STATISTICS OF MIXING DISTRIBUTIONS IN FILLED ELASTOMERS PROCESSED BY TWIN SCREW EXTRUSION

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Abstract

Continuous processing of filled elastomers by twin screw extrusion and achievement of viable mixing distribution characteristics present formidable challenges. In this work a thermoplastic elastomer, HyTemp, was plasticized with DOA and filled with ammonium perchlorate powder and additives. It was found that the extruder geometry, the order of ingredient addition and die pressurization have profound effects on the mixing distribution characteristics of the elastomer based extruded profiles. The mixing distribution characteristics were quantitatively determined by x-ray diffraction techniques.

Background

During continuous processing the ingredients of filled formulations have to be metered accurately and mixed adequately in order to secure a uniform mixing distribution throughout the extruded profile. Inadequate mixing or segregation of the ingredients during processing lead to production of inhomogeneous extrudates with localized "sensitive" regions which may degrade ultimate properties. In order to optimize processing conditions and product quality reliable analytical techniques need to be employed for characterization of mixing distribution.

Various theoretical and experimental methods have been developed to study the development of the microstructure and the degree of mixing in simpler materials (1-8). Although some of these techniques are useful for understanding and modeling of the mixing process, their applicability to the industrial production environments is highly limited. Kalyon et al. (9) have employed magnetic resonance imaging, wide-angle x-ray diffraction and x-ray radioscopy for characterization of suspensions consisting of a polymeric binder solid fillers. Yazici and Kalyon (10-15) have developed and applied electron probe and x-ray diffraction techniques to the analysis of degree of mixing in concentrated suspensions (13-16).

In this study, a plasticized thermoplastic elastomer HyTemp filled with ammonium perchlorate powder and additives was processed with twin screw extruder under controlled extruder geometry, order of ingredient addition and die pressurization. The effects of these extrusion conditions on the mixing distribution characteristics were quantitatively determined by wide-angle x-ray diffraction techniques developed by the authors. The statistical parameters of the distributive mixing achieved throughout a given run and as a function of location on the extrudate cross-sections were determined.

Experimental Procedures

Materials

The formulation of the filled elastomer of this study involved HyTemp [crosslinked (butryl and ethyl) acrylic acid ester] elastomer with DOA (dioctyl adipate) plasticizer filled with 84% ammonium perchlorate (AP) and additives Fe_2O_3, graphite (Gr) and ZrC. This formulation was twin screw extruded using an annular die with a star-shaped mandrel (see Fig.1).

Three control samples were prepared by batch mixing and used for calibration of the wide-angle x-ray diffraction (WAXD). The batch designations of the control materials were BL, for the baseline batch with 84% ammonium perchlorate (AP), BL-2 for the baseline-2% Batch (82% AP), and BL+2 for the baseline + 2% Batch (86% AP). For these three control formulations the concentrations of AP, iron oxide (Fe_2O_3) and the additives zirconium carbide (ZrC) and graphite (Gr) were kept constant, however, the concentrations of the binder ingredients HyTemp 4404 and plasticizer DOA were altered in proportion to the variations in the concentration of AP.

Characterization of the Mixing Indices

The relative volume-fractions of the ingredients were utilized as the basis for the measure of the degree of mixing and mixing distribution of the extruded profiles. Here ϕ represents the volume fraction of a given ingredient.

$$AP\ relative\ volume\ fraction\ = \frac{\phi_{AP}}{\phi_{HyTemp}} \qquad (1)$$

In general, the quantitative description of the mixing quality of a given mixture can be given by comparison of the state of the mixture to the most complete mixing state attainable (16). This complete mixing corresponds to statistical randomness of the ultimate properties of the ingredients being mixed which would follow the binomial distribution. 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 c. The variance arising from the individual concentration measurements provides such an index to quantitatively assess the quality of mixing. Relative variability is defined with coefficient of variation, which is the ratio of standard deviation to the mean.

