Quantitative characterization of degree of mixedness of lova grains

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QUANTITATIVE CHARACTERIZATION OF DEGREE OF MIXEDNESS OF LOVA GRAINS

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ABSTRACT

A wide-angle x-ray diffraction technique developed earlier by the authors to characterize the degree of mixing in concentrated suspensions is applied to the quantitative characterization of the distributive mixing achieved in extruded LOVA grains, to demonstrate the applicability of the technique towards total quality assessment of energetic grains. The samples included LOVA grains which were either processed in a batch mixer and ram extruded or processed and extruded using co-rotating twin screw extrusion.

INTRODUCTION

The ingredients of energetic formulations, including the oxidizer, fuel, polymeric binders, plasticizers, catalyzers, wetting agents, and burning rate modifiers have to be metered accurately and mixed adequately in order to secure their uniform distribution throughout the microstructure of the extruded grain. Inadequate mixing of the ingredients and formation of defects associated with such inadequate mixing lead to the production of inhomogeneous grains with localized "sensitive" regions which seriously degrade their performance characteristics. In order to improve quality and to reduce waste, reliable analytical techniques need to be developed and employed for "degree of mixing" and defect distribution analysis in extruded grains.

Various theoretical and experimental methods have been developed to study the development of the microstructure and the degree of mixing in model materials[1-14]. Although some of these techniques are useful for understanding and modeling of the mixing process, their applicability in the industrial production environments is highly limited. Kalyon et al.[15] have employed magnetic resonance imaging, wide-angle x-ray diffraction and x-ray radioscopy for characterization of composite suspensions. Yazici and Kalyon[16] have developed and applied electron probe and x-ray diffraction techniques to the analysis of degree of mixing in concentrated suspensions. The magnetic resonance imaging and x-ray diffraction can provide detailed mixing analyses on any type of energetic material.

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In this study, a wide-angle x-ray diffraction technique developed by the authors to assess the degree of mixing in concentrated suspensions[16] is applied to the quantitative characterization of the distributive mixing achieved in extruded live LOVA grains following continuous and batch mixing operations.

EXPERIMENTAL PROCEDURES

Materials Processing and Sample Preparation

The formulation of the LOVA involved 30% by volume polymeric binder cellulose acetate butyrate (CAB) plasticized with acetyl triethyl citrate and 70% by volume solids. Same formulation was used in both the continuous and the batch mixing. The solid content was primarily cyclotrimethylene-trinitamine (RDX) that contained few volume percent octahydro-tetranitro-tetrazocine (HMX) as a by-product of RDX synthesis. The average particle size of the solid phase was 4 microns.

Both the continuously processed, i.e., twin-screw mixed and extruded, and the batch processed, i.e., batch mixed and ram extruded profiles, contained internal perforations as seen in Figure 1. Sections of the extruded profiles each measured 0.3" in diameter and 1" long, were randomly chosen from the continuous (C-1) and batch processed (B-1) lots. Each grain was sectioned as shown in Figure 1b, prior to characterization with x-ray diffraction. In addition to the extruded profiles, samples of the raw ingredients that were used in the processing, i.e., CAB, plasticizer and RDX + HMX powder were also analyzed as reference materials.

Characterization of the Mixing Indices

Various mixing indices were determined at different scales of examination by varying the sampling area through alterations of the size of the x-ray probe by several orders of magnitude as shown in Figure 1b. The relative volume-fractions of the filler and the plasticized binder, i.e.,

$$\frac{\phi_{CAB}}{\phi_{CAB} + \phi_{RDX}} \tag{1}$$

was utilized as the basis for the measure of the degree of mixing of the grains. Here ϕ_{CAB} is the volume fraction of the binder, cellulose acetate butyrate and ϕ_{RDX} is the volume fraction of RDX.

In general, the quantitative description of the mixing quality or goodness of mixing of a given mixture can be developed by comparison of the state of the mixture to the most complete mixing state attainable[17]. This complete mixing corresponds to statistical randomness of the ultimate properties of the ingredients being mixed which would follow the binomial distribution[18].

