Solid State C-13 NMR Characterization of Textiles: Qualitative and Quantitative Analysis

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Synopsis

Cross-polarization magic angle spinning (CP/MAS) carbon 13 NMR was used to qualitatively and quantitatively characterize textiles of various compositions. Rapid and accurate determination of cotton/polyester blends was accomplished with minimal sample preparation using an empirical peak height relationship. Qualitative identification was demonstrated for various fiber blends.

INTRODUCTION

Only within the past decade has the textile industry replaced wet chemical analysis for composition of fabrics and fibers with modern instrumental techniques. The advantages of these new techniques are that they are quick, generally nondestructive, less operator intensive, do not require difficult sample handling procedures, and are almost always more precise and more accurate. Previous instrumental analysis in the textile industry has included X-ray diffraction, infrared spectroscopy (IR), and electron spectroscopy for chemical analysis (ESCA).[1] Nuclear magnetic resonance spectroscopy (NMR) has also been utilized to study textiles,[2] and the advent of powerful solid state NMR spectrometer systems allows characterization with little or no sample preparation.

Specific NMR applications have included both qualitative and quantitative analyses. Proton broad line NMR was used to examine segment mobility in synthetic fibers[3] and the adsorption of water in oriented fibers.[4] Cellulose and regenerated cellulose were also studied with wide line proton NMR[5] as well as with solid state carbon-13 NMR.[6,7] Recent work has defined the cross-polarization process in detail,[8] and examined the two crystalline forms of cellulose by CP/MAS.[9-11] Cotton/polyester blends have been examined quantitatively by IR,[1] X-ray diffraction,[12] density measurements,[13] and ESCA.[14]

The technique presented here allows rapid, accurate, and nondestructive compositional determination of cotton/polyester blends and general qualitative identification of textile fibers.

EXPERIMENTAL

Textile samples were obtained from clothing and cut into approximately 5 × 2 cm pieces. The actual composition of the fabric was taken to be that on

the garment label. Each sample was rolled and placed in a rotor and tamped for best packing and spinning. If a sample did not spin well, a small amount of fine silica gel was put into the spinner to help balance it.

The carbon-13 NMR spectra were recorded at 50.32 MHz on a Bruker MSL-200 Spectrometer equipped with a magic angle spinning probe and cross polarization circuitry to satisfy the Hartmann–Hahn condition. Spectra were acquired with a contact time of 5 ms, an acquisition time of 50 ms, and a recycle time of 3 s. The 90° pulse was set at 5 μs, and the magic angle was set using potassium bromide. Between 1000 and 3000 FIDs were collected for each sample. Adamantane was used to set the Hartmann–Hahn relationship and as the chemical shift reference. Fused alumina rotors with Kel-F caps were spun at 4.9 kHz. Total scanning time was between 30 and 60 m, with about 15 m necessary to pack the sample and start spinning. All measurements were taken at a temperature of 300 K.

RESULTS AND DISCUSSION

The quantitative aspects of the ^{13}C magic angle spinning NMR experiment have already been shown.[15,16] The determination of the cotton/polyester content of commercial blends was accomplished by a peak height ratio method. The peaks at 104 and 162 ppm, for cotton (C-1 of cellulose)[17,18] and for the polyester carbonyl, respectively, were chosen since they are free of overlap with other peaks. Cotton/polyester blends examined included nominal ratios of 85 : 15, 75 : 25, 63 : 37, 60 : 40, 55 : 45, 53 : 47, 50 : 50, and 35 : 65. The ratio of the nominal cotton/polyester content was then plotted against the ratio of the cotton and polyester peak heights. Analysis by linear regression produced a straight line plot with a slope of 0.71, a y-intercept of -0.13, and a correlation coefficient of 0.993 (Fig. 1). Eliminating the highest point and recalculating the straight line gave a slope of 0.67, a y-intercept of -0.08, and a correlation coefficient of 0.963.

A plot of the ratio of the respective peak areas was also generated. Linear regression produced a slope of 0.72, a y-intercept of 0.35, and a correlation
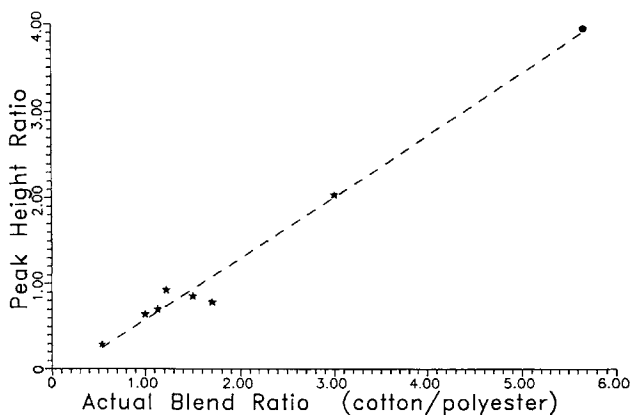

Fig. 1.   Peak height ratio versus cotton/polyester blend ratio.

coefficient of 0.969. Peak areas apparently do not correlate as well, perhaps due to differences in noise and baseline linearity. More careful setting of the integration regions and baseline and a greater number of acquisitions to reduce noise may give more precise integration values.

It should be emphasized that the relationship described by Fig. 1 is entirely empirical. Peak heights will depend on a variety of sample variables and acquisition parameters such as thermal history, water content, contact time, recycle time, and r.f. field strength. In this particular system, however, use of peak heights is easy, rapid, and gives excellent results.

The spectra of 100% cotton, 100% polyester, a 35 : 65 and a 50 : 50 cotton/polyester blend are all shown in Fig. 2. The peak height ratio does not exactly equal the actual blend ratio due to variations in cross-polarization efficiency between cotton and polyester, and certainly due to the differences in the ratios of crystalline to amorphous content for each polymer component.

In addition to the clothing samples used to establish the relationship in Fig. 1, additional samples were obtained from a fabric store. Cotton/polyester
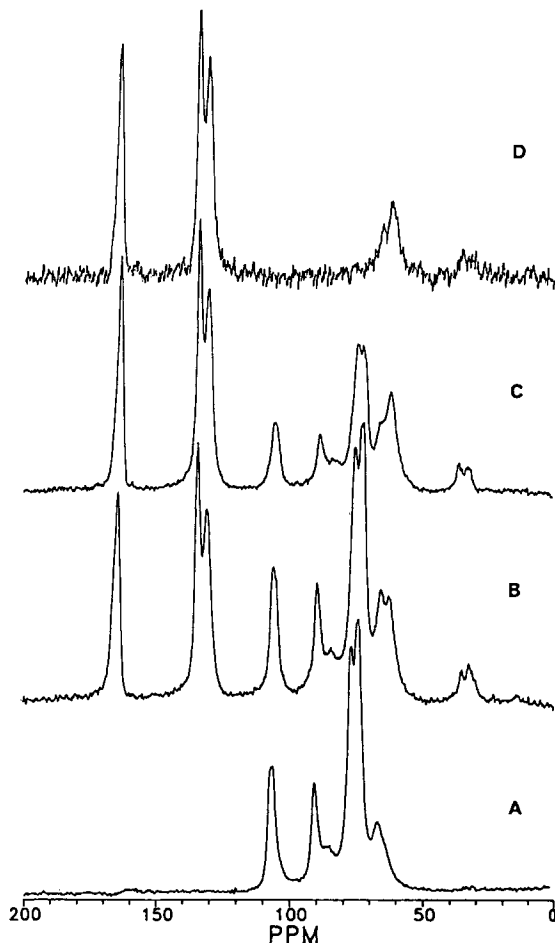

Fig. 2. Carbon CP/MAS spectrum of: (A) 100% cotton, (B) 50 : 50 and (C) 35 : 65 cotton/polyester blend, (D) 100% polyester.

blends with nominal ratios of 86 : 14, 84 : 16, 73 : 27, 72 : 28, and 20 : 80 were evaluated but did not correlate at all with the earlier data. In fact, one sample labeled as containing only 20% cotton was clearly almost all cotton; the cotton content calculated from measured peak heights corresponded to a ratio of 85 : 15. We are suggesting that these samples are mislabeled, either deliberately or through careless handling. In any event, fabric purchasers are not receiving the fabrics they think they are getting. It is also clear, especially from the nonzero intercept obtained from the peak height data, that careful determination of known sample blends would greatly improve the accuracy of this technique.

The utility of ^{13}C CP/MAS for qualitative analysis of textile fabrics was demonstrated for a number of clothing samples. These included fabrics nomi-
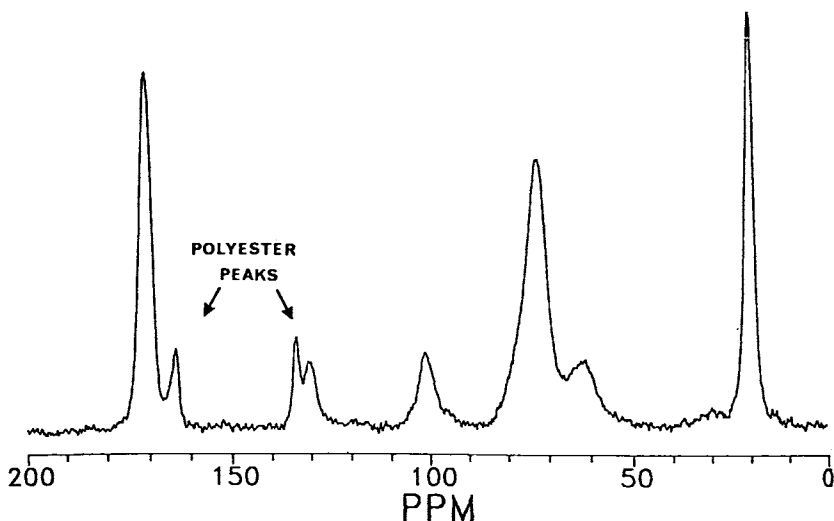

Fig. 3.   Carbon CP/MAS spectrum of a nominal 80 : 20 Arnel/nylon blend.
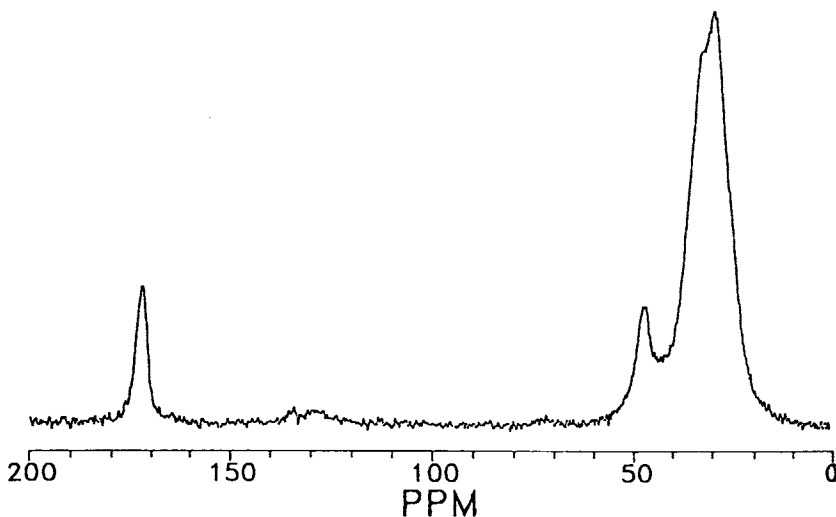

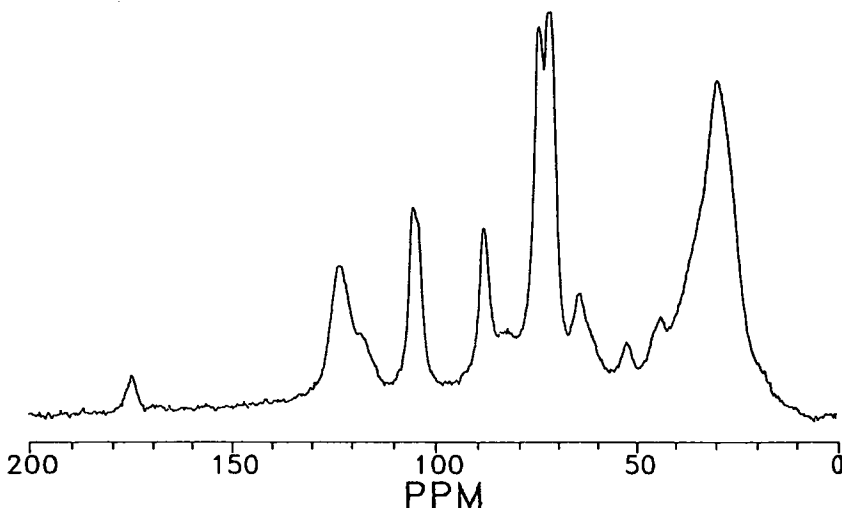
Fig. 4.   Carbon CP/MAS spectrum of Qiana nylon.

Fig. 5.   Carbon CP/MAS spectrum of 50:50 cotton/Creslan acrylic.

nally containing 100% rayon, 100% Qiana nylon, 100% Shetland wool, and blends of 95:5 cotton/polyurethane, 50:50 cotton/Creslan acrylic, 82:12:6 cotton/acrylic/viscose rayon, 44:44:12 cotton/polyester/rayon, and 80:20 Arnel/nylon. In all the spectra, peak assignments were made for each component of the blend by comparison with the spectra of individual fiber component and representative model compounds. Interestingly, it was found that the spectra of the garment labeled 80:20 Arnel/nylon did not contain peaks for nylon. Instead it showed peaks for polyester; compare Fig. 3 and the polyester spectrum in Fig. 2. The spectra of Qiana nylon and the 50:50 cotton/Creslan acrylic blend are shown in Figs. 4 and 5, respectively.

These solid state carbon NMR examples demonstrate the value of this technique for rapid quantitative analysis of textile blends, and for quick, positive identification of fabrics and blends. This technique has great promise for routine screening of fabric samples to confirm the identity and composition of domestic and especially imported textile products.

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