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Determination of Shrink-Resist Polymers on Wool Fabric by DSC

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ABSTRACT

Many reactive polymers used to shrink-resist wool fabric are derived from poly(propylene oxide) (PPO). Shrink-resist polymers derived from PPO were identified on wool by their oxidation characteristics using differential scanning calorimetry. The amount of PPO-based polymers on the fabric was estimated using isothermal scans after calibration with suitable standards. Polyacrylates applied with the PPO did not interfere with the oxidation of the PPO component, but a polyester-polyurethane dispersion suppressed PPO oxidation and made identification and estimation of the PPO component unreliable. The technique was used to determine the distribution of shrink-resist polymer on men's trousers.

INTRODUCTION

A number of polymer systems have been proposed as shrink-resist treatments for wool. The chlorine-Hercosett process [1], which is used to shrink-resist wool in top form, entails mild chlorination of the fiber followed by application of a polyamide-epichlorohydrin resin.

More recently, multifunctional reactive prepolymers for which no prechlorination is required have been developed for wool-containing

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fabrics [2, 3]. These prepolymers are usually derived from poly(propylene oxide) polyols (PPO) or polysiloxanes, although some experimental ones based on poly(tetramethylene oxide), polyesters, polybutadiene, and polyamides have been reported [4]. The hydroxyl endgroups of PPO are capped to produce prepolymers with reactive terminal groups such as thiols, isocyanates, or carbamoyl sulfonates. The product containing the latter grouping is also used in combination with soft acrylic emulsions, vinylidene chloride-based emulsions, or polyurethane dispersions to shrink-resist wool fabrics.

There have been difficulties in identifying and quantifying polymers on wool. Chemical-analytical techniques, such as hydrolysis and chromatographic separation of the components [5] can be used on some polymers, but are very time-consuming. Some dye-staining techniques have also been described, but these do not distinguish polymer types and are not quantitative [6]. Thermal analytical techniques have been used to identify interfacially deposited nylon on wool [7] but have been less successful for other polymers [8]. This communication describes the use of differential scanning calorimetry to identify and determine the type and amount of shrink-resist polymers on wool by examining its thermo-oxidative behavior.

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EXPERIMENTAL

A plain-weave, pure wool fabric (150 g/m^2, R60/2 tex yarn, 13 ends/cm × 12 picks/cm) was used. The polymers listed in Table 1 were applied to the fabric and cured according to recommendations [9-12].

The following hindered-phenol antioxidants were also used: Irganox 415 (Ciba Geigy); Anullex PBA 15 (William Pearson); Plastanox 2246 (American Cyanamid).

DSC scans were made by using a Perkin-Elmer DSC-1B instrument. Approximately 2.8 mg of fabric, conditioned at 65% RH, 20°C and accurately weighed, was placed in an aluminum pan and covered with a disk of stainless-steel gauze. Unless otherwise stated, an oxygen atmosphere (flow rate 30 ml/min) was used.

Two procedures were used. Scanning experiments were conducted at 16°C/min from room temperature to 350°C. In the isothermal experiments, treated fabrics were rapidly heated at 64°C/min to the required temperature and held there until the exotherm was complete.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry of Shrink-Resist Wool

Earlier thermal analyses [7, 8] of polymer-treated wool were performed under nitrogen or continuous evacuation. Thermal transitions

TABLE 1. Polymers Used

Polymer	Manufacturer	Type
Synthappret LKF	Bayer	Poly(propylene oxide)-based urethane prepolymer
Synthappret BAP	Bayer	Bisulfite adduct (water-soluble) of Synthappret LKF
Primal K3	Rohm & Haas	Soft polyacrylate emulsion
Primal HA20	Rohm & Haas	Acrylate - vinylidene chloride copolymer emulsion
Impranil DLN	Bayer	Polyester-based urethane dispersion
Hercosett 57	Hercules	Polyamide-epichlorohydrin resin
DC109	Dow Corning	Dimethylsiloxane-based silicone prepolymer

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in the polymer (such as the melting of a polyamide) that made up only a small part of the sample were very small and easily masked by the transitions associated with the wool.

