

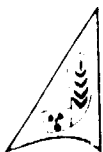
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**RADIATION-INDUCED GRAFTING ONTO WOOL
FUNDAMENTAL STUDIES AND PRACTICAL APPLICATIONS**

by

D. Müller-Schulte



ATOMIC ENERGY BOARD
Pelindaba
PRETORIA
Republic of South Africa

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SAMEVATTING

Stralingsgeïnduseerde hegtoetse is op afsonderlike wolvesels uitgevoer. Verskillende vinylmonomere is vir hierdie doel gebruik en hulle is in twintig verskillende oplosmiddels geheg wat vir hulle swel- en oplosvermoë gekies is. Die toetse is beide in die teenwoordigheid en afwesigheid van water uitgevoer.

Die teenwoordigheid van water veroorsaak dat die polimeeropname aansienlik verhoog word. Daar is bevind dat metanol en miersuur/metanol die mees geskikte oplosmiddels met die hoogste waterstofbindingvermoë is. Die vogopname van wol is van die hidrofiliese en hidrofobiese eienskappe van die gehegte polimere afhanklik. Die toetse met afsonderlike vesels dien as grondslag vir die analoë hegtoetse op wolprodukte. Die permanente plooië is deur hegting met hidrofobiese polimere en polimere met 'n hoë glasoorangstemperatuur verbeter.

ABSTRACT

Radiation-induced grafting tests were done on single wool fibres. Different vinyl monomers were used for this purpose and they were grafted in twenty different solvents which were selected for their swelling efficiency and solvent parameters. The tests were done once with and once without the addition of water. The presence of water causes the polymer uptake to increase considerably. Formic acid/methanol and methanol were found to be the most suitable solvent systems, as they have the highest hydrogen-bond interaction efficiency. The moisture uptake of wool depends on the hydrophilicity and hydrophobicity of the grafted polymers. The single-fibre tests serve as a basis for analogous grafting tests on wool fabrics. The permanent-press was improved by grafting with hydrophobic polymers and polymers with a high glass-transition temperature.

1. INTRODUCTION

Whereas until 1970 only 7.3% of the fabrics used in the textile sector consisted of wool, the trend nowadays is to return to natural fibres [1]. This has had a negative effect on the production of synthetic fibres and the industry is faced with serious problems at present [2]. Although natural fibre possesses a better wearing quality, as well as other favourable textile properties, a number of finishing processes have been developed over the past two decades. Shrink resistance is one of the major improvements. Developments in the field of nuclear technology have made radiation technology available to the textile sector [3]. Several possibilities have been created by modifying the structure of wool through the radiation-induced graft copolymerisation of vinyl monomers. Since Burke *et al* [4] published their first test results most papers have dealt with basic fundamental aspects such as graft kinetics [5–8], modification of chemical and physical properties [9–14], structure interrelationships [11,12,15,16,17], solvent influence [13,18–22], etc. Whereas several radiation-grafting processes are already being applied on an industrial level in the cotton and synthetic-fibre sector (Deering-Milliken, Dow Chemical, Burlington [23–26]), similar processes in the wool sector have not progressed beyond the laboratory stage. Garnett and Leeder [27], Needles *et al* [28] and McLaren [12] are the only research workers who have dealt with some aspects that could be of industrial significance.

Fundamental studies on single fibres to determine the effect of solvents as well as solvents and monomers on wool, serve as a basis for the present study. The objective was to develop radiation-induced grafting processes for the improvement of permanent-press that can be applied on a technological level. Although all the studies on single fibres and later on fabrics had to be done with the aid of a ^{60}Co radiation source, and since basically only an electron accelerator can be used for an industrial application of the process, the experiments were planned in such a manner that full attention could be paid to potential technological aspects. The test procedure was kept as simple as possible, and an attempt was made to keep the polymer uptake of the fabrics below 30%. The test conditions described in the literature, e.g. high vacuum rates and polymer uptakes of more than 100%, are quite unacceptable for commercial applications.

Ten different monomers and 20 different solvent systems were used for the treatments on single fibres. In this manner some details were obtained of the wool/solvent/monomer interactions that are vital to the optimisation of the graft test on wool fabrics.

2. EXPERIMENTAL

2.1 Materials and Preparation

Commercial grade wool was continuously extracted for 12 h with methanol and petroleum ether and then dried for 6 h at 50 °C in a vacuum oven (12 mm Hg). The wool

fabrics used were in an unextracted state, as supplied by the South African Wool and Textile Research Institute.

2.2 Irradiation Sources

An AECI Gammabeam 650 (50 kCi) and a Gammacell 220 (10 kCi) irradiation source were used for the irradiation work.

2.3 Grafting Tests

Round-bottomed flasks with gas inlets were used for the grafting tests. After the components had been put inside the flasks, nitrogen was added for 3 min; the dose rate amounted to 6–7 kGy/h and the total dose 18–21 kGy. Thereafter the single fibres were extracted for 16 h in a suitable solvent in a Soxhlett unit, benzene was used for styrene, 2-vinylpyridine (2-Vpy) and 4-vinylpyridine (4-Vpy), chloroform was used for butyl methacrylate (BMA), iso-butyl methacrylate (i-BMA), methyl methacrylate (MMA), and vinyl acetate (V-acetate). The samples grafted with acrylonitrile (AN) and acrylic acid (AA), 1-vinyl-2-pyrrolidone (V-Pdon) were each stirred in dimethylformamid (DMF) in water at room temperature. During this procedure the solvent was renewed three times. The extraction was followed by vacuum drying of 5 h at 50 °C under 12 mm Hg. The wool fabrics were kept for 16 h in these solvents which were renewed three times. The drying process was the same as in the case of single fibres.

2.4 Calorimetric Tests

A Perkin Elmer DSC-1b differential scanning calorimeter was used for this purpose. The experimental conditions were as follows: Heating rate 16 °C/min, sensitivity 5–10 mcal/s, mass 2–5 mg and the thermograms were recorded in nitrogen.

2.5 X-ray Tests

The X-ray tests were done with the aid of a Debye Scherrer Powder Camera Phillips PW 1024 (wide angle) and a Kiessig camera with nickel-filtered $\text{K}\alpha$ radiation (small angle). The distance between film and preparation was 50 cm. The X-ray diagrams were recorded on film (Agfa-Gevaert Structurix D7P).

2.6 Amino Acid Analyses

The amino acid analyses were performed with an automatic Beckman amino acid analyser. Samples were hydrolysed with 6N HCl at 110 °C for 24 h in sealed evacuated tubes. Phenol was added to prevent the destruction of tyrosine.

3. RESULTS AND DISCUSSION

3.1 Radiation-Induced Grafting on Single Wool Fibres

The swelling capacity of the solvents is a decisive factor in grafting processes. Details are supplied in the literature of

the effect of a variety of organic solvents as well as organic and inorganic acids [13,18 - 22,27]. If the solvent has a high affinity for the fibre and is able to penetrate into it, absorption of a dissolved substance can be improved provided it has a high affinity itself. On the other hand, if the dissolved substance has a low affinity, its absorption can be hindered. If, however, the solvent is not able to penetrate into the fibre, a dissolved substance still has a good change of being absorbed if it has a limited affinity for the fibre. The preceding facts also apply to wool, even though different interactions (hydrophilic, hydrophobic, salt and hydrogen bonding) occur because of the heterogeneous structure of wool.

As was mentioned earlier, systematic tests were initially done on single fibres to determine the fibre-solvent-monomer interaction. The various solvents were selected on the basis of swelling capacity, as determined by Koenig [29,20], Atkinson [31,32], Blankenburg [33] and Böhme [34] etc.; the solubility-parameter concept of Hoy [35] was also used. These parameters consist of polar, non-polar and hydrogen bonding and are based on the average cohesive energy density.

The monomers were selected on the basis of hydrophobicity, hydrophilicity and glass-transition temperatures. These criteria have a decisive effect on the

permanent-press properties to be discussed later on. The total polymer uptake of the various solvents appear in Table I.

The best grafting results were obtained with hydrophobic monomers such as MMA, styrene and BMA. The effect of water which increases the polymer uptake on average by 36% is also very strong in hydrophobic monomers. No unambiguous evidence is available that the graft kinetics themselves are affected by the presence of water, but it can be safely accepted that certain micro areas in wool swell more after the addition of water and monomer diffuses into these areas. This observation is supported by observations made by Speakman [36]; he discovered that n-octanol molecules diffuse into a fibre that has been preswelled by methanol. Tests made by Abbot [37] also showed that no swelling occurs in anhydrous acetic acid and pyridine after a 15 min treatment. As soon as water was added, 50% swelling occurred after 3 min for acetic acid and 25% swelling for pyridine.

The standard deviation values can be accepted as a measure for the large number of different possible fibre-solvent-monomer interactions.

The following sequence of the best graft-accelerating solvents or solvent mixtures is based on the above data.

