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Using Rheology to Achieve Co-Extrusion of Cement-Based Materials with Graded Cellular Structures

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Co-extrusion involves simultaneous extrusion of multiple layers and can be used to produce functionally graded materials whose layers have different properties. Rheological control is vital for successful co-extrusion. During extrusion, flow in the barrel and die land in a ram extruder should be plug-like, while the paste should be sheared and uniformly elongated in the die entry region. In the barrel of the extruder, the paste flow velocity field was inferred by direct observation of the paste left in the barrel, and evidence for plug flow in the barrel was seen only at low-extrudate velocities. In the die land, the Benbow nonlinear model was employed to assess the paste flow behavior, and plug flow was achieved only when the shear stress applied to the paste by the die land wall was smaller than its yield stress. For co-extrusion, a simple method using thin-walled tubes was found to be effective to prepare layered feedrods. Functionally graded cellular structures of cement-based materials were successfully co-extruded by using a low-extrudate velocity when the paste had decreasing shear viscosity from inner to outer layers.

Introduction

Concrete offers potential advantages in residential construction—it is economical, durable, and fire resistant—but a key disadvantage of concrete is its high density, typically 2300 kg/m^3. To overcome this disadvantage, light-weight concrete has been produced through either aeration or light-weight fillers, but such concrete is usually associated with high permeability and low strength.[1–3] This investigation utilizes an advanced co-extrusion process to engineer a functionally graded cellular microstructure, highly porous in the center and dense on the outer surface, to produce light-weight cement-based material without the disadvantage of high permeability and low strength.

Extrusion is a process in which a stiff plastic paste is forced to pass through a rigid die generating high shear which produces a fluid behavior. A very high volume fraction of cement is utilized in extruding cement-based materials, which is beneficial to the ultimate strength of the extrudates. Co-extrusion involves simultaneous extrusion of multiple layers. High shear applied to the paste during co-extrusion can improve the interfacial bonding between particles and layers. Extrusion has been successfully applied in production of many cement-based products, for example, pressure pipe,[4] plate,[5] and fiberboard.[6] Extrusion can also be used to manufacture complicated shapes.[7] Extru-

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sion has been shown to enhance properties such as toughness, tensile strength, and flexural strength.[8,9]

Extrusion is generally believed to require control of rheology to obtain good-quality products, and researchers have gained some knowledge of the rheological properties of cementitious pastes required for successful extrusion. Peled *et al.*[10] measured the pressure applied to pastes during extrusion to compare the effects of fiber type and fly ash addition on the rheological properties. Srinivasan *et al.*,[11] Shen,[12] and Kuder[13] applied the physically based paste flow linear model developed by Benbow and his colleagues[14,15] to describe the rheology of fiber-reinforced cementitious pastes. Zhou and Li[16] characterized the rheology of similar pastes using the nonlinear model developed by Benbow and his colleagues[14,15] and explored the influence of such parameters as the water content, fiber content, and fiber category, on the extrusion behavior. Li and colleagues[17,18] studied the rheological behavior of cementitious pastes based on a nonlinear viscoelastic constitutive relationship.

Rheology control is especially important for successful co-extrusion. If rheology does not match between layers, successful co-extrusion cannot be achieved. There is relatively little literature on rheology and co-extrusion. When doing microfabrication of ceramics, Hoy *et al.*[19] and Crumm and Halloran[20] reported that all the materials in the green body should have similar rheological behavior. On the other hand, Schrenk *et al.*[21] and Kim and Kriven[22] reported that inner layers should be stiffer than outer layers for co-extrusion of certain ceramic materials. No literature was found describing co-extrusion of cement-based materials.

This paper focuses on using rheology to improve the fabrication of functionally graded cementitious paste. Co-extrusion of multiple layers with different cellular contents was performed to fabricate functionally graded cellular rods. The flow velocity field in the barrel of the extruder was inferred by direct observation of paste remaining in the barrel after extrusion was terminated. The paste-flow behavior in the die was studied by ram extrusion tests and the experimental data were analyzed using the nonlinear Benbow model.[14,15] The structure of extrudates was examined by both optical and scanning electronic microscope.

