows a much more suppressed peak due to moisture at a lower temperature (78°C). This is because the PANi molecules occupy about 50% of the region available for moisture absorption, leaving little space for actual moisture to be absorbed. The thermograms of the composite fabrics show more stability in that the heat uptake is steadier up to ~200°C, whereas in the control cotton fabric samples, heat uptake continuously increases from 125°C. This suggests that the composite fabric samples are more thermally stable after the incorporation of PANi molecules.

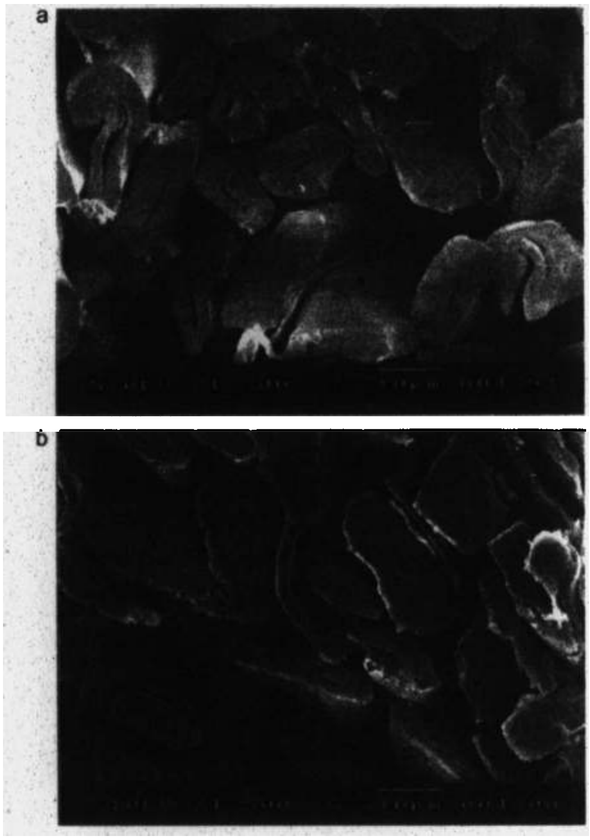


FIGURE 4. SEM micrograph of cross sections of (a) control cotton fiber and (b) cotton + PANi fiber.

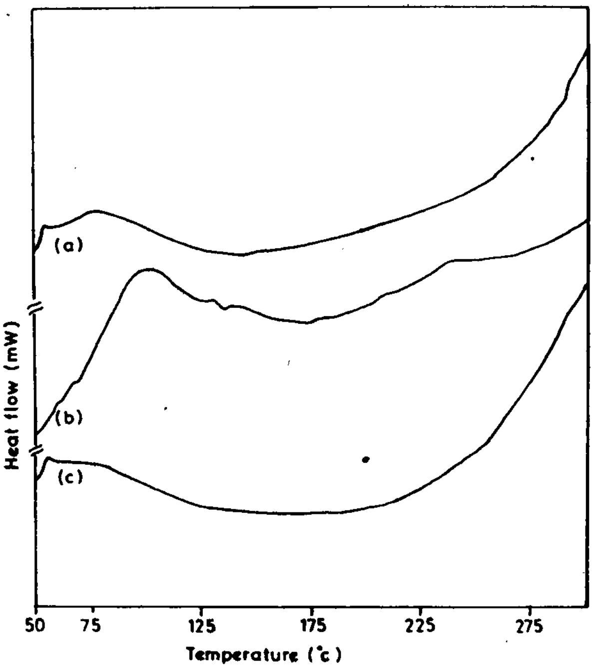


FIGURE 5. DSC thermograms of (a) control cotton, (b) PANi-Std., (c) cotton + PANi.

CONDUCTIVITY STUDIES

We studied the electrical conductivity of the samples in a normal environment at 65 RH and also in a vacuum. Note that the current in the sample in the vacuum is at least one order of magnitude less than that in air. These results may be seen in terms of the environmental humidity and the fact that both cotton and PANi salt can absorb moisture. The presence of moisture will assist the electron transfer because of proton formation. This can also be due to chlorine being removed.

