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Analysis of Polysaccharide–Poly(ethylene-*co*-acrylic acid) Composites by Fourier-Transform Infrared Spectroscopy

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ABSTRACT

*A method, based on absorbances in FTIR spectra of the C—O single-bond stretch band of the polysaccharide and the C—H stretch band of poly(ethylene-*co*-acrylic acid) (EAA) at 2851 cm^{-1}, was developed for the determination of EAA in composites with either dextran or starch. Spectral subtraction of the polysaccharide component was necessary for quantitative determination of EAA. The accuracy of this analytical procedure is affected by the fact that absorbances of these two bands are not equally dependent on particle size of the sample in the KBr pellet; the absorbance ratio, as calculated from FTIR spectra therefore varies with sample preparation conditions. To ensure the necessary particle size uniformity during the preparation of KBr pellets, a method based on relative intensities of two bands in the C—O region of the spectrum was developed as an indicator of particle size in the pellet. This method was also used for monitoring sample size in the polysaccharide standard used for spectral subtraction, since particle size uniformity between sample and polysaccharide standard was also necessary for accurate determination of EAA.*

INTRODUCTION

Composite systems containing starch and poly(ethylene-*co*-acrylic acid) (EAA) have been under investigation at the Northern Regional

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*The mention of firm names or trade products does not imply that they are endorsed or recommended by the US Department of Agriculture over other firms or similar products not mentioned.

Research Center for a number of years, and Otey and coworkers have described the preparation and properties of films from these composites (Otey *et al.*, 1977, 1980, 1987; Otey & Westhoff, 1984). Extrusion-blown starch–EAA films containing about 40% starch are uniform, flexible and transparent and have good physical properties in spite of the obvious differences in physical and chemical properties between the two polymers. Although polyethylene is incompatible with starch and gives poor quality films when extrusion-blown under conditions used for EAA mixtures, Otey and coworkers found that it was possible to incorporate polyethylene into an EAA–starch composite and obtain good film properties.

Composites of this type are currently receiving increased attention because of the ability of the starch component to biodegrade. We are thus undertaking a detailed study of interactions between starch and EAA and have presented preliminary evidence that the ability of the two polymers to form uniform blends might be due to formation of a complex similar to known helical inclusion complexes between starches and fatty acids (Fanta *et al.*, 1988). As evidence for complex formation we have observed that a significant percentage of EAA cannot be solvent-extracted from starch, whereas EAA is readily extractable from mixtures with dextran. Although dextran is a poly(glucopyranose) like starch, the two polymers are structurally different. In starch, α-(1→4) linkages between glucopyranosyl units cause the polymer chains to assume a helical configuration, whereas no such configuration is possible with dextran, which has α-(1→6) linkages.

Since we wished to study the apparent complexing of EAA with different starch varieties and under different conditions of starch gelatinization, a rapid and accurate method was needed for determining the amount of EAA in blends with either starch or our dextran control. Previously (Fanta *et al.*, 1988), we used weight loss on acid hydrolysis; however, this method was not only time consuming, but complete removal of polysaccharide was often difficult to achieve. Since FTIR analyses of samples in KBr pellets can be both rapid and accurate, we examined this technique to determine the important variables and pitfalls that affect its successful use.

Infrared analyses of polymers in a KBr matrix can be subject to errors and lack of reproducibility. For example, results are affected by non-uniform sample distribution in the pellet (Jones, 1952) and by non-uniform path-length of the light beam (Siesler & Holland-Moritz, 1980). Absorption values will also be affected by insufficient grinding of the sample (George & McIntyre, 1987; Price, 1972) due to light scattering by particles larger than the wavelength of IR radiation. The influence of particle size (as determined by length of time used to grind the sample) on the sharpness and intensity of absorption bands has been clearly shown by Brügel (1962). When sample and KBr have a sufficiently different index of refraction, absorbance of the sample may actually be more a function of particle size than of absorption coefficient (Henniker, 1967), and variations in refractive index may be greatest in the neighborhood of strong absorption frequencies.

