Analysis Method

A UV-Vis spectroscopic method for monitoring of additive particle properties during polymer compounding

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ABSTRACT

Determination of the dispersion characteristics/or morphology of additives in polymer melts by fast, reliable and accurate on-line methods is highly desired in the polymer industry. An ultraviolet-visible (UV-Vis) spectroscopic methodology is described which meets these demands. It is demonstrated that the applied methodology may be developed on a cheap, packaging grade of Polylactic Acid (PLLA), an important bioresorbable polymer for the medical device industry, and still be accurate when implemented on a production line using a more expensive (medical) grade of the polymer compound. Simple chemometric algorithms are applied allowing the data processing step to be carried out in near real time, thus providing vital information to process operators which allows any out of control process to be identified and rectified without product loss.

1. Introduction

The addition of a particulate material to a polymer matrix is useful for many reasons. Additives can be incorporated to improve mechanical properties, barrier properties, aesthetics or just to reduce costs where the polymer is relatively expensive. For particulate additives within a polymer melt there are two main states; aggregated (or agglomerated) and suspended dispersion [14]. Effective mixing is essential to ensure that the additive is well dispersed, ideally in a homogeneous fashion, to obtain improved performance of the polymer composite. Non-homogeneous dispersion may be encountered due to agglomeration and also when the forces acting on the melt cause breakdown of larger particles or when an inconsistent feed rate is seen. Ensuring effective dispersion of additives often means laboratory testing of samples after compounding which can be time consuming, in the meantime a batch of product may have been produced to unacceptable quality or long lead-times can ensue. In some cases re-compounding is necessary, resulting in extra time, energy and expense for the manufacturer. This becomes particularly problematic in the case of polymer compounds for the medical industry where quality demands are extremely high.

Medical devices, specifically implantable devices, made from bioresorbable polymeric materials offer a number of advantages over their traditional counterparts made from metallic materials including an ability to release drugs/bio-active agents at controlled rates [29].

Additive materials in this case are commonly used to aid healing of the area where the device is implanted [1] or tune degradation rates [4]. The medical device industry demands that stringent quality control mechanisms are in place where high development costs can effect financial viability. This is especially the case where medical grades of polymers have material costs reaching into thousands of euros per kilogram, as such high development and waste costs can lead to production of a device being deemed unviable. On-line monitoring techniques have the capacity to overhaul the current, wasteful and expensive trial and error approach taken to the processing of bioresorbable polymers. Using these techniques, quality parameters may be fed back to the user at the earliest stage of development allowing processes to be optimised before material is wasted. This reduction in wastage leads to a reduction in energy, man hours and subsequently development costs.

1.1. Monitoring of particle size in compounding of filled polymer systems

On-line monitoring of the composition of polymer blends during extrusion has been investigated by both ultrasound measurements of polyethylene (PE)/polypropylene (PP)/polystyrene (PS) blends [18] and Small angle light scattering of PE/PS blends [21] and PP/polyolefin elastomer (POE) blends [3]. While the ultrasound measurements provided information on the % loading only, small angle light scattering

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has shown potential for monitoring the morphology of the blend (size and shape of different domains in the melt). Monitoring of particulate additives in a polymer compound has also been carried out during extrusion. The volume fraction of calcium carbonate ($CaCO_3$) in PS was monitored on-line using dielectric measurements [11]. Volume fraction of $CaCO_3$ in PP and also volume fraction of PA6-glass fiber filled compounds have been studied by terahertz (THz) spectroscopy [20]. Content (w/w %) of Magnesium Hydroxide in low density polyethylene (LDPE) was monitored during an extrusion process by near infrared (NIR) spectroscopy [5]. For the most part these studies used some form of multivariate data (MVDA) analysis in order to extract the relevant data from the measurements, the use of MVDA and chemometrics for extrusion monitoring is relatively widespread in the modern literature [26] [2]; [6] [31]; [33].

A number of workers have also addressed the problem of determining the particle size of additives in a polymer compounding process, as a key measure of the degree of dispersion. Several studies have focussed particularly on the exfoliation of nanoclay (breakdown of micro-sized agglomerates of the clay into nano-thick platelets) during extrusion in a polymer matrix [12]. and [8] studied this via light intensity measurements, whereby, following Mie theory, exfoliated nano-particles scatter less light than agglomerated micro-particles and result in a higher intensity light signal being transmitted through the melt. UV-vis [3], fluorescence [13] and NIR-transmission spectroscopy [34] have also been used to monitor dispersion of polymer/clay nano-composites.

Monitoring of the morphology of micro-additives in a polymer compound during extrusion has been achieved by in-process ultrasound measurements [28]. reported the use of a neural network to relate degree of dispersion to ultrasonic velocity, attenuation, melt temperature and pressure measurements. Ultrasonic attenuation spectroscopy was applied to monitoring of particle size in compounding of $CaCO_3$ with PP [3]. This work differed from the previous study in that here use was made of the fact that the ultrasonic attenuation at different frequencies is dependent on particle size [3]. argue this is more directly related to particle size than integral attenuation or velocity measurements and hence required less data and less complex chemometric modelling for calibration of the measurements to particle size.

1.2. Model system

The chosen polymer material for this study, Polylactic acid, is a type of polyester which belongs to a group of materials known as bioresorbable polymers which are slowly becoming more prevalent in the medical device industry.

The additive material chosen for the present study represents a type which has been used extensively with PLA. This was chosen to ensure that the composites represented a relevant material within the medical field. Beta-Tricalcium phosphate ($Ca_3(PO_4)_2$) or β-TCP, a biodegradable, bioactive ceramic material commonly used in orthopaedic devices, has been investigated in composites of: PLGA [15], PLLA [19] and PDLLA [22]. Particle dispersion has been identified in the mentioned studies as a parameter which effects final properties of a product, therefore a robust tool to measure this during processing would be greatly advantageous. Additionally dimensions of medical devices can be in the micro-scale (tubes, membranes, tissue scaffolds *etc.*), as such it is important that agglomerations of filler particles are kept small relative to the product dimensions. In this work we are focussing on monitoring of the size of particulate agglomerates (represented by fixed particle size additives), and ensuring that they do not exceed a specific size where they become significant relative to the product dimensions and hence could potentially result in aesthetic or mechanical defects. Traditional monitoring regimes focus on monitoring fluctuations in percentage loading, however with controlled pre-mixing or if using modern controlled feeding technology, controlling percentage loading is much less of an issue. Monitoring of PLA based polymers by

spectroscopic methods reported in the literature focusses on material degradation [32], this demonstrates the adaptability of the UV-Vis measurement system and suggests that future work may be able to combine filler and degradation monitoring using a single technique.

In this manuscript we aim to demonstrate an on-line measurement technique which is capable of determining in real time if particle (and by extension agglomerate) sizes are within a specified range and are not forming large agglomerates or are breaking down into smaller particulates. The technique has the further advantage of 100% sampling and validating of the filler dispersion in a non-invasive manner.

As defined agglomeration is difficult to control, the methodology was tested using a model system of defined particle sizes of β-TCP. The additive with a small mean particle size represents well dispersed, and large mean particle size represents fully agglomerated additives. These were tested individually, and then in a mixture of sizes to closer represent a real compounding process whereby small numbers of large agglomerates may be present among a majority of well-dispersed particles. Additionally we report the successful use of multivariate calibration models (using linear discriminate analysis (LDA) and partial least squares (PLS) regression), developed on a cheap packaging grade material for prediction of the same properties in a more expensive medical grade material without the need for a corrective transfer methodology. These two materials exhibit different optical properties (*i.e.* colour) which can be problematic for spectroscopies which rely on light transmission. This difference means that a calibration model built for one material may not be directly applicable to the other.

1.3. Multivariate analysis

A single spectrum usually contains a large number of variables; two approaches are possible to utilise spectral information for calibration of quantitative models, univariate or multivariate methodologies. In univariate analysis, covariation with other variables is explicitly neglected and this may lead to important features being ignored [9]. For this reason within the analytical chemistry field it is standard practice to carry out multivariate analysis on spectroscopy data [10]. In general multivariate models are more adequate than univariate models – however, it is always possible to discard variables, with a mathematical justification, such that a univariate approach is re-obtained.

Multivariate data analysis (MVDA) describes the practice of using mathematical and statistical tools to extract information from data tables where each observation contains a large number of variables. In such cases, the desired information lies in the correlation structure between variables, this often leads to erroneous results when tested independently. MVDA by means of projection methods is able to analyse data where challenges such as multidimensionality of the data set, multicollinearity, missing data and variation introduced by deviating factors such as experimental error and noise occur. Principal Component Analysis (PCA) is a commonly used projection method in MVDA, this projects data onto a lower dimensional space where is can be easily inspected. Linear Discriminant Analysis (LDA) is a commonly used technique to classify data into discrete sets i.e. yes/no, working/broken or running/faulty. Regression modelling such as partial least squares (PLS) regression is another type of MVDA where the aim is prediction of a response (quantity) rather than classification [16].

1.4. Transferability of multivariate models

Multivariate calibration models are utilised in combination with these spectroscopic techniques, allowing only relevant data to be used to inform the predictive models. This causes problems when transferring a model between instruments, material grades or even when using the same instrument under different environmental conditions (temperature, relative humidity etc.). Various methods of calibration transfer exist and are summarised in a review by Ref. [17].