TABLE I

Polymer uptake of single wool fibres, depending on different monomers and solvents. Grafting conditions: 0.2 g wool, 14 ml solvent, 7 ml monomer (+ 1 ml water) under nitrogen; dose rate 6 - 7 kGy/h, total dose 18 - 21 kGy.

Solvent	Monomer	MMA	MMA/Water	6-Vpy	6-Vpy/Water	Styrene	Styrene/Water	AA ^H	AA/Water ^H	2-Vpy	2-Vpy/Water	V. acetate	V. acetate/Water	AB	AN/Water	BMA	BMA/Water	V. P. am	V. P. am/Water		
DMF		95	90	5	62	9	27	20	15	13	9 ₂	4	5	69	94	40	203	106	0	36	
Trichloroethane ²⁾																					
n-Propan		32	95	4	17	3	31	12	1	3	48	1	5	31	62	3	47	2	146	12	30
Pyridin		17	87	4	45	6	32	2	22	3	50	3	3	10	27	5	242	2	178	1	0
DMSO		3	117	28	59	6	33	12	0	22	122	4	3	0	0	108	17	69	58	9	12
Methylacetone		0	218	21	228	18	11	15	0	4	34	3	4	7	51	2	107	1	62	41	17
Nitrobenzene		0	19	0	12	0	4	3	2	30	2	9	2	2	5	2	3	1	1	1	51
Butanol		0	30	13	12	0	10	0	24	3	19	1	2	12	37	1	22	1	116	7	7
Tetrahydrofuran		0	33	8	51	0	13	27	18	1	19	2	3	14	63	1	4	1	1	1	11
Propylalcohol		8	27	13	21	10	55	6	18	3	21	2	1	11	48	2	10	0	13	17	2
Methanol		369	132	133	174	252	208	78	0	40	74	5	7	64	62	151	47	137	173	6	2
Dioxan		10	32	19	119	6	72	16	0	1	12	0	5	5	52	2	228	0	203	1	15
1,2-Dichlorobenzene		0	22	12	120	6	0	10	0	3	22	0	7	18	37	3	16	0	16	0	0
Amylalcohol		0	4	19	28	3	118	22	0	2	9	3	5	6	30	2	38	0	54	0	0
1,2-Dichloroethane		47	51	2	142	0	0	9	0	1	18	3	4	12	57	4	9	0	130	0	0
Acetic Acid		239	799	7	8	111	325	0	0	7	5	7	5	121	108	281	257	241	118	25	15
Chloroform																					
Methylene chloride		51	781	4	59	0	31	27	0	5	13	3	2	121	11	112	100	83	82	6	16
7 Vol % Formic Acid																					
Formic Acid, Methanol		152	627	7	14	1 640	46	0	0	6	4	1	3	17	18	11	445	1 113	627	9	8
Acetic Acid		0	172	0	0	186	211	0	0	10	7	8	3	170	115	198	162	457	592	26	1
Acetone		0	43	2	30	0	115	0	0	0	22	0	0	34	38	3	162	1	1 066	1	8
		Σ = 61	Σ = 175	Σ = 16	Σ = 63	Σ = 125	Σ = 79	Σ = 17	Σ = 16	Σ = 7	Σ = 32	Σ = 3	Σ = 4	Σ = 39	Σ = 49	Σ = 50	Σ = 122	Σ = 171	Σ = 209	Σ = 6	Σ = 18
		S = 104	S = 255	S = 29	S = 64	S = 385	S = 90	S = 19	S = 9	S = 10	S = 32	S = 2	S = 2	S = 49	S = 30	S = 41	S = 118	S = 131	S = 271	S = 11	S = 22

- a) 0.2 g wool, 14 ml solvent, 3 ml acrylic acid
- b) only carried out with these four monomers
- c) solution polymerised

TABLE II
List of solvent systems used in order of decreasing polymer uptake, plus their polar, non-polar and hydrogen-bonding parameters after Hoy [35].

Solvent	Average uptake (%) for all monomers	Solvent parameter (cal/cm ³) ^a		
		Polar	Non-polar	Hydrogen-bonding
Formic acid-Methanol	273.5	5.3	6.7	11.7
Methanol	164.1	5.9	6.8	11.7
Acetic acid	159.3	5.9	6.8	9.3
Acetic acid-chloroform	149.9	5.9/6.9	6.8/5.6	9.3/2.1
Acetone	101.7	5.2	6.4	5.4
Methylene chloride 2 vol % Formic acid	82.5	5.7	6.6	4.7/-
DMF	63.7	5.9	8.1	6.0
DMSO	49.4	-b)	-	-
Methylene chloride	44.2	5.7	6.6	4.7
1,4-dioxane	42.1	4.9	8.0	3.8
Pyridine	36.8	5.0	8.6	3.7
1,2-dichloroethane	33.2	5.9	7.5	2.5
n-propanol	27.6	4.3	7.5	8.6
i-propylalcohol	20.2	4.3	7.5	8.6
Amyl alcohol	20.0	3.7	7.7	7.2
1,2-dichlorobenzene	18.2	4.8	8.8	0.0
Butanol	16.4	4.1	7.8	7.5
Trichloroethylene ^b	13.8	6.9	5.7	2.1
Trichloroethane	8.1	6.3	6.8	3.4
Nitrobenzene	7.2	-b)	-	-

a) used only for 4 monomers

b) no details available

The above Table shows that the grafting efficiency increases with an increase in the hydrogen bonding parameter. The alcohol values partly supplied by this correlation, viz. high parameter values together with relatively low grafting efficiencies, can be explained by the growing size of the alcohol molecule and the corresponding steric hindrance. This is confirmed by investigations done by King [38], Speakman [36] and Bradbury [39,40], who observed a diffusion delay as with an n-propanol related molecule size. No such correlation is possible with polar and non-polar parameters. The grafting process is affected by the acids by a complex mechanism. To begin with, the hydrogen bonds and salt bridges are ruptured, resulting in drastic conformation changes. Garnett and Leeder [27] write of a rupture of histological or macromolecular regions which changes the original diffusion-controlled grafting into a bulk reaction. Apart from this mechanism, Williams and Stannett [41] give a purely radiation-chemical explanation. H atoms are formed by the secondary electrons accompanying the radiation process, which created new graft sites after reacting with the fibre protein or the grafted polymer.

3.2 The Effect of Radiation on the Fibre Structure

3.2.1 Amino acid analyses

One important aspect of the application of ionizing radiation in the textile sector is the damage caused by the

radiation in the form of partial destruction of the molecule chain. Although wool, unlike a large number of synthetic fibres, is considered to be relatively non-sensitive to radiation, the technological implications of the behaviour still have to be studied.

The first work in this connection was done by Satlow [42] and Zahn *et al* [43]. They set the critical exposure dose for wool at 100 - 200 kGy. Cystine bridges, tyrosine and tryptophane, in particular, are involved here. In the presence of atmospheric oxygen, oxidation of cystine into cysteine acid is observed, as well as a decrease of the sorption capacity. The 10% loss of tensile strength and elongation at break is explained by cleavage of the disulphide bridges. In the absence of oxygen, on the other hand, the dissociation of cystine occurs at much lower rates than is generally accepted. Although the relevant dose rates of 100 - 200 kGy are higher by one order of magnitude than the maximum radiation doses required for the grafting processes (20 kGy), the latest investigations by Beevers and McLaren [17] reveal that even in the case of small doses (50 - 100 kGy), sufficient covalent break occurs, which makes the fibre more susceptible to swelling and disordering agents. These radiation-induced effects hardly have any effect on the mechanical strength. However, the absorption and penetration properties which can be significant for chemical modifications or radiation-induced grafting of wool, are permanently affected.

We began our investigations by analysing the amino acids of various solvent-treated wool samples, and then a series of grafted samples were analysed. The results appear in Table III. They reveal the deviations in composition with a non-treated sample.

of the treated wool. This is confirmed by the results of the solvent-treated sample which undergo no detectable modification. The deviations of the grafted samples could, in most instances, be ascribed to solvent-induced changes in composition as well as to the grafting process.

TABLE III
Results of amino acid analyses of a few solvent-treated and radiation-grafted wool samples, as compared with untreated wool

Treatment ^(a)	Percentage of amino acid content deviating from untreated sample ^(b)
Original wool	21.5% (mean) of amino acid changes
Trifluoroacetic acid	1.5% (mean) of amino acid changes, lysine and tyrosine slightly changed
Trifluoroethanol	1.5% (mean) of amino acid changes
TREATED WITH SOLVENT	
Acetic acid	10% reduction of tyrosine by about 30% and lysine by about 20%
1,2-dichlorobenzene	10% reduction of tyrosine and lysine
DMSO	10% reduction of aspartic acid and 20% of tyrosine
MMA/methanol	10% reduction of aspartic acid and tyrosine, insignificant reduction of lysine and valine
4-Vpy/methanol	12% reduction of tyrosine, insignificant change of lysine
GRAFTED SAMPLES	
AA/methanol	40% reduction of tyrosine and lysine
Styrene/methanol	18% reduction of tyrosine and lysine
Styrene/methanol/water	18% reduction of tyrosine and lysine
V-acetate/methanol	12% reduction of lysine and tyrosine
2-Vpy/methanol	18% reduction of tyrosine and lysine

(a) The sample (0.1 g wool, 5 ml solvent) was allowed to swell for 1 h at room temperature and then dried under vacuum. The grafted sample resembles that described under "Experimental".