To obtain the necessary particle size uniformity from sample to sample, one might initially consider developing a single mixing and pelletizing procedure that would be optimum for a broad EAA concentration range. However, for samples containing varying amounts of polysaccharide and EAA, this could be an impossible task, since increasing amounts of the tough EAA component renders a mixture of the two polymers increasingly difficult to pulverize. For example, with extruded films containing high EAA concentrations, samples might require prolonged grinding at low temperature to attain the same particle size that could be easily achieved with short grinding times when films are cast rather than extruded and when EAA concentrations are low. The major problem in preparing an empirical curve from known mixtures is therefore the uncertainty in whether known mixtures used to construct the curve have the same particle sizes as the unknowns to be analysed. Although addition of an internal standard is a widely used technique for quantitative IR analysis, this would not eliminate the problem, since variations in absorption with particle size can be different at different regions of the spectrum.

In this publication, we will discuss the use of a ratio of absorbances between two polysaccharide bands as a simple technique for monitoring particle size in the KBr pellet. This method ensures that pelletizing procedures are reproducible and provides maximum accuracy when empirical curves are used to determine %EAA in mixtures with polysaccharides. These methods and principles can no doubt be applied to other polysaccharide-synthetic polymer composites with minimal modification.

EXPERIMENTAL

Materials

Dextran (industrial grade, average mol. wt $5-40 \times 10^6$) was from Sigma Chemical Co. Cornstarch was Buffalo 3401 from CPC International Inc. EAA was Primacor 5981 from Dow Chemical Co. This polymer contains about 20% acrylic acid by weight and has a melt index of 300, $\bar{M}_w$ of about 18 000, and $\bar{M}_n$ of about 7000 (Dow Chemical Co., 1984). Aqueous EAA solution was prepared by stirring 25·00 g EAA, 250 ml concentrated NH_4OH, and 250 ml water for about 5 h under gentle reflux. The resulting opalescent solution was then cooled and diluted with concentrated NH_4OH to a total weight of 500·0 g. Potassium bromide used for the preparation of pellets was from Spectra Tech, Inc.

Preparation of polysaccharide–EAA mixtures

A mixture of 25·00 g (dry basis) polysaccharide (starch or dextran) in 470 ml water was stirred and heated in a 1 litre resin flask for 1 h at 95°C. The dispersion/solution was cooled to 55°C, water was added to give 500·0 g of dispersion, and the mixture was stirred and cooled to 25°C. Portions of both the 5·0% polysaccharide solution/dispersion and the 5·0% EAA solution were weighed into beakers to give the required polysaccharide:EAA ratio, and mixtures were stirred for 10 min. Mixtures were spread onto polyethylene sheets and were allowed to air-dry at room temperature. The resulting brittle films were readily pulverized. A portion of the polysaccharide dispersion/solution was also freeze-dried to obtain samples for standard spectra.

Preparation of KBr pellets for FTIR

Samples were ball-milled in a Wig-L-Bug amalgamator (Crescent Dental Manufacturing Co.) equipped with a stainless-steel capsule and two $\frac{1}{4}$-in diameter stainless-steel ball pestles.

Film samples were broken into pieces and ball-milled for 30 s with the capsule roughly one-quarter full. Powdered samples were then further dried under vacuum at 60°C.

The following procedures were used to ball-mill samples with KBr for the preparation of pellets:

(A) Powdered film sample (about 10 mg) was ball-milled for 15 s with about 350 mg KBr. A portion of this mixture needed to give 1·3 mg of polysaccharide (or 1·3 mg of total sample when EAA contents were above 20%) was then blended with KBr to give a total weight of 391 mg, and this mixture was ball-milled for 120 s.

(B) This was similar to (A), except that the second ball-milling was carried out for 240 s.

(C) Powdered film sample (20–25 mg) was ball-milled for 120 s in the absence of KBr. About 10 mg of this pulverized material was mixed with about 350 mg KBr and ball-milled for 15 s. A portion of this mixture needed to give 1·3 mg polysaccharide (or 1·3 mg of total sample when EAA contents were above 20%) was then blended with KBr to give a total weight of 391 mg and this mixture was ball-milled for 120 s.

(D) This was similar to (C), except that the powdered film sample was ball-milled for 240 s in the absence of KBr.

(E) A freeze-dried sample of polysaccharide (43 mg) was ball-milled for 75 s with 442 mg of KBr. A portion of the mixture needed to give 1·3 mg of polysaccharide was then blended with KBr to give a total weight of 391 mg and this mixture was ball-milled for 60 s.

(F) This was similar to (E), except that the second ball-milling was carried out for 240 s.

The ability to pulverize polysaccharide–EAA composites successfully by ball-milling often varies with temperature and moisture content of the sample (and thus with the relative humidity of the room). We have found that ball-milling may be facilitated by briefly cooling the stainless-steel capsule in a refrigerator-freezer.