The average conductivity values for the treated samples are 10^{-5} and 10^{-6} S/cm, respectively, for the first and second sets of samples with higher and lower concentrations of monomer and oxidant. This is a significant improvement in the conductivity levels compared to the control cotton, whose conductivity is about 10^{-10} S/cm. The I–V plot of the control cotton at room temperature in a vacuum shows that it is linear in nature, which is typical of an insulator, and shows the ohmic nature of conduction. We studied the I–V plots along with the log I versus log V and log σ versus $1/T$ plots for the treated samples to determine the nature of conduction. The I–V plot has a nonlinear nature, and the log I versus log V plots also show different slopes at different regions, indicating that the conduction mechanism is space charge limited current with many traps.

As the temperature increases from room temperature to 90°C, there are transition temperatures at which different trends in the current are observed. For example, up to about 50–60°C, the current value decreases with increasing temperature from room temperature upwards, but after the transition temperature, the current starts increasing with temperature. This transition might be due to the adsorbed and absorbed water molecules present in the samples, since only a vacuum is ineffective in drying the samples, which have an affinity to water molecules. Also, DSC studies reveal that the water molecules are eliminated at about 80°C in the conductive fabrics in N_2 atmosphere, which in a vacuum might be eliminated at a lower temperature. But this kind of conduction behavior is almost the same as for the virgin conducting polymer PANi, whose I versus V plots and log I versus log V plots are also nonlinear in nature, showing the presence of distinct regions well defined at higher temperatures. This shows that the conduction mechanism is space charge limited current filled with traps. Although some of the chlorine might also be removed, the important point to note is that the conduction mechanism of the composite is similar to that of the virgin conducting polymer. The current values decrease with increasing temperature up to 70°C, above which the current steadily increases with temperature. Hence, this behavior might be characteristic of PANi and is probably due to the increased chain mobilities. This leads to a greater number of charge carriers in the conduction band at higher temperatures and hence the semiconductor-like behavior at such temperatures. The temperature dependence can be seen in the log σ versus $1/T$ plot (Figure 6). A positive slope in the low temperature region shows metal-like behavior from 29 to 60°C, in that the current decreases as the temperature increases. Above 60°C up to 90°C, the fabrics show semiconductor-like behavior, *i.e.*, there is a negative slope for the log σ versus $1/T$ plot.

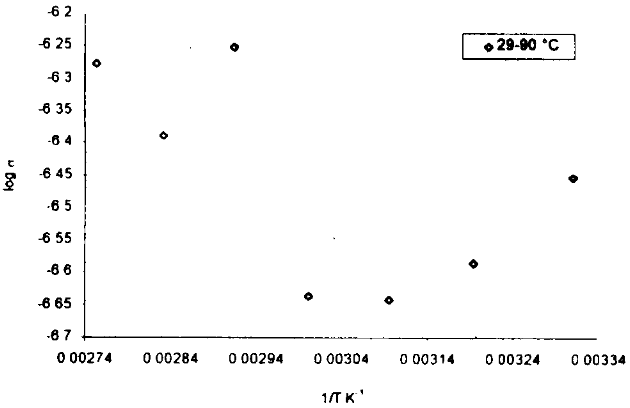


FIGURE 6. Log σ versus $1/T$ plot of cotton + PANi.

The variation of log σ in the low temperature region suggests that it is metal-like behavior and may be due to the presence of metallic islands formed by PANi molecules. The conduction mechanism seems to be electron hopping between the localized states on the metallic sites. The presence of moisture will affect the barriers between the metallic islands and increase the hopping mechanism.

WASHABILITY OF COTTON + PANi FABRICS

Washing with water and detergents is a normal process for all fabric types. After ensuring that our treatments yielded good fabric impregnation with the conducting polymer PANi, we thought it would be interesting to determine the stability of such fabrics. The composite (cotton + PANi) fabric was therefore subjected to repeated washing in by distilled water, since only one wash may not cause much change.