(b) Cysteine acid could not be determined in all cases; histophane was not determined.

Clearly, three amino acids in particular are liable to changes, viz. tyrosine, lysine and, especially in a few cases, aspartic acid. In the case of solvent-treated samples, DMSO and acetic acid in particular, show a distinct reduction of the aspartic acid or tyrosine and lysine. These solvents therefore have a damaging effect. This agrees with the test results of Koenig *et al* [29] and Friedman [30], who observed supercontraction and felting in wool treated with DMSO. A very important observation is made by comparing solvent-treated and radiation-grafted samples. The changes in solvent-treated wool samples are generally more serious than those in grafted samples which in many cases are only slightly modified. This observation can be explained by the fact that the apparent reduction of the amino acid contents is caused not so much by radiation as by the solvent

3.2.2 Calorimetric analyses

Thermoanalytic studies have been used to identify the physical and chemical properties of polymers. Similar studies have been carried out on fibrous proteins and peptides and important details of the structure and the chemical behaviour of fibre proteins were obtained [44-47]. For this reason this method was used for the chemical and physical characterization of treated wool samples. By virtue of the large number of thermograms of the wool-treated and grafted samples (about 450), a statistical evaluation was done with the object not so much of interpreting separate results, but of determining the characteristic features of a given monomer or solvent system. The dehydration peaks in the 20-130 °C range (a

distinctive feature of all hydrophilic polymers) which represent the entire amount of absorbed water, were first used for the evaluation. This amount of absorbed water is of significant importance because of the moisture exchange taking place between textile and skin. The shift of the α -helix peak is also recorded. The α -helix peak is another distinctive feature of all vertebrate keratins and it is tied up with the melting point, i.e. the collapse of the helical area in wool. The physical structure in general is destabilised as the α -helix peak shifts towards lower temperatures or disappears completely [48]. The third distinctive feature is based on the entire thermogram which records the modifications of the morphological structure of wool.

Analysing the solvent-treated samples, a whole series of solvents causes the helix melting point to be lowered considerably; these are trifluoroacetic acid (-40°C), trifluoroethanol (-22°C), DMF (-20°C), DMSO (-28°C), acetic acid/chloroform (-16°C), DMF/water (-25°C), methylene chloride/2 vol % formic acid (-11°C), perhydrol (-13°C), i-propanol/water (-15°C), i-propanol (-10°C). The results of amino acid tests are used to determine whether physical effects and/or chemical dissociation are responsible for the partial destabilisation of the physical structure. No significant losses of amino acid were determined for trifluoroacetic acid and trifluoroethanol. Physical interactions, e.g. the rupturing of hydrogen bonds and salt bridges, can mainly be held responsible for the lowering of the helix melting peak. On the other hand, in the case of DMSO and acetic acid which suffer extensive losses of amino acid, chemical dissociation

mechanisms can play a part in the destabilisation of the helical range. Let us examine the grafted wool samples. In Table IV appear the average helix peak shift, the percentage of undetectable peaks, the number of complete changes of the thermogram characteristics, and the modification of the moisture absorption as compared with an untreated wool sample.

Lowering of the melting temperature is observed more often in the case of hydrophobic monomers, whereas for hydrophilic monomers such as AA, V-acetate and V-Pdon the melting point rises. The melting point drops again when the grafting process is carried out in the presence of water. This phenomenon runs virtually in line with an increase in polymer uptake when water is added. Apparently, stabilising and destabilising interactions occur, and the destabilising effects predominate whenever the polymer uptake increases. The hydrogen bonds, hydrophobic and hydrophilic interactions, as well as the salt bonds, are responsible for these interactions. The hydrogen bonds, as well as the salt bond between the carboxyl groups and the lysine, arginine and histidine side-groups, could be responsible for the distinct rise in the melting temperature in the case of AA. Similar interactions with a stabilising effect on the helix conformation are found during the interaction between sulphate and perchlorate ions and proteins or polyamino acids [49]. Additional hydrophobic interactions acting as a stabilising factor occur in the case of V-acetate, V-Pdon and AN, while hydrophobicity occurs in the case of BMA.

TABLE IV
Shift of the α -helix melting peak, percentage of undetectable helix peaks, percentage of water absorption and number of total modifications of thermogram characteristics of grafted wool samples

WOOL GRAFTED WITH	α -helix ($^{\circ}\text{C}$)	% undetected helix peaks	Number of modified thermograms	% water absorption
MMA	- 2.7	21	4	64
MMA/water	- 5.9	50	9	35
4-Vpy	- 7.4	0	0	50
4-Vpy/water	- 7.0	10	2	51
Styrene	- 1.7	40	4	56
Styrene/water	-	37	4	57
AA	+ 5.7	60	0	90
AA/water	+ 12.0	71	0	96
2-Vpy	+ 1.1	0	0	94
2-Vpy/water	- 0.8	0	0	72
V-acetate	+ 0.6	5	0	44
V-acetate/water	- 2.9	5	0	48
AN	- 2.9	37	13	37
AN/water	+ 4.0	94	18	34
i-BMA	+ 2.3	25	5	43
i-BMA/water	+ 3.5	40	10	25
BMA	+ 1.5	35	6	28
BMA/water	- 4.3	42	10	34
V-Pdon	+ 2.2	0	0	55
V-Pdon/water	- 0.9	0	0	44

These stabilising interactions are, however, compensated for in such a manner by the steep increase of the graft uptake during the addition of water, that the original conformation and configuration of the peptide chains are disrupted by the increasing incorporation of foreign polymer molecules, resulting in the disruption of the keratin structure. This can also be proved by the percentage of undetectable peaks, because the increase of graft uptakes in the presence of water occurs in line with the increase of undetectable peaks. The same tendency is observed in the number of totally modified DSC thermograms – more modifications take place as the polymer uptake increases.

The AN-grafted samples occupy a special position in this respect. The distinct peak appearing in the 240 – 280 °C range (Fig. 1), which has a marked effect on the thermogram characteristics, is not caused by a graft-induced destabilisation of the keratin structure.

This is a well-known [50,51] specific intra- and intermolecular reaction of the nitrilo groups into cyclic tetrahydronaphthydrine during which the cleavage of low-molecular compounds is accompanied by the formation of the so-called propagation cross-links (ladder polymers) (see Fig. 2). This is also the reason why acrylonitrile-grafted samples have a fairly strong yellow colour as a result of the conjugated C-N sequences that act as chromophor [52].

The water sorption of treated samples is reduced in all cases. This also applied to all hydrophilic polymers. Williams *et al* [13] had similar results, since they found a considerable decrease in the drained-water content. This conclusion is opposed by the results obtained by other authors [11,53,54] who determined that the equilibrium absorption of moisture by grafted wool is unaffected by the presence of hydrophobic polymers. However, it must be borne in mind that the relative humidities of these tests differed from ours.