A 301·0-mg portion of each of the KBr mixtures prepared by procedures (A) through (F) was pressed under vacuum into a 13-mm diameter pellet with a Perkin–Elmer evacuable potassium bromide die (186-0025). A Carver press was used to attain 22 000 pounds on the plunger. Each pellet thus contained 1·0 mg polysaccharide for samples containing 20% EAA or less, and 1·0 mg of total sample when the EAA content was above 20%.

Spectroscopy

Spectra were recorded on a Mattson Polaris FTIR equipped with an He–Ne laser and DTGS detector to provide a resolution of 0·5 cm^{-1}. Mattson ICON analytical software was used for spectral manipulation and subtraction.

RESULTS AND DISCUSSION

Physical mixtures of polysaccharide and EAA were prepared in film form by first blending aqueous solutions (or dispersions) of polysaccharide with aqueous ammonia solutions of EAA and then allowing the blends to air-dry. The resulting brittle films were then pulverized for various periods of time in a small rapidly reciprocating ball-mill.

We chose the KBr method for FTIR analysis because both sample and KBr could be accurately weighed to give uniform and reproducible pellets. Internal standards were not used for the quantitation of EAA;

instead we constructed empirical curves based on an absorbance ratio between selected bands of the EAA and polysaccharide components.

Dextran-EAA mixtures

FTIR spectra of dextran and EAA are shown in Fig. 1. To quantitate the amount of EAA in blends with dextran, we searched for bands in the spectra of both components where overlap was minimal. Bands chosen were 2851 cm^{-1} (C—H stretch of EAA) and 1018 cm^{-1} (C—O stretch of dextran), and the absorbance ratio A_{2851}/A_{1018} was used as a measure of EAA content. This ratio should theoretically be independent of the weight of polymer in the KBr pellet, and this fact was confirmed experimentally for sample weights between 0·5 mg and 2·0 mg per pellet.

The 2851 cm^{-1} band of EAA was sharper and easier to quantitate than the carbonyl band at 1705 cm^{-1}; moreover, use of the C—H stretch band eliminated any concern about minor amounts of ammonium carboxylate possibly remaining in our samples. Although A_{1018} could be accurately determined directly from the spectrum without the need for

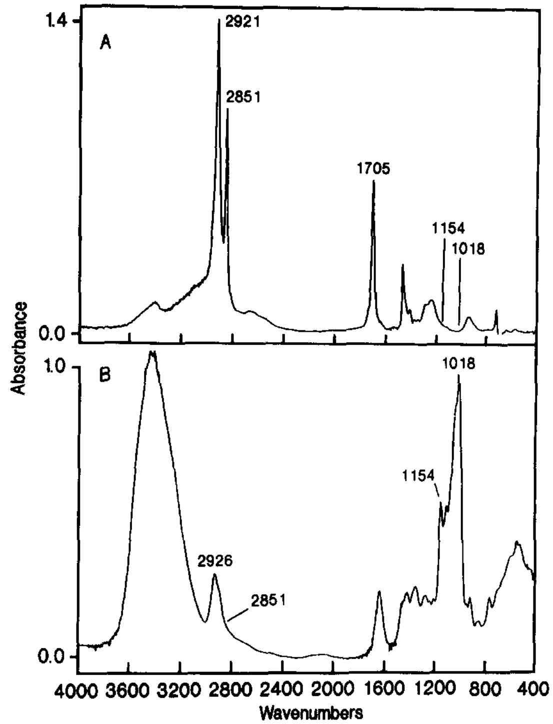

Fig. 1. FTIR spectra of (A) poly(ethylene-*co*-acrylic acid) and (B) dextran.

spectral manipulation, the 2851 cm^{-1} band of EAA was partially obscured by the dextran band at 2926 cm^{-1} and could therefore be accurately measured only after subtracting a standard spectrum of dextran.

It immediately became apparent that values obtained for A_{2851}/A_{1018} depended on how finely our samples were pulverized by ball-milling during the preparation of KBr pellets. The reason for these variations is apparent from Fig. 2, which shows how extensive ball-milling of the sample sharpens and intensifies the 1018 cm^{-1} band of the dextran component. A lesser increase in the 2851 cm^{-1} band of EAA results in lower values for A_{2851}/A_{1018}.

