

# Quantitative Analysis of Polymer Blends using Breadths of Overlapping X-Ray Diffraction Lines

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## Synopsis

A method is developed to estimate the composition of a powder mixture using breadths of overlapping x-ray diffraction (XRD) lines. The application of the method is illustrated for analyzing blends of cotton and jute.

## INTRODUCTION

Methods of quantitative analysis of crystalline powder mixtures using x-ray diffraction (XRD) techniques are fairly well developed.<sup>1</sup> The analysis is relatively easy if the XRD pattern of the mixture exhibits component lines which do not overlap. Methods of analysis for mixtures with overlapping XRD lines have also been developed.<sup>2</sup> In the latter, each of the intensities of  $n$  lines in the pattern of the mixture consisting of  $n$  components is expressed in terms of expressions of the form

$$I_j = \sum_{k=1}^n C_{jk} p_k \quad (1)$$

where  $I_j$  is intensity of the  $j$ th line in the pattern of the mixture,  $p_k$  is the weight fraction of the  $k$ th component, and  $C_{jk}$  are constants, which can be experimentally evaluated. Using the set of  $n$  equations of type (1), the weight fractions of the components can be determined. In the present article, a somewhat different approach to the problem is presented, wherein the diffraction profile of a single line in the pattern of the mixture is expressed in terms of the profiles of the components and quantitative analysis is attempted using the breadths of the same line in the patterns of the mixture and its components. For the sake of simplicity, only a bicomponent system, with both the components having the same x-ray absorption, is considered; however, the method can be extended to cover more complex cases.

## Derivation of Analytical Expressions

The present approach requires a knowledge of the profile shapes of the chosen analytical line in the XRD patterns of the components. The treatment that follows, therefore, is divided to encompass the three line shapes normally encountered, viz., Gaussian, Cauchy, and a mixture of these two forms.

*Gaussian*

The profile may be represented in this case by

$$I = I_0 \exp(-H^2 x^2) \quad (2)$$

where  $I$  is the intensity at any distance  $x$  from the center of the profile situated at  $x = 0$ ,  $I_0$  is the intensity at the peak (at  $x = 0$ ) and  $H^2 = \ln 2/\alpha^2$ , where  $\alpha$  is the half-width at half-maximum intensity in the full profile. The intensity  $I_c$  of a composite line in the pattern of the mixture at any value of  $x$  may be written

$$I_c = I_1 + I_2 \quad (3)$$

where  $I_1$  and  $I_2$  represent the intensities of the components 1 and 2 at the same distance  $x$ . Rewriting  $I_1$  and  $I_2$  using eq. (2), we get

$$I_1 = I_{10} \exp(-H_1^2 x^2) \quad (4)$$

$$I_2 = I_{20} \exp(-H_2^2 x^2) \quad (5)$$

where  $I_{10}$  and  $I_{20}$  refer to the peak heights of the component profiles and  $H_1$  and  $H_2$  refer to their breadths. Now, eq. (3) may be written

$$I_c = I_{10} \exp(-H_1^2 x^2) + I_{20} \exp(-H_2^2 x^2) \quad (6)$$

Using the fact that  $I_c = 0.5 I_{c0}$  at  $x = \alpha_c$ , where  $I_{c0}$  is peak height of the composite profile and  $\alpha_c$  is half the half-maximum width of the entire composite profile, we get

$$0.5 I_{c0} = I_{10} \exp(-H_1^2 \alpha_c^2) + I_{20} \exp(-H_2^2 \alpha_c^2) \quad (7)$$

From eq. (3), we have

$$I_{c0} = I_{10} + I_{20} \quad (8)$$

On combining eqs. (7) and (8) and rearranging terms, we get

$$\left( \frac{\exp(-H_1^2 \alpha_c^2) - 0.5}{\exp(-H_2^2 \alpha_c^2) - 0.5} \right) = - \frac{I_{20}}{I_{10}} \quad (9)$$

If  $(I_{10})_n$  and  $(I_{20})_n$  represent the peak heights in the profiles of the components normalized to equal mass and  $p_1$  is the mass fraction of component 1, then

$$I_{10} = p_1 (I_{10})_n \quad (10)$$

and

$$I_{20} = (1 - p_1) (I_{20})_n \quad (11)$$

Substituting the above in eq. (9), we get

$$\left( \frac{\exp(-H_1^2 \alpha_c^2) - 0.5}{\exp(-H_2^2 \alpha_c^2) - 0.5} \right) = \frac{-(1 - p_1) (I_{20})_n}{p_1 (I_{10})_n} \quad (12)$$

Knowing  $H_1, H_2, \alpha_c, (I_{10})_n$ , and  $(I_{20})_n$ ,  $p_1$  can be determined using eq. (12).