A basic measure of the homogeneity of a mixture is the extent to which the concentration values of the ingredients of the formulation found at various regions of the volume of the mixture differ from their mean concentration $\bar{c}$. The variance, s^2, arising from the individual concentration, c_i, measurements, provides such an index to quantitatively assess the degree of mixedness. Relative variability is defined with coefficient of variation, v, which is the ratio of standard deviation to the mean[19].

$$v = \frac{s}{\bar{c}} \tag{2}$$

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The maximum variance occurs if the components are completely segregated. Maximum variance is given by

$$s_0^2 = \bar{c}(1 - \bar{c}). \tag{3}$$

The intensity of mixing, I_{mix}, can be defined by normalizing the variance with its maximum value, and an amplitude of mixing or mixing index, MI, can be obtained by normalizing the standard deviation with its maximum value:

$$MI = 1 - \frac{s}{s_0} \tag{4}$$

Both the intensity of mixing and the mixing index values range from zero, for completely segregated system, to one, for ideally homogeneous system. The objective of any mixing/processing operation, whether batch or continuous, is to homogenize the distribution of the components of the formulation; thus, to achieve mixing index values as close to one as possible at the desired scale of examination.

The Analytical Technique: Wide-Angle X-Ray Diffractometry

X-ray diffractometry has been successfully applied for both qualitative and quantitative phase analysis in multi-phase materials[20,21]. The technique and its application in mixing analysis have been reviewed elsewhere[16] and only a brief description will be given here. Upon irradiation with x-rays, a given substance produces a characteristic diffraction pattern. Qualitative analysis by x-ray diffraction is accomplished by identification of the particular diffraction pattern of a substance from the standard diffraction tables[22]. Quantitative analysis is possible, because the intensity of the diffraction pattern of a particular phase - in a mixture of phases - depends on the concentration of that phase in the mixture. Degree of mixing

analysis is achieved by carrying out systematic "window" measurements at various locations of the extruded grains.

The relation between the integrated intensity I_x and the volume fraction ϕ_x of a phase in a mixture depends on the absorption coefficient of the mixture, μ_m:

$$I_1 = K_1\phi_1/\mu_m, \tag{5}$$

where K_1 is a constant which depends on the material and the incident beam used but not on the concentration. The relative ratio of intensities from phases 1 and 2, however, is independent of μ_m

$$\frac{I_1}{I_1 + I_2} = \frac{K_1\phi_1}{K_1\phi_1 + K_2\phi_2} \tag{6}$$

K values can be determined either from the $I_x/I_{corundum}$ values listed by JCPDS[22] or by preparing standard samples of known composition.

The ingredients of the extruded grains of this demonstration study constitute similar elements C-H-O and N, and similar molecules, making it difficult to differentiate the ingredients by other analytical methods. On the other hand, as listed in Table 1, the ingredients of this formulation exhibit distinct crystallinity characteristics: RDX(I) and β-HMX exhibit unique crystal structures and plasticized CAB exhibits a unique amorphous structure. The wide-angle x-ray diffraction technique that is chosen as the principal tool for this study is, therefore, a very effective method to differentiate and quantify these ingredients.

TABLE 1: Formulae and Structures of Ingredients

Name	Formula	Crystal	Constants
RDX(I)	$C_3H_6N_6O_6$	Orthorhombic	a=13.19
			b=11,592
			c=10.714
β-HMX	$C_4H_8N_8O_8$	Monoclinic	a=6.537
			b=11.052
			c=8.702
			β=124.4
CAB	$.5\ C_6H_{10}O_5$	Amorphous	—
	$.13\ CH_3CO$		
	$.37\ CH_3(CH_2)_3$		

In this study, the relative volume fractions of the plasticized binder (CAB) and the fillers RDX and HMX were calculated from the relative intensity fraction values given by Eq. 6. These measurements were carried-out utilizing relatively high number of crystal-plane reflections of the crystalline fillers in order to eliminate texture effects and to increase accuracy. For the amorphous, plasticized binder CAB, the entire broad amorphous peak was utilized. Standard samples of the raw ingredients, i.e., the live powder and the polymer binder were prepared and utilized to calibrate the measurements. A software package by Rigaku, Images, was used for quantitative analysis. The contributions from the additives which total less than 4% by volume were considered in these calculations; however, the effects of the micro-voids and perforations were omitted. A Rigaku DXR-3000 wide-angle diffractometer system was used. Crystal monochromatized CuK_α radiation at 40 KV and 20mA was applied with 0.15 and 0.6 degree receiving slits. The x-ray

probe sizes (defining the scale of examination) used were 0.1, 1, and 10 mm^2, respectively. The depth of penetration of the technique was in the order of 0.5 mm.