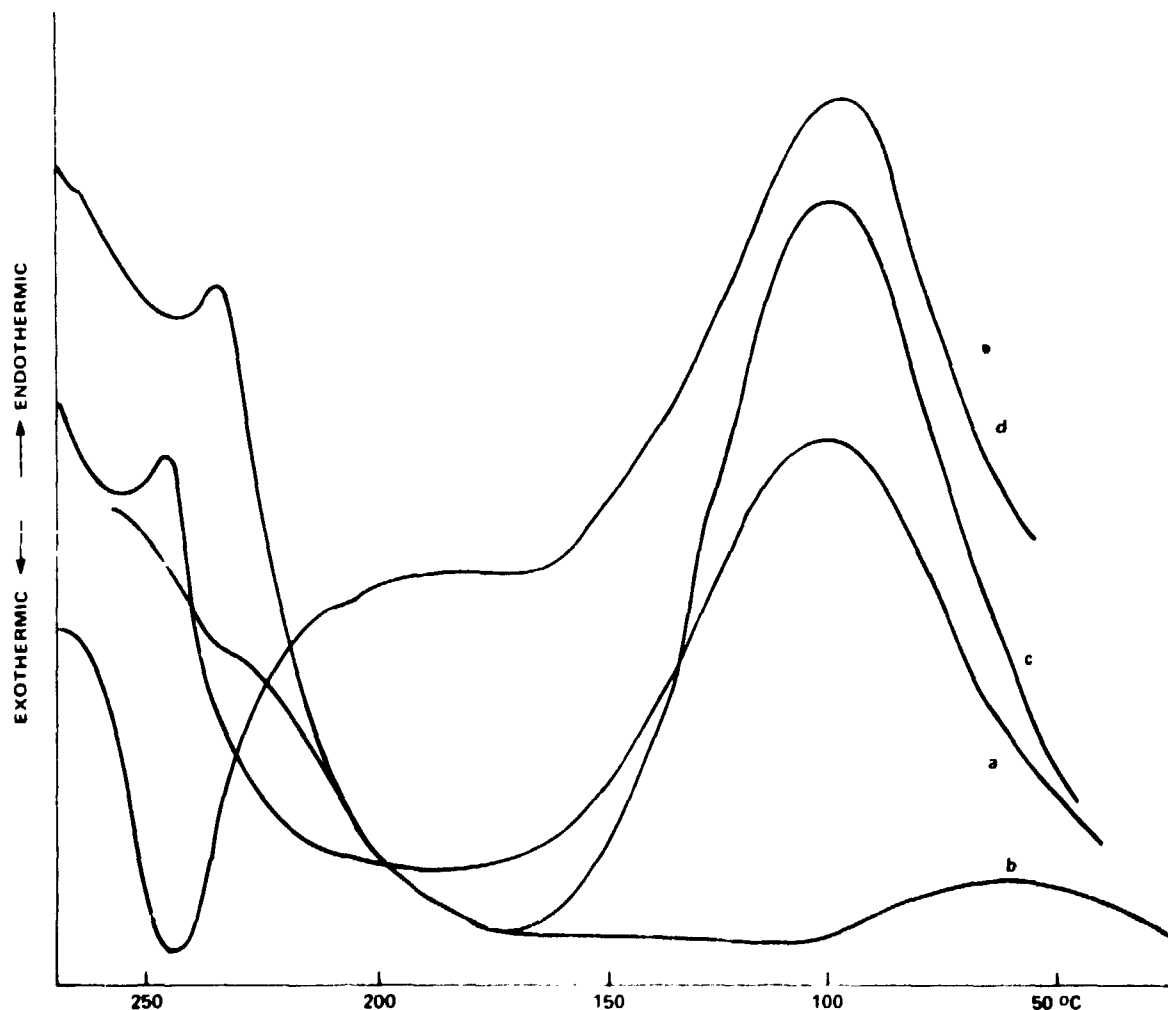


Figure 1

DSC curves of original (a) and three different grafted samples (b) grafted with styrene in methanol (showing the total change of thermogram) (c) grafted with 4-vinylpyridine in acetone (d) grafted with acrylonitrile in butanol; heating rate 16 °C/min under nitrogen.

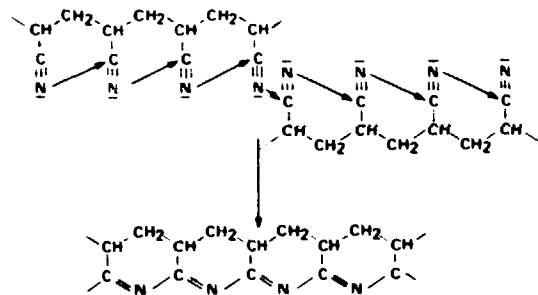


Figure 2

Simplified formula diagram of the intra- and intermolecular nitrilgroup formation during the thermal treatment of polyacrylonitrile [51].

3.2.3 X-ray measurements

The small-angle measurements on the wool yielded only very weak reflexes, and consequently mohair fibres will probably have to be used as they have sharper scattering patterns [55]. Our investigations are therefore based only on wide-angle X-ray measurements (WAX). The tests are evaluated on the strength of the characteristic meridian reflex at 5,15 Å and the equator reflex at 9,8 Å. The diffraction pattern is analysed purely qualitatively by comparison with the characteristic pattern of the initial material. In this manner the specific modifications of the wool structure resulting from the various grafts, can be determined. The characteristic modifications of the WAX diffraction pattern appear in Table V.

With the aid of the preceding details certain classifications can be made into annular widening, annular blurring and total blurring. All samples have one thing in common, viz. the originally crescent-shaped reflexes are widened annularly as a result of the grafting process. This phenomenon can generally be explained by a disorientation of fibrillar ranges that run along the fibre axis. The haloes of the grafted predominantly amorphous material are, in addition, responsible for progressive blurring of the reflexes until completely diffused patterns are reached. This observation is confirmed by the hypothesis of paragraph 3.2.2, viz. parallel distortion of the organic microscopic morphology of the fibres as a result of rising polymer uptake. Arai *et al* [16] came to the same conclusion after similar X-ray tests had been done on grafted fibres. Some interesting observations are made on comparing these results with V-acetate and V-Pdon-grafted samples. Both samples have a comparatively low polymer uptake; nevertheless the scattering patterns are distinctly divergent. Whereas in the vinylacetate-grafted sample the 9,8 Å reflex is clearly visible as crescent-shaped intensity, it is annularly blurred in the vinylpyrrolidone-grafted sample. This observation can be explained by the fact that vinylpyrrolidone, an extremely hydrophilic polymer, can penetrate close to protofibrils in certain hydrophilic structure ranges which are impenetrable to V-acetate. This could serve as confirmation of electron-microscopic examinations by which the alteration of the arrangement of protofibrils in crystalline microfibrils was determined [15,16].

TABLE V
Modifications of the WAX diffraction characteristics of a few grafted wool samples and percentage relevant polymer uptake

Wool grafted with	Characteristic modifications	Polymer uptake
Styrene/methanol/water	annular cleavage of both reflexes	208
MMA/methanol/water	completely blurred diagram	132
4-Vpy/methanol	9,8 reflex distinctly visible annular cleavage of blurred 5.15	173
AA/methanol	annular cleavage of both reflexes; pronounced blurring	77
2-Vpy/methanol/water	annular cleavage of both reflexes	74
V-acetate/methanol/water	crescent-shaped cleavage of 9,8 reflex, annular cleavage of 5.15	6,5
AN/methanol/water	annular cleavage of reflexes and pronounced blurring	62
i-BMA/methanol/water	annular cleavage of reflexes; pronounced blurring	47
V-Pdon/methanol/water	annular cleavage of reflexes; pronounced blurring	7,3

4. GRAFTING ONTO WOVEN FABRICS

The tests on woven fabrics were done under the same test conditions as the grafting tests on single fibres. This applies especially to the selection of suitable solvent systems which are of major importance for the optimisation of the grafting process. The system methanol or methanol/water was found to be the most suitable solvent mixture for the preceding tests. In a few cases, a few other solvents or solvent mixtures, e.g. acidic systems and DMSO, accelerated the grafting process significantly (see Table I). However, analyses proved that virtually all of these solvents caused irreversible fibre damage and would be unsuitable for technological application. Consequently, the grafting tests on fabrics were done in the above system, viz. methanol or methanol/water. The test procedure is very similar to the one used for single fibres.

Woven fabrics of a size 5 x 5, 7 x 7 and 10, x 10 cm were used for the first tests to determine the conditions for a suitable polymer uptake which should not exceed 30%. This value is limited by the roughness of the textile surface (touch) which increases with polymer uptake.

Finally, 30 x 30 cm fabrics were used to determine, in particular, the textile properties. These tests were done at the South African Wool and Textile Research Institute. Grafting tests were done on untreated as well as chlorinated wool. Chlorination is a well-known process in the textile industry and serves to ensure shrink resistance.

4.1 Results and Discussion

4.1.1 Radiation-induced grafting of untreated wool fabrics

The grafting tests were done under nitrogen as well as air. The object of the parallel tests series was to determine the effect of both media on the grafting process in order to simplify the test conditions whenever necessary. Quite apart from high-vacuum conditions, the use of nitrogen should cause no unsolvable technical problems with a view to industrial applications; it would, however, raise costs and thus reduce the chances of commercial application. In addition, Burke *et al* [4] found no difference in the polymer uptake of the samples grafted under nitrogen or vacuum. Campbell *et al* [56] were able to prove that no differences exist between air and vacuum grafting.

The polymer uptake of untreated wool fabrics appears in Fig. 3.

