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Effects of rheology on the interface of $Pb(Zr, Ti)O_3$ monofilament composites obtained by co-extrusion

M.R. Ismael [a,b], F. Clemens [a,*], W.M. Bohac [a], T. Graule [a], M.J. Hoffmann [b]

[a] *Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland*

[b] *Institut für Keramik im Maschinenbau, Universität Karlsruhe, Heid-und-Neustr. 7, 76131 Karlsruhe, Germany*

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Abstract

The production of lead zirconate titanate (PZT) fibres, 1-3, 3-1 and 2-2 composites for actuator and sensor applications through the thermoplastic co-extrusion process can be achieved by using a macro-scale preform shaped by two different extrudable mixtures. The main challenge of this method is the optimization of materials that can be co-extruded and at the same time maintain the preform geometry in the final product, without axial and cross-sectional deformation. In this work, rheological characterizations of PZT/polyethylene and carbon black/polyethylene feedstocks were carried out to produce monofilament composites by the co-extrusion process. To explore the interface instabilities resulting from the viscosity mismatch between the processed materials, the co-extrusion tests were performed varying the velocity of the piston during extrusion. Successful co-extrusion, with well preserved fibre morphologies and defined interface between the co-extruded materials, was achieved for viscosity ratios between the feedstocks ranging from 0.98 to 1.16. Outside of this range, interface distortions were observed.

Keywords: Extrusion; Fibres; PZT; Rheology

1. Introduction

Lead zirconate titanate [$Pb(Zr_xTi_{1-x})O_3$; PZT] materials in fibre form are suitable for an incorporation into composite structures for actuator and sensor applications. Fine-scale diameter fibres (<25 μm) are desirable for such composites, due to the fact that they can be operated with increased magnification and actuation.[1] To overcome the difficulty of handling these thin fibres, different methods for forming fine-scale piezoelectric ceramic–polymer composites have been developed.[2] In this context, semi-finished 1-3, 3-1 and 2-2 connectivity composites for ultrasonic transducers and hydrophones have been produced using a thermoplastic co-extrusion process.[3–5] The principle of this technique consists of initially fabricating a macro-scale preform composite and afterwards, extruding it through a die to generate fine composite structures which are identical in their geometry and composition to the original preform with reduced cross-sectional dimensions. The process can be repeated to reduce the size and multiply the number of shaped patterns. However, the method is limited by the particle size of the starting powders.

The production of PZT fibres, 1-3, 3-1 and 2-2 composites through the co-extrusion process can be achieved by using two different extrudable mixtures (feedstocks). The primary material is the ferroelectric ceramic which is to be micro-fabricated. The secondary is a fugitive substance with the function to fill the space between the green filaments, provided that it can be completely removed after the micro-fabrication. After co-extrusion, the final composition is thermally treated to eliminate the organic binders and the ceramic is densified using conventional methods. The co-extrusion process offers several advantages over the single standard extrusion. By careful choice of the reduction ratio, the exact diameter of the fibre can be obtained and conveniently modified. Additionally, it is a mass production process, allowing numerous fibres to be made simultaneously. Using such technique it is possible to scale down the diameter of the fibres to less than 20 μm, without increasing the extrusion pressure dramatically. This technology had been proven

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* Corresponding author. Tel.: +41 44 8234821; fax: +41 44 8234150.
E-mail address: frank.clemens@empa.ch (F. Clemens).

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Table 1
Raw materials used for processing.

Raw-material	Density (g/cm^3)	SSA (m^2/g)	Supplier
$Pb(Zr_x,T_i1_{-x})O_3$ PZT-SKN	8.10	1.97 ± 0.01	CeramTec AG, Germany
Carbon black (CB) BP® 120	1.90	30.33 ± 0.03	Cabot Corporation, USA
Low density polyethylene (LDPE)[a] PEBD-1700MN 18C	0.92	–	Lacqtene, Elf Atochem S.A., Switzerland

[a] Melting temperature = 108 °C; melt flow rate-2160 at 190 °C = 70.0 g/10 min.

Table 2
Formulations of the different thermoplastics compounds.