Variations in A_{2851}/A_{1018} with particle size of the ball-milled sample complicates the use of this ratio as an indicator for EAA content. Particle size distributions might vary with such factors as sample origin, pretreatment, and moisture content and thus might not be the same within a series of samples, even though an identical procedure was used for sample preparation. A simple method was therefore needed for establishing how finely a sample had been pulverized during preparation of the KBr pellet. If such a method were available, EAA in an unknown sample could then be determined from a plot of A_{2851}/A_{1018} versus %EAA in which known samples used to construct the plot had been pulverized to the same extent as the unknown.

We have found that the relative absorbance values of two polysaccharide bands at 1018 cm^{-1} and 1154 cm^{-1} can be correlated with conditions used for ball-milling and can thus be used to compare particle

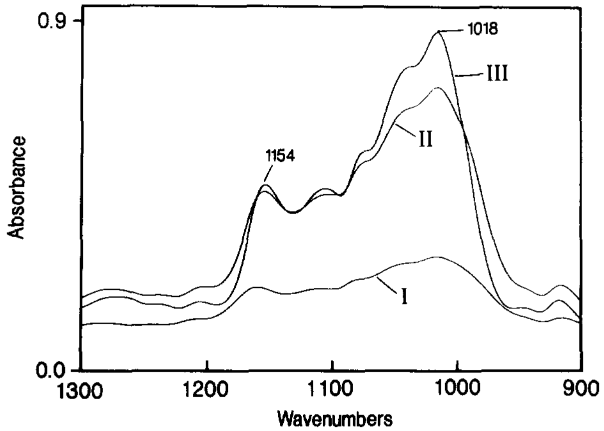

Fig. 2. Effect of ball-milling procedure (see Experimental section) on the spectrum of dextran. (I), procedure A; (II), procedure C; (III), procedure E.

sizes within a given series of KBr pellets. As samples are pulverized to an increasingly fine consistency, the increase in absorbance of this doublet is accompanied by an increase in the value of A_{1018}/A_{1154}. For EAA–dextran blends (Table 1), this absorbance ratio depends largely on conditions used for ball-milling and is less affected by EAA content of the sample. For example, values of A_{1018}/A_{1154} for sample preparation method C (see Experimental section) were 1·79–1·91 while for method A, in which samples were not as extensively ball-milled, these ratios ranged from 1·39 to 1·45. Within each series, A_{1018}/A_{1154} was lower for samples containing no EAA, suggesting that the presence of 15% or less EAA facilitates the ball-milling process.

As mentioned earlier, accurate measurement of EAA absorbance at 2851 cm^{-1} required spectral subtraction of the dextran component to remove interfering absorption of the polysaccharide. Figure 3(A) shows the spectrum of a 95:5 (by weight) blend of dextran and EAA, while the difference spectrum after subtraction is shown in Fig. 3(B). Expanded C—H stretch regions of both spectra are presented in Fig. 4. To obtain consistent spectral subtractions, the dextran reference was arbitrarily subtracted from the spectrum of the dextran–EAA blend until positive- and negative-directed peaks in the 1000 cm^{-1} region of the difference spectrum were about equal.

Although distortion of subtraction spectra is always evident, distortion could be minimized by choosing a reference spectrum in which the absorbance ratio A_{1018}/A_{1154} was as close as possible to that of the sample being analysed. Since identical conditions of ball-milling give lower A_{1018}/A_{1154} values for pure dextran than for EAA–dextran blends

TABLE 1

Dependence of Dextran Absorbance Ratio A_{1018}/A_{1154} on the Method Used to Ball-mill Samples with KBr

Sample preparation method[a]	*A_{1018}/A_{1154} for samples with different dextran: EAA ratios*								
	100:0	*99:1*	*98:2*	*97:3*	*95:5*	*93:7*	*90:10*	*88:12*	*85:15*
A	1·36		1·40	1·41	1·40	1·45	1·42	1·39	1·42
B	1·47								
C	1·59	1·85	1·81	1·84	1·85	1·81	1·82	1·79	1·91
D	1·62								
E	1·84								

[a] See Experimental section.

