The Chemistry of a Polyamide–Epichlorohydrin Resin (Hercosett 125) Used to Shrink-resist Wool

G. B. GUISE and G. C. SMITH, *CSIRO Division of Textile Industry, Belmont, Geelong, Victoria 3216, Australia*

Synopsis

A polyamide–epichlorohydrin resin used to shrink-resist wool [Hercosett 125 (Hercules Inc.)] was separated by ultrafiltration into fractions A, B, and C (in the approximate proportions 60, 40, and 2 by weight), which correspond to the three peaks in size exclusion chromatograms (SEC). Viscosity, spectra, and SEC results as well as results of experiments on the reaction of the parent polyamino–polyamide (PAA) with epichlorohydrin indicated that fraction A was high-molecular-weight crosslinked material whereas fraction B was essentially uncrosslinked. Fraction C was minor impurity, possibly a mixture containing a triazine, and it was also found in the PAA from which the original resin was prepared. High-resolution proton NMR spectra of the Hercosett 125 indicated that chlorohydrin or epoxy groups were absent, and thus confirmed an earlier ^{13}C-NMR study that only azetidinium reactive groups were present. Two reactions are believed to occur in Hercosett 125 on storage: hydrolysis of azetidinium to dihydroxypropyl groups and hydrolysis of backbone amides. The small differences in the properties of wool treated with either A or B fractions, and those of wool treated with unfractionated Hercosett 125, were related to the extent of crosslinking before and after curing. As the extent of crosslinking increased, the amount of staining by an anionic dye decreased, and the shrink resistance improved slightly.

INTRODUCTION

Cationic polyamide-epichlorohydrin (PAE) resins prepared by reaction of epichlorohydrin with polyamides derived from adipic acid and diethylenetriamine (Fig. 1) are widely used as wet-strength additives for paper,[1] and are the type of polymer used most extensively to shrink-resist wool.[2,3]

Most of the information published on PAE resins has concerned their applications, and there are some unresolved questions about their chemistry.[4–9] In particular, the nature of the reactive side groups derived from epichlorohydrin is not clear. One study[5] using proton NMR concluded that azetidinium, epoxy, and chlorohydrin groups were present in approximate proportions of 60:20:20. A more recent, detailed ^{13}C and ^{15}N NMR study[9] concluded that only azetidinium groups and their hydrolysis product, dihydroxypropyl groups, were present.

It is also not known why only 70% of the side groups react with mercaptans.[4] The presence of polymers of different structures and of low-molecular-weight impurities was suggested from SEC studies,[6–8] but structures were not assigned.

Hercosett 125 (Hercules Inc.) is a PAE resin used to shrink-resist wool.[2,3] The aim of the work described below was to explain the presence of multiple SEC peaks and to relate this to the chemical reactions that can occur with this product.

Journal of Applied Polymer Science, Vol. 30, 4099–4111 (1985)
 CCC 0021-8995/85/104099-13$04.00