Thermoplastic compound	PZT powder (vol.%)	Carbon black (vol.%)	Stearic acid (vol.%)	LDPE (vol.%)
Feedstock 1	58.0	–	3.9	38.1
Feedstock 2	–	–	–	100.0
Feedstock 3	–	25.0	–	75.0
Feedstock 4	–	35.0	–	65.0

successfully for devices such as ultrasonic motors,[6] hollow piezofibres,[7] PZT fibres with internal electrodes,[8] multilayer tubes for use in tubular SOFCs,[9,10] alumina fibres,[11] multiphase alumina/zirconia components[12] and fibrous monolithic composites.[13,14]

The main challenge of the co-extrusion method is the optimization of materials that can be co-extruded and are capable of maintaining the preform geometry in the final product without axial and cross-sectional deformation. Due to this fact, to our knowledge no continuous co-extrusion of advanced ceramics is, up to date, practiced commercially. Defect-free products require a detailed rheological characterization of the compositions to be co-extruded. Differences in the flow behaviour of the materials being processed can lead to the formation of a number of instabilities depending on other parameters such as process settings and die-details. A common problem which is often reported in polymer co-extrusion literature[15,16] is the encapsulation phenomena, caused mainly by the tendency of the less viscous material to migrate towards the region of highest shear since this minimises energy dissipation. Interface instabilities might also occur due to discrepancies in the rheology of the compositions.[17] However, in ceramics these instabilities have not been widely reported. Hence, this study focuses on examining how rheology affects the interface of PZT monofilament composites obtained by thermoplastic co-extrusion. Considering that the step of compounding the feedstocks to be co-extruded plays an important role on the flow behaviour of the materials, this stage of the process is discussed in detail. The results attained will be the basis for further studies to optimize the manufacture of composites for both structural and functional applications using the co-extrusion process.

2. Experimental

A description of the raw materials used in this work is listed in Table 1. Carbon black (CB) was selected as the fugitive material since it is inexpensive and usually added to improve dispersion in polymers.[3] The thermoplastic binder was chosen based on previous work.[18] The density values were obtained using a helium pycnometer (Micromeritics, AccuPyc 1330). The specific surface area (SSA) was determined from a five point N_2 adsorption isotherm obtained from BET measurements (Beckman-Coulter SA3100, Beckman-Coulter, USA). To stabilize the mixture against agglomeration and promote proper binder wetting on the PZT ceramic, stearic acid (Fluka AG) was used as a surfactant. Further details concerning this coating procedure have been described previously.[18]

The feedstocks described in Table 2 were prepared using a high shear mixer (HAAKE PolyLab Mixer, Rheomix 600, Thermo Scientific). The total volume of the compounds was formulated to fill 70% of the volume of the mixer chamber (69 cm^3). The mixing was carried out using a two step sequence: first at 10 rpm and 130 °C for 30 min and subsequently at 10 rpm and 120 °C until the torque reached steady state conditions. Since a stable torque is a qualitative indication that the filler is uniformly distributed in the polymer binder, adding particles to the system increased the time to achieve torque equilibrium.

A torque rheometer (HAAKE PolyLab Rheometer, Thermo Scientific) was used to record rheological data of the compositions presented in Table 2. After preparing the feedstocks, equilibrium torque values were recorded at rotor speeds ranging from 10 rpm to 100 rpm, at 120 °C. A pair of parallel aligned roller rotors counter-rotating at a speed ratio of 3:2 was used (only the higher speed is indicated on the dial). A representation of the torque rheometer and its geometric dimensions are shown in Fig. 1.

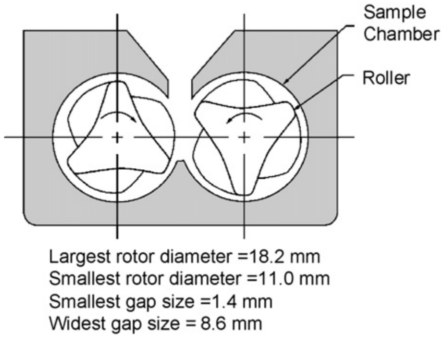

Fig. 1. Schematic front view of the torque rheometer and its geometrical dimensions.