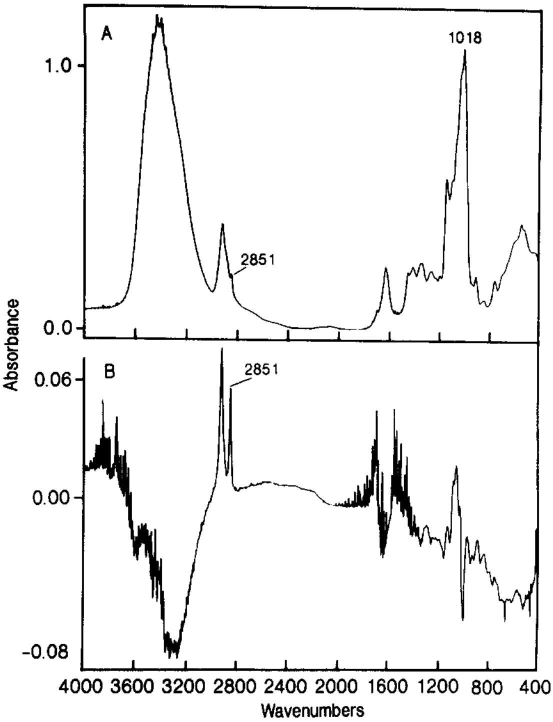

Fig. 3. (A) Spectrum of a 95:5 (by weight) blend of dextran and EAA (B) same spectrum after subtraction of a reference spectrum of dextran.

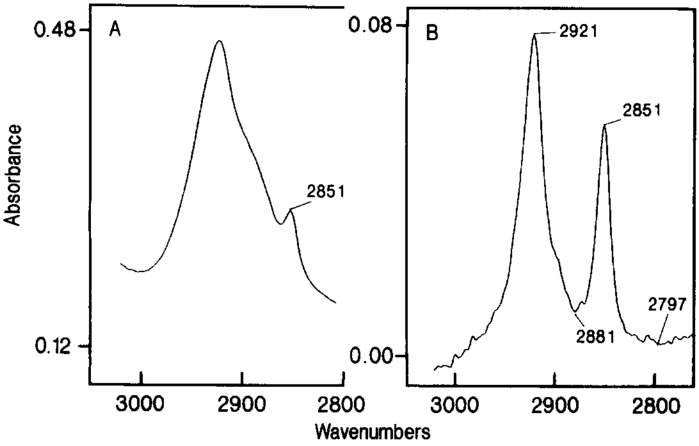

Fig. 4. (A) 95:5 (by weight) blend of dextran and EAA expanded in C—H stretch region. (B) Same spectrum after subtraction of a reference spectrum of dextran.

(Table 1), it was usually necessary to use different ball-milling procedures for sample and reference to attain the desired similarity of absorbance ratios. For example, a dextran reference ball-milled by method E (Table 1) was used as the difference standard for EAA-containing samples prepared by method C.

The accuracy of our FTIR method also depends on the establishment of a reproducible baseline for the 2851 cm^{-1} band in our difference spectra. For simplicity, we chose two points on either side of the 2851 cm^{-1} band, and in Fig. 4(B) these points are at 2881 cm^{-1} and 2797 cm^{-1}. Selection of alternate baseline points on the left-hand side of the 2921 cm^{-1} band proved difficult because of spectral distortion in this area caused by differences in water content (and therefore hydroxyl absorption) between samples and dextran references. Moisture variability could no doubt be minimized by preparing KBr pellets under an atmosphere of dry nitrogen; however, the strong affinity of polysaccharides for water would make it difficult either to eliminate water or to maintain a constant water content within a given sample series.

Effects of variations in (1) the procedure used to ball-mill samples during pellet preparation and (2) the selection of a dextran reference for spectral subtraction can be seen by examining plots of %EAA versus A_{2851}/A_{1018}. Results with samples ball-milled by method A in Table 1

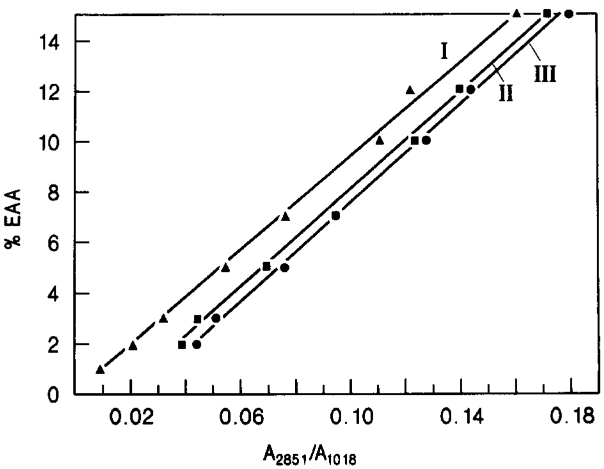

Fig. 5. Dependence of A_{2851}/A_{1018} versus %EAA on the methods used to ball-mill dextran standards for spectral subtraction. EAA–dextran mixtures ball-milled according to A in Table 1. (I) Dextran standard ball-milled according to E in Table 1. (II) Dextran standard ball-milled according to B in Table 1. (III) Dextran standard ball-milled according to A in Table 1.