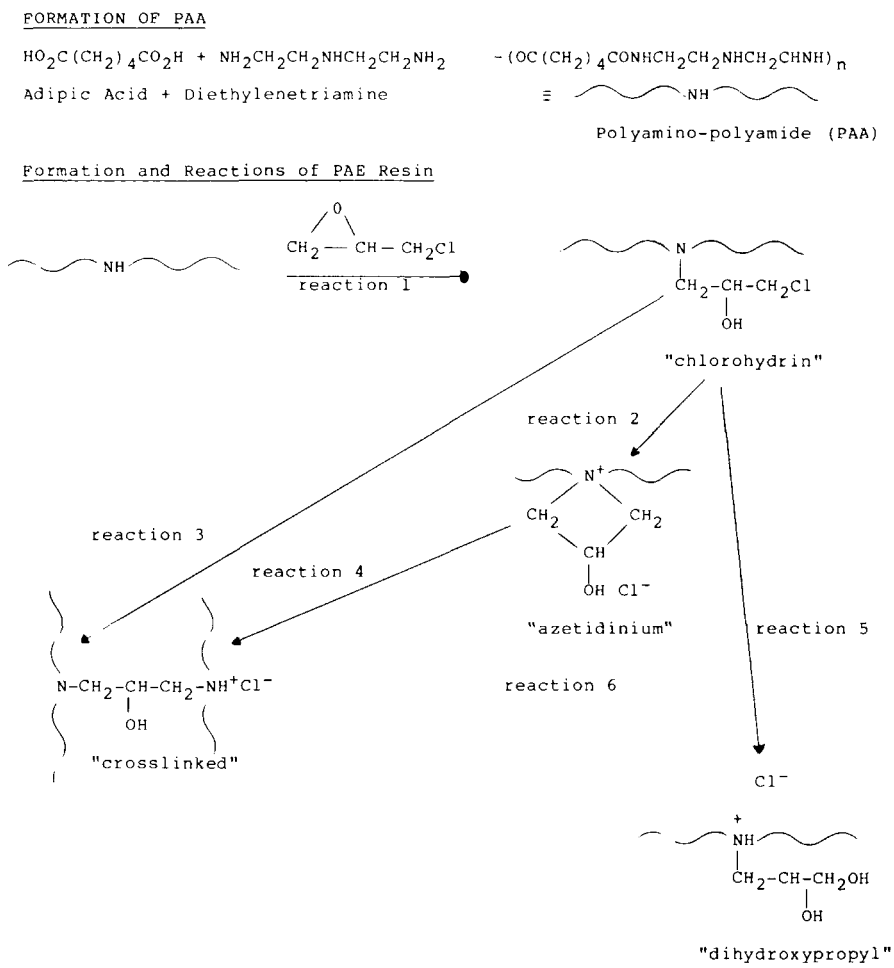


Fig. 1. Chemistry of PAE resins.

EXPERIMENTAL

Materials

The PAE resin was a fresh sample of Hercosett 125 provided by Hercules Australia Ltd. This was used within a month of receipt unless stated otherwise. The polyamino–polyamide (PAA) was a sample provided by Hercules Inc. (U.S.A.).

Size Exclusion Chromatography

Full details have been given previously.[7,8] A combination of TSK 4000SW and TSK 3000SW columns was used with 0.3*M* triethylammonium dihydrogen phosphate, pH 3, as eluent, unless stated otherwise. To prepare this eluent, triethylamine was dissolved in water and the pH 3 was adjusted with 85% phosphoric acid.

Viscosity

Viscosities were determined with a Ubbelohde viscometer at 25°C or with a Brookfield Synchro-electric LVT viscometer at room temperature.

NMR Spectra

Natural abundance ^{13}C-NMR spectra were measured at 40°C on a Bruker WM 250 spectrometer. Spectral widths of 12195 Hz, with 16391 data points, were used with complete proton decoupling.

Spin-lattice relaxation times (T_1) were determined using the standard $\pi-\tau-2$ sequence. ^{1}H spectra were obtained on the Bruker WM250 (250 MHz) and on a Varian T60A (60 MHz) spectrometer.

Chemical shifts were referenced to sodium 3-trimethylsilyl propionate [2,2,3,3-D_4] (TSP). Spectra were run of solutions either diluted with water or prepared by precipitation of the polymeric material with acetone and dissolution of the precipitate in deuterium oxide to give approximately 10% solution.

Molecular Weights

$\overline{M}_w$ were determined using a Chromatrix KMX6 low-angle laser light-scattering instrument with 0.5M sodium chloride as solvent. The estimation of $\overline{M}_w$ from SEC has been described previously.[7]

Fractionation of PAE Resin

Ultrafiltration

Ultrafiltration was carried out on an Amicon TCF10A unit with either an X100 membrane (nominal cutoff MW = 100,000) or a UM2 membrane (nominal cutoff MW = 2000). Separation of Hercosett 125 was carried out as follows: Hercosett 125 (50 g) was diluted with water (450 mL) and the solution was adjusted to pH 3 with dilute hydrochloric acid. Ultrafiltration was commenced with the X100 membrane. Evaporation of the filtrate gave fraction C. The solution (50 mL) retained by the membrane was then diluted with 0.5M sodium chloride (450 mL) and adjusted to pH 3 with hydrochloric acid, and ultrafiltration was continued with the same membrane. The filtrate and retentate were termed fractions B and A, respectively; both fractions contained sodium chloride. Membrane UM2 was then used to desalt and concentrate fractions A or B.

Precipitation

Fraction C was also obtained by dissolving sodium chloride (to give an approximate 20% solution) in Hercosett 125. This solution was added slowly with rapid stirring to 80–100 volumes of acetone to precipitate polymeric material and sodium chloride. The acetone solution was decanted and evaporated to leave a sticky solid which was extracted with methanol. The methanol extract was evaporated to give fraction C as brown oil, with identical spectral properties to that prepared by ultrafiltration.