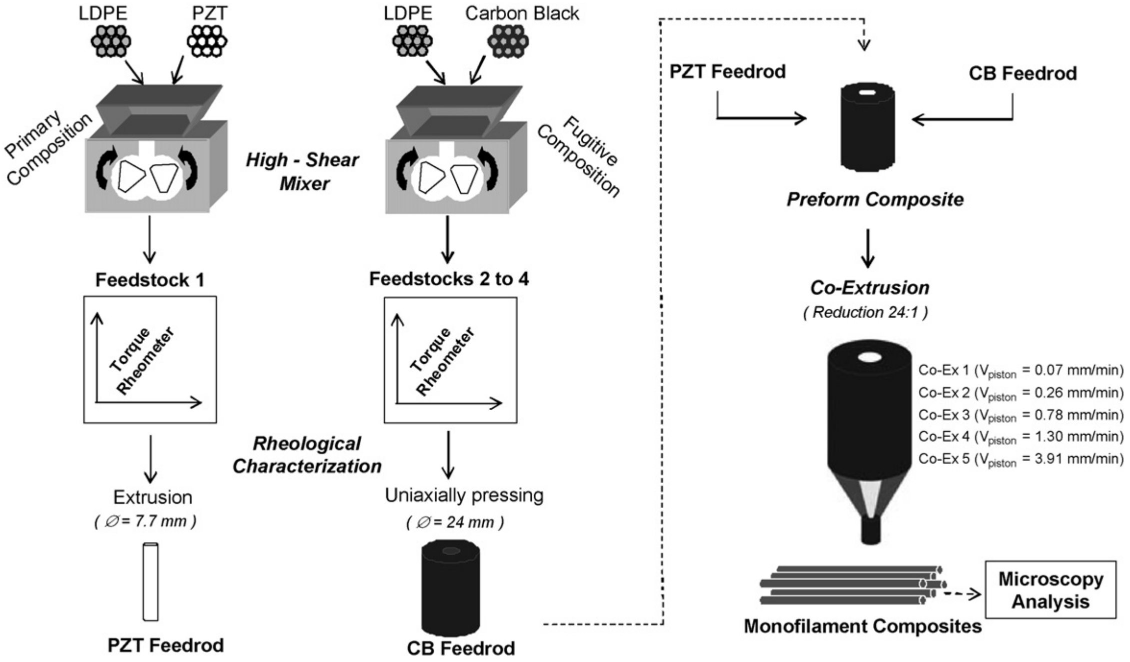

Fig. 2. Experimental overview. PZT and carbon black powders are blended with LDPE and rheologically characterized. The feedstocks are either extruded (PZT) or uniaxially pressed (CB). The preform materials are co-extruded and the monofilament composites analysed.

The PZT feedstock (Feedstock 1) was extruded through a 7.77 mm diameter die using a capillary rheometer (RH7-2, Malvern; velocity of the piston = 5.0 mm/min, $T = 110\,^{\circ}\mathrm{C}$). The selected carbon black feedstock was first placed in an oven at 130 °C for 1 h and afterwards uniaxially pressed (OPUS, Römheld) into a cylinder shaped feedrod (diameter = 24 mm, length = 45 mm). A hole with the same diameter of the PZT feedrod was drilled in the center of the CB cylinder in order to structure the preform composites.

The co-extrusion tests were carried out using the capillary rheometer stated before (24 mm bore diameter). A die with a half cone angle of 60°, 1 mm diameter and 16 mm length was used, so that the extrudate was 24 times smaller than the initial preform. Varying the speed of the piston (V_{piston}), 5 different tests were performed: Co-Ex 1 ($V_{\mathrm{piston}} = 0.07$ mm/min), Co-Ex 2 ($V_{\mathrm{piston}} = 0.26$ mm/min), Co-Ex 3 ($V_{\mathrm{piston}} = 0.78$ mm/min), Co-Ex 4 ($V_{\mathrm{piston}} = 1.30$ mm/min) and Co-Ex 5 ($V_{\mathrm{piston}} = 3.91$ mm/min). Lengths of 15 cm of each of the co-extruded materials were collected. The area of the PZT fibre (inner part) and the outer area of the carbon part was measured using an optical microscope (Leica–Wild M3Z) equipped with a micrometer. The cross-sections (perpendicular to the extrusion direction) of the monofilament composites were investigated by scanning electron microscopy (Tescan TS51368 M). It is important to note that, to avoid distortion of the ceramic–thermoplastic green bodies, the monofilament composites were fractured under liquid nitrogen. An overview of the experimental setup is given in Fig. 2.