The Analytical Technique

X-ray diffractometry has been successfully applied for both qualitative and quantitative phase analyses in multi-phase materials. The technique and its application in mixing analysis have been reviewed elsewhere (10-13) 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 from the standard references. Quantitative analysis is possible, because the intensity of the diffraction pattern of a particular ingredient in a mixture of ingredients depends on the concentration of that phase in the mixture. Quality or degree of mixing analysis is achieved by carrying out systematic "window" measurements at various locations of the extruded profiles.

Samples from randomly chosen extruded profiles were analyzed to assess the mixing distributions achieved by twin screw extrusion. As a part of this investigation, samples from three control formulations prepared by batch mixing with varied AP concentrations were also analyzed. The results were utilized to calibrate the measurement techniques applied.

Results and Conclusions

The measurements carried-out on the control formulations exhibited a linear dependence between the AP concentration and the measured values obtained by x-ray diffraction techniques. The twin screw extruded composite profile exhibited a relatively good state of mixing compared to those grains processed in previous extrusion during the optimization of the process parameters. The concentration of the burn modifier iron oxide (Fe_2O_3) was 1.53% by weight, almost at the target value and its degree of mixing was one of the highest observed, with a coefficient of variation of 0.12 and a mixing index of 0.98. The concentration of AP was 1% higher than the target value. The mixing index of AP was 0.85 and its coefficient of variation, was 0.06. Only 1% deviation of the AP from the target value is indicative of the adequate processing of the extruded suspension in the twin screw extruder.

The results of the WAXD measurements carried-out on these control batch samples are shown in Fig. 2. In this figure, three calibration curves relating the relative concentrations of the binder/oxidizer c_{binder}/c_{AP}, to relative x-ray diffraction intensities of the binder/oxidizer I_{binder}/I_{AP} are shown. Three different calibration methods were applied: 1-, 3- and 4-peak relating to the number of AP diffraction peaks utilized. All three methods exhibited linear variation of the XRD measurements with linear variation of the AP concentration.

Sampling of the twin screw extruded annular profile for WAXD analysis was carried-out by sectioning from multiple transverse locations until a good representation of the whole extrudate was secured. Each one of the samples was further cut multiple times to obtain 3 mm-thick samples for effective XRD measurements. All measurements that are presented in this report were carried-out on the "longitudinal cut" surfaces of the extruded profile.

The average results of the XRD measurements carried-out on the extruded profile samples are shown in Fig. 3. Here the binder/AP WAXD intensity ratios (I_{binder}/I_{AP}) obtained by 1-, 3- and 4-peak methods are superimposed on the calibration curves obtained from the three control formulations. The intensity ratio (I_{binder}/I_{AP}) values of the twin screw extruded profile are marked with arrows obtained via each method.

As shown in Fig. 3, the agreement between the results of the three measurement methods was excellent. All three measurements indicate an elastomer/AP concentration ratio of 0.14-0.142, which indicates an AP concentration in between those of the 84% and 86% control formulations. The AP concentration that can be obtained from this chart would be correct only if the concentrations of the other ingredients, Fe_2O_3, ZrC and Gr, are the same as in the control formulations. The concentrations of these other ingredients were determined via similar calibration procedures, which make use of WAXD intensities emanating from each ingredient.

The results of this x-ray diffraction intensity based quantitative degree of analysis results are given in Plate 1 for the entire extruded filled-elastomer profile run. In Plate 1, the concentrations of each ingredient and the degree of mixing parameters are listed in the table. The variations of the concentrations (in weight fractions) of the two important ingredients ammonium perchlorate (AP) and the modifier iron oxide (Fe_2O_3) are also shown graphically in Plate 1.

The concentration of Fe_2O_3 is 1.53% and is very close to the target value. The state of mixing parameters for Fe_2O_3 were 0.12 for coefficient of variation, which is relatively low, and 0.98 for mixing index which is relatively high. Both indicate a very good state of mixing. The coefficient of variation value of 0.06 is very low, indicating a good mixing state. The mixing index value 0.85 is one of the higher values obtained in the other twin screw extrusion runs carried out during process optimization. For the plasticized binder the coefficient of variation value of 0.20 and the mixing index value of 0.93 are among the best obtained in such filled elastomer materials. The concentrations of the other two additives graphite Gr and ZrC were slightly lower than the target formulation values.