Spectral data for fraction C: γ max. 3400, 1600, 1540, 1030 cm^{-1}; λ max. (H_2O), 315 nm (ϵ = 1100). ^{13}C-NMR: (D_2O) (63 mHz) 179(m), 168.09(s), 88.38(s), 73.57(d), 65.05(t), 54.26(t), 50.19(t), 48.36(t), 47.06(t), 45.09(t), 38.22(t), 35.79(s), 33.22(t), 23.77(t) ppm. ^1H-NMR: (60 mHz) 3.8 (m) ppm.

Textile Experiments

The plain-weave fabric (150 g/m^2) used in these experiments was chlorinated with 2.5% owf dichloroisocyanuric acid as described before.[8] This level of chlorination was chosen such that there was a significant improvement in shrink resistance when the PAE resin was applied and is lower than used in many industrial treatments. The polymers were exhausted onto chlorinated wool at 30°C, pH 7.5 for 30 min as described before.[8] SEC of a sample from the bath at this point indicated complete exhaustion of the polymeric material. Samples were washed in 15 L of pH 7.5 wash liquor at 40°C in a 50-L Cubex International machine.

Samples were stained for 5 min in a solution of 1 g/L Cibacron Pront Turquoise G (Ciba-Geigy) adjusted to pH 3.5 with acetic acid and rinsed for 1 min in cold water. Reflectance spectra were measured at 640 nm using a Kollmorgen Color-Eye KCS-18 spectrophotometer and the Kubelka-Munk function K/S was calculated. To reduce the variability in staining experiments, samples were treated at the same time, left for 1 day, and stained together in the same solution.

RESULTS AND DISCUSSION

Fractionation of Hercosett 125

In size exclusion chromatograms of Hercosett 125, the polymeric material eluted to two peaks,[7,8] a sharp peak at high molecular weight (peak A) and a broad peak at low molecular weight (peak B). In addition, a third peak (C), with an ultraviolet adsorption maximum at 315 nm, was eluted after the total permeation limit. The positions and intensities of the A and B peaks depended on the pH and ionic strength of the eluent. When either or both the pH and the ionic strength were raised, the A peak decreased in area and the B peak increased. This was attributed[7] to a change from an extended to a more compact conformation. This conformational change is typical of polyelectrolytes in solution.[10,11]

Hercosett 125 was divided by ultrafiltration into three fractions (termed A, B, and C) which showed [Fig. 2(b)–(d)] on SEC only an A, B, or C peak, respectively, and contained approximately 60%, 40%, and 2% of the original material. The peak C material passed through an ultrafiltration membrane with nominal 100,000 MW cutoff while A and B were retained. However, when 0.5M sodium chloride was added to the PAE solution, only the peak A material was retained by this membrane. A membrane of nominal 2000 MW cutoff could be used to remove salts (and also fraction C) from fractions A or B.

A simpler way to prepare the C fraction involved precipitation of the polymeric material with acetone; the solvent was removed from the acetone

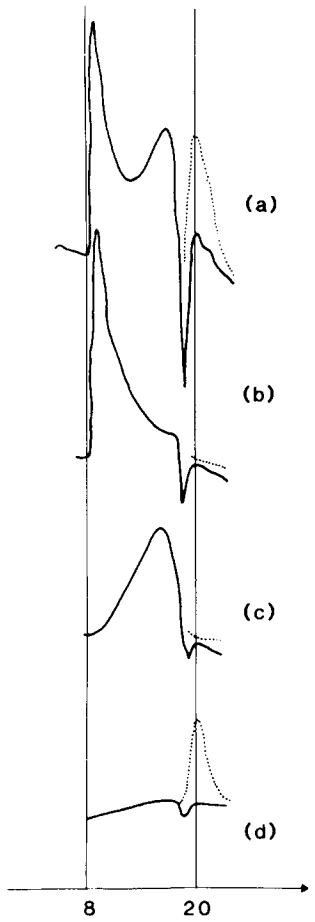


Fig. 2. Gel permeation chromatography: Eluent, pH 3, 0.3*M* triethylammonium phosphate. (a) Unfractionated Hercosett 125; (b) fraction A; (c) fraction B; (d) fraction C; (—) refractive index detector; (· · ·) ultraviolet absorption 315 nm.

solution, and the residue was extracted with methanol. Concentration of this methanol extract gave a brown oil with only peak C in SEC. The polymeric material precipitated by acetone still contained a small C SEC peak.