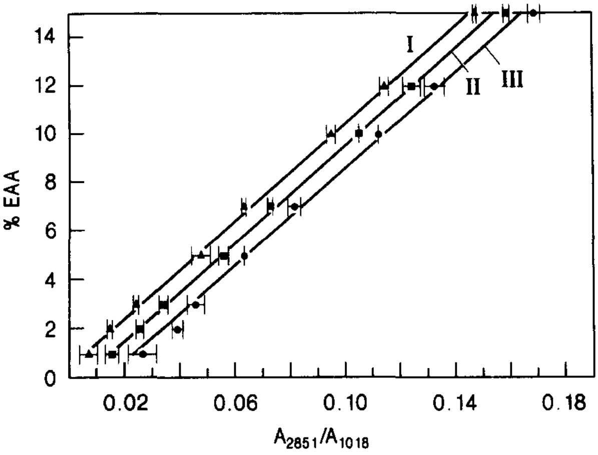

Fig. 6. Dependence of A_{2851}/A_{1018} versus %EAA on the methods used to ball-mill dextran standards for spectral subtraction. EAA–dextran mixtures ball-milled according to C in Table 1. (I) Dextran standard ball-milled according to E in Table 1. (II) Dextran standard ball-milled according to C in Table 1. (III) Dextran standard ball-milled according to A in Table 1.

are plotted in Fig. 5, while Fig. 6 shows similar plots for samples ball-milled by method C. Figure 6 also shows the reproducibility of duplicate determinations and suggests that the lowest measurable concentration of EAA is about 1%. Both figures show the variations in straight-line plots obtained by using differently ball-milled dextran references for spectral subtractions. These differences are caused by minor variations in the shape and width of the 2926 cm^{-1} band with ball-milling conditions. During spectral subtraction, these variations become obvious in the 2851 cm^{-1} region of the difference spectrum, particularly in the depth of the minimum absorbance at 2881 cm^{-1} (Fig. 4(B)). Since the 2881 cm^{-1} minimum is one of the two points used for baseline correction, measured absorbance at 2851 cm^{-1} also varies by a significant amount.

For both curve II of Fig. 5 and curve I of Fig. 6, dextran references chosen for spectral subtraction had A_{1018}/A_{1154} ratios similar to those of EAA–dextran mixtures. These two plots, shown together in Fig. 7, thus provide a good example of how ball-milling conditions used for EAA–dextran samples can influence the empirical relationship between composition and the measured absorbance ratio A_{2851}/A_{1018}. Either curve can obviously be used to determine EAA content of an unknown mixture, provided that the unknown and the EAA–dextran blends used to construct the curve are ball-milled to the same extent, as measured by the similarity in A_{1018}/A_{1154} ratios.

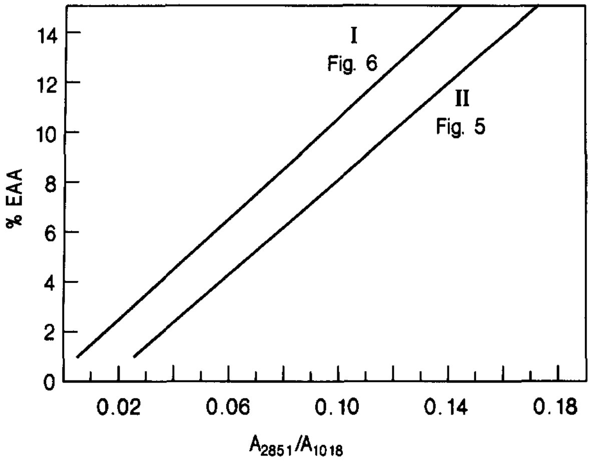

Fig. 7. Dependence of A_{2851}/A_{1018} versus %EAA on the method used to ball-mill EAA-dextran mixtures. Curve I in Fig. 6 (A_{1018}/A_{1154} = 1·79–1·91) compared with Curve II of Fig. 5 (A_{1018}/A_{1154} = 1·39–1·45).

