
Analysis of Degree of Mixing in Filled Polymers by Wide-Angle X-Ray Diffraction

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INTRODUCTION

The ingredients that go into extruded suspensions, such as solid fillers, polymeric binders, plasticizers, dyes, catalyzers and wetting agents have to be metered accurately and mixed rigorously in order to secure a uniform microstructure throughout the extruded profile. Inadequate mixing of the ingredients and formation of defects lead to production of inhomogeneous profiles with localized "sensitive" regions that seriously degrade the product performance. In order to improve product quality and to reduce waste, reliable analytical techniques need to be developed and employed for "degree of mixing" and defect distribution analysis in extruded profiles, amenable to on-line utilization.

Various experimental methods have been developed to study the development of microstructure and the degree of mixing in model materials [1-6]. 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. [7] have employed magnetic resonance imaging, wide-angle x-ray diffraction and x-ray radioscopy for characterization of composite suspensions. Yazici and Kalyon [8] have developed and applied electron probe and x-ray diffraction techniques to the analysis of degree of mixing in concentrated suspensions.

In this study, a wide-angle x-ray diffraction technique developed by the authors to assess the degree of mixing in concentrated suspensions [8] is applied to the quantitative characterization of the distributive mixing achieved in two lots of extruded filled polymers, with the extrusion step following continuous and batch mixing operations, respectively.

EXPERIMENTAL PROCEDURES

Materials Processing and Sample Preparation

The filled polymer consisted of 30% by volume plasticized polymeric binder cellulose acetate butyrate (CAB) and 70% by volume solid fillers. The filler 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 filler was 4 microns. Same formulation was used in both the continuous and the batch mixing followed by extrusion through a die.

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 0.3" in diameter and 1" long, were randomly chosen from the continuous (C-1) and batch processed (B-1) lots. In addition to the extruded profiles, samples of the raw ingredients that were used in the processing, i.e., plasticized CAB binder and RDX filler 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.,

$$\frac{\phi_{CAB}}{\phi_{CAB} + \phi_{RDX}} \quad (1)$$

was utilized as a measure of the degree of mixing of the samples.

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 [9]. This complete mixing corresponds to statistical randomness of the ultimate properties of the ingredients being mixed which would follow the binomial distribution [10].

A basic measure of the homogeneity of a mixture is the extent to which the concentration values at various regions of the volume of the mixture differ from the 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 mean [11].

$$v = \frac{s}{\bar{c}} \quad (2)$$

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

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

An 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:

$$MI = 1 - \frac{s}{s_0} \quad (4)$$

Both the intensity of mixing and the mixing index values range from zero, for completely segregated system, to one, for ideally homogeneous system.

The 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 [12,13]. The technique and its application in mixing analysis have been reviewed elsewhere [8] 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 [14]. 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 extrudates.

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 :

$$I_1 = K_1 \phi_1 / \mu_m, \quad (5)$$

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

$$\frac{I_1}{I_1 + I_2} = \frac{K_1 \phi_1}{K_1 \phi_1 + K_2 \phi_2} \quad (6)$$

K values can be determined by preparing standard samples of known composition.

The ingredients of the extruded profiles of this 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 I, the ingredients of this formulation exhibit distinct crystallinity characteristics: RDX(I) and β -HMX each exhibit unique crystal structure and CAB + plasticizer exhibit a unique amorphous structure. The wide-angle x-ray diffraction technique chosen as the principal tool for this study is, therefore, a very effective method to differentiate and quantify these ingredients.

In this study, the relative volume fractions of the plasticized binder (CAB) and the filler RDX 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 amorphous plasticized binder CAB, the entire broad amorphous peak was utilized (see Fig. 2). Standard samples of the raw ingredients, i.e., filler powder and polymer binder were prepared and utilized to calibrate the measurements. 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 $\text{CuK}\alpha$ radiation at 40 KV and 20mA was applied with 0.15 and 0.6 degree receiving slits. The x-ray probe sizes used were 0.1, 1 and 10 mm², 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 filled polymer is shown in Figure 2a. This is a convoluted pattern which includes diffraction information from all the ingredients present in the formulation. Computer search/match methods were applied utilizing the documented crystallographic data and XRD patterns listed in the JCPDS files [14] and in the published literature [15]. In Fig. 2b, the XRD of the amorphous plasticized CAB binder is also shown to demonstrate the phase identification process.