Properties of A and B Fractions

Hercosett 125, fraction A, and fraction B were stable only in dilute solution; freeze-dried material or solutions concentrated to contain more than 20% polymer slowly formed an insoluble gel after a few days at room temperature.

The B fraction on SEC at very low pH and ionic strength, e.g., $10^{-3}M$ H_3PO_4 (conditions which maximize the area of peak A in the SEC of Hercosett 125), showed only a B peak. The A fraction on SEC under the normal analysis conditions used for molecular-weight determination (pH 3,0.3*M* $Et_3N \cdot H_3PO_4$) showed only an A peak, but the A peak was reduced on SEC

in eluents with either a higher pH or ionic strength, and a broad peak was eluted later in the region where the B peak normally appeared.

The ^{13}C NMR spectra of the A and B fractions were very similar, apart from intensity differences of some minor peaks, and the main peaks had identical spin lattice (T_1) relaxation times. The ^{13}C NMR spectra of the A and B fractions were both very similar to the spectra of the unfractionated material and to those published by Kricheldorf[9] for a similar PAE resin.

The effect of ionic strength on the intrinsic viscosities of the A and B fractions is shown in Figure 3. Fraction B did not change, whereas fraction A showed typical polyelectrolyte behavior.[10,11] This difference perhaps relates to the higher molecular weight of A than B; differences in polyelectrolyte behavior with molecular weight are known.[10,11]

Molecular Weights of A and B Fractions

In the previous[7,8] SEC work, values of $\overline{M}_w = 11{,}000$ and $\overline{M}_n = 2{,}000$ were estimated for the B peak of unfractionated Hercosett 125 in $0.3M$ phosphate buffer; the A peak was eluted at the SEC exclusion limit and the molecular weight could not be estimated. In the present study, low-angle light-scattering measurements in $0.5M$ NaCl solutions suggested that $\overline{M}_w$ of fraction A was about 20 times that of fraction B, based on the assumption that the change of refractive index with concentration (dn/dc) was the same for both. If dn/dc was assumed to be 0.14 (a typical value for polyamides and polyelectrolytes[10]), the $\overline{M}_w$ calculated for fraction A was ~13,000 and for B was 600. The value of 0.14 for dn/dc might be low, but the use of higher values would at most double $\overline{M}_w$.

Several sources of error are possible in the molecular weight estimates from SEC and light scattering, particularly due to branching. One problem

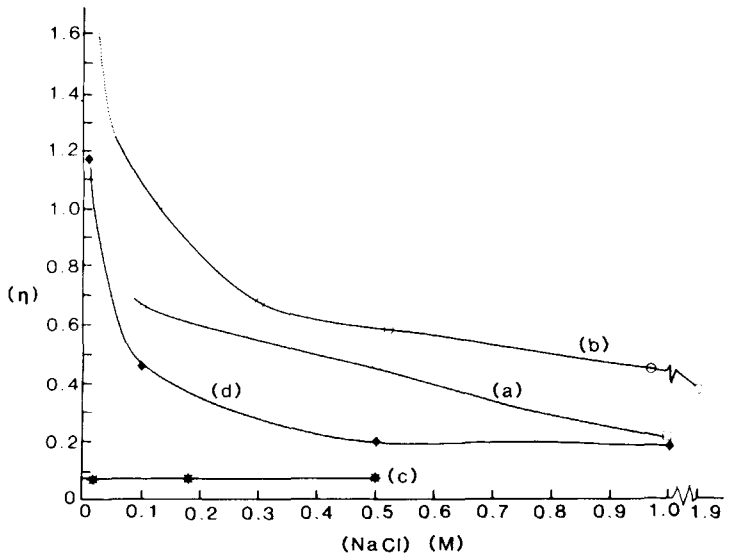


Fig. 3. Effect of ionic strength on intrinsic viscosity: (a) Unfractionated Hercosett 125; (b) fraction A; (c) fraction B; (d) PAA.

was that these measurements were made at the different ionic strengths, although the error from this is likely to be small in view of the viscosity results in Figure 3. The SEC could have given an anomalously high value due to ion-exclusion effects, but the system used gave the correct values for some polyvinylpyridine standards of known molecular weight. Another possibility is that the two peaks overlapped and the low-molecular-weight material of A may have been included in the SEC average of peak B. The ratio of the areas of the A and B SEC peaks (using the eluent used in molecular-weight assignments) was 40:60, whereas the weights of the A and B fractions from ultrafiltration were in the proportions 60:40. In support of this contention was the finding that the $\overline{M}_w$ of the isolated fraction B determined by SEC was approximately 7000, but $\overline{M}_n$ was very similar to that determined for unfractionated material.