Starch–EAA mixtures

There are only minor differences between the FTIR spectra of starch and dextran. One such difference is in the C—O stretch region, where starch bands occur at 1022 cm^{-1} and 1153 cm^{-1}. Also, the C—H stretch band of starch at 2928 cm^{-1} is somewhat sharper than the comparable 2926 cm^{-1} band of dextran. This difference between the two polysaccharides produced difference spectra for starch-containing samples that were less sensitive than dextran-containing samples in the 2851 cm^{-1} region to variations in ball-milling of the polysaccharide reference.

As in the dextran series, an absorbance ratio (A_{1022}/A_{1153}) was used as an indicator of particle size in KBr pellets after ball-milling. Values for this absorbance ratio under different ball-milling conditions are shown in Table 2. If these values are compared with those in Table 1 for the dextran series, the starch-containing samples have higher absorbance ratios and are thus apparently reduced to smaller particle size under comparable ball-milling conditions.

Figure 8 shows the relationship between %EAA and A_{2851}/A_{1022} for starch–EAA mixtures ball-milled according to method C. Each sample was run in duplicate, and horizontal bars show the variations observed in absorbance ratios. The starch standard used for spectral subtraction was prepared according to method E (A_{1022}/A_{1153} = 1·84); however, use of starch standards ball-milled by method C (A_{1022}/A_{1153} = 1·75) and method F (A_{1022}/A_{1153} = 1·95) gave curves that were virtually identical.

TABLE 2

Dependence of Starch Absorbance Ratio A_{1022}/A_{1153} on the Method Used to Ball-mill Samples with KBr

Sample preparation method[a]	*A_{1022}/A_{1153} for samples with different starch: EAA ratios*												
	100:0	*98:2*	*95:5*	*94:6*	*93:7*	*92:8*	*91:9*	*90:10*	*88:12*	*86:14*	*84:16*	*82:18*	*80:20*
B	1·50												
C	1·75	1·86	1·95	1·96	1·96	1·95	1·94	1·97	1·93	1·93	1·86	1·86	1·83
E	1·84												
F	1·97												

[a] See Experimental section.

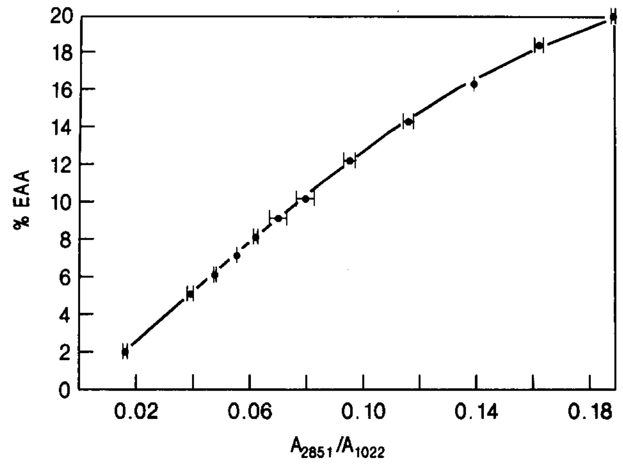

Fig. 8. Relationship between %EAA in starch–EAA mixtures and A_{2851}/A_{1022}. Starch–EAA mixtures were ball-milled according to Method C, and starch standard was ball-milled according to Method E.

TABLE 3

Dependence of Starch Absorbance Ratio A_{1022}/A_{1153} on the Method Used to Ball-mill Samples with KBr

Sample preparation method[a]	*A_{1022}/A_{1153} for samples with different starch: EAA ratios*					
	100:0	*80:20*	*75:25*	*65:35*	*55:45*	*45:55*
A		1·52	1·49	1·43	1·42	1·48
C	1·75	1·83	1·82	1·70	1·58	1·52

[a] See Experimental section.

Contrary to comparable curves for dextran–EAA, the curve for starch-containing mixtures deviates from linearity above about 12% EAA.

A series of samples containing up to 55% EAA (by weight) was also prepared, and values for A_{1022}/A_{1153} under different ball-milling conditions are shown in Table 3. Although absorbance ratios did not vary greatly with EAA content when samples were ball-milled in the presence of KBr (method A), ball-milling in the absence of KBr (method C) caused this ratio to drop significantly in samples containing more than about 35% EAA. This drop is probably due to reduced brittleness of high EAA samples.