The state of mixing distribution of the ingredients as a function of radial location on the cross sections of the extrudates was determined by carrying out WAXD measurements at one-mm intervals. The results of these measurements are given in Plate 2. As shown in Fig. 1 the distribution of AP concentration across the full thickness of the annular extrudate was within $\pm$2% of the mean value (84%). AP concentration was higher than the mean at 22^{nd}–25^{th} mm location, about 1/3 of thickness away from the outer wall. The AP concentration was lower than the mean at both of the wall regions, inner and outer. The distribution of Fe_2O_3 concentration across the full thickness of the annular extrudate was within $\pm$0.3% of the mean value (1.56-%). Fe_2O_3 concentration was in general higher near the inner wall regions and lower near the outer wall regions, with respect to the mean value.

These experiments demonstrate the importance of quantitatively determining the concentrations of ingredients of formulations and their spatial distributions. Such measurements will enable a detailed understanding of the development of various properties of processed articles.

Acknowledgement

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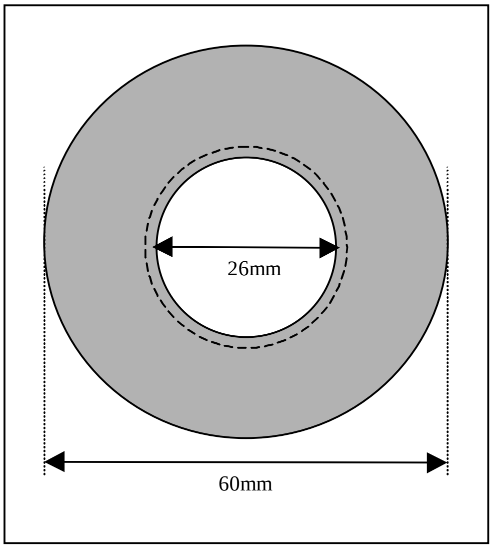


Fig. 1 Annular extrudate

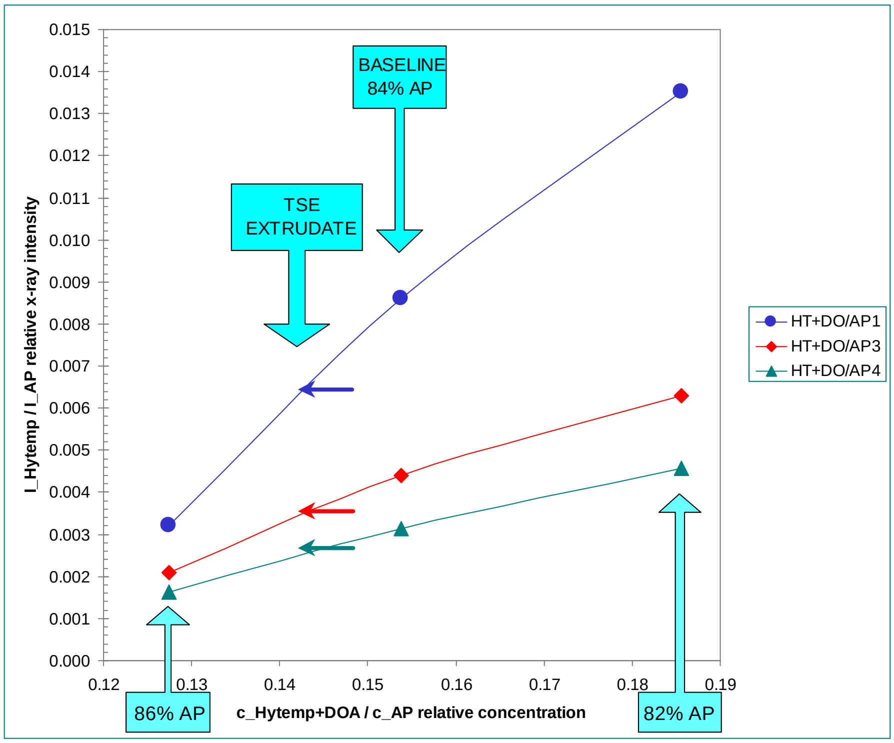
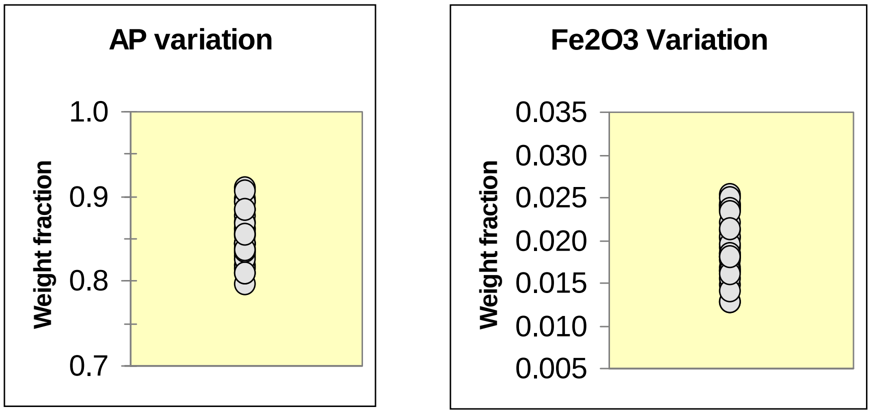