The present study highlights the problems in the absolute determination of the molecular weight of polyelectrolytes. The main conclusion that can be drawn concerning Hercosett 125 and related PAE resins is that the molecular weight is low, there is a broad molecular-weight distribution, and some very low-molecular-weight material must be present. A low degree of polymerization must be expected, since in the preparation of the polyamino–polyamide (Fig. 1) there was excess of amino groups. However, a value of 600 for a PAE resin corresponds to only 2 repeat units in the polymer and is obviously too low, but at this stage it is not possible to say if the value determined before [7,8] by SEC for the PAE resin is more realistic.

Chemistry of Preparation of Hercosett 125

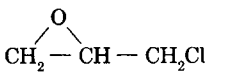
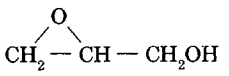
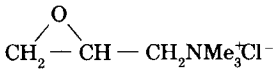
A sample of the polyamino–polyamide (PAA) used to prepare Hercosett 125 was provided by Hercules Inc. and its reaction with epichlorohydrin has been followed by NMR and SEC. The polymeric material in PAA showed only one broad SEC peak (even at low pH and ionic strength), and, from the SEC data, an $\overline{M}_w \sim 10{,}000$ was calculated using the previous[7] calibration method.

In the reaction of the PAA with 80% excess epichlorohydrin in water at 20°C, the proton NMR peak due to the $-CH_2-$ protons on the epoxide ring of the epichlorohydrin disappeared after a day, but the peak corresponding to the methylene groups on the azetidinium ring increased more slowly and reached a maximum after 3 days. This indicated that cyclization to form the azetidinium group (reaction 2) was slower than the addition of the epoxide (reaction 1).

In this reaction mixture, after 2 weeks at 20°C (Table I), there was only a very small shoulder corresponding to the A peak in the SEC. It was necessary to heat the reaction mixture before a significant A peak was observed in the SEC and the intensity of the A peak increased with reaction time and/or temperature. Reaction of the PAA and epichlorohydrin at high dilution or with excess (e.g., 1.8) epichlorohydrin gave no peak (Table I).

Reaction of PAA with 0.7 of epichlorohydrin gave a product with a larger A peak than the product from the reaction with 0.9 eq under the same conditions.

TABLE 1
GPC of Reaction Products of Polyamide–Polyamide (PAA) with Epoxides

Reactant	No. of equivalents epoxide for amino group of PAA	Reaction conditions[a]	GPC[b] area of A peak (% of total polymer)
None	—	—	Nil
	0.7	22° 7 days	Small shoulder
	0.9	22° 7 days	v-Small shoulder
	1.8	22° 7 days	Nil
	0.9	50° 14 days	30
	0.9	50° 14 days	Nil[c]
	0.9	70° 1 day	45
	0.9	90° 7 h	50
	0.9	90° 13 h	80
	1.0	20° 14 days	Nil
	1.0	20° 14 days	Nil

[a] Reaction in water at 10% solids content.
[b] Eluent pH 3, 0.3*M* trethyl ammonium phosphate.
[c] 1% solids reaction mixture.

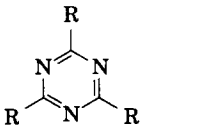
Structure of A and B Fractions

To account for the previous results, we propose that the fraction A was crosslinked (perhaps more correctly termed chain-extended) material in which two (or more) PAA molecules have been joined together by reaction of both functional groups in epichlorohydrin (reactions 3 or 4, Fig. 1), whereas the B fraction was essentially uncrosslinked low-molecular-weight material. The chemistry of the preparation of the PAA is expected to give a broad molecular-weight distribution, and chain-extension reactions during formation of the PAE resin should cause further broadening and/or skewing of the molecular-weight distribution. The main problem with this hypothesis about crosslinking is not that these reactions should occur, but how it results in two distinct SEC peaks and fractions separable by ultrafiltration. This may be explained by the different polyelectrolyte behavior of the A and B fractions (this is shown in the viscosity results in Figure 3). The high-molecular-weight material (fraction A) changes dimensions in solution with changes in ionic strength much more than the low-molecular-weight material (fraction B).