Figure 9 shows the relationship between %EAA and A_{2851}/A_{1022} for the mixtures in Table 3. As observed in earlier samples, the empirical curve that one obtains depends on the method used for pellet prepara-

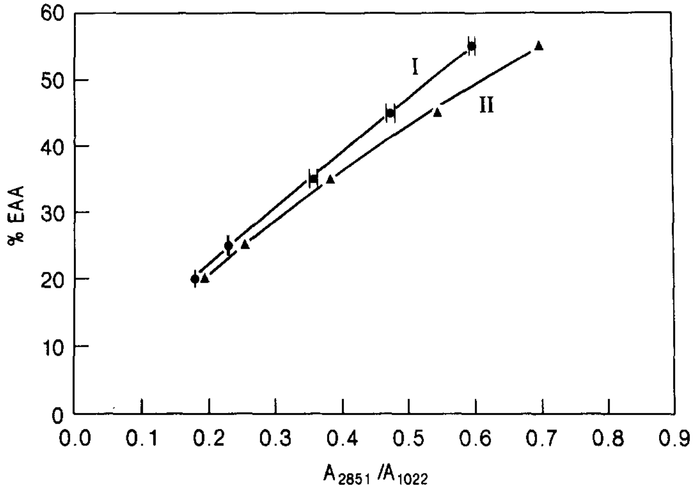

Fig. 9. Relationship between %EAA in starch–EAA mixtures and A_{2851}/A_{1022}. Curve I, starch–EAA mixtures were ball-milled according to Method C, and the starch standard was ball-milled according to Method E. Curve II, starch–EAA mixtures were ball-milled according to Method A, and the starch standard was ball-milled according to Method B.

tion; however, there was little or no dependence on the particular standard used for spectral subtraction. A starch standard with $A_{1022}/A_{1153} = 1{\cdot}60$ gave results nearly identical to curve I, in which the standard used had an absorbance ratio of 1·84. Similarly, the same curve II was obtained with two subtraction standards having absorbance ratios of 1·50 and 1·31.

To determine whether the empirical curves shown in Figs 8 and 9 could indeed be used to analyse unknown composites of starch and EAA, a validation set consisting of starch–EAA mixtures ranging from 3–53% EAA was prepared and analysed by FTIR (Table 4). The standard error of prediction was 0·767, and the correlation coefficient was 0·9997. To obtain the accuracy shown in Table 4, it is necessary that particle size in each unknown sample (as measured by A_{1022}/A_{1153}) be the same as that of a comparable known mixture used as a data point in the construction of the empirical curve. This requirement sometimes makes it necessary to carry out repeat determinations with different ball-milling times and thus arrive at an extrapolated value of A_{2851}/A_{1022}.

CONCLUSIONS

Empirical curves can be constructed relating %EAA in mixtures with either dextran or starch to a ratio of the absorbance of the C—H stretch

TABLE 4
Validation Set for Analysis of Starch–EAA Mixtures

Wt% EAA in mixture	*Measured value*
3·00	3·2
7·52	7·9
12·50	12·7
12·50[a]	12·8
17·96	18·1
22·00	22·6
22·00[a]	22·6
27·00	27·5
32·08	32·4
37·16	38·3
42·27	43·6
53·00	55·6
Average (CO_y) = 24·08	Average (CO_x) = 24·8

Standard error of prediction = 0·7670
Correlation coefficient = 0·99970

[a] Repeat determinations on the same synthetic mixture.

band of EAA at 2851 cm^{-1} to the C—O stretch band of the polysaccharide. Spectral subtraction of the polysaccharide component is necessary before the EAA absorbance can be accurately determined.

A number of experimental variables affect the accuracy and reproducibility of this analytical method. Of primary importance is particle size of the sample in the KBr pellet, and thus the method used to ball-mill samples during pellet preparation. Variations in particle size resulting from differences in pellet preparation conditions can be easily monitored by observing changes in the absorbance ratio of two bands in the polysaccharide region of the spectrum. When analysing dextran–EAA mixtures, it is especially important that both the mixture and the dextran standard used for spectral subtraction be ball-milled to about the same particle size. It is equally important that unknown samples be ball-milled to the same particle size as the known samples used to construct the empirical curve. Moreover, relative amounts of sample and KBr present during ball-milling must be the same for standards and unknowns. We also have preliminary evidence that FTIR analysis of extruded films (as opposed to cast films) requires the use of extruded film standards for construction of the empirical curve.

Principles outlined in this study should be applicable to FTIR analyses of other polysaccharide–synthetic polymer composites.

ACKNOWLEDGMENT

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