3. Results and discussion

The step of compounding the feedstocks has an important role on the manufacture of PZT fibres using thermoplastic co-extrusion process. The two step sequences applied were in order to improve homogeneity and reduce particle agglomeration.[18] An inhomogeneous feedstock can result in density gradients directly affecting the rheological properties causing defects in the final product. The breakdown of agglomerates was indicated by a decrease and a subsequent stabilization in torque readings. The mixing temperature was accurately controlled to avoid degradation by thermal scission of the thermoplastic binder. This phenomenon, whereby molecular chain bonds are ruptured, leading to a decrease in the binder molecular weight and consequently diminishing the resistance to shear, might also modify the rheological performance of the compositions. It is worth noting that the rheological and the co-extrusion tests were carried out at the same temperature (120 °C). This temperature was selected based on the melting point of the LDPE used (Table 1). The temperature dependency of viscosity has a pronounced effect on the choice of the processing conditions as well as on the quality of the final product.[19] The use of higher temperatures might induce very low viscous compositions, since the chains in the random polymers have a higher thermal energy that leads to a more disentangled state, which affects the ceramic particle mobility, allowing the material to flow by gravity during the co-extrusion process. On the other hand, processing at lower temperatures would increase the pressure during co-extrusion considerably.

According to the Ostwald-de Waele power–law model[19] a rheological non-Newtonian model proposed for representing the polymeric flow behaviour, the relation between shear stress, τ, and shear rate, $\dot{\gamma}$, is given by Eq. (1):

$$\tau = \bar{\kappa}\dot{\gamma}^{n} \tag{1}$$

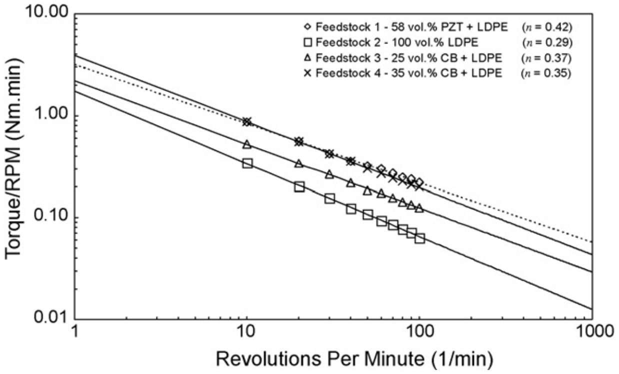

Fig. 3. Torque/rpm as a function of revolutions per minute for Feedstocks 1–4, measured using a torque rheometer at 120 °C. The power law index is the negative slope of the curve.

where $\bar{\kappa}$ reflects the consistency index of the material, and n is the power law index, giving a measure of the degree of non-Newtonian behaviour, with values smaller than unity showing shear-thinning characteristics. With the use of torque rheometry, based on Eq. (1), Blyler and Daane[20] derived the following equation:

$$M = C(n)\bar{\kappa}N^n \tag{2}$$

where M is the torque, $C(n)$ is a temperature-dependent constant, N is the roller speed in revolutions per minute (rpm) and $\bar{\kappa}$ and n are parameters similar to Eq. (1). Eq. (2) enables us to plot the logarithm of torque (M) *versus* the logarithm of roller speed (N) yielding a linear correlation, where the power law index n represents the slope of the curve. Considering that the measured torque (M) is related to the imposed shear stress (τ) and the roller speed (N) is proportional to the shear rate ($\dot{\gamma}$):

$$\tau = K_1 M \tag{3}$$

$$\dot{\gamma} = K_2 N \tag{4}$$

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{K_1 M}{K_2 N} \tag{5}$$

where η is the apparent viscosity and K_1 and K_2 are constants which depend on the dimensions of the rheometer.[21] Fig. 3 presents the data obtained using torque rheometry, applying the approach described above.

Following Heiber et al.,[22] a solid loading of 58 vol.% of PZT was selected for the Feedstock 1 since it should provide high sintered densities and electromechanical properties while generating suitable flow behaviour for the extrusion step. To determine a carbon containing composition with similar rheological behaviour as Feedstock 1, a composition with 100% LDPE was initially analysed (Feedstock 2, Fig. 3) and, subsequently, carbon black powder was progressively added (Feedstocks 3 and 4, Fig. 3). All the feedstocks exhibited shear-thinning behaviour for the test temperature and velocity range analysed, as the power law indices n were smaller than 1. The lower degree of shear-thinning observed for the filled systems (Feedstock 1, 3 and 4) in comparison to the pure polymer feedstock, is attributed to the fact that more friction is created with higher solid loading, since the inter-particle separation distance reduces, increasing the resistance to shear. However, when comparing the CB containing feedstocks (Feedstocks 3 and 4), the resistance to shear decreased when adding carbon black powder. This could be explained assuming that the probability to ensue in a laminar flow increases with the presence of particles in the filled polymer mixtures. When the particles are oriented by the laminar flow, the resistance to shear decreases.[23] Accordingly, the Feedstock 1 should present a smaller power law index than the CB feedstocks, since it contains a greater amount of ceramic particles. Nevertheless, the size and shape of the particles are important factors to be considered when investigating the rheology of high solid loading mixtures.

From the torque rheology of the compounds (Fig. 3), it can be seen that Feedstocks 1 and 4 will have a high flow compatibility for a given roller speed, and therefore they were selected for the co-extrusion tests. It is well known that for successful co-extrusion, viscosity matching is necessary between the processed materials.[3–17] Any variation will result in rearrangement of the interface and instabilities during flow. To explore these variations, different co-extrusion tests were performed varying the velocity of the piston during extrusion, which provided different viscosity ratios between the materials. The different speeds applied for the tests were selected using Eq. (6) where the velocity of the piston (V_{piston}) and the apparent shear rate at the wall of the die ($\dot{\gamma}_A[s^{-1}]$) can be established.

$$\dot{\gamma}_A = \frac{4Q}{\pi R^3} \tag{6}$$

with Q as the volumetric flow rate ($Q = V_{\text{piston}}\,A$, where V_{piston} is the velocity of the piston, A the area of the piston [mm^3/s]) and R the die radius [mm]. Taking into account the geometrical dimensions of the torque rheometer (Fig. 1), the apparent shear

Table 3
Parameters considered for the co-extrusion tests, using Feedstocks 1 and 4.

Co-extrusion tests	Capillary rheometer		Torque rheometer	
	Piston velocity (mm/min)	Shear rate (1/s)	Correspondent rpm range (1/min)	Viscosity ratios range (PZT/CB)
Co-Ex 1	0.07	5	4–37	0.90–1.05
Co-Ex 2	0.26	20	15–149	0.98–1.16
Co-Ex 3	0.78	60	44–448	1.06–1.25
Co-Ex 4	1.30	100	73–747	1.10–1.30
Co-Ex 5	3.91	300	220–2241	1.19–1.40

rate can be related to the rpm (N) applying Eq. (7).

$$\dot{\gamma}_A = \frac{2\pi rN}{60y} \tag{7}$$

where r is the roller diameter and y is the gap between the roller and the chamber wall. The smallest gap between the roller and the chamber wall provides the maximum shear rate and the widest gap, the lowest one. Table 3 summarizes the parameters used for the co-extrusion tests. The viscosity ratio of the feedstocks is expressed as a torque/rpm ratio of the PZT compound (Feedstock 1) and the carbon black composition (Feedstock 4) for the correspondent range of rpm.

Fig. 4 shows the characterization of the co-extruded monofilament composites. The dotted lines represent PZT inner fibres that achieved their theoretical diameter, i.e., exactly 24 times smaller than the preform ($\varnothing \approx 325\,\mu\text{m}$). At lower shear rates, i.e., Co-Ex 1, 2 and 3, it is noted that the process starts to become stable only after a volume proportional to the volume of the cone part of the die was extruded (approximately 2400 mm^3). As the piston moves downward it is expected that the PZT feedrod, which lies on the center of the preform, firstly comes out of the orifice of the die, because of the chosen geometry proportion. In addition, a static zone in which the extrudate is not squeezed out is produced at the die entry region.[24] Hence, co-extruded fibres with good qualities were observed only after the static region was formed and the flow became steady. At higher shear rates (Co-Ex 4 and 5) the stability was not achieved, attributed to the fact that high extrudate velocity may generate unsteady flow. The results indicate that successful co-extrusion, with well shaped fibre morphologies and defined interfaces between the co-extruded materials, was obtained for the second co-extrusion test (Co-Ex 2, $V_{\text{piston}} = 0.26$ mm/min). With the range of viscosity ratio worked (Table 3), the co-extrusion process was stable after a short initialized period (co-extruded volume = volume of the cone part of the die) up to the end of the experiment, and a good correlation with the PZT fibre area and total monofilament composite area was obtained.

For all the other co-extrusion tests, interface instabilities were observed which were attributed to the mismatch of viscosity between the primary and fugitive material. The co-extrusion tests 3, 4 and 5 were carried out with a carbon black/LDPE composition revealing a smaller viscosity than the primary material as recommended by Schrenk et al.[25] The aim was to minimize the velocity difference between the co-extruded layers by using an inner layer with a higher viscosity. However, in our study, the CB material indicates only lower viscosities at higher shear rates, which led to two drawbacks. First, the tests were done applying high piston speed. In accordance to Chen et al.,[26] co-extrusion of pastes should be performed at a relatively low extrusion rate to achieve high quality products. Second, increasing the shear rate the difference in viscosity of the compositions was enhanced as well. We attribute this more pronounced difference in viscosity between the Feedstocks 1 and 4 with increasing shear rate due

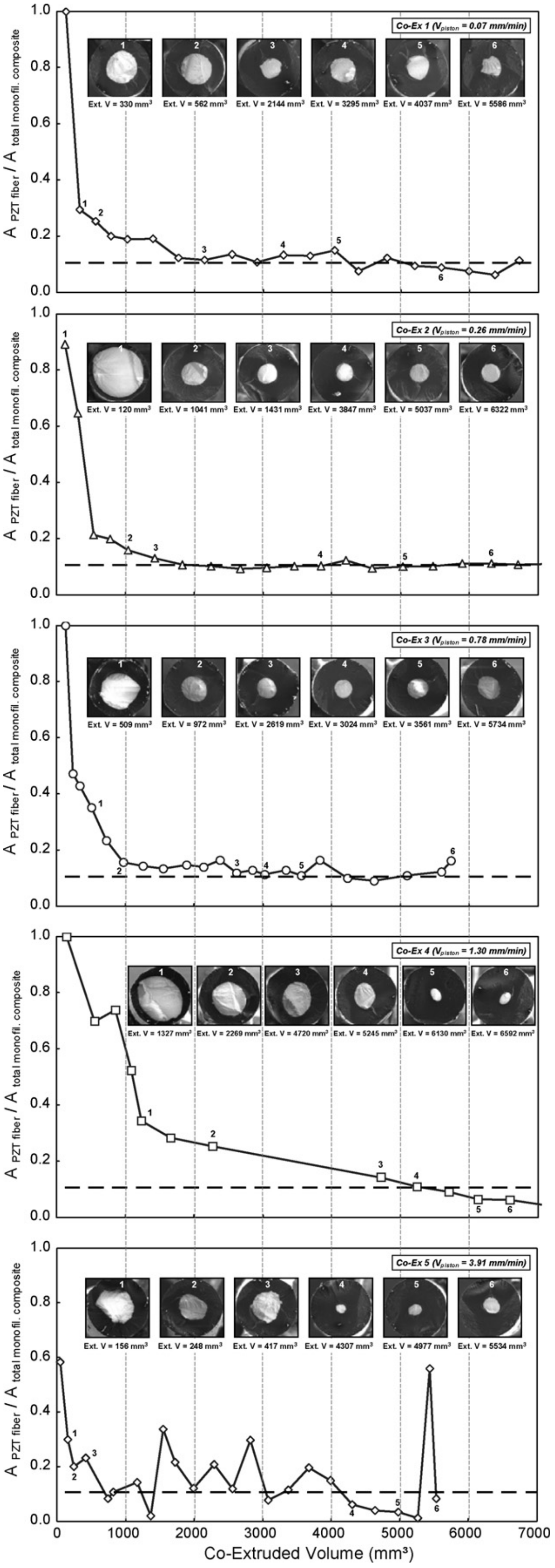

Fig. 4. Ratio between the co-extruded PZT fiber area and the total monofilament composite area as a function of the co-extruded volume for the co-extrusion tests carried out applying different velocity of the piston (V_{piston}). The micrographs show the cross-section (perpendicular to the extrusion direction) of the monofilament composites for different extruded volume (Ext. V).

to the higher specific surface area of the carbon black powder used (Table 1). Feedstocks containing high specific surface area particles are more susceptible to surface phenomena, which can cause agglomeration between the particles. The agglomerates are porous structures formed due to the bonding of primary particles that absorbs a part of the polymer originally destined for the inter-particle separation, increasing the viscosity of the composition. By increasing the shear rate, there is a breakdown of the agglomerates, which releases the absorbed polymer that will contribute to the inter-particle separation, therefore decreasing the viscosity. Nevertheless, when comparing Co-Ex 1 with Co-Ex 3, where the difference in viscosity between the materials was less than 10% and the tests were attained at lower shear rates, our results were quite similar to Schrenk et al.[25] Co-Ex 1 was carried out with the inner part having a lower viscosity than the CB material, while for Co-Ex 3 the opposite was observed and as a result, interfacial flow instabilities were reduced, but not eliminated, due to the viscosity mismatch between the compounds.

Due to the difference on the power law index of the feedstocks, the Co-Ex 3, 4 and 5 tests were performed when the carbon black/LDPE composition presented a smaller viscosity than the primary material. Therefore, it was reasonable to assume that it would be the first extrudate to come out of the die, encapsulating the PZT fibre. However, the die and preform geometry should be taken into account, as previously discussed. Moreover, in the case of Co-Ex 3, the difference in viscosity between the materials was probably not enough for the encapsulation phenomena to occur. In the case of Co-Ex 4 and 5, due to the high speed applied, the residence time was not sufficient. However, the oval shape of the inner fibre obtained at the end of the Co-Ex 4 process, is an indication of this instability. As follows, it is valuable to consider that in addition to the viscosity match between the materials, the velocity of the piston during co-extrusion should also be taken into account. High velocity extrusion can lead to unsteady flow conditions.

4. Conclusions

The rheological behaviour of a $Pb(Zr_x,Ti_{1-x})O_3$/polyethylene feedstock and carbon black/polyethylene mixtures was examined applying torque rheometry. A feedstock containing 58 vol.% of PZT + polyethylene and another containing 35 vol.% of carbon black powder + polyethylene were selected for co-extrusion tests. After assembling the preform materials, 5 co-extrusion tests were carried out using different velocities of the piston. Considering that the torque reading obtained from the torque rheometer is related to the shear stress imposed and the roller speed is proportional to the shear rate, the speed of the piston during extrusion was selected to achieve a range of different viscosity ratios between the materials. Hence, the structure instabilities due to viscosity mismatch could be investigated on green monofilament composites. Successful co-extrusion, with well preserved fibre morphologies and defined interfaces between the co-extruded materials, was obtained for a viscosity ratio between the feedstocks ranging from 0.98 to 1.16. Outside of this range, interface distortions were observed. Despite the viscosity mismatch between the compounds, interfacial flow instabilities were reduced when the lower viscosity material was in contact with the die wall, considering the viscosity difference between the materials not higher than 10%. In general, co-extrusions carried out at lower shear rates were more satisfactory when compared to high piston speeds, due to the fact that high velocity extrusion may generate unsteady flow conditions. Finally, it could be demonstrated that the torque rheometer is a practical tool to identify the rheology requirements for the successful co-extrusion of ceramic–polymer compounds. Preserving the microfabricated PZT fibre during sintering is the subject of further studies.

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