Experimental Procedure

This section addresses the experimental methods used to fabricate the extrudates. It includes a discussion of materials, mix proportions, mixing procedure, the ram extruder, and the actual co-extrusion process.

Materials

A commercial Portland cement (Essroc Cement, Nazareth, PA) was used in all cementitious mixtures, which meets the Type I specification of ASTM Standard Specification for Portland Cement (C 150-05). The cement was mixed with water to form a paste. Methyl hydroxyethyl cellulose (MHEC, WALOCEL M-20678, Wolff Cellulosics, Willowbrook, IL) was employed to make the paste dough-like and extrudable. Cenospheres, which are hollow spherical particles of fly ash (XL-150, Sphere Services, Clinton, TN, mean size 63 μm and specific density 0.57 g/cm^3), were blended into the mixture to produce cellular pores.

Mixture Proportions

Extrudates with three and five layers were fabricated. The water content in the outer layer was fixed, and the extrudates with good quality were made by adjusting the water content of inner layers to the final values shown in Table I. The MHEC content was adjusted in each layer so that the MHEC concentration in the water was constant.

Mixing Procedure

For pastes used in extrusion (including the test for the application of the Benbow model), solid powders (cement, MHEC, and cenospheres if used) were first mixed dry for 3 min at a low speed of 136 rpm using a planetary mixer (Model N-50, Hobart Corporation, Troy, OH). Water was then added and mixing continued at the low speed until a dough-like paste was formed. The dough-like paste was further mixed at a higher speed of 281 rpm for 1 min.

Ram Extruder

The ram extruder shown in Fig. 1 was used to characterize the paste-flow behavior and to fabricate the functionally graded cellular products. The piston was connected to a 10 kN load cell. The barrel had an inner diameter of 60 mm and a height of 150 mm. The die had an inner diameter of 12 mm. Die lengths for characterizing the paste flow behavior varied from 12 to

Table I. Composition of Layered Extrudates

Number of layers	Layer (g)	Cement (g)	Cenosphere (g)	Water (g)	MHEC (g)	MHEC% based on water
3	Core	70	30	38	1.65	4.35
	Middle	90	10	28	1.30	4.35
	Outer	100	0	25	1.09	4.35
5	Core	50	50	45	1.96	4.35
	Second	70	30	38	1.65	4.35
	Third	80	20	34	1.48	4.35
	Fourth	90	10	28	1.30	4.35
	Outer	100	0	25	1.09	4.35

MHEC, methyl hydroxyethyl cellulose.

192 mm, such that the ratios of die length/die diameter were 1, 4, 8, 12, and 16. For co-extrusion, a single die length was used, such that the ratio of die length/die diameter was.[8]

As the piston moves downward, the feed paste inside the barrel is forced into the die and the extrudate comes out the die exit. A static zone in which the paste is not squeezed out forms a natural cone at the die entry region. For co-extrusion, extrudate with good quality was obtained only after the static zone was formed and the flow became steady.

Co-extrusion

A simple and cost-effective method was employed to make a layered feedrod for co-extrusion. Using the thin-walled tubes, rods and alignment jigs shown in Fig. 2, and using the barrel of the extruder as the outermost tube, the layered feedrod was prepared as shown in Figs. 3 and 4. First, the innermost paste rod was prepared using the smallest tube. The next paste rod was made using the next bigger tube and a hole was drilled longitudinally using the smallest tube. The innermost paste rod was inserted into the hole to make a two-layered feedrod. Feedrods with more layers were prepared by extending the sequence. After all the layers were stacked according to this process, a multiple-layered feedrod was ready for co-extrusion.

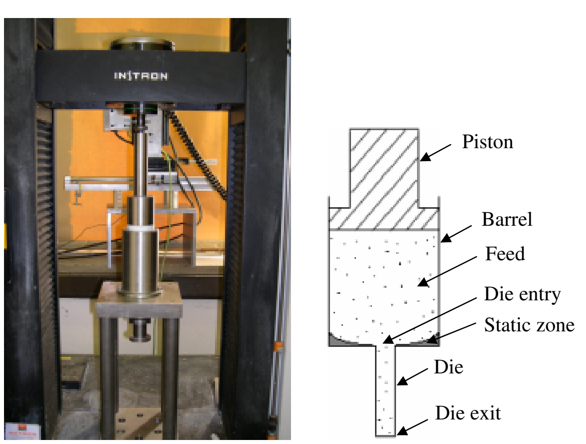

Fig. 1. Ram extruder. Left, set-up of the real ram extruder; right, schematic illustration of the ram extruder.