Fig. 2 Calibration curves for binder/filler relative concentration vs x-ray measurements obtained by 1-, 3- and 4-peak methods. And the superimposed values of the twin screw extruded filled elastomer.



TSE Extrudate	HyTe+DOA	Gr	Fe2O3	ZrC	AP
MEAN	0.1226	0.0035	0.0198	0.0052	0.849
STDEV	0.0282	0.0016	0.0069	0.0020	0.0367
COF.VAR	0.234	0.457	0.349	0.387	0.043
MIX.INDX.	0.913	0.973	0.950	0.972	0.897

Plate 1. Degree of mixing parameters of the twin screw extruded filled-elastomer ingredients.

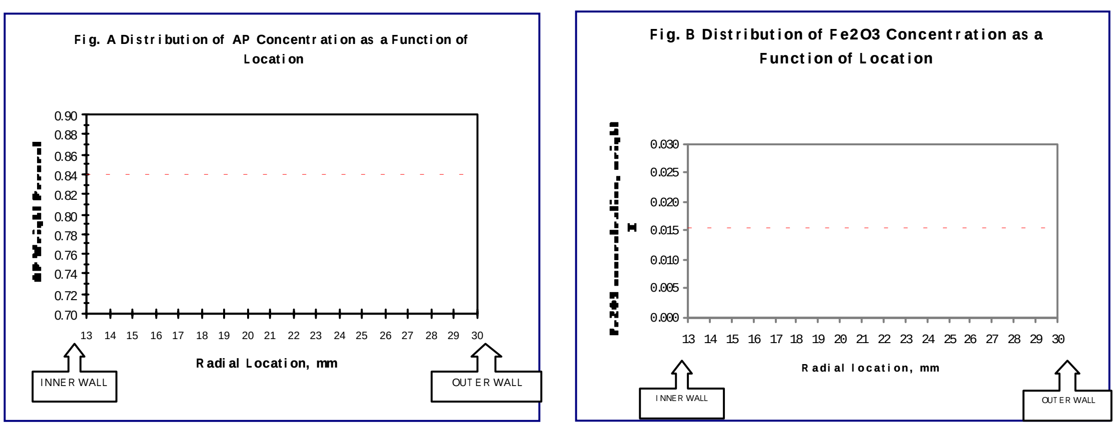


Plate 2. Mixing distribution of main ingredients in filled elastomer extrudate as a function of radial location.