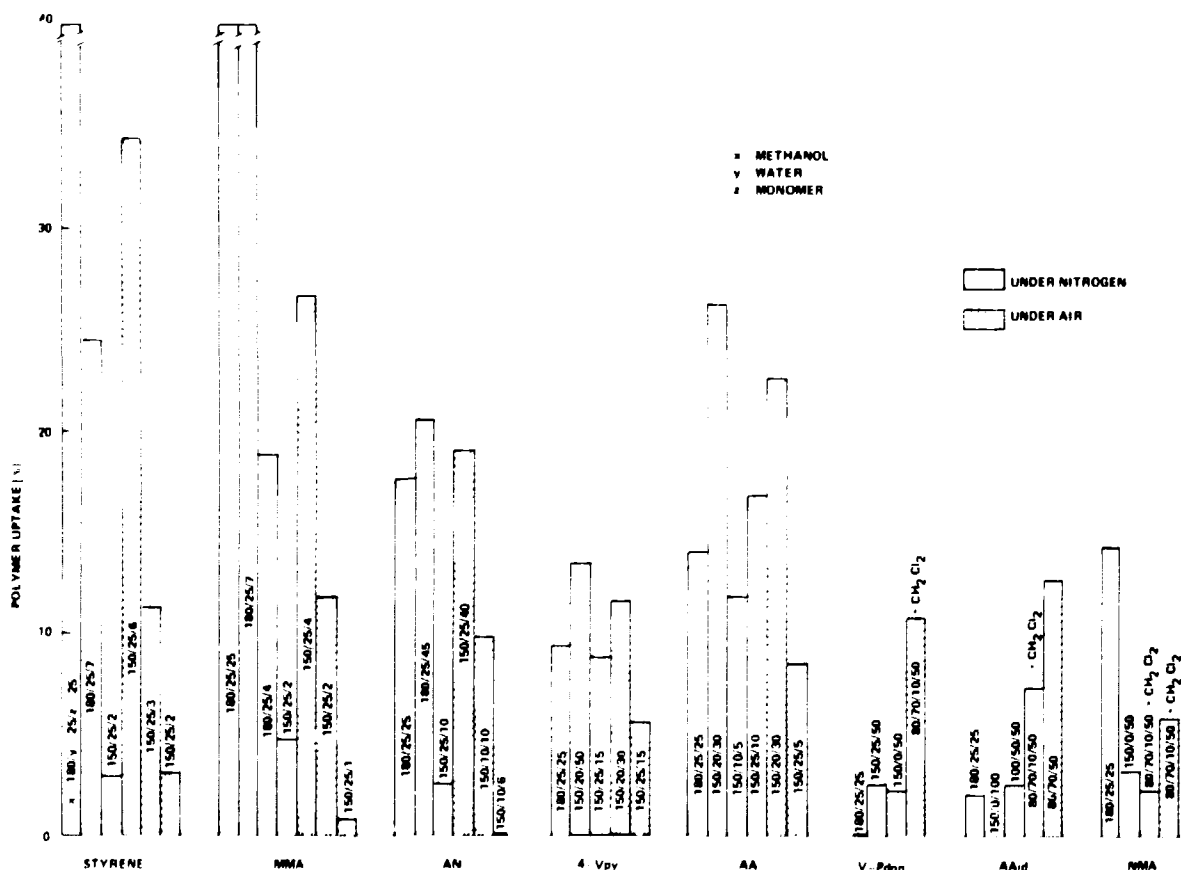


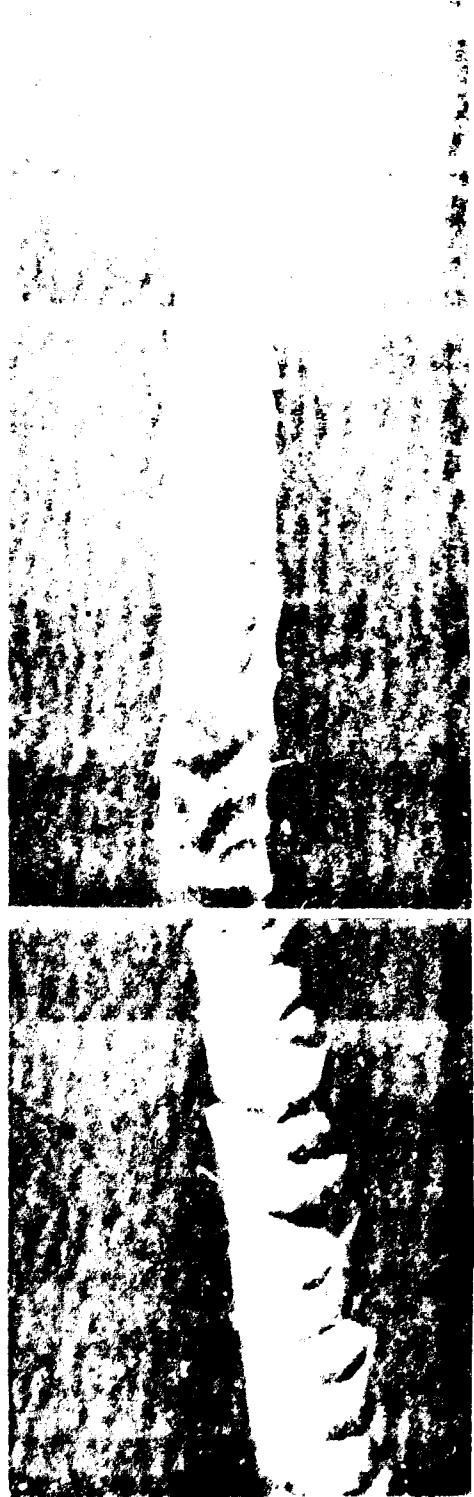
Figure 3
Polymer uptakes of 30 x 30 cm wool fabrics grafted under air and nitrogen (x, y, z in ml).

As can be seen from the histogram, the uptakes can be increased quantitatively by varying the amount of monomer in the relationship. In the case of V-Pdon, methyl methacrylate and N-methylolacrylamide (NMA) the uptakes are very low; they can be increased by increasing the monomer. The results of initially similar preparation of the samples grafted under air and nitrogen are shown in Table VI. The samples grafted under nitrogen show a lower uptake. The relationship is reversed for styrene, MMA and methyl methacrylate. Some explanation can be given since the grafting conditions that cannot be quantified are of the following nature.

MMA grafting closely resembles the Deering-Milliken Deering grafting process, an industrial process combining grafting and radiation treatment. As a first step the monomer MMA is grafted onto the fibre with the aid of an electron beam, followed by chemical cross-linking by addition of H_2O_2 . This ether cross-link comes into effect as soon as the wool is pressed, ensuring a permanent-press. It is well known, however, that the acid employed to neutralise the cross-link during the subsequent pressing of the wool has a severely damaging effect on wool, even if used in small amounts. Co-grafting experiments were carried out with MMA and acrylic acid, the acrylic acid serving as a cross-linker to form the ether cross-link. Subsequent pressing tests revealed, however, that no better improvement had been achieved than in the case of other monomers as described later on.

4.1.3. Grafting and co-grafting on chlorinated wool fabrics

The shrink resistance of wool is one of the main problems from a textile point of view. Processes were developed to improve shrink resistance, e.g. chlorination of wool with the aid of hypochlorite. This type of treated wool was also used for our studies. Although, as electron-microscopic tests have shown (see Fig. 4), the grafting processes take place in the interior of the fibre at adequate polymer uptakes, the handle of the wool is considerably impaired, depending on the polymer as well as polymer uptake (see Table VI). For this reason co-grafting tests were done in addition to the homo-grafting tests, specifically with the intention of improving the handle of the textile. Only one highly hydrophobic polymer could be used for this purpose, viz. AA. The uptake of the various co-grafted and homo-grafted wool samples appear in Fig. 5.



(c)

Figure 4
Electron micrograph ($\times 800$) of some wool samples shadowed with aluminium: (a) original wool; (b) grafted with methacrylic acid n-butyl ester in methanol/water (47% uptake); (c) grafted with vinylacetate in methanol/water (6% uptake) showing that the scale structure of the wool fibre is not covered by the grafted polymer.