Further support for the crosslinked structure of fraction A was the observation (Table I) that the reaction products of PAA with glycidyl alcohol and glycidyl trimethylammonium chloride (neither of which can crosslink) showed in the SEC only one peak (a broad peak eluted in the same region as the PAE B peak) before the exclusion limit even at low pH and ionic strength. This crosslinked hypothesis was also consistent with the observation (Table I) that conditions that favored crosslinking, e.g., concentrated reaction mixtures, a deficiency of epichlorohydrin, or long reaction times, gave products with an increased A peak.

Fraction C

Fraction C is a minor (2% by weight) component in Hercosett 125 which does not exhaust onto wool and is responsible for most of the ultraviolet absorption of Hercosett 125 above 240 nm. A peak corresponding to the C peak in Hercosett 125 was also observed in SEC of the PAA from which Hercosett 125 was prepared, and at a similar concentration to that in the PAE resin. An aromatic structure was consistent with the ultraviolet and infrared spectra (see Experimental section). There were no aromatic protons in the NMR spectra, but there was a ^{13}C-NMR peak close to that reported[12] for 1,3,5-triazine. This suggested a structure such as I, but the ^{13}C-NMR also contained minor amide carbonyl peaks and suggested that fraction C was a mixture and might contain, for example, the products of reaction of adipic acid with one or two molecules of diethylenetriamine.



I, R = $CH_2CH_2NHCH_2CH_2CH_2NH_2$

Structure of Side Groups in the PAE Resins

The early papers on shrink-resisting wool with PAE resins (e.g., Ref. 2) suggested the presence of chlorohydrin, epoxy, and azetidinium groups, and this has subsequently been repeated in numerous textile papers. Chlorohydrin and epoxy side groups were inferred[5] from 60 MHz proton NMR and chlorohydrin from determinations of free and covalent chloride. Kricheldorf[9] interpreted the ^{13}C-NMR of a PAE resin (which had an identical spectrum with the Hercosett 125 studied here) on the basis of only azetidinium groups. Our ^{13}C-NMR spectra of Hercosett 125 clearly ruled out epoxy rings, but chlorohydrin—if present in low concentration—could not be excluded. A higher resolution (250 MHz) proton NMR spectrum of Hercosett 125 has now been examined and was inconsistent with the presence of either chlorohydrin or epoxy groups. The peaks in the 60 MHz proton spectrum previously assigned to these groups are possibly due to the hydrolysis product or to acetone used to precipitate the PAE resin. If this interpretation is correct, the method[5] used to determine covalent chlorine in the PAE resin must give anomalous results. Also the material used in some of the earlier studies[4,5] may not have been fresh and may have hydrolyzed; this would account for the incomplete reaction with thiols.[4]

Changes to Hercosett 125 on Storage

The manufacturer's literature assigns a 6-month shelflife to Hercosett 125. The Brookfield viscosity of Hercosett 125 dropped markedly after several months (Fig. 4) and a fall in viscosity is noted in the manufacturer's literature. We could not detect any change in the shrink resistance when

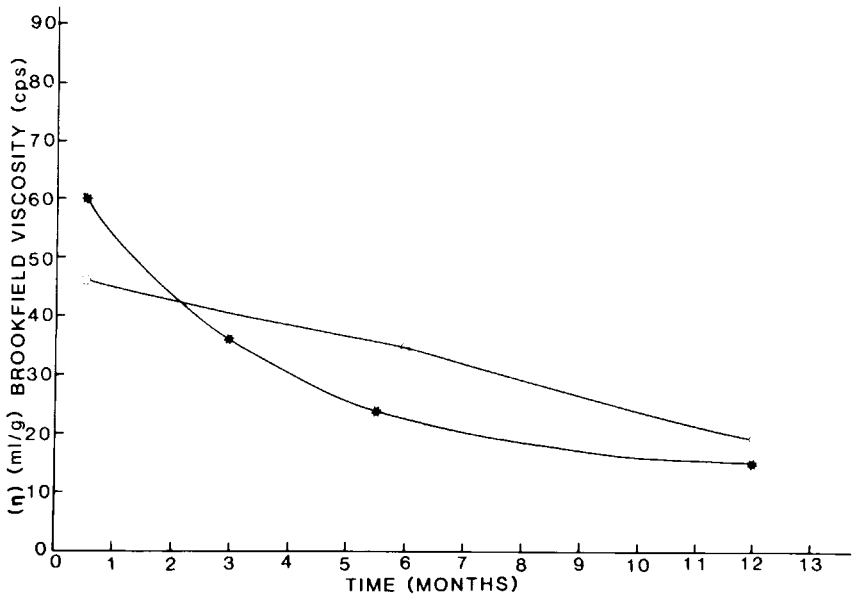


Fig. 4. Changes in viscosity of Hercosett 125 on storage at 20°C: (a) intrinsic viscosity in 0.5*M* NaCl; (b) Brookfield viscosity of 12.5% Hercosett 125.