Velocity Profile Analysis During Extrusion

In a nonslip condition, the flow velocity of fluid in a pipe varies across the section perpendicular to the flow direction due to wall shear. For Newtonian liquids this velocity profile is parabolic, and for power-law liquids

Fig. 2. A set of molds for making layered feedrod.

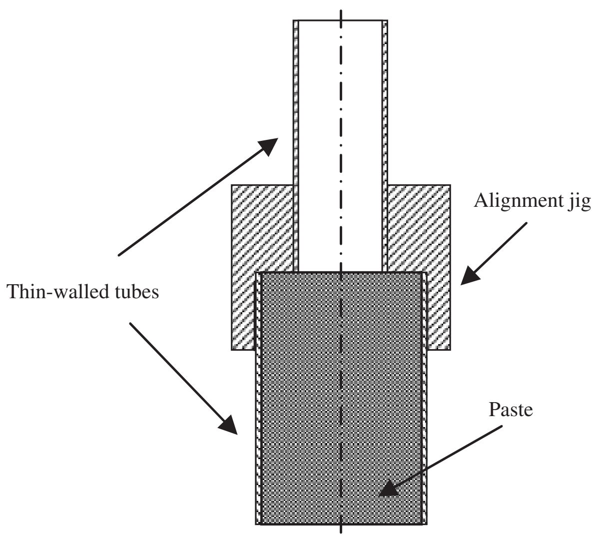

Fig. 3. Schematic assembly of molds.

this velocity profile is given by[23]

$$v(r) = \frac{Q(3n+1)}{\pi R^2(n+1)}\left[1 - \left(\frac{r}{R}\right)^{(n+1)/n}\right] \quad (1)$$

where Q is the volume flow rate, n is the power-law index in the power-law expression of viscosity and shear rate, R is the radius of the pipe, and r is the distance of the liquid to the center of the pipe. Figure 5 presents the velocity profiles for different power-law indices. It is seen that the velocity increases toward the pipe center. In addition, as the power-law index decreases (which indicates a higher degree of shear thinning), the plug-nature of the flow increases until only a thin layer near the wall is sheared.

Plug flow requires that the shear stress be lower than the yield stress of the paste. The shear stress in a

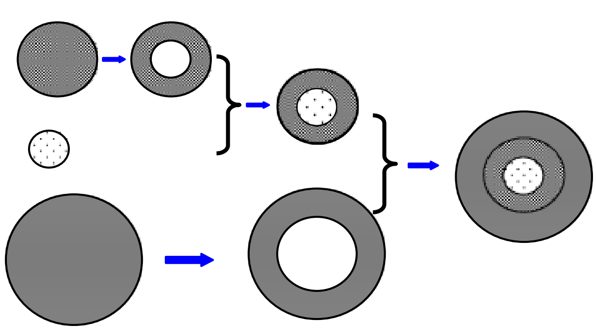

Fig. 4. Schematic diagram for multiple-layer feedrod preparation.

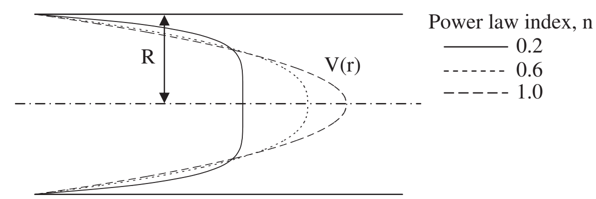

Fig. 5. Velocity profiles for pipe flow of power-law liquids. The same volume flow rate was used for the three calculations (after Barnes et al.[23]).

pipe is highest at the wall and is approximated by

$$\tau_w = PD/(4L) \quad (2)$$

where τ_w is the apparent shear stress at the wall, D and L are the diameter and length of the pipe, and P is the pressure drop in the pipe. The pressure drop is presumed to be related to the velocity of the fluid such that a lower velocity generates a smaller pressure drop and therefore a smaller resultant shear stress. Zhou and Li[24] calculated the apparent shear stress of short fiber-reinforced cementitious composites using Eq. (2).