RESULTS AND DISCUSSION

A typical wide-angle x-ray diffraction (XRD) pattern of the extruded profiles is shown in Figure 2a. This is a convoluted pattern which includes diffraction peaks from all the ingredients present in the formulation. Computer search/match and manual identification/elimination methods were applied utilizing the documented crystallographic data, and XRD patterns listed in the JCPDS files[22] and in the published literature[23]. The available diffraction patterns of RDX(I) and β-HMX are shown in Figures 2b and 2c. In Figure 2d, the x-ray diffraction pattern of the amorphous binder, i.e., plasticized CAB, is shown to demonstrate further the phase identification process.

The results of the quantitative x-ray diffraction analysis of the relative volume fractions of the binder and RDX from the systematic "window" measurements at two scales of examination are shown in Figures 3 and 4, respectively. In both figures the data from the batch-mixed sample (B-1) is given in (a) and the data from the continuously-mixed sample (C-1) is given in (b), for comparison.

The statistical analysis of these results are presented in Tables 2 and 3 for the relative volume ratios of the binder and RDX, respectively. Overall, the average volume fractions of the ingredients were very close to their target values in both batch (B-1) and continuously processed (C-1) lots. However, the amplitude of the

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dispersion or variance of the measured relative volume fraction values differed significantly. As can be seen in Figures 3 and 4, the dispersion of the data is relatively narrow for 10 mm^2 scale of examination; however, when the scale of examination is reduced to 1 mm^2 the dispersion of the data increases substantially and the differences in dispersion between the B-1 and C-1 lots become pronounced.

TABLE 2: Plasticized CAB Mixing Parameters

| | Batch Mixed (B-1) | | Twin Screw Extruded (C-1) | |
| | Scale of Examination | | Scale of Examination | |
	10 mm^2	1 mm^2	10 mm^2	1 mm^2
mean	24.73	24.71	25.1	25.5
s	2.183	6.321	1.98	3.44
v	.09	.26	.08	.13
MI	.95	.85	.95	.92

TABLE 3: RDX+HMX Mixing Parameters

| | Batch Mixed (B-1) | | Twin Screw Extruded (C-1) | |
| | Scale of Examination | | Scale of Examination | |
	10 mm^2	1 mm^2	10 mm^2	1 mm^2
mean	71.41	71.06	70.4	69.8
s	2.215	4.967	1.95	3.48
v	.03	.07	.03	.05
MI	.95	.89	.96	.92

The immediate inferences one can make from these results include the fact that the quality of mixing in the continuous mixed (C-1) lot is better than the batch

mixed (B-1) lot. How much better is the C-1 lot from the B-1 lot? The answer to this question can be found in the statistical parameters of the measurements listed in Tables 2 and 3. For example, the parameters for the binder volume fraction at 1 mm^2 scale of examination show that the dispersion or standard deviation of the data is almost twice as large for the B-1 lot than the C-1 lot. Since the mean values for the two lots are almost identical, the coefficient of variation is also twice as large for B-1 than C-1, suggesting the superior distributive mixing achieved by the continuous processing method in comparison to batch mixing. The difference between the two lots is also evident in the index of mixing values. The relatively lower sensitivity of the index of mixing in differentiating the two lots is due, by definition, to its normalization with respect to the totally segregated state. The mixing index value for the continuously mixed (twin screw extruded) grains are greater than those of the batch mixed and ram extruded LOVA grains.

How significant are these results, which statistical parameter is more important and which scale of examination is more relevant? The answer to these questions can only come from the performance characteristics of extruded grains for a given application. However, the technique and the parameters generated can accurately classify a given extruded suspension with respect to ideally mixed and/or totally segregated states and quantify the "degree of mixing."

This comparative study was completed with no prior information about the two lots, and, only after presentation of the results some of the vital information related to the performance properties of the two lots were obtained from the sponsors. According to this information, the batch mixed B-1 lot had apparently failed the burn-rate-based performance test and was discarded. Another batch

mixed lot B-2 which passed the performance test was also evaluated with our technique and gave similar results as the continuous mixed C-1 lot. Therefore, the results that are presented in this study are very significant not only in determining the degree of mixing with quantitative parameters but also in indirectly providing information on the performance of a given energetic grain. The results indicate that the relevant scale of examination is 1 mm^2 (or lower) for the LOVA grains; and the index of mixing has to be significantly high (better than 0.9) at this scale of examination, for adequate mixedness and performance.