The results of the quantitative x-ray diffraction analysis of relative volume fractions of the polymer from systematic "window" measurements at two scales of examination are shown in Fig. 3. In Fig. 3 the data collected from different locations from the batch-mixed sample is given in (a) and from the continuously-mixed sample is given in (b), for comparison.

The statistical analysis of these results are presented in Tables II and III for the polymer and the filler, respectively. Overall, the average volume fractions of the ingredients were very close to their target values in both lots. However, the amplitude of the dispersion or variance of the measured relative volume fraction values differed significantly. As can be seen in Fig. 3, the dispersion of the data is relatively narrow for 10 mm² scale of examination; however, when the scale of examination is decreased to 1 mm² the dispersion of the data increase substantially and the differences in dispersion between the batch, B-1, and continuous, C-1, lots become pronounced.

These results indicate that the quality of mixing in the continuous mixed C-1 lot is better than the batch mixed B-1 lot. The quantitative comparison of the degree of mixedness of the two lots are shown in the statistical parameters of the measurements listed in Tables II and III. For example, the parameters for the binder volume fraction at 1 mm² 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. The difference between the two lots is also evident in the index of mixing values.

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 the filled polymers for a given application. However, the technique and the parameters generated can accurately classify a filled polymers with respect to ideally mixed and/or totally segregated states and quantify the "degree of mixing".

Qualitative microstructural examples, i.e. SEM micrographs, are shown in Fig.s 4a and 4b. These micrographs are taken at locations which were probed with WAXRD, i.e., (a) average binder content (25%) and (b) inadequate binder content (<10%), respectively. The lack of binder between the particles in micrograph 4b in contrast to 4a is a qualitative demonstration of the inferior degree of mixing measured in B-1 Lot by the x-ray diffraction method applied in this study.

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 was obtained from the sponsors. According to this information, the batch mixed B-1 lot had

apparently failed the 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 predicting the performance of a given filled polymer. The results indicate that the relevant scale of examination is 1 mm² (or lower) for these materials; and the index of mixing has to be significantly high (better than 0.90) at this scale of examination.

It should also be noted that our technique generates degree of mixedness measures which are amenable to prediction using numerical simulation of polymer processing operations [16-18]. Thus, future development in mixing theory can be linked naturally to our technique.

CONCLUSIONS

Our degree of mixing analysis technique based on wide-angle x-ray diffraction was successfully applied to analyze filled polymers 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 specific application.

In the profiles 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 mm²) the quality of mixing of the binder and the filler was significantly better in continuous mixed lot than batch mixed lot.

The parameters defined, variation coefficient and mixing index, were highly effective in quantifying the degree of mixing and predicting the ensuing performance of the extruded profiles.

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Table I: Formulae and Structures of Ingredients

<u>Name</u>	<u>Formula</u>	<u>Crystal</u>	<u>Constants</u>
RDX(I)	C ₃ H ₆ N ₆ O ₆	Orthorhombic	a=13.19 b=11.592 c=10.714
β-HMX	C ₄ H ₈ N ₈ O ₈	Monoclinic	a=6.537 b=11.052 c=8.702 β=124.4
CAB	.5 C ₆ H ₁₀ O ₅ .13 CH ₃ CO .37 CH ₃ (CH ₂) ₃	Amorphous	ó

Table III: RDX+HMX Mixing Parameters

	B1		C1		
	Scale of Exam.		Scale of Exam.		
	<u>10 mm²</u>	<u>1 mm²</u>	<u>10 mm²</u>	<u>1 mm²</u>	
mean	71.41	71.06	70.4		
	2.215	4.967	1.95		
	.03	.07	.03		69.8
MI s	.95	.89	.96		3.48
v					.05