The important property that is being investigated is the electrical conductivity of a composite fabric. The electrical conductivity of the control cotton at room temperature in air is of the order of about 10^{-10} S/cm, and after impregnation with PANi, it increases to about 10^{-6} S/cm for the lower concentration of monomer samples and a maximum of about 10^{-4} S/cm. This shows that there is a significant increase in the electrical conductivity with very small amounts of PANi.

We monitored the changes in the electrical conductivity of such repeatedly washed conductive cotton fabric samples through their I–V characteristic plots. Figure 7 shows a typical I–V plot of the cotton + PANi fabric for the sample with monomer and oxidant of 0.5 M each and the diffusion time and polymerization time of 4 hours each. There is quite a significant decrease in the electrical conduction due to the number of washes. These samples were tested after every five washing cycles and their I/V characteristics were recorded. We observed that after washing the current decreased, and by fifteen cycles the current reached an almost steady value.

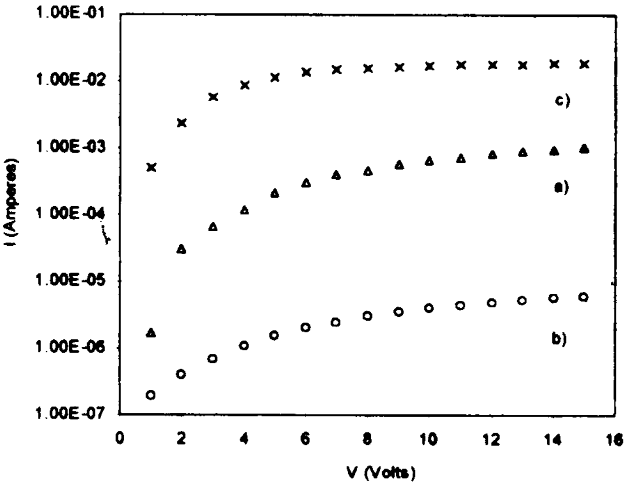


FIGURE 7. I/V response of cotton + PANi fabrics: (a) as prepared, (b) after 15 cycles of washing with distilled water, (c) after redoping with 1M HCl for 2 hours.

Since after washing with water, the current decreased by two orders of magnitude, but visibly there was no color change in the fabric samples and the solution, it was necessary to ascertain the exact reason for such a decrease. We therefore redoped these samples with chloride ions by dipping in a 1 M HCl solution for about 2 hours, then drying under ambient conditions for 24 hours, and measured their conductivity values. The results show that the conductivity imparted by our process is not permanent. We anticipate that the conductivity decrease is either due to the removal of dopant molecules or polyaniline. Since we did not see much change in the color of the fabric (deep green), PANi removal seems to be less probable.

PERFORMANCE OF WASHED FABRICS ON REDOPING WITH 1 *M* HCl

After redoping with 1 *M* HCl for only 2 hours, there was a sudden rise in current compared to the washed samples (Figure 7). The current values reached one order more than that for the prepared samples, *i.e.*, overall there was an increase of three orders of magnitude in the current. If the PANi molecules had been removed in the washing process, then the current wouldn't have risen to the same order and the washing water would have been colored green, which did not happen. The increased conductivity with redoping with HCl shows that the dopant chloride ion is responsible for such changes. Further additional increases in the prepared sample can be explained as follows: It is likely that while preparing these samples, they were extensively washed, so some sites where chloride ions could have been residing were vacant. These sites would be filled upon redoping, hence the rise in current. This is normally the case with polyaniline prepared by the standard method, where the as-prepared samples are not fully doped and reach a saturation level only after redoping in an HCl solution of 1 *M* or higher concentration.

FLAME RETARDANT BEHAVIOR OF COTTON + PANi FABRICS

We tested the flame retardancy of these samples by suspending 20-cm long yarns from them and applying a flame to them at the lower end. The yarns showed very good results compared to the control cotton. The results are given in Table I.