CONCLUSIONS

Our degree of mixing analysis technique based on wide-angle x-ray diffraction was successfully applied to analyze extruded LOVA grains which were pre-mixed with batch and twin screw extrusion processes. The technique can: i) identify various components present in an extruded formulation, ii) quantitatively determine the volume fraction of each component at various locations in extruded profiles, iii) quantitatively characterize the degree of mixing of each component at the desired scale of examination for a given application.

In the grains studied, the average volume fractions of the ingredients were close to their target values in both batch and continuous mixed lots. At smaller scale of examination (1 mm^2) the quality of mixing of the binder and the energetic solid powder was significantly better in continuous mixed lot than batch mixed lot.

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The parameters defined, i.e., the variation coefficient and mixing index, were highly effective in quantifying the degree of mixing of extruded grains, which is related to their performance.

ACKNOWLEDGMENTS

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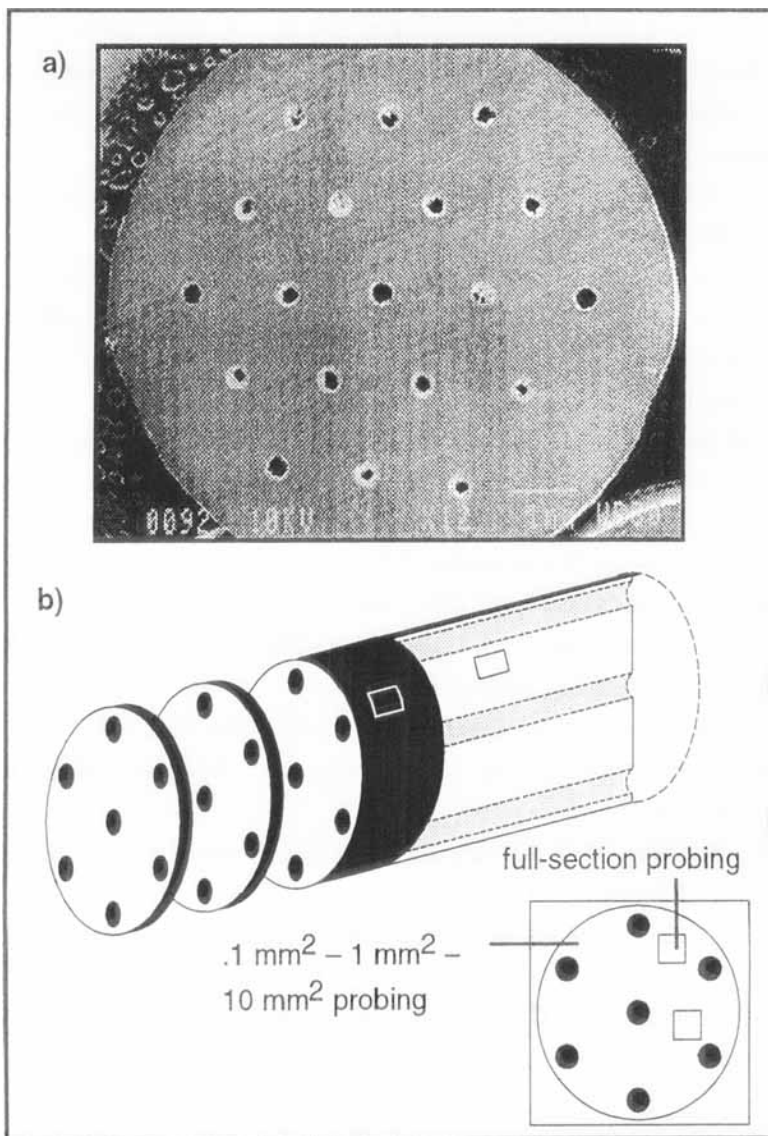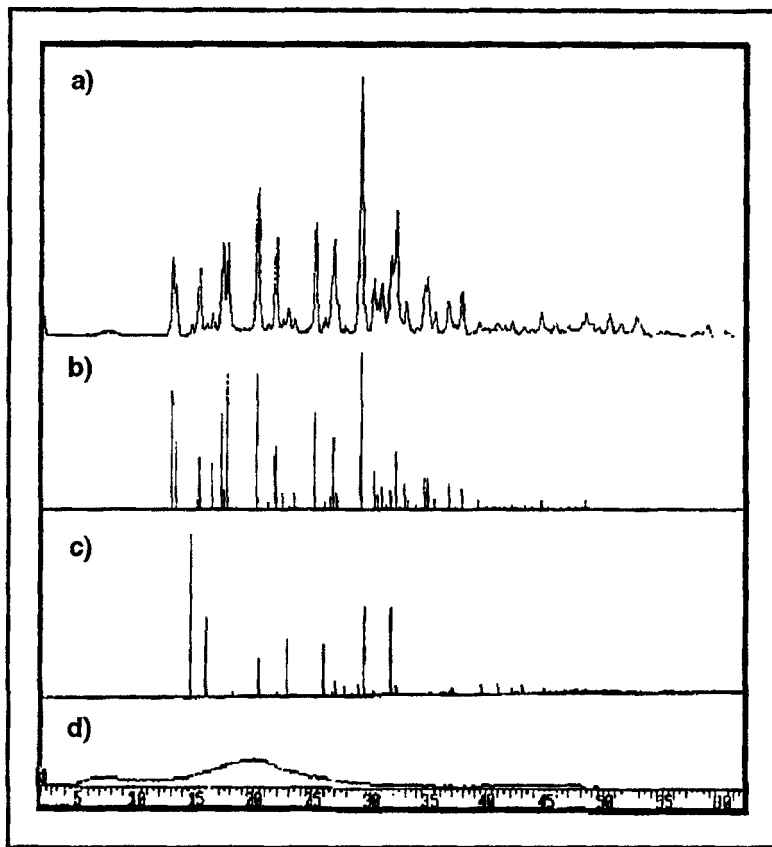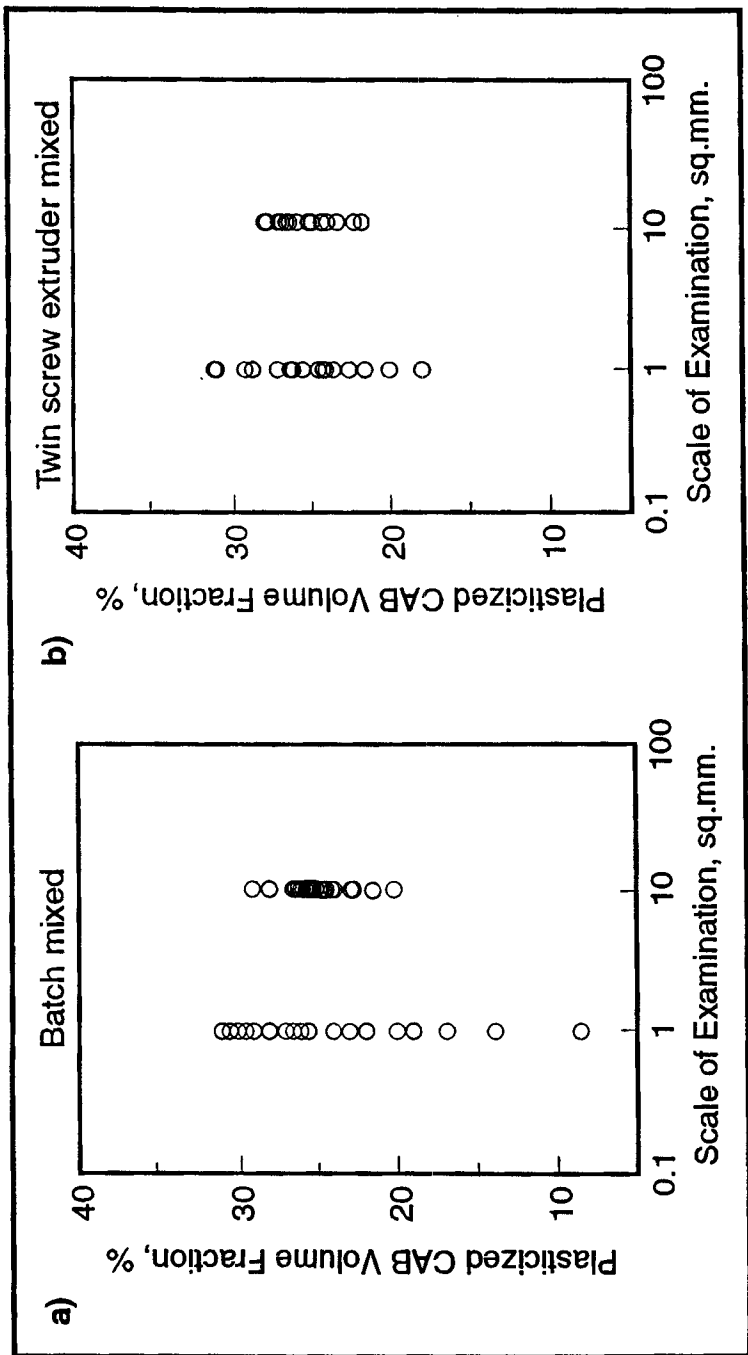23. D. B. Sullenger, J.S. Cantrell and T. A. Beiter, Powder Diffraction, 9, 2 (1994).