*Cauchy*

In this case, the profile shape is of the form

$$I = I_0 \alpha^2 / (\alpha^2 + x^2) \quad (13)$$

Following through the same steps as in the Gaussian case, we get

$$0.5I_{c0} = I_{10} \left( \frac{\alpha_1^2}{\alpha_1^2 + \alpha_c^2} \right) + I_{20} \left( \frac{\alpha_2^2}{\alpha_2^2 + \alpha_c^2} \right) \quad (14)$$

From eqs. (8) and (14), we get

$$\frac{\alpha_1^2 - \alpha_c^2 \alpha_2^2 + \alpha_c^2}{\alpha_2^2 - \alpha_c^2 \alpha_1^2 + \alpha_c^2} = \frac{-I_{20}}{I_{10}} \quad (15)$$

Combining eqs. (10), (11), and (15), we derive

$$\frac{\alpha_1^2 - \alpha_c^2 \alpha_2^2 + \alpha_c^2}{\alpha_2^2 - \alpha_c^2 \alpha_1^2 + \alpha_c^2} = \frac{-(1 - p_1)(I_{20})_n}{p_1 (I_{10})_n} \quad (16)$$

Thus,  $p_1$  may be determined from eq. (16).

### *Mixture of Gaussian and Cauchy*

In this case, the profile of the components are of the form

$$(I_1)_n = f_1(I_G)_n + (1 - f_1)(I_C)_n \quad (17)$$

and

$$(I_2)_n = f_2(I_G)_n + (1 - f_2)(I_C)_n \quad (18)$$

The subscript  $n$  in the above indicates that the heights of the profiles considered are all normalized to the same value at the peaks. Equation (17) expresses the normalized profile of component 1 as a linear combination of fraction  $f_1$  of a normalized Gaussian profile  $(I_G)_n$ , and fraction  $(1 - f_1)$  of a normalized Cauchy profile  $(I_C)_n$ . Equation (18) similarly expresses the profile of the component 2 in terms of fractions  $f_2$  and  $(1 - f_2)$  of normalized Gaussian and Cauchy profiles. The intensity of the composite profile from the mixture may be written

$$I_c = p_1(I_1)_n + (1 - p_1)(I_2)_n \quad (19)$$

and its intensity at half maximum as

$$0.5I_{c0} = p_1 \left( f_1(I_{G0})_n \exp(-H_1^2 \alpha_c^2) + (1 - f_1)(I_{C0})_n \frac{\alpha_1^2}{\alpha_1^2 + \alpha_c^2} \right) \\ + (1 - p_1) \left( f_2(I_{G0})_n \exp(-H_2^2 \alpha_c^2) + (1 - f_2)(I_{C0})_n \frac{\alpha_2^2}{\alpha_2^2 + \alpha_c^2} \right) \quad (20)$$

where  $(I_{G0})_n$  and  $(I_{C0})_n$  are the peak heights of the normalized Gaussian and Cauchy profiles, respectively. We also have

$$I_{c0} = p_1 (I_{10})_n + (1 - p_1) (I_{20})_n \quad (21)$$

and

$$(I_{10})_n = (I_{20})_n = (I_{G0})_n = (I_{C0})_n \quad (22)$$

On combining eqs. (20), (21), and (22) and rearranging terms, we get

$$\left( \frac{f_1 \exp(-H_1^2 \alpha_c^2) + (1 - f_1) \alpha_1^2 / (\alpha_1^2 + \alpha_c^2) - 0.5}{f_2 \exp(-H_2^2 \alpha_c^2) + (1 - f_2) \alpha_2^2 / (\alpha_2^2 + \alpha_c^2) - 0.5} \right) = - \frac{1 - p_1}{p_1} \quad (23)$$

If the values of  $f_1$  and  $f_2$  are separately determined, the above expression can be used to analyze the sample.

### EXPERIMENTAL

Our interest was in analyzing textile materials produced from blends of cotton and jute, each having a cellulose I lattice. The fibers of each material, weighing about 150 mg, were cut into fine powder, passed through a 150-mesh screen, and filled in a rectangular specimen holder. The sample was then subjected to a nominal pressure of about 5 kg/cm<sup>2</sup> and the holder was inserted in place in a vertical diffractometer set up in the reflection mode on a Philips stabilized x-ray generator having rate-meter and recording accessories. Ni-filtered Cu  $K\alpha$  radiation was used in the experiments and the XRD patterns were recorded employing 0.5° divergence and antiscatter slits, 0.1 mm receiving slit, 1°/min scan rate, and 600 mm/hr chart speed. Mixtures with different proportions of cotton and jute, prepared from the sieved powders, were also examined similarly. No corrections were made on the recorded data except that for the nonlinearity of response of the detector. The intensity values in the range 10°–40° ( $2\theta$ ) were all normalized to the same area in order to minimize errors arising from small mass and instrumental variations. The diffraction patterns of cotton and jute thus obtained are given in Figure 1.