The time taken to burn the samples after incorporating polyaniline was significantly higher than for the control samples. Note that the treated fabric did not start burning immediately when the flame was applied, but took a considerable time to start the burning process and burned very slowly. Thus the thermal stability of the fabric impregnated with polyaniline was indeed good, and the fabric acquired good stability against flame as well. Note that regardless of the diffusion and polymerization times, the time taken to burn a fixed length of the sample was constant for a particular combination of concentrations of monomer and oxidant. However, it was higher for samples treated with higher concentrations (0.5/0.5) of aniline than those with lower concentrations (0.05/0.05).

The delayed ignition shows good flame retardancy, although the samples are not fully fireproof. Table I shows that even for a very small loading or incorporation of conducting polymer, there was a greater than 100% increase in the time taken to burn, which shows that these fabrics have excellent flame retardancy. Also, when the loading increased to about 7–9% of the conducting polymer from about 2%, the time taken to burn the sample increased further by 100%.

EMI SHIELDING EFFICIENCY OF COTTON + PANi FABRICS

The EMI shielding efficiency values in terms of the percent attenuation after inserting the sample in the path of the frequency generator and detector are given in Table I. There is a marked effect on shielding efficiency with respect to diffusion/polymerization time as well as the frequency range employed. In general, as the diffusion time or polymerization time decreases, the shielding efficiency decreases for all concentrations and all frequency ranges. This shows that as the polymerization time decreases, the amount of converted monomer decreases. As the diffusion time decreases, we can report that since the diffused monomer content itself is decreasing, polymer formation is less compared with the sample prepared with greater diffusion time. Further, as the frequency increases, the efficiency decreases for all frequency ranges studied.

Since conductivity of cotton + PANi fabric samples showed an increase in conductivity after redoping, we also performed EMI shielding experiments after redoping of the fabric samples with 1 *M* HCl for 2 hours and then drying in ambient conditions for 24 hours. The EMI shielding efficiency values for the fabric samples before and after redoping are shown in Table I, and they have increased after redoping for all treatments.

USING COTTON + PANi COMPOSITE FABRICS AS GAS SENSORS

It is interesting to study the performance of such composite conductive fabrics for their gas sensing ability. The principle for such responses is as follows: the electronic cloud of incoming gaseous molecules interacts with the charged species present on the conducting polymer backbone, leading to either more delocalization if the molecule has atoms that are electron-accepting in nature like oxygen, or disturbing the delocalization if the molecule has atoms that are electron-donating in nature like NH_3.

The response of the cotton + PANi fabrics to ammonia vapors is shown in Figure 8. Note that when the ammonia vapors pass into the chamber, the current sharply decreases and then stabilizes for an exposure of 10 minutes. When the inflow of gas stops and pumping starts, the current values again start to increase, but not to the same extent as that of the unexposed composite conductive fabric. This behavior is similar to that of PANi prepared by the standard method and exposed to ammonia gas, indirectly proving that the response is because of

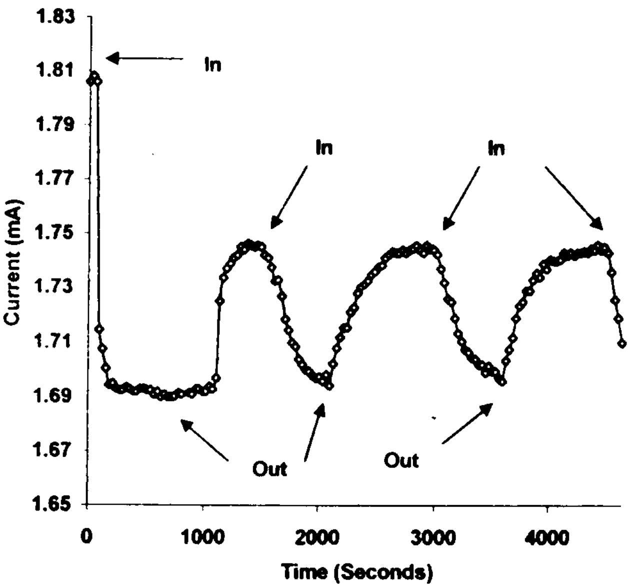


Figure 8. Response of cotton + PANi to repeated adsorption and desorption of ammonia vapors.

interactions with PANi molecules only. The slow rise in current during desorption proves that gas effusion is a very slow process.