FIGURE 1
Extruded profile (a) and sampling (b).

FIGURE 2
X-ray diffraction patterns of the (a) multi-phase extruded profile, (b) RDX,
(c) HMX, (d) plasticized cellulose acetate butyrate (CAB).

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FIGURE 3

Plasticized CAB volume fraction dispersion at two scales for grains processed with batch mixing and twin screw extrusion. Each point represents a different location.
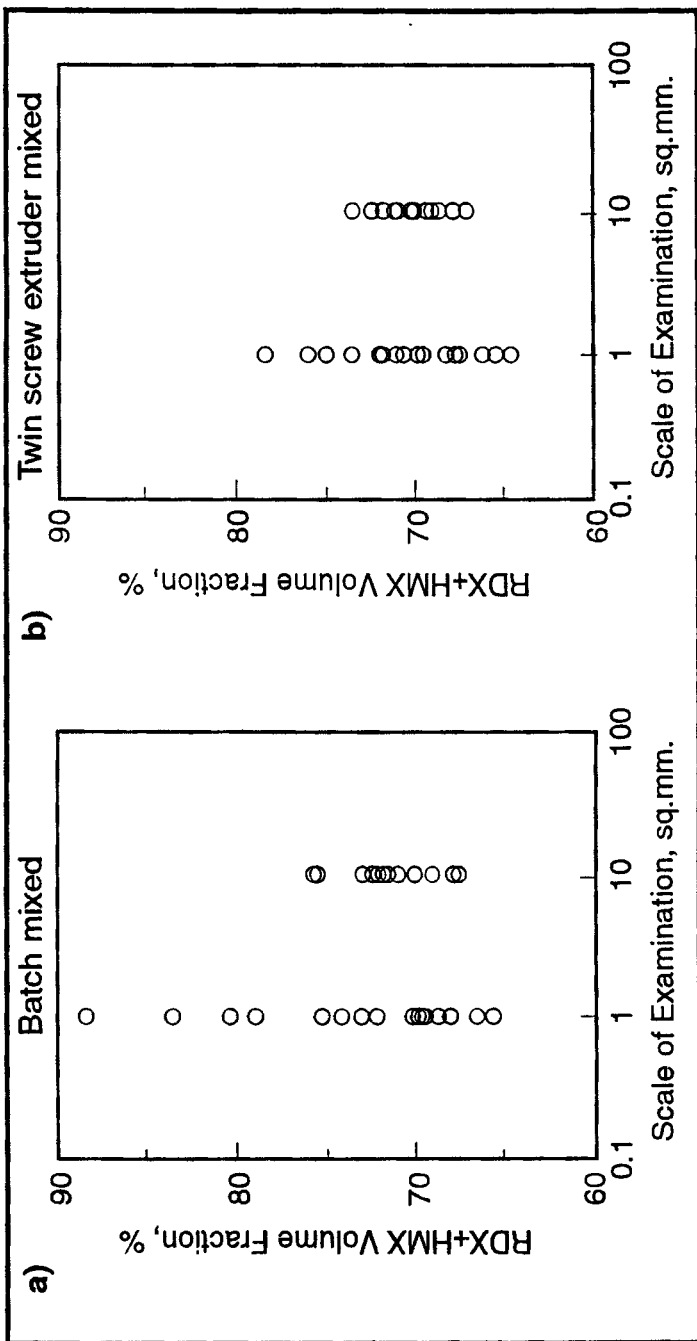
FIGURE 4

RDX+HMX volume fraction dispersion at two scales for grains processed with batch mixing and twin screw extrusion.