Benbow and colleagues[14,15] developed models to describe the constitutive relationship between pressure drop and velocity during extrusion. The idealized nonlinear Benbow model has been applied to some materials including cement paste:

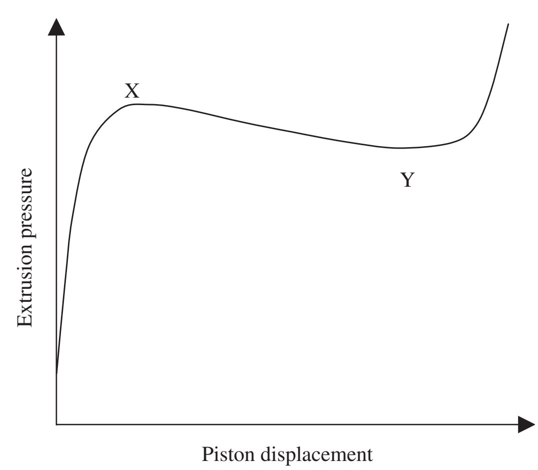

Fig. 6. Typical curve of extrusion pressure versus piston displacement at a constant extrusion rate (after Benbow and Bridgwater[15]).

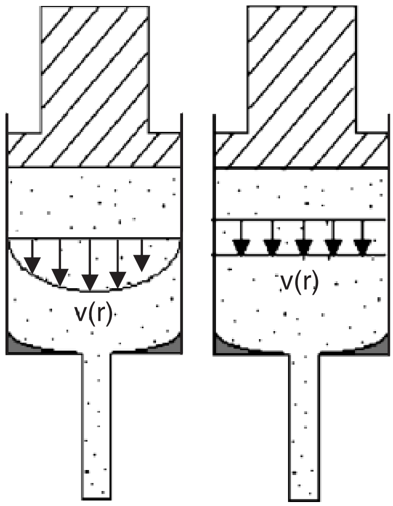

Fig. 7. Expected velocity profile in the barrel. Left, differential flow at high extrudate velocity; Right, plug flow at low extrudate velocity.

$$P_{tot} = P_1 + P = 2(\sigma_0 + \alpha V^m)\ln(D_0/D) + 4(\tau_0 + \beta V^n) \times (L/D) \quad (3)$$

where the first term P_1 is the pressure drop in the die entry region, the second term P (the same as that in Eq. (2)) is the pressure drop in the die land. The geometrical parameters D_0 and D are the diameters of the barrel and the die, respectively, L is the length of the die land, V is the extrudate velocity, σ_0 is the yield stress of bulk material, α is a parameter characterizing the velocity effect in the die entry region, τ_0 is the wall yield stress, and β is a parameter characterizing the velocity effect in the die land region. The power indices m and n account for the nonlinear features of the paste. All six parameters, σ_0, α, τ_0, β, m, and n, were regarded as material.

The Benbow model ignores any pressure drop in the barrel. Indeed, the pressure drop in the barrel during extrusion is small and can be neglected when compared with the total pressure drop. As the piston moves downward, the extrusion pressure increases rapidly to X (Fig. 6), where the piston fully contacts the paste and the paste is extruded out. As displacement increases from X, the condition is steady state, but the pressure decreases slightly because the friction in the barrel decreases as less and less paste remains in the barrel. When the piston reaches the static zone, the pressure increases rapidly again.

The Benbow model assumes plastic deformation in the die entry region and plug flow in the die land. In the die land, only a very thin-layer liquid near the wall is sheared and the bulk material is almost shear-free.[14,15,25] Plug flow can occur in the barrel at low extrudate velocities when the shear stress is smaller than the yield stress of paste, as previously discussed. However, at high extrudate velocity, the flow in the barrel is expected to be laminar instead of plug, as illustrated in Fig. 7. Figure 8 presents evidence concerning the velocity field in the barrel observed at different extrudate velocities of the outer paste in Table I. The paste was divided into two portions. Each portion was formed into a cylinder and stacked in the barrel. After the extrusion was terminated, the two cylinders in the barrel were taken apart. High extrudate velocity produced laminar flow in the barrel, while low extrudate velocity gave plug flow. High extrudate velocity may even introduce turbulent flow, which is not desired for co-extrusion of multiple layers. Therefore, co-extrusion

Fig. 8. Observed velocity profile at different extrudate velocities in the barrel. Left, differential flow at extrudate velocity of 116 mm/s; Right, plug flow at extrudate velocity of 3 mm/s.

