

Low shear compounding process for thermoplastic fabrication of ferroelectric lead-free fibres

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Abstract

The thermoplastic ceramic extrusion process involves the shaping of a polymer highly filled with inorganic powder, the so-called ceramic–thermoplastic feedstock. The limitation faced with the process is the amount of raw material required to produce the feedstock. Depending on the density and desired volume of the materials used, the typical amount of ceramic powder required is a minimum of ~100 g. The validation of a low shear feedstock preparation method against a standard high shear mixing method occurred. Microstructure investigation and single electromechanical fibre characterization of low shear produced KNN ($d_{33} - 49$ pC/N; $P_r - 3.7$ μ C/cm³) and PZT ($d_{33} - 392$ pC/N; $P_r - 32.4$ μ C/cm³) fibres, in terms of PE, SE loops and d_{33} measurements, demonstrating the reproducibility of the results when compared to a standard ceramic–thermoplastic high shear mixing process. The repeatability of the measurements showed the proposed procedure to be robust, validating the new compounding method for wide-scale use.

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1. Introduction

Composites of piezoelectric ceramics and polymers have been produced, combining the dielectric constant and the piezoelectricity of the ceramics with the low density and flexibility of polymers. Applications of these smart ceramic–polymer composites include rod composites (1–3 composites) and active fibre composites (AFCs). In these systems ceramic fibres are embedded in a polymeric matrix and their electromechanical properties depend on fibre content, distribution, diameter and material composition.¹ 1–3 composites are typically used for transducer applications like sonar, hydrophones, energy harvesting systems, medical diagnostic applications as well as large area actuators,^{2–4} while AFC structures are used for sensor and actuator applications such as structural health monitoring, structural actuation and energy harvesting systems.^{5–9}

Especially for the transducer applications various processing techniques have been developed to surmount the difficulties involved in handling fibres with such small dimensions; these include the injection moulding method,¹⁰ tape casting technique,¹¹ the ‘dice and fill’ approach.¹² The advantage gained with the use of the thermoplastic fibre extrusion method is the ability to produce thin fibres without significant pressure increase, e.g. co-extrusion¹³ or by the pull-off technique.¹⁴ The big advantage of fibre transducers is the realization of longer length/diameter ratios which can be used in lower frequency ultrasonic devices. The process chain of thermoplastic ceramic shaping technique includes the following steps: (a) feedstocks compounding, which involves the mixing of a ceramic powder with an organic vehicle, (b) extrusion, which shapes the material into the final geometry (c) debinding, which is the removal of the organic vehicle and finally, (d) sintering of the body to achieve sufficient density and grain size.¹⁵

The main limitation for research work faced with the process is the minimum amount of raw material required to produce the feedstock. Depending on the density and desired volume of the materials used, the typical amount of ceramic powder required

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is a minimum of ~ 100 g. Therefore the process is useful for the production of a large number of samples, but not for the development of novel ferroelectric powders, especially for fibre applications where prototyping of small numbers of low volume experimental powder samples is sufficient. Due to the high surface to volume ratio for fibre applications, the material composition in relation to the fibre diameter after sintering process tends to change and therefore special tailoring of powder for fibre applications is necessary.^{14,16} Earlier experiments with low volume processing units like micro-compounders have shown that either homogeneity of the feedstock is insufficient or powder loading is too low. Due to this an alternative processing method has to be investigated.

Additionally a special device for single fibre piezo- and ferroelectric measurements (hereafter FerroFib) based on the aixPES instrument, developed in conjunction with aixACCT System GmbH (Germany), working with low powder quantities (i.e. few grams) is very interesting. The equipment allows the determination of small and large signal electromechanical properties, such as piezoelectric charge coefficient (d_{33}), polarization evolution (P-E) loop, longitudinal free strain evolution (S-E) loop and blocking force on single fibres. A new processing method in combination with the FerroFib analytic device will help to optimize ferroelectric raw material especially for future fibrous applications.

In the present paper we validate a low shear feedstock preparation method against a standard high shear mixing method. A commercial lead zirconate titanate (PZT) powder was used to prepare a feedstock with both techniques for the first evaluation of useful thermoplastic binder systems. In a second step, potassium sodium niobate (KNN) was synthesized by a molten salt synthesis method and the optimal powder content for the feedstock was evaluated by the low shear mixing method. Finally the optimized feedstock was compounded by the high shear mixing method to compare microstructure and electromechanical properties of the sintered fibres processed with the two different methods. Single ferroelectric fibre characterization, in terms of PE, SE loops and d_{33} measurements, demonstrating the reproducibility of the results when compared to the standard ceramic–thermoplastic high shear mixing process was carried out.

2. Experimental procedure

PZT based green fibres were produced by mixing 58 vol.% of a commercially available PZT powder (CeramTec Sonox P505) with a thermoplastic binder; low-density polyethylene–LDPE (1700MN18C Lacqtene PEBD, Arkema Group, Cedex, France).¹⁴ The PZT powder had a mean grain size of $2.66\text{ }\mu\text{m}$, a specific surface area (BET) of $2\text{ m}^2/\text{g}$ and a density of 8.1 g/cm^3 .¹⁵ Additionally the same powder was used to prepare a feedstock by the low shear mixing method which involved mixing the ceramic powder, a polyethylene oxide – PEO (Polyox WSR301, Dow Chemicals) thermoplastic binder, dispersant (Hypermer KD1, Uniqema) and a solvent (toluene) for one hour, just below the boiling point of the solvent. In this study a weight ratio of 1:0.3:20 was used for ceramic, dispersant and solvent.

The mixture was dried for 24 h at $60\text{ }^\circ\text{C}$ and the feedstock collected for extrusion. The fully dried sample was inspected by weight loss analysis.

Un-doped KNN based green fibres were produced with in house produced molten hydroxide synthesized (MHS) KNN powder. The MHS method, involves mixing stoichiometric ratios of K_2CO_3 and Nb_2O_5 with a molar excess of KOH [2:1; KOH:reactants] ($\geq 90\%$ flakes – Sigma–Aldrich) according to the $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ formula which are placed in an alumina crucible and heat treated at $500\text{ }^\circ\text{C}$ for 2 h; on cooling, the reactants are mixed with a molar excess of Na ions [from Na_2CO_3 or NaCl (1.4:1; Na ions:K and Nb-ions)] and calcined for 2 h at $700\text{ }^\circ\text{C}$. The final product was washed to remove the water soluble species like KOH, NaCl, alkali niobates, etc. and dried. The final KNN powder had a mean grain size of $2.8\text{ }\mu\text{m}$, a specific surface area (BET) of $0.9\text{ m}^2/\text{g}$ and a density of 4.5 g/cm^3 . Further powder processing details are reported by Lusiola et al.¹⁷

To optimize the powder content of the high shear KNN feedstock the low shear mixing method was used to carry out the investigation. Feedstocks with a ceramic powder–thermoplastic PEO loading of 50:50, 52:48, 54:46, 56:44 and 58:42 were investigated by the low shear mixing process. The dispersant content was fixed to a weight ratio of 1:0.3 against the KNN powder. After the sintering of the extruded fibres, electromechanical results were used to select the optimal KNN powder loading level. Finally the selected optimal KNN powder content was used to produce a high shear mix feedstock of KNN with the thermoplastic LDPE binder. For the high shear mixing procedure powders were previously coated with stearic acid (Sigma–Aldrich – W303518-K) [stearic acid represents 7.7 vol.% of ceramic feedstock], by dissolving stearic acid in toluene, adding the KNN powder, ball milling the mixture for 20 h and eventually evaporating the solvent; in order to enhance their dispersion in the polymer.¹⁴ The two feedstocks (PZT:LDPE and KNN:LDPE) were obtained by mixing the raw materials in a high-shear mixer (Haake PolyLab Mixer Rheomix 600, Thermo Fisher Scientific).¹⁸ The flow chart (Fig. 1) shows the investigation plan for the validation of the low shear feedstock preparation method, benchmarked against the high shear feedstock preparation method. Thermo-gravimetric analysis (TGA) was performed on the LDPE and PEO using a Mettler Toledo TGA/SDTA 851e.

Large volume extrusion (LVE) green fibres were obtained by extruding the feedstock vertically with a capillary rheometer (RH7 Flowmaster, Rosand Precision Limited) through a $300\text{ }\mu\text{m}$ die. Small volume extrusion (SVE) green fibres were obtained with the same machine, but with an adapter to reduce the diameter of the cylinder from 24 mm to 4 mm. It is worthwhile to mention that reduction of diameter is necessary otherwise the amount of feedstock would be not sufficient to be able to extrude the small quantity of material. More details about the fibre production can be found in Heiber et al.¹⁴

Debinding and sintering of the green fibres occurred in a zirconia crucibles with V-shaped grooves; closed in an alumina crucible and sealed with alumina powder. In order to reduce the lead volatilization during sintering of PZT fibres, a Pb-rich ($\text{PbZrO}_3 + \text{ZrO}_2$) atmosphere was used for the PZT fibres.

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