In general, the ammonia molecules interact with the charge on the nitrogen atom, disturbing the charge delocalization. ESR experiments by Kang *et al.* [11] showed that when a conducting polymer like PANi is exposed to oxygen gas, there is a decrease in conductivity. The reasons are the reduction in charge carriers and also their mobility, but the latter is more influential. This is true when the metallic island theory is considered to explain the conduction mechanism of PANi. These metallic islands are formed by the polarons on the PANi chain, which is the place where the incoming gas molecules interact with the PANi chain. In the case of ammonia, because of the partial reduction in the charge, the number of such metallic islands decreases, leading to decreased conductivity.

Conclusions

Preparing conductive cotton fabrics by the DPMB process is possible due to *in-situ* polymerization of the aniline monomer by an oxidative polymerization reaction at low temperatures. These fabrics show significant weight uptake, revealing that the diffusion of aniline monomers at room temperature is taking place and subsequent polymerization is possible even at low temperatures. The diffusion is actually more penetrating in the case of a dilute monomer solution. From the structural studies, we can conclude that the crystalline regions of the cellulose structure are not easily affected, and the cellulose molecules interact with the PANi molecules. SEM studies reveal a very uniform and dense deposition of the PANi molecules, even after thorough washing. The thermal studies show that PANi-impregnated cotton fabrics have better thermal stability. The conductivity studies clearly show that the conduction mechanism is that of the virgin conducting polymer, even though it has been incorporated within a nonconducting insulating matrix.

From the results of washability, redoping, flame retardancy, and EMI shielding before and after redoping with 1 *M* HCl, we see that these conductive fabric samples are excellent materials for applications in industry, stealth technology, and special anti-flammable clothing.

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Investigating the Drape Behavior of Seamed Knit Fabrics with Image Analysis

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ABSTRACT

Drape is one of the most important fabric aesthetic properties. Although there are many studies related to the drape structure of seamless fabrics, knowledge about the drape behavior of seamed fabrics is very limited. This study analyzes the effect of five-thread overlock seams (stitch type 516, seam type Ssa-1) on the drape behavior of heavy weight knit fabrics to provide prediction equations for drape. Results are statistically analyzed. From the regression analysis, the drape coefficients of seamed heavy weight knit fabrics and the rating values obtained from a subjective analyses are predicted with 0.80 and 0.86 correlation coefficients, respectively.

Drape is the deformation of fabric produced by its own weight when only part of it is directly supported [9]. The drape behavior of fabric is very important for apparel design and fabric quality and also for composite textiles when a fabric is draped over a mould surface before consolidation under heat and pressure.

Studies of this subject began with Chu *et al.* [7, 8], then Cusick [9] developed an instrument based on the principle of the Drapemeter described by Chu *et al.* [7]. Many experimental [13, 16, 17, 19] and theoretical studies, including computer simulations [1, 3–6, 10, 12, 14, 18, 20, 22] have followed them.

All these studies involved seamless fabrics, except for Hu *et al.* [15]. They studied the effect of a plain seam (lockstitch) on the drape structure of a woven fabric. They showed that the drape coefficient (DC) increases with the number of seams, but it is slightly affected by increases in the seam allowance. Changes in DC % with the number of seams and the seam allowance are more noticeable for heavy weight fabrics than for light weight fabrics. Among these studies, Gaucher and King [13] presented equations for predicting the drape coefficient of seamless knit fabrics, depending on their bending and thickness.

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