samples of Hercosett 125 aged for 2 years at 20°C were applied to wool. Also, fraction A, after 3 months storage at pH 4, developed a substantial B peak in the SEC, whereas the SEC at fraction B on similar storage was unchanged.

Kricheldorf's NMR studies[9] established that the azetidinium groups in a PAE resin hydrolyzed to dihydroxypropyl groups (reaction 6, Fig. 1) during storage. Other chemical reactions are also possible although the acidic pH should prevent further crosslinking reactions 3 and 4 due to protonation of amino groups. In the SEC of Hercosett 125 solution aged for more than 3 months at 20°C, the A peak had decreased and the B peak increased. The crosslinking reactions 3 and 4 are not reversible, and, if our postulated structure of the A and B fractions is correct, the reduction of the viscosity and the A peak in the SEC on storage could indicate that hydrolysis of the polyamide backbone also occurs. This was not unexpected for a polyamide in aqueous solution at pH 3–4. It is unlikely that SEC could detect hydrolysis, unless it was very extensive, of the B fraction, due to the broad molecular-weight distribution and the poor resolution of the SEC at very low molecular weights.

Treatment of Wool with Fractions A and B

The properties of chlorinated wool treated with fraction A, fraction B, and unfractionated Hercosett 125 were quite similar (Table II), and, at low levels of chlorination, the shrink resistance was improved marginally by an increase in the curing temperature. To explain this improvement and the relative shrink resistance of the A and B fractions, we postulate that an increase in crosslinking results in improved shrink resistance, as has been suggested for other types of shrink-resist polymers.[13] However, with

TABLE II
Properties of Chlorinated Wool Treated with PAE Resins and Products Derived from PAA

Polymer treatment (1% owf)	Shrinkage, Wash time to exceed 10% shrinkage[c]		Dye staining, *K/S*	
	Cure, 5 min, 120°C	Cure, 5 min, 150°C	Cure, 5 min, 120°C	Cure, 5 in, 150°C
None	0.7 (2)	—	0.2	—
Hercosett 125	2.5 (>15)	2.5–3.0	2.1	1.0
Fraction A	2.5 (>15)	2.5–3.0	2.0	1.2
Fraction B	1.5 (15)	1.5–2.0	3.5	1.2
PAA	1 (10)	1	10.7	10.5
PAA + 1.0 equiv. GTMAC[a,b]	1	1	1.4	1.7
PAA 1.0 equiv. glycidol[b]	1	1	6.9	6.6
PAA 2.0 equiv. glycidol[b]	1	1	11.4	9.5

[a] GTMAC = glycidyltrimethylammonium chloride.
[b] Reaction conditions: 10% solution in water 20°C, 1 day.
[c] Figures in brackets are for fabric chlorinated with 3.0% dichloroisocyanuric acid.

PAE resins the level of chlorination appears to have a much greater influence on the level of shrink resistance than does the extent of crosslinking of the PAE resin. Crosslinking may not be the only factor involved, as high-temperature curing could also promote reactions between the polymer and the wool and this should improve the shrink resistance. Also, noncrosslinkable cationic polymers (e.g., the PAA and its reaction product with glycidol) improved the shrink resistance of chlorinated wool, as also recently found by De Boos.[14]

Anionic dyes with a high affinity for the resin but a low affinity for chlorinated wool are used in staining tests[14] to detect cationic polymers on wool. In the present study (Table II) chlorinated wool treated with fraction B stained more than that treated with either unfractionated Hercosett 125 or fraction A, but, after curing at 150°C, the staining of all three was similar. White[15] has observed that the curing conditions markedly influence the extent of staining of Hercosett-125-treated wool with other acid dyes. The general trend (observed here and by White[15]) was that the staining of PAE-resin-treated wool decreased as the extent of curing increased (e.g., by curing for longer times or at higher temperatures), but the level of staining of the noncrosslinkable products (e.g., PAA) did not change greatly with the curing conditions.