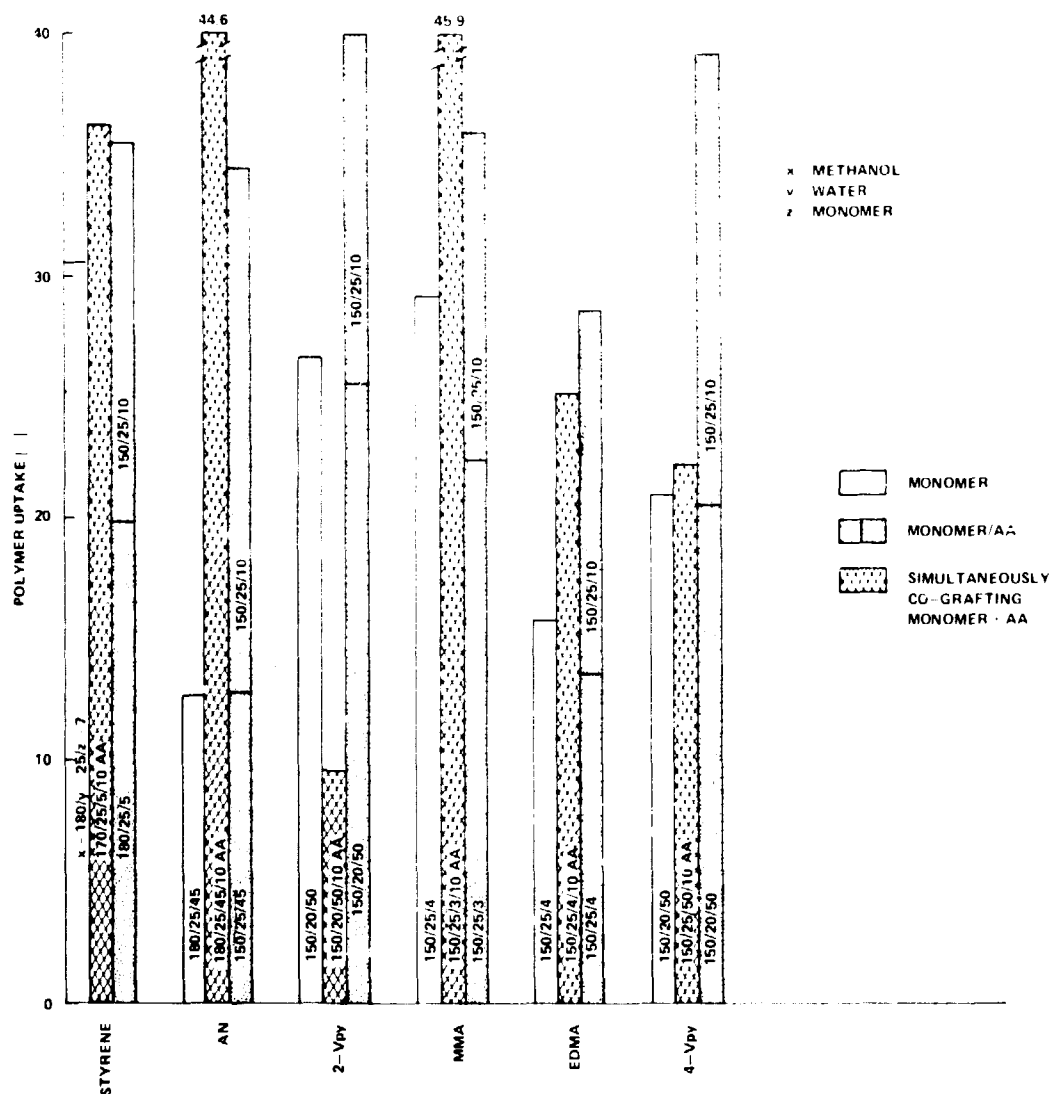


Figure 5
 Polymer uptake of 30 x 30 cm chlorinated wool fabrics that were simultaneously and successively homo- and co-grafted under nitrogen (EDMA: ethylenedimethacrylate).

On comparing the values of homo-grafted samples of chlorinated wool with those of untreated wool from previous tests, it appears that in the case of samples (styrene, MMA, AN, 4-Vpy) grafted under similar grafting conditions, the uptakes of chlorinated wool are higher, except for AN. Although these differences are not very large (about 10%) and cannot be considered to be representative, the conclusion could nevertheless be drawn that reactive centres are formed by the chlorination where additional grafting can take place. The samples grafted successively with acrylic acid, cannot be used for a similar comparison since the chemical structure of wool was changed too much by the preceding grafting process, and

because partial grafting of acrylic acid onto the grafted polymer could have taken place. The grafting tests that were done successively and simultaneously cannot be compared quantitatively with regard to different grafting behaviour, because the solvent/monomer relationship of the two processes differs basically. Both co-grafting processes have the same polymer uptake. Distinct differences are observed only in the two samples that were grafted with vinylpyridine. In both cases the uptakes of the simultaneously co-grafted samples are considerably below the successively grafted material. This can be attributed to the effects of salt-bridge formation between the two monomers, acrylic acid and vinylpyridine, which inhibits polymerisation.

TABLE VI
Sett, cantilever bending length and area-shrinkage measurements on grafted 30 x 30 cm unchlorinated wool fabrics

Monomer	Uptake %	Grafted in nitrogen or air	Sett (threads/cm)		Cantilever bending length (cm)	Area shrinkage (%) after washing for		
			Ends	Picks		30 min	60 min	180 min
Control			12.6	11.4	1.57	46	68	76
Styrene	24	N ₂	13.0	11.8	1.76	14	22	44
Styrene	3	N ₂	12.6	11.8	1.69	28	48	71
Styrene	34	air	13.0	11.8	1.76	9	14	33
Styrene	3	air	12.6	11.8	1.69	26	49	71
MMA	19	N ₂	12.2	11.4	1.72	25	39	62
MMA	5	N ₂	12.2	11.8	1.60	30	56	72
MMA	27	air	12.6	11.4	1.64	20	34	59
MMA	12	air	13.0	11.4	1.63	32	52	73
AN	20	N ₂	12.6	11.8	1.79	5	7	18
AN	3	N ₂	12.2	11.8	1.63	14	29	64
AN	20	air	12.6	11.8	1.70	6	15	52
AN	10	air	13.0	11.8	1.63	14	33	64
AA	27	N ₂	12.6	11.4	1.80	49	58	63
2-Vpy	13	N ₂	12.6	11.4	1.70	17	32	64
2-Vpy	9	N ₂	12.6	11.4	2.87	8	19	54
NMA	2	N ₂	13.0	11.8	1.65	40	62	75
AArd	7	N ₂	13.0	11.8	1.70	37	59	74
V-Pdon	3	N ₂	12.6	11.8	1.65	30	55	74
AA	23	air	13.0	11.4	1.78	49	60	67
2-Vpy	12	air	12.6	11.4	2.63	6	18	52
NMA	6	air	13.0	11.8	1.65	31	59	76
2-Vpy	5	air	12.6	11.8	1.67	19	40	69
AA	8	air	12.6	11.8	1.72	40	58	72
V-Pdon	10	air	13.0	11.8	1.79	9	59	73
AArd	13	air	13.0	11.4	1.69	35	58	73

4.2 Textile Testing of Wool Fabrics

The main parameters used for the characterisation of textiles are all covered by the test methods used. First of all, these tests describe the modifications of wool during the grafting tests. The Sett results outline the extent of shrinkage during these modification processes. The stiffness of the textile, which determines the quality of wear, is tested by means of bending-length measurements. Area-shrinkage tests determine the behaviour of the modified material during washing. In the last series of tests (Table VII) crease-recovery angles, abrasion and relaxation shrinkage of chlorinated homo- and co-grafted wool fabrics are tested.

Shrinkage of the wool during the grafting process is negligibly small, as is proved by the Sett values. If the values are high in comparison with the control sample, the shrinkage rate is also high. The stiffness of the material is determined by bending-length measurements. Generally, grafting increases stiffness, and a direct relationship exists between rising uptake and increasing stiffness. Strangely enough, highly hydrophilic polymers such as AA, V-Pdon

and Vpy have relatively high bending values. This is in direct contrast to the handle of wool, which is generally softer in the case of hydrophilic polymers than hydrophobic polymers. Values of between 1.6 and 1.7 are acceptable from a textile point of view.

A reduction of area shrinkage is observed during washing tests. Here again there is a direct relationship between polymer uptake and physical test parameters, so much so that a rising uptake is accompanied by reduced shrinkage, especially in the case of styrene, AN and MMA. A significant reduction of shrinkage is found in the sample grafted with 2-Vpy. Although the uptake is relatively low in these polymers, it can be assumed that specific stabilising interactions, e.g. salt-bond interactions, occur between the grafted polymer and wool. No significant differences are observed on comparing samples with similar polymer uptake grafted under nitrogen and air (Table VIa).

The main objective of the present research work was to improve the permanent-press properties. In this respect wool is at a disadvantage in comparison with cotton or synthetic textiles, mainly as a result of cross-linking. No

textile fibre is as amenable to different types of cross-linking as wool. Residual cystine is the main agent in this respect as it is a double amino acid and a natural principal valence cross-link. Thirteen other trifunctional amino acids contain so-called side-chain functions which are capable of forming cross-links. The formation of hydrogen bridges between side-chain functions and peptide bonds within the peptide chain supplies an even wider spectrum of possible secondary valence bridges. The structure of wool is highly stabilised and it is extremely difficult to modify the structure, as has to be done, for example, to obtain a permanent crease.

TABLE VIa
Comparison of average shrinkage values of wool samples grafted under air and nitrogen

Samples grafted in (graft uptake range)	Average shrinkage value (%) after washing for		
	30 min	60 min	180 min
N ₂ (20 - 35 % uptake)	20.9	31.5	46.7
Air (20 - 35 % uptake)	21.0	30.7	52.7
N ₂ (2 - 10 % uptake)	27.6	48.3	70.2
Air (2 - 10 % uptake)	26.3	50.3	70.4

Starting with experiments in the field of synthetic fibres, polymers with a high glass-transition temperature seem to be the best to improve the permanent-press. Water exchange within the textiles is another important aspect, since water is an excellent swelling agent and plasticiser.

Moisture sorption is very high in wool which is a hydrophilic polymer.

Simple pressing tests were done during preliminary tests to select suitable monomers on a purely qualitative basis. These monomers were applied for grafting tests on larger fabrics which were to be used for further textile tests.

The pressing conditions were similar to those used on an industrial scale (5 s at 120 °C). After pressing, the samples were treated with a soap solution for about 24 h at room temperature. These treatments revealed that the best permanent-press results were obtained with styrene, MMA and AN, whereas in the case of hydrophilic monomers such as AAid, AA, V-acetate, V-Pdon, the crease disappeared very quickly after washing (1 - 2 h). This is probably due to the increased water uptake, leading to enhanced chain-relaxation processes.

On the other hand, hydrophobic polymers such as BMA, 1,3-butadiene also yield a non-permanent crease because of the low glass-transition temperatures. The good results obtained with AN, a more hydrophilic polymer, can be explained by the relatively high glass-transition temperature (~100 °C), and by either the reaction of the cyanide groups resulting in ladder polymers, or the reactions taking place with peptide side-groups.

A summary of the textile tests of chlorinated homo- and co-grafted 30 x 30 cm wool fabrics is given in Table VII. It

TABLE VII
Crease-recovery angle, abrasion and relaxation-shrinkage results of the different homo- and co-grafted chlorinated wool fabrics

Wool samples Monomer uptake (%)	Monsanto crease recovery angle ^{a)}		Martindale abrasion (% mass loss) (5 000 circles)	Relaxation shrinkage (%)	
	"dry"	"wet"		IWSTM 9	IWSTM 186
Control	305	274	9.6	0.5	3.1
Styrene 30.4	312	268	7.81	0.0	- 0.6
Styrene 19.2, AA 16.4	304	249	6.55	6.9	9.5
Styrene/AA 36.2	309	252	7.11	3.2	5.0
AN 12.7	297	235	6.51	3.1	3.8
AN 12.9, AA 21.7	296	203	5.63	8.2	12.9
AN/AA 44.6	298	193	7.41	6.9	9.5
2-Vpy 26.8	308	253	12.48	- 2.5	- 1.3
2-Vpy 25.6, AA 14.9	298	207	9.95	5.6	3.8
2-Vpy/AA 9.7	302	261	12.72	- 4.4	- 3.8
MMA 29.2	308	251	7.52	- 1.9	0.6
MMA 22.5, AA 13.5	307	230	7.53	7.5	8.8
MMA/AA 45.9	300	197	6.71	2.5	7.5
EDMA 15.9	307	238	-b)	1.2	0.6
EDMA 13.6, AA 15.0	299	196	>7.18	8.1	10.0
EDMA/AA 25.2	298	209	6.36	10.1	10.8
4-Vpy 21.1	299	196	6.19	1.3	4.4
4-Vpy 20.6, AA 18.6	292	172	5.10	2.5	6.3
4-Vpy/AA 22.3	289	261	7.48	0.0	3.1

a) De-aged at 20 °C, 65 % rel. humidity

b) Fabric destroyed

can be stated in general, that the best treatments are those giving high crease-recovery angles, low mass losses and low shrink results. On analysing the crease-recovery angle measurements, parallels are found between these values and the pressing tests done on a laboratory scale. In this case, too, hydrophobic monomers such as styrene and methylmethacrylate yield the best values. Contrary to the pressing results, the AN-grafted sample has a surprisingly low value. This seems to support the preceding hypothesis whereby PAN is involved in reactions during the pressing process, resulting in stabilisation of the wool texture.

Co-grafting with acrylic acid reduced the crease-recovery angles, which confirms the relationship mentioned earlier between relaxation phenomena and water sorption. The abrasion tests do not vary significantly, except for the material grafted with 2-Vpy, of which the values are above average.

Values of less than 8% are acceptable from a textile point of view for relaxation shrinkage. In a few cases (styrene, MMA and 2-Vpy) even negative shrinkage occurs, i.e. the surface increases. The effect of the co-grafted acrylic acid on the relaxation behaviour of the fibre is very obvious

from the increase of the shrinkage value. The effect of grafting, and especially AA, on moisture sorption, is shown in Fig. 6 which lists the moisture sorption of different wool samples.

The 30 x 30 cm fabrics were folded three times, dried for 1 h at 60 °C under vacuum (12 m.m Hg) and then weighed. The starting mass was calculated on the assumption that the moisture uptake is the same between 45 and 45 + 60 s as during the first 45 s.

The sorption rate of wool grafted with styrene is distinctly lower than that of the non-treated sample, thereby complying with the requirement mentioned at the outset, viz. to improve the permanent-press by reducing the moisture sorption. The effect of AA is quite clear when styrene and styrene/AA homo- and co-grafted samples are compared. Initially the sorption process is highly accelerated by the presence of this hydrophilic polymer; after 4 min there is a sudden slowing down, this being the point at which AA saturation is reached. The rest of the sorption kinetics resemble those of material homo-grafted with styrene.

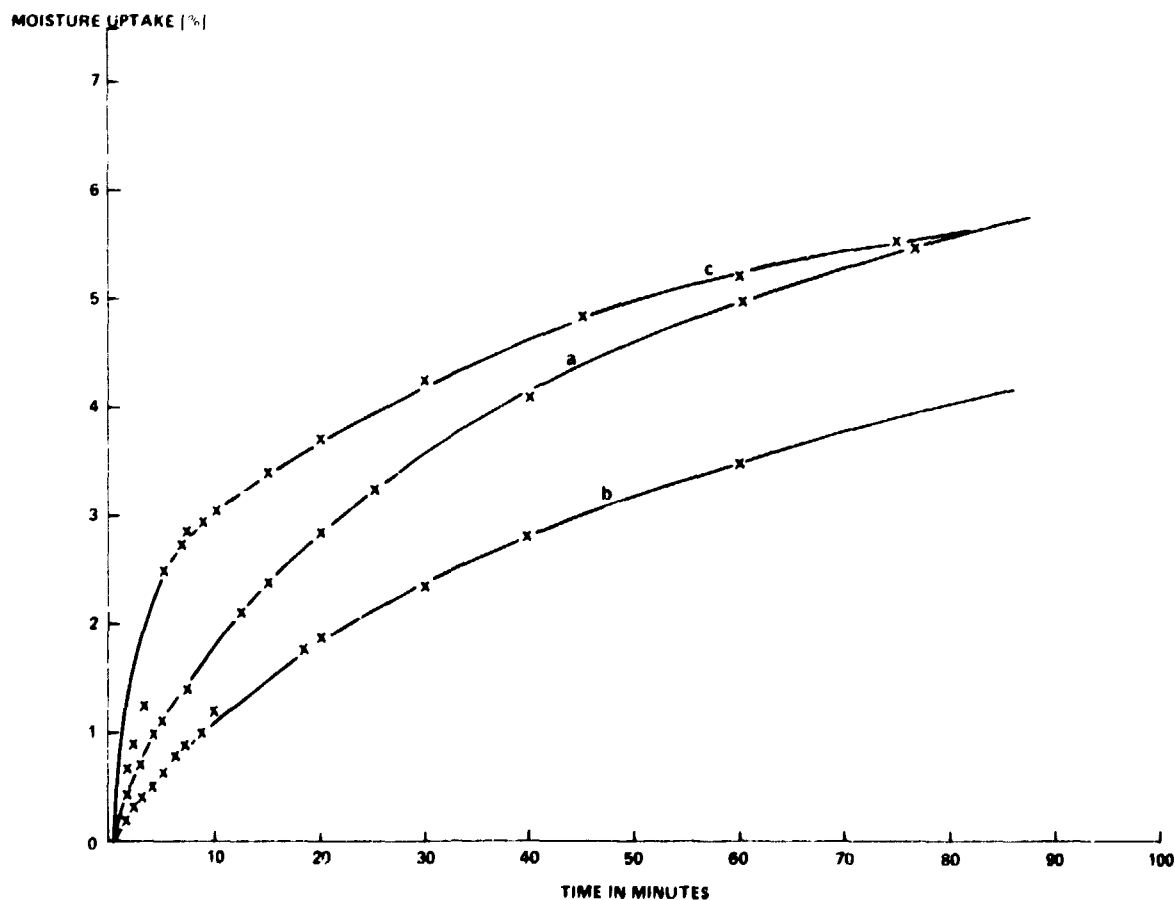


Figure 6

Moisture sorption of three 30 x 30 cm chlorinated wool samples (a) control sample; (b) wool grafted under nitrogen with styrene (methanol 180 ml, water 25 ml, styrene 7 ml); (c) wool co-grafted with styrene, AA under nitrogen (methanol 180 ml, water 25 ml, styrene 5 ml/methanol 150 ml, water 25 ml, AA 10 ml).