Table II: Plasticized CAB Mixing Parameters

	B1		C1	
	Scale of Exam.		Scale of Exam.	
	<u>10 mm²</u>	<u>1 mm²</u>	<u>10 mm²</u>	<u>1 mm²</u>
mean	24.73	24.71	25.1	

s	2.183	6.321	1.98	3.44
v	.09	.26	.08	.13
MT	.05	.05	.05	.05

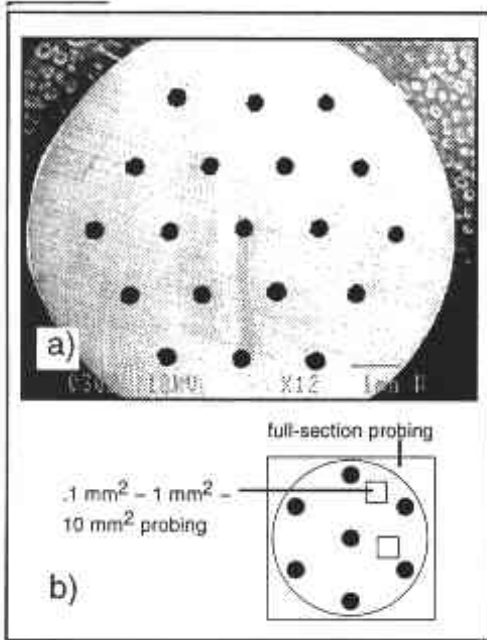


Fig. 1. Extruded profile cross section (a) and systematic x-ray measurements (b).

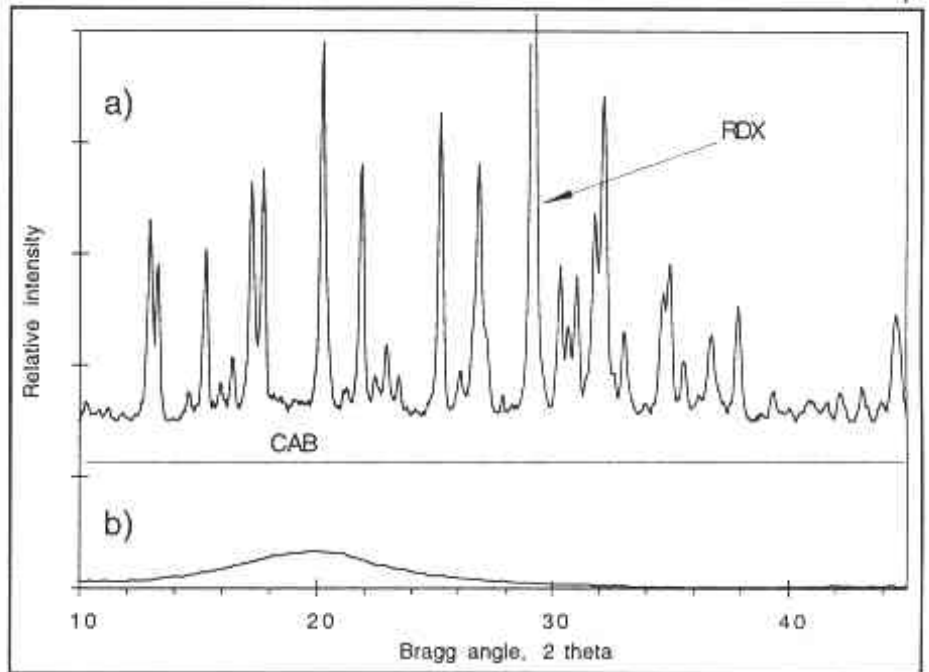


Fig. 2. X-ray diffraction patterns of (a) the filled polymer suspension and (b) plasticized binder (CAB) alone.