In the present study, an oxygen atmosphere was used. Thermograms of various shrinkproofed wool fabrics are shown in Fig. 1. Fabrics treated with PPO-based polymers had a distinct exotherm between 180 and 220°C which was not observed on untreated wool or when the polymer-treated fabrics were heated in a nitrogen atmosphere. Similar exotherms were obtained with PPO-treated wool or glass filter cloth. Chlorinated wool and wool treated with polyacrylates, polyamides, or polysiloxanes did not show an exotherm. Consequently, the exotherm was interpreted as being due to the oxidation of the poly(propylene oxide). A similar exotherm was also observed in a study of the flammability properties of wool treated with Synthappret LKF [13]. The exact position of the oxidative exotherm depended on the concentration of antioxidant, the polymer, and the heating rate. Shrink-resist treatments involving application of a mixture of a polyacrylate (Primal K3 or Primal HA20) and Synthappret BAP exhibited the oxidation peak for the PPO component, but when Synthappret BAP was applied in mixture with a dispersion of a polyester-based polyurethane (Impranil DLN) the oxidative exotherm was suppressed. Oxidative exotherms were also observed in wool treated with other polyether-based polymers such as poly(ethylene oxide) and poly(tetramethylene oxide) but only those based on PPO are commercially available for shrink-resist applications.

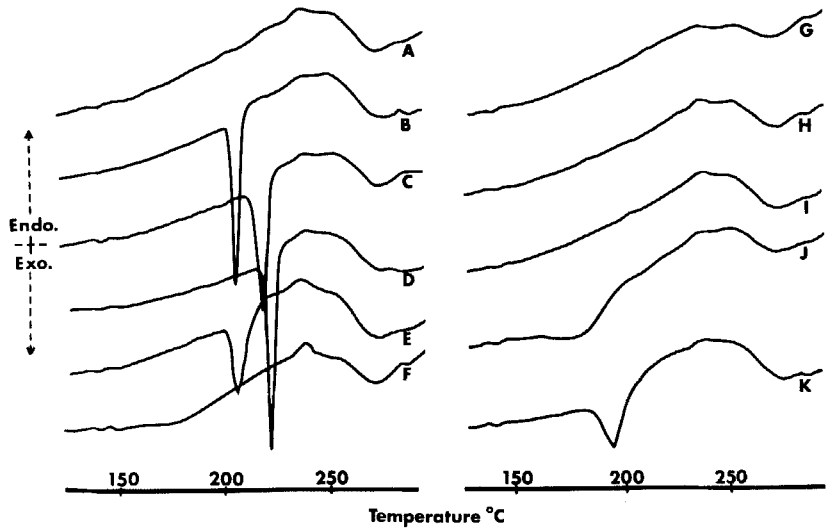

FIG. 1. Thermograms of treated wool fabrics: (A) untreated wool or chlorinated wool (4% DCCA); (B) 3% omf poly(propylene oxide) polyol (MW 3000) + 1% omp Anullex PBA 15; (C) 3% omf Synthappret LKF + 1% omp Anullex PBA 15; (D) 3% omf Synthappret BAP + 1% omp Anullex PBA 15; (E) 3% omf 1:1 Primal K3/Synthappret BAP + 0.5% omp Anullex PBA 15; (F) 3% omf 1:1 Impranil DLN/Synthappret BAP + 0.5% omp Anullex PBA 15; (G) chlorinated wool (4% DCCA) + 2% omf Hercosett 57; (H) 3% omf Primal K3; (I) 3% omf Silicone DC109; (J) 3% omf poly(ethylene oxide) polyol (MW 4000), no antioxidant; (K) 3% omf poly(tetramethylene oxide) polyol (MW 2000), no antioxidant.

Determination of the Amount of Polyether on Wool

Because only the polyether-based polymers appeared to be involved in the oxidation, the energy of the oxidative exotherm was used as a measure of the amount of PPO polymers on the wool. Preliminary experiments indicated that more reproducible exotherms were obtained if samples were oxidized under isothermal conditions. Consequently, treated fabrics were rapidly heated to the required temperature and held at that temperature until the exotherm was observed. Under these conditions, oxidation occurred after an initial induction period. The energy of oxidation (measured as the area of the exotherm) was proportional to the amount of polymer applied to the fabric (Fig. 2), but the relationship between polymer content and energy differed between PPO and the PPO-based shrink-resist polymers. However, when allowance was made for the end groups (between 14 and 21% by

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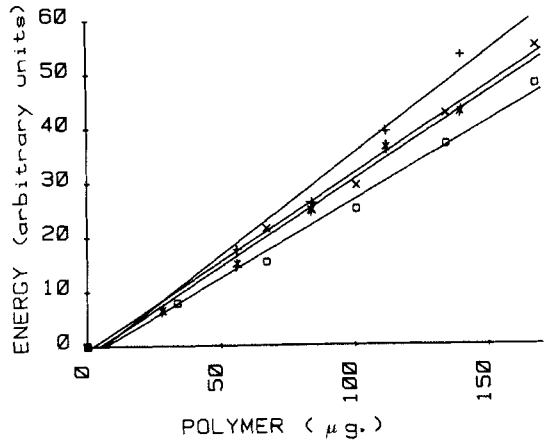

FIG. 2. Energy of oxidation of various polymers by isothermal experiments at 155°C: (○) Synthappret BAP (r = 0.99); (×) 1:1 Synthappret BAP/Primal K3 (r = 0.99); (*) Synthappret LKF (r = 0.99); (+) PPO polyol, MW 3000 (r = 0.99).

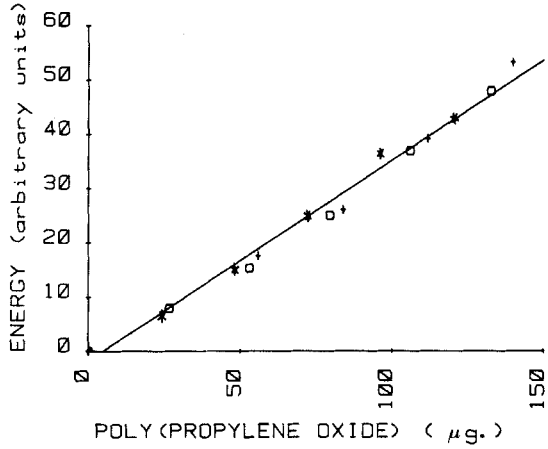

FIG. 3. Energy of oxidation for the PPO component of various polymers.

weight of the polymer), the polymers all fitted the same line (Fig. 3). Thus, it appears that the end groups did not participate in the oxidation. The polyacrylate in 1:1 Synthappret BAP/Primal K3 system [10] had little effect on the energy of oxidation of the BAP component.

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However, the errors in the determination were greater for the mixed polymer system than for BAP alone. The energy of oxidation was independent of the antioxidant, the antioxidant concentration and the presence of wool.

The variability of exotherm energy (±10% at 95% confidence) did not appear to be due to uneven polymer application, as similar variations were observed when measured amounts of polymer solutions were added directly to fabric in the sample pans. This appears to be the limit of accuracy for the determination of PPO-based polymers on fabric using DSC. A similar spread of results has been reported for the estimation of stabilizer efficiency in polypropylene by DSC [14].

Use of DSC to Determine Antioxidant Effectiveness

Because PPO-based shrink-resist polymers are prone to oxidative attack, hindered-phenolic antioxidants [15, 16] are included to protect the polymer against thermal or photo-degradation during processing or in wear. In isothermal DSC experiments, the induction period increased with the concentration of antioxidant in the polymer film (Fig. 4) and depended on the structure of the antioxidant.

DSC analysis ranked the antioxidants in the same order (415 > PBA-15 > 2246) as obtained by tests of thermal stability (Table 2). However, the effectiveness of Anullex PBA15 in stabilizing the polymers to light was slightly greater than that of Irganox 415. Differences in the initiation of the thermo-oxidative and light-activated oxidative degradation for the Anullex PBA15 and Irganox 415 stabilized

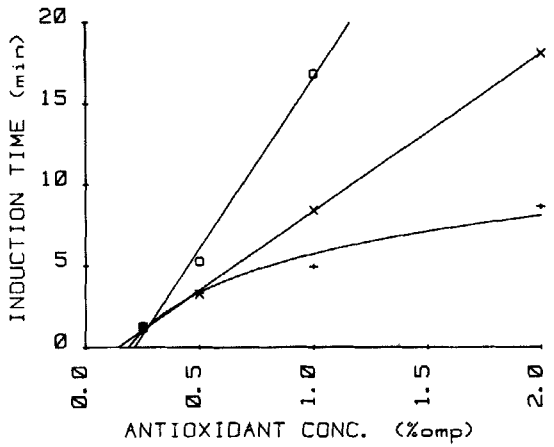

FIG. 4. Effect of antioxidant and antioxidant concentration on induction time in Synthappret BAP (1.5% omf): (○) Irganox 415; (×) Anullex PBA 15; (+) Plastanox 2246.

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TABLE 2. Antioxidant Concentration Required to Stabilize Polymer-Shrinkproofed Wool

Polymer (1.5% omf)	Antioxidant	Antioxidant concn at various exposure times (%)				
		Heat[a]			Light[b]	
		2.5 hr	4 hr	8 hr	3 days	6 days
Synthappret BAP	Irganox 415	0.4	0.8	~1.3	0.6	~2
	Anullex PBA 15	0.5	1.1	~2	0.3	>2
	Plastanox 2246	0.9	~1.5	>2	~2	>2
BAP-K3	Irganox 415	0.5	0.9	~1.8	0.4	>2
	Anullex PBA 15	0.4	1.2	~1.8	0.2	>2
	Plastanox 2246	>2	>2	>2	>2	>2
BAP-DLN	Irganox 415	0.6	0.9	~1.8	0.4	>2
	Anullex PBA 15	0.7	1.1	>2	0.2	~1.5
	Plastanox 2246	>2	>2	>2	>2	>2

[a]Held at 173°C in a forced-draft oven for time shown.
[b]Exposed to MTBF lamps at 25°C for time shown.

systems may be responsible for this effect. Nevertheless, DSC remains a useful tool for predicting large changes in light stability. The induction period for a given antioxidant also varied with the polymer (Fig. 5) and the amount applied to wool. The difference in effectiveness of a given antioxidant in various polymers may have been the result of the differences in crosslink density of the polymers or differences in the compatibility of the antioxidant with the polymer. The effectiveness of the antioxidant in the 1:1 Primal K3/Synthappret BAP, based on total weight of polymer, was only slightly greater than that of the antioxidant in the BAP alone. This suggested that the antioxidant had distributed itself between the two components. If the antioxidant had remained in the BAP component, the effective antioxidant concentration and hence the induction time would have doubled.

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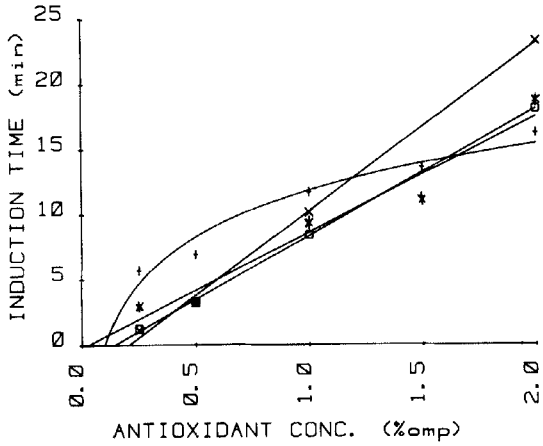

FIG. 5. Effect of polymer and Anullex PBA 15 concentration on induction time (1.5% omf): (○) Synthappret BAP; (×) 1:1 Synthappret BAP/Primal K3; (*) Synthappret LKF; (+) PPO polyol, MW 3000.

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Distribution of Polymer in Garments

Synthappret LKF applied from perchloroethylene in a drycleaning machine is used to shrink-resist garments [17] and to give durable-press effects in men's trousers [6]. When shrinkage occurs in polymer-treated men's trousers it is usually uneven, occurring first in the seams and near the waist band (Fig. 6). This unevenness is thought to result from an uneven distribution of the polymer. Samples were taken from the felted and non-felted areas of the garment (given a nominal 1.5% Synthappret LKF treatment), and the amount of polymer and the antioxidant concentration were determined with the DSC techniques outlined above. No polymer was detected in the seams of the trousers, either by isothermal or scanning DSC. By using isothermal DSC, the unfelted areas of the legs were found to have ~1.6% omf polymer, whereas the felted area on the hem had ~ 0.4% omf. The felted areas of the trousers near the pocket had the same amount of polymer as the unfelted areas. These differences were qualitatively confirmed by a dye-staining technique [6]. No difference was detected in the antioxidant concentration of the polymer in the various regions.

These results indicate that the felting along the leg seams and at the join of the waistband was caused by the low concentration of polymer in these areas. A possible cause of the felting in the leg area of the garment adjacent to the pockets was additional mechanical action in that area as the result of the configuration adopted by the garment in the machine. In this example, staining allowed only

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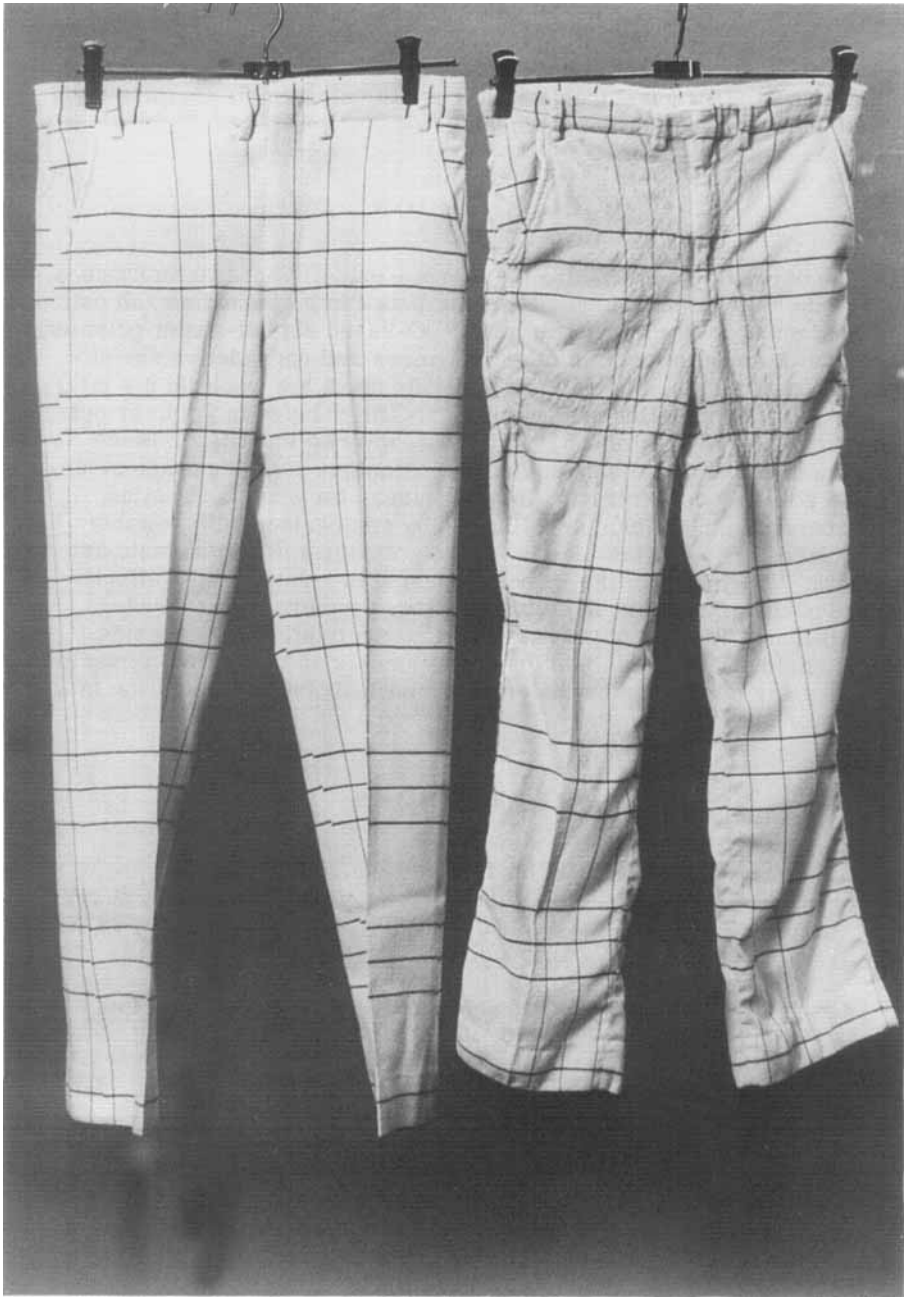

FIG. 6. Trousers treated with Synthappret LKF (1.5% omf nominal) before (left) and after (right) machine washing (2 cycles Kelvinator machine).

subjective assessment and then only on white or lightly dyed garments. In contrast, DSC gave quantitative results using small samples from well-defined areas of the garment.

CONCLUSION

By using DSC to measure the thermo-oxidative characteristics, polyether-based shrink-resist treatments can be identified and estimated on wool fabric. In this way PPO-based shrink-resist polymers can be differentiated from other polymers and degradative shrink-resist treatments. Under the conditions used, the wool did not interfere with the oxidation of the polymer. Differences in polymer concentration in excess of 0.5% omf can readily be identified. Since only a small sample is required, the technique can be used to determine polymer concentration in small areas for spots and stains. Antioxidant content can be estimated by comparison with suitable standards provided the identity of the polymer and antioxidants are known. The length of the induction period is related to the effectiveness of the antioxidant in stabilizing the polymers under service conditions. The technique has practical application in assessing polymer distribution in fabrics and garments and the effect of various processing conditions on the effective antioxidant concentration in the polymer.

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