5. CONCLUSIONS

Fundamental grafting tests on single fibres were done to study fibre-monomer-solvent interactions, in order to determine the conditions for developing an optimum grafting process. This applies especially to the selection and composition of the monomer-solvent system. The chemical and physical modifications of the wool structure as a result of the effect of the solvent and/or the grafting process were studied at the same time. These tests were done to determine the extent to which wool is exposed to damage or other modifications which, from a commercial point of view, can or cannot be tolerated. This aspect which has so far been neglected must be studied in order to determine its industrial possibilities for modification processes. It was proved unambiguously that a whole series of solvent systems cannot be used because of their damaging effect on wool, although they accelerate the grafting process considerably. Methanol/water is the only system that accelerated the grafting process and is also commercially inexpensive.

On the basis of these fundamental investigations on single fibres a program for radiation-induced modification of wool fabrics was initiated. Improvement of the permanent-press was the main objective. Polymers with a high glass-transition temperature of hydrophobic polymers were favoured for this purpose in view of experience gained with regard to the physical processes which affect the permanent-press in synthetic fibres. Tests on wool fabrics confirmed the above hypothesis. The best pressing and crease-recovery angle results were in fact obtained with hydrophobic polymers or polymers with a high glass-transition temperature, e.g. polystyrene and polymethylmethacrylate. Another important point is wearing quality or wearing comfort of the textiles after treatment, which refers to the softness or the handle of the fibres. The grafting technique causes problems in this respect in so far as the handle of the textile is impaired by the incorporation of foreign polymers. Co-grafting tests intended to soften the handle with hydrophilic monomers such as AA, were also unsuccessful. It would also complicate any potential industrial process, as well as raise the costs thereof. Consequently, for commercial application the polymer uptake would have to be kept as low as possible, i.e. values of about 10% would be realistic.

As is the case with all textile modification processes, a certain compromise has to be reached between tolerable impairment and improvement of certain textile properties. Electron accelerators are the only radiation facilities that can be used for an industrial application of this process. A high-dose output together with a short radiation period, less extensive radiation-protection measures than in the case of a ^{60}Co source, and adaptability to the dimensions of the articles to be irradiated, are points that favour electron accelerators [57]. Whether the preceding process has any chance of commercial application will depend on the marketing situation in the textile sector, rather than on technological points of view.

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7. REFERENCES

1. Hölzel, K.A. *Ciba-Geigy Rundschau* 1, 2 (1972).
2. Blankenburg, G. German Wool Research Institute, private communication.
3. "Referatesammlung zur Bestrahlungstechnik in der Textilindustrie", Bureau Eurositop, Euratom, Arbeitsunterlage Nr. 52.
4. Burke, M., Kenny, P., Nicholls, C.J. *J. Text. Inst.* (1962) 53, 370.
5. Arai, K., Shimizu, M., Shimada, M. *J. Polym. Sci.* (1973) 11, 3 283.
6. Arai, K., Shimizu, M., Shimada, M. *J. Polym. Sci.* (1973) 11, 3 271.
7. Arai, K., Kiho, H., Stannett, V. *Makromolek. Chem.* (1966) 95, 106.
8. Schnautz, N.G., du Plessis, T.A. *J. Polym. Sci.* (1975) 19, 2 099.
9. Stannett, V.T., Williams, J.L. *J. Macromol. Sci.-Chem.* (1976) A10(4), 637.
10. D'Arcy, R.L., Watt, I.C. *J. Macromol. Sci.-Chem.* (1972) A6(4) 689.
11. Arai, K., Negishi, M., Suda, R., Doi, K. *J. Polym. Sci. Part A-1*, (1971) 9, 1 879.
12. McLaren, K.G., Watt, I.C. *J. Polym. Sci.* (1976) 14, 257.
13. Williams, J.L., Stannett, V., Armstrong, Jr. A.A. *J. Appl. Polym. Sci.* (1966) 10, 1 229.
14. Williams, J.L., Stannett, V., Roldan, L.G., Sello, S.B., Stevens, C.W. *Int. J. Appl. Radiation and Isotopes* (1975) 26, 169.
15. Ingram, P., Williams, J.L., Stannett, V., Andrews, M.W. *J. Polym. Sci. Part A-1*, (1968) 6, 1 895.
16. Arai, K., Negishi, M., Suda, T., Arai, S. *J. Appl. Polym. Sci.* (1973) 17, 483.

17. Beevers, R.B., McLaren, K.G. *Text. Res. J.* (1974) 44, 986.
18. Gervasi, J.A., Stannett, V., *J. Appl. Polym. Sci.* (1966) 10, 1 217.
19. Stannett, V., Araki, K., Gervasi, J.A., McLeskey, S.W. *J. Polym. Sci. Part A*, (1965) 3, 3 763.
20. Garnett, J.L., Kenyon, R.S. *Polym. Letters Ed.* (1977) 15, 421.
21. Kenyon, R.S., Garnett, J.L. *Polym. Letters Ed.* (1973) 11, 651.
22. Williams, J.L., Woods, D.K., Stannett, V., Sello, S.B., Stevens, C.V. *Int. J. Appl. Radiation and Isotopes*, (1975) 26, 159.
23. Dasgupta, S. *J. Polym. Sci., Part C* (1972) 37, 333.
24. Hoffman, A.S. *Isotopes and Radiation Techn.* (1970) 8, 84.
25. Shinohara, J. *J. Appl. Polym. Sci.* (1959) 1, 253.
26. Okamura, S. "Large Radiation Sources in Industry", Warsaw, IAEA, (1960) 1, 459.
27. Garnett, J.L., Leeder, J.D. *Text. and Paper Chem. Techn.* (1977) 49, 197.
28. Needles, H.L., Sarsfield, L.J., Dowhaniuk, D.M. *Text. Res. J.* (1972) 42, 558.
29. Koenig, N.H., O'Connell. *Text. Res. J.* (1960) 30, 712.
30. Friedman, M., Koenig, N.H. *Text. Res. J.* (1971) 41, 605.
31. Atkinson, J.C., Filson, A., Speakman, J.B. *Nature* (1959) 184, 444.
32. Atkinson, J.C., Speakman, J.B. *J. Text. Inst.* (1964) 55, T 433.
33. Blankenburg, G. *Melliand Textilber.* (1967) 48, 686.
34. Böhme, H. Ph.D. Thesis, University Aachen (1975).
35. Hoy, K.L. "Tables of Solubility Parameters", Union Carbide Corp. South Charleston, W.VA., July 1969.
36. Speakman, J.B. *Proc. Roy. Soc.* (1931) A132, 167.
37. Abott, N.J., Temin, S.C., Chunghi Park, *Text. Res. J.* (1968) 38, 1 026.
38. King, G. *Trans Faraday Soc.* (1947) 43, 552.
39. Bradbury, J.H. *Text. Res. J.* (1957) 27, 829.
40. Bradbury, J.H. *J. Appl. Polym. Sci.* (1963) 7, 557.
41. Williams, J.L., Stannett, V.T. *Polym. Letters* (1970) 8, 711.
42. Satlow, G. *Melliand Textilber.* (1960) 41, 1 525.
43. Zahn, H., Fritze, E.H., Pfannmüller, H., Satlow, G. Repr. from 2nd UN Geneva Conference Session C-12 and C-B (1960).
44. Crighton, J.S., Happey, F., Ball, J.T. "Conformation of Biopolymers", (G.N. Ramachandran ed.) Part II, 623.
45. Crighton, J.S., Findon, W.M. *J. Thermal Analysis* (1977) 11, 305.
46. Müller-Schulte, D. *South African J. Chem.* (1978) 31, 77.
47. Crighton, J.S., Findon, W.M., Happey, F. *Appl. Polym. Symp.* (1971) 18, 847.
48. Müller-Schulte, D. *South African J. Chem.* (1978) 31, 131.
49. Ebert, Ch., Ebert, G. *Progr. in Colloid and Polymer Sci.* (1975) 57, 100.
50. Grassie, N., McGuchan, R. *Europ. Polym. J.* (1971) 7, 1 357.
51. Fitzer, E., Müller, D.J. *Chemiker Zeitung*, (1972) 1/2, 20.
52. Alger, K.W., Anne, Tai. *Text. Res. J.* (1978) 48, 123.
53. Armstrong, Jr A.A. Stannett, V. *Makromol. Chem.* (1966) 90, 145.
54. Watt, E.C. *J. Macromol. Sci.* (1970) A4 1079.
55. Spei, M. Forschungsbericht Land Nordrhein-Westfalen (1975) No. 2 455.
56. Campbell, D., Williams, J.L., Stannett, V. *Adv. Chem. Series* (1967) 16, 221.
57. Bobeth, W., Heger, A., Pässler, H. *Lenzinger Ber.* (1975) 38, 98.

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