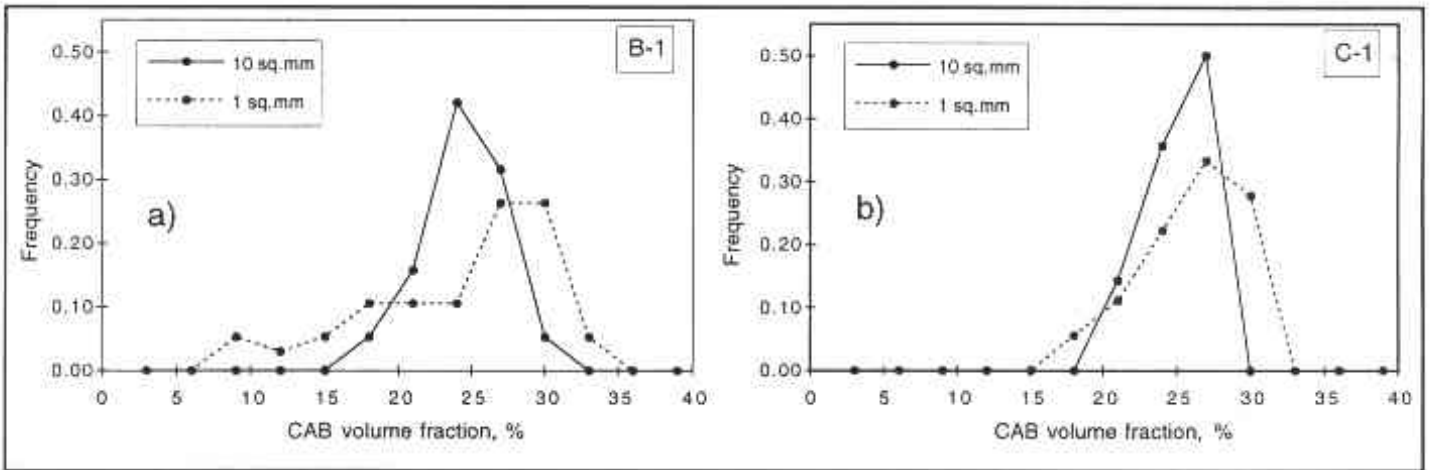


Fig. 3. Plasticized CAB volume fraction variance at two different scales of examination for (a) batch-processed B-1 Lot and (b) continuous-processed C-1 Lot.

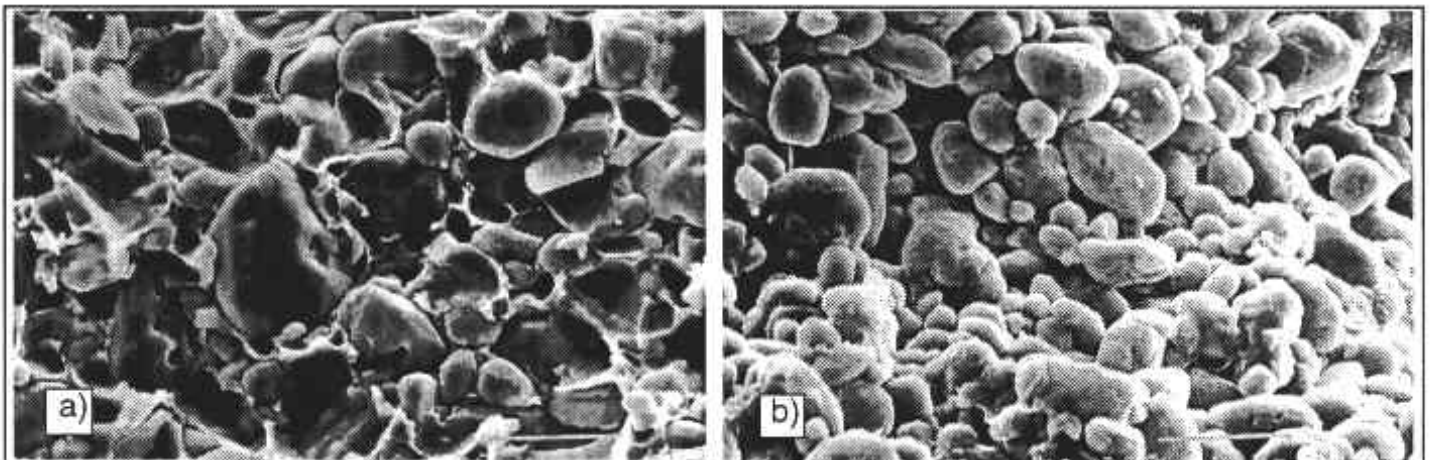




Fig. 4. Microstructures of filled polymer regions (2,000X) with (a) average binder content (25%) and (b) inadequate binder content (<10%), as measured by x-ray diffraction.