The strong (002) line, occurring at about 22.6° ( $2\theta$ ) was chosen for carrying out the analysis. A linear background connecting the intensities at 18° and 28° ( $2\theta$ ) was drawn under the (002) line and this background was subtracted from the profile to yield a "true" (002) line. Because of ambiguities regarding the background from amorphous scatter and contributions from the neighboring reflections occurring at lower  $2\theta$  values, only that half of the profile at the higher angle side was considered for profile analysis and measurement of  $\alpha$ 's.

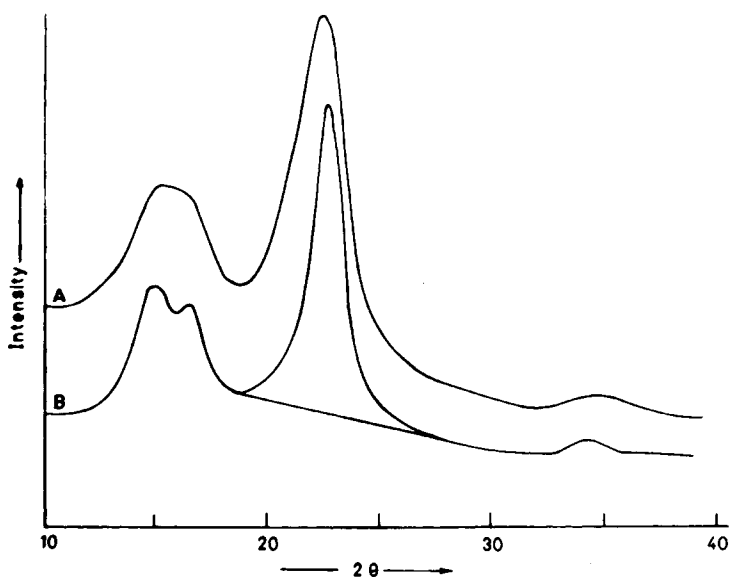


Fig. 1. XRD patterns of (A) jute and (B) cotton.

## RESULTS AND DISCUSSION

### Analysis of Profile Shapes

In order to decide which one of eqs. (12), (16), and (23) would be most appropriate for estimating compositions of cotton-jute blends, the (002) profiles of these materials were first examined. For this purpose, averaged profiles from five scans of cotton as well as jute were first drawn. It was noted that neither the Gaussian nor the Cauchy forms satisfactorily fitted the (002) profile for cotton or jute. On the other hand, profiles of the type given by eqs. (17) and (18) were found to be more relevant. Assigning the subscripts 1 and 2 for cotton and jute, respectively, the values of  $f_1$  and  $f_2$  were obtained as 0.69 and 0.22. It is interesting to note that an earlier study<sup>3</sup> on the (002) profile of jute yielded a value of 0.3 which is close to the present one. The difference between the two values could probably be due to the differences in procedures of processing raw diffraction data and drawing the background. It is also noteworthy that a value of 0.7 has been reported for ramie.<sup>4</sup> The experimental and the Gaussian-Cauchy profiles, the latter generated with the same normalized peak height and half-width as the former, are shown in Figures 2 and 3 for cotton and jute, respectively.

### Quantitative Analysis of Blends

Using eq. (23) and employing the  $\alpha$ 's from the averaged profiles of cotton and jute, a calibration curve was drawn (Fig. 4). The values of  $\alpha_c$  obtained for mixtures with known composition are shown in the same figure as open circles. It may be noted that these points lie fairly close to the calibration curve.

The maximum deviation between the actual and estimated values of either

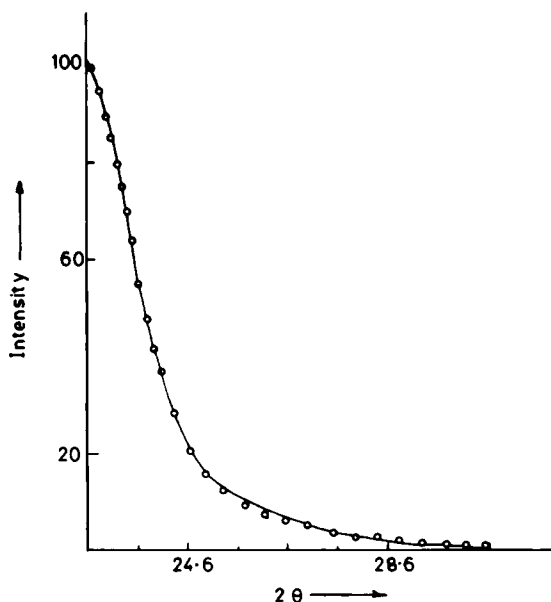


Fig. 2. Experimental (—) and fitted (○) (002) profiles of cotton. The latter is 69% Gaussian and 31% Cauchy.

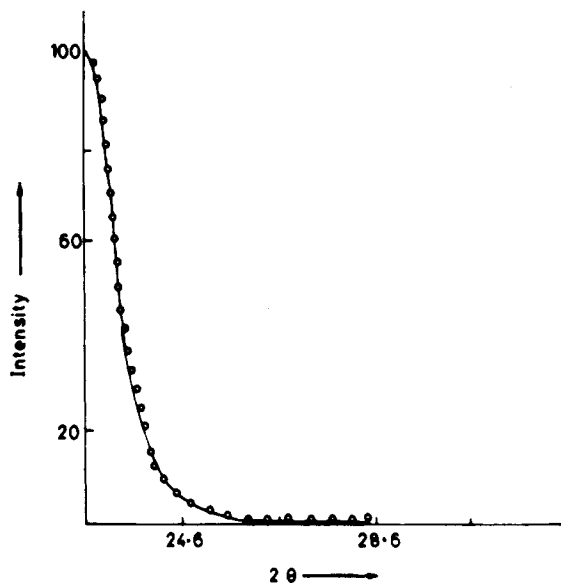


Fig. 3. Experimental (—) and fitted (○) (002) profiles of jute. The latter is 22% Gaussian and 78% Cauchy.

component was about 5%, when the analysis was based on two scans each per mixture. Part of this error may be attributed to the uncertainty in the choice of the background line. Unfortunately, it is very difficult to fix this background line unambiguously for cellulosic fibers. It may be possible, however, to improve

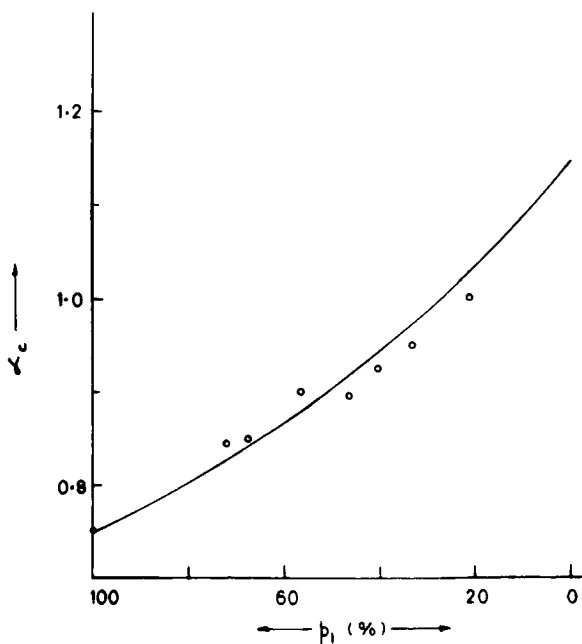


Fig. 4. Relationship between cotton content  $p_1(\%)$  and half the half-maximum breadth  $\alpha_c$  of (002) peaks from cotton-jute blends. Solid line is the theoretical curve; the circles indicate experimental values.

the accuracy of estimate by applying the usual corrections for instrumental and absorption effects and by employing proper counting statistics. For the types of cotton-jute blends that are likely to be analyzed, however, these limitations may not be very serious, and the accuracy obtained presently may be generally acceptable.

It may also be mentioned that equations similar to those used by Copeland and Bragg<sup>2</sup> can be written to express the composite line profile from the mixture in terms of the intensities of the profiles from the components, and analyses can be made. For a bicomponent system, the expressions take the form

$$I_{cj} = p_1 I_{1j} + (1 - p_1) I_{2j} \quad (24)$$

where  $I_{cj}$ ,  $I_{1j}$ , and  $I_{2j}$  are the intensities in the normalized profiles of the sample, component 1 and component 2, respectively, at any value of  $2\theta$  ( $=j$ ). Equations of this type can be set up to cover the entire profile and  $p_1$  evaluated. When this approach was tried, however, the error in analytical results was considerably higher, apparently due to the errors introduced in estimating intensities from rate-meter scans. Perhaps, owing to the same reason, a calibration curve drawn using  $\alpha_c$  values obtained from profiles generated graphically from those of the components (for various compositions) was also not satisfactory. While these errors can be reduced by using step scanning for data collection, routine and fast quantitative analysis can perhaps be better performed using breadths of diffraction lines, measured from rate-meter scans.

Quantitative analysis using breadths of x-ray diffraction lines may particularly suit semicrystalline polymeric materials which are characterized by relatively broad diffraction profiles. In cases of blends for which the analytical x-ray lines of the components do not overlap, the equations used for analysis will have to be modified by incorporating the difference in peak positions into the equations. We are extending the application of this method, with such suitable modifications where needed, to other polymer blends.

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