These staining results for fractionated and unfractionated Hercosett 125 (in particular, the differences between the A and B fractions cured at 120°C) may be explained by the increased crosslinking of the cationic polymer. Presumably, the greater the crosslinking the slower is the diffusion of dye into the polymer.

It is difficult to reconcile the level of staining (Table II) of Hercosett with that of uncrosslinked cationic polymers. The PAA and the PAA glycidol reaction product, which should both have a similar number of cationic

groups, both stained more than Hercosett, whereas the more cationic reaction product of PAA with glycidyl trimethylammonium chloride stained less. De Boos[14] recently observed that chlorinated wool treated with another highly cationic polymer, polyvinylbenzyltrimethylammonium chloride, stained less than Hercosett-125-treated wool.

CONCLUSIONS

The results of the work described in this paper suggest that:

Only azetidinium reactive groups are present in the PAE resin, Hercosett 125. Previously postulated epoxy and chlorohydrin groups are absent.

Hercosett 125 is a mixture of fraction A, which contains high-molecular-weight species formed by crosslinking reactions of both functional groups of one epichlorohydrin molecule, and fraction B, which is essentially not crosslinked.

The UV absorption of Hercosett is due mainly to a low-molecular-weight species, probably a triazine.

Fraction A shows more extensive polyelectrolyte behavior of large dimensional changes with pH or ionic strength than fraction B.

These postulates help explain the appearance of three peaks in the SEC, the changes in the SEC of the polymeric peaks with pH and ionic strength, and the separation of fractions corresponding to these peaks by ultrafiltration. Crosslinking can also account for the observations in the reaction of the polyamino–polyamide with epichlorohydrin that the A peak (chain-extended material) increased with the extent of heating, in concentrated reaction mixtures, and when the concentration of epichlorohydrin was reduced.

The shrink-resistance and dye staining of wool treated with the A and B fractions of Hercosett 125 were only slightly different and this is explained in terms of different extents of crosslinking. However, in this system, a much greater improvement in the shrink resistance was obtained by increasing the level of chlorination of the wool than by changing the extent of crosslinking during either manufacture (i.e., before application to wool) or during curing (i.e., after application to wool). Hence, changes to the manufacturing conditions, which could alter the proportions of the A and B fractions in a PAE resin, offer no practical advantages in terms of shrink resistance.

Another point that emerges from this study is that chemical reactions occur in Hercosett 125 during storage. We have not been able to detect any change in shrink resistance after 2 years at 20°C, although a reduction was expected since the number of potential crosslinks should be reduced by hydrolysis of the reactive azetidinium groups to dihydroxypropyl groups, while backbone hydrolysis should negate crosslinking.

^{13}C and high resolution proton NMR spectra were kindly determined by Mr. I. Willing of CSIRO Division of Applied Organic Chemistry, Melbourne.

References

1. G. I. Keim, U.S. Pat. 2,926,154 (1960).
2. R. H. Earle, Jr., R. H. Saunders, and L. R. Kangas, *Appl. Polym. Symp.*, **18**, 707 (1971).
3. P. Smith and J. H. Mills, *Chem. Tech.*, **3**, 749–755 (1973).

4. N. A. Bates, *Tappi*, **52**, 1162–1168 (1969).
5. M. E. Carr, W. M. Doane, G. E. Hamerstrand, and B. T. Hofreiter, *J. Appl. Polym. Sci.*, **17**, 721–735 (1973).
6. W. de Fries, thesis, Rheinisch Westfaischen Technischen Hochschule, Aachen, 1979.
7. G. B. Guise and G. C. Smith, *J. Chromatog.*, **235**, 365–376 (1982).
8. G. B. Guise and G. C. Smith, *Textilveredlung*, **18**, 334–338 (1983).
9. H. R. Kricheldorf, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2195–2214 (1981).
10. A. Eisenberg and M. King, *Ion Containing Polymers*, Academic, New York, 1977, Chap. 5.
11. C. Tanford. *Physical Chemistry of Macromolecules*, Wiley, New York, 1963, p 306.
12. G. C. Levy and G. L. Nelson. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley-Interscience New York, 1972.
13. G. B. Guise and M. A. Rushforth, *J. Soc. Dyers Col.*, **92**, 389–394 (1975).
14. A. G. De Boos, *J. Text. Inst.*, **75**, 184–190 (1984).
15. M. A. White, unpublished results.

Received October 10, 1984
Accepted February 13, 1985