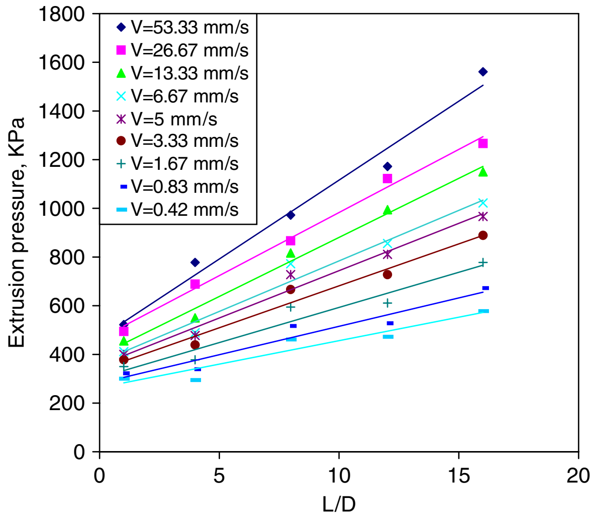

Fig. 9. Extrusion pressure P_{tot} versus L/D for various extrudate velocities of the outer paste in Table I. The correlation coefficients (R^2) for the linear regressions were higher than 0.93.

should be performed at a relatively low extrusion rate to maintain plug flow in the barrel.

The Benbow model, Eq. (3), has the total extrusion pressure P_{tot} in a linear relationship with L/D. Figure 9 shows measured extrusion pressures of the outer paste (shear is highest in the outer paste during extrusion) as a function of L/D at various extrudate velocities. The extrusion parameters, σ_0, α, m, τ_0, β, and λ, can be obtained from this plot. A linear regression is performed for each velocity. The intercepts of these lines plotted as a function of the extrudate velocity gives the bulk material parameters, σ_0, α, and m, when analyzed using nonlinear regression. Likewise, the wall shear stress parameters, τ_0, β, and λ, can be obtained analysis of the slopes of these lines plotted as a function of the extrudate velocity. The Benbow rheological parameters for the outer paste are listed in Table II. The pressure drop in the die land with $L/D=8$ at extrudate velocity of 1.67 mm/s for this paste was calculated to be 239.68 kPa using the second term in Eq. (3). Substituting the pressure drop value into Eq. (1), the shear stress at the wall was found to be 7.49 kPa. This value is far less than its bulk yield stress σ_0 (73.71 kPa, see Table II). Thus, even without a thin-slip layer, plug flow was likely in the die land.

Co-Extrusion of Graded Cellular Structures

This section addresses the co-extrusion of graded cellular cementitious materials, including the actual products obtained. The discussions include rheology requirements for co-extrusion, and structural and microstructural examination of extrudates.

Rheology Requirement for Co-Extrusion

The functionally graded cellular material in this study was fabricated using different layers with different cellular contents and was designed to become increasingly dense toward the surface. The layers in the feedrod need to elongate uniformly during co-extrusion in order to obtain good quality extrudates. Ideal conditions for co-extrusion include plug flow in the barrel and die land, and paste shearing and elongating only in the die entry region. A simplified analysis shows that plug flow can be achieved in both the barrel and die land at low extrudate velocities (discussed above). Shear and elongation are necessary so that the interfaces between layers pass through gradually and smoothly into the die and so that the extrudate is densified. Even in the die entry region, where the material contracts from the barrel to the die and is highly sheared, it is expected that the paste exhibits a velocity profile as shown in Fig. 5. The die entry region should not be too long; otherwise the layers in the extrudate would not elongate uniformly because the shear and hence the velocity would be different in each layer. The length of the die entry region has been shown to be related to the extrudate velocity,[26] with a

Table II. Benbow Parameