Effects of Aroma Chemical Vapor Pressure and Fiber Morphology on the Retention of Aroma Chemicals on Cotton and Poly(ethylene terephthalate) Fabrics

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ABSTRACT: Aroma chemicals with vapor pressure in the range of 10–7460 mPa were applied onto cotton and poly(ethylene terephthalate) (PET) fabrics. Retentions on these two fabric substrates were measured using gas chromatography/mass spectrometry (GC/MS), while distribution on and within fiber was graphically demonstrated by backscattered electron microscopy (BSE). Aroma chemicals with low vapor pressures were retained on the fabrics to a larger extent than aroma chemicals with higher vapor pressures. Larger amounts of aroma chemicals were retained on cotton than on PET. Effect of fiber type on retention was largest for aroma chemicals with higher vapor pressures; for example, 20% of allyl cyclohexyl propionate (1360 mPa) was retained on cotton fabric after 480 min, while none was detected on PET as compared to ambrettolide (30 mPa) that had no difference between cotton and PET after 480 min. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1720–1723, 2006

Key words: fibers; vapor pressure; surface; cotton; polyester

INTRODUCTION

In our previous research,[1] we found that the distribution of aroma chemical on cotton, lyocell, and poly(ethylene terephthalate) (PET) fabrics varied with the following fiber characteristics: molecular structure, surface and internal morphology, capillary structure, and fiber packing in the yarn structure. Aroma chemicals were deposited and retained on the fiber surfaces, within the micro pores or voids in the fibers, in capillary structures such as the crenulation of cotton, and between closely space fibers within the yarn and fabric structure. Aroma chemical was observed on internal surfaces for both cotton and lyocell fibers because of the pores and voids in their structures. Deposition, adsorption, and retention of aroma chemicals were influenced by the relative surface energies of the fibers and aroma chemicals. Chemical properties also influence retention and release of aroma chemicals from fabric. The goal of this research is to study the effect of a key chemical physical parameter, vapor pressure, on the distribution and retention of aroma chemical on cotton and PET textiles.

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EXPERIMENTAL

Fabric

Bleached cotton print cloth (style 400) and PET (100% Dacron®, type 54, style 777) fabrics, from Testfabrics (West Pittiston, PA), were rinsed in running tap water for 1 h, followed by washing with distilled water, air-dried at 23°C, and conditioned at 65% ± 2% relative humidity for at least 24 h. Cotton is a naturally occurring cellulose fiber that has characteristic surface roughness, microporous and capillary structure,[2,3] and distinct morphological regions including lumen, secondary wall, and crenulation.[4–8] PET fiber is synthetic usually with a round cross-sectional shape, very few or no voids and irregularities.[9]

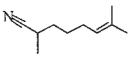
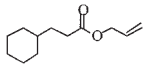
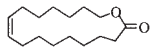
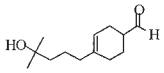
Chemicals

Aroma chemicals (given in Table I) (International Flavors and Fragrances) and ethanol (VWR Scientific, West Chester, PA, HPLC grade) were used as received. Their vapor pressures were measured, according to a method reported by Rittfeldt.[10] Aroma chemical/ethanol solutions were prepared at a concentration of 1% (w/v). Osmium tetroxide aqueous solution (2% w/v) was purchased from Electron Microscopy Sciences (Hatfield, PA).

Application method

The pipette method for aroma chemical delivery was described previously.[1] Briefly, 0.2 mL of 1% (w/v)

TABLE I
Aroma Chemical Properties and Cotton Fabric Retention Data

Aroma chemical	Structure	Vapor pressure at 295 K, 760 mmHg mPa	Retention on fabric (%)			
			Cotton		PET	
			70 (min)	480 (min)	70 (min)	480 (min)
Agrunitrile		7460	43	5	35	0
Allyl cyclohexyl propionate		1036	78	20	70	0
Rosalva		790	80	26	77	10
Ambrettolide		30	97	94	96	94
Lyral		10	92	75	91	70

aroma chemical/ethanol solution was delivered by pipette onto each fabric swatch, followed by air-drying to allow the evaporation of ethanol. At selected time intervals of 70 or 480 min, the fabric was extracted twice with 5 mL of ethanol. The extracts and original aroma chemical solutions were analyzed by gas chromatography/mass spectrometry (GC/MS).

Quantitative analyses of aroma chemicals were performed on an Agilent Technologies GC/MSD 6890N equipped with a HP-5MS (5% phenyl methyl siloxane) capillary column of 30 m $\times$ 250 μm $\times$ 0.25 μm and autosampler. The temperature of injection port was 220°C. Splitless mode was used for both SCAN and SIM (selected ion monitoring) acquisition. The oven temperature program was as follows: initial temperature was 60°C, temperature ramps of 23°C/min to 210°C and 30°C/min from 210 to 300°C. Carrier gas was helium at a flow rate of 1 mL/min. An aliquot of 1 μL of aroma chemical in ethanol was injected for quantitative analyses. Integrated areas of the target gas chromatogram peak were used for all quantification.

Microscopy analysis

Fabric specimens were exposed to osmium tetroxide vapor for several hours in an enclosed container. Osmium tetroxide reacted with the unsaturated aroma chemicals, providing a tag for backscattered electron imaging. Treated warp yarns were embedded in resin and cured at 70°C for about 10 h. Thick cross sections (~5 μm) were prepared with a microtome. Yarn specimens were mounted on carbon stubs using carbon tape. Before the microscopical analysis, specimens were carbon coated using an Edwards Auto 306 High Vacuum Evaporator (Edwards High Vacuum International, Wilmington, MA). Backscattered electron images were recorded on a Scanning Electron Microscopy JEOL 440 (LEO Electron Microscopy, Japan) in the Cornell Center for Materials Research. An accelerating voltage of 15 kV and a working distance of 20 mm were used. X-ray maps were obtained using a JEOL Superprobe JXA-8900R WD/ED combined Microanalyzer. Net X-ray counts from Os at an energy range of 1.64–2.11 keV at selected locations were provided by conducting energy dispersive X-ray analysis (EDX) on the same instrument. Control specimens were not treated with aroma chemical but were exposed to osmium tetroxide vapor. As osmium tetroxide does not react with cellulose or PET, the net X-ray counts from Os on these controls were zero.

RESULTS AND DISCUSSION

An inverse relationship was observed between vapor pressure and aroma chemical retention on fabric. For ambrettolide with vapor pressure of 30 mPa, 94% of that applied was retained on cotton fabric after 480 min, while within the same time period only 5% of agrunitrile with vapor pressure of 7460 mPa was retained. Retention for Lyral and rosalva on cotton fabric showed a similar trend, i.e. less rosalva with vapor pressure of 790 mPa was retained after 480 min than Lyral with a vapor pressure of 10 mPa (Table I).

Backscattered electron microscopy (BSE) images of cotton yarn treated with rosalva and Lyral are shown in Figure 1. More Lyral with a lower vapor pressure was retained on cotton surfaces after storing at room condition for 480 min than rosalva that has a higher vapor pressure. This is in agreement with the low amount of rosalva (26%) retained on the fabric, as measured by GC/MS (Table I). Similar results were obtained when comparing the other three aroma chemicals that had varying vapor pressures (Fig. 2). After 480 min, no deposits of high concentration were observed on fibers treated with aroma chemicals agrunitrile and allyl cyclohexyl propionate with higher vapor pressures. However, we observed large concentrations on yarn treated with aroma chemical ambrettolide that has the lowest vapor

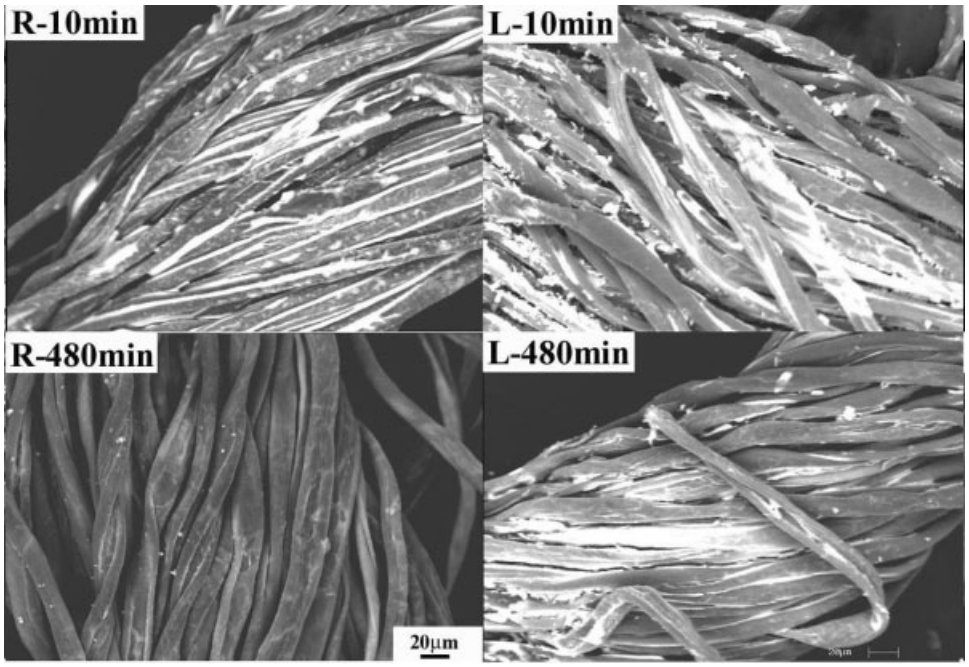


Figure 1 BSE images of treated cotton yarn with rosalva (R) and lyral (L) after 10 and 480 minutes.

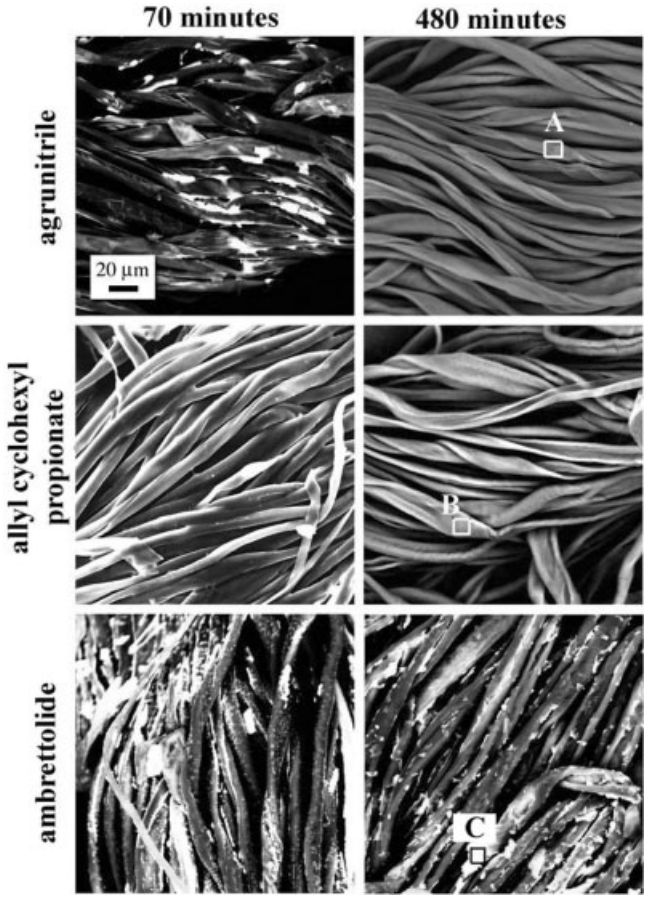


Figure 2 BSE images of cotton fabric treated with agrunitrile (top), allyl cyclohexyl propionate (middle), and ambrettolide (bottom). Data was collected 70 and 480 min. after application of aroma chemical on the fabric.

pressure of 30 mPa. We believe that small amounts of aroma chemical remain on the treated surfaces, as GC results showed 5 and 20% aroma chemical retained on the fabrics for agrunitrile and allyl cyclohexyl propionate, respectively. Backscattered electron images are less effective in determining the presence of lower concentrations of aroma chemical such as areas marked in Figure 2(A, B). To determine the presence of aroma chemical, we measured the relative net X-ray intensities at these two locations; they were 59 and 218 for agrunitrile and allyl cyclohexyl propionate, respectively, confirming the presence of low concentrations of aroma chemicals on these surfaces. The bright spot in Figure 2(C) for ambrettolide had a relative net X-ray intensity of about 1000 under the same measurement condition.

Retention of aroma chemicals was studied on two fibers that differ in chemistry and morphology—-our data indicate that evaporation behavior of aroma chemical on cotton was different from that on PET, particularly for the aroma chemicals with the higher vapor pressures. In general, a larger amount of aroma chemical was retained on cotton than on PET fabrics at both time periods (Table I). At the shorter time period of 70 min, retentions of all five aroma chemicals on cotton and PET fabrics did not differ as much as they did for the longer time period of 480 min. When storing time was extended, retention on PET was less than on cotton for agrunitrile, allyl cyclohexyl propionate, and rosalva with vapor pressure of 7460, 1360, and 790 mPa, respectively. Aroma chemicals were released at a faster rate from PET than from cotton. This difference may be attributed to other factors in

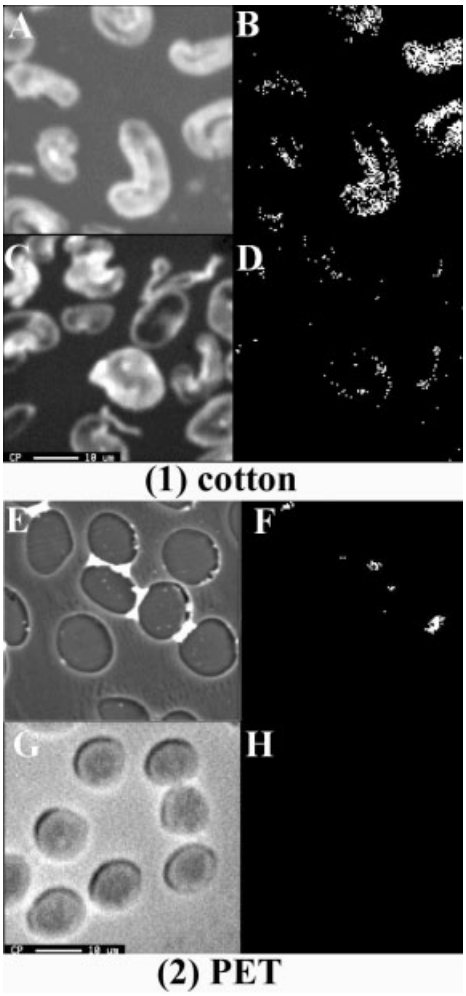


Figure 3 BSE images (A, C, E, G) and X-ray maps (B, D, F, H) of cross-section of (1) cotton and (2) PET fabrics treated with rosalva after 70 min. (A, B, E, F) and 480 min (C, D, G, H).

addition to evaporation rate and vapor pressure of the aroma chemical, such as distribution of aroma chemical in the external and internal fiber and molecular interaction between aroma chemical molecules and polymers of the fiber.

Distributions of aroma chemicals varied on and within cotton and PET fibers. Location and concentration of aroma chemical rosalva on and within fibers are presented in the backscattered electron images and X-ray maps of the fibers cross sections in Figure 3. Aroma chemical rosalva is distributed through the whole cotton fiber from external fiber surface to internal fiber structure including the secondary wall, crenulation, and lumen [Fig. 3(A, B)], while it is deposited only on the external PET fiber surface, with no penetration into the bulk of the PET fiber [Fig. 3(E, F)]. As fewer strong polar forces are expected between rosalva and PET than between rosalva and cotton, volatilization of the aroma chemical on PET fabric is expected to behave much like that of a pure liquid. Thus, retention would be predominately related to vapor pressure of aroma chemical. After 480 min, most rosalva had evaporated from the PET fibers [Fig. 3(H)].

Cotton fibers exhibit a complex morphology, and capillary forces as well as pore structures influence the adsorption of liquids. It is anticipated that the evaporation of a liquid that is adsorbed on an internal surface, e.g., within a small pore or capillary, will be hindered relative to volatilization from an external surface. In addition, the cotton surface is very hydrophilic, and strong polar interaction forces likely play important roles in influencing retention of aroma chemicals on textile fibers. As seen in Figure 3(D), low concentration of rosalva were still observed on and within cotton fibers after 480 min, which is in agreement with the GC/MS result, showing 26% rosalva retention (Table I).

CONCLUSIONS

Vapor pressure of aroma chemicals had the expected effect on retention of aroma chemical on fibers, and this effect is graphically presented in the microscopy. Lower vapor pressure of the aroma chemical resulted in increased retention of the aroma chemicals on the fiber surfaces. Retention of aroma chemicals—agrunitrile, allyl cyclohexyl propionate, and rosalva—with higher vapor pressure was different for cotton and PET fabrics. This difference between cotton and PET may be related to differences in polar and hydrogen bonding interactions with the fabric substrates and in morphological structures. For cotton fabric, the distribution of the aroma chemicals was on the external fiber surfaces and within the pore structure of the fiber, or internal surfaces, while for PET fibers the aroma chemicals were distributed on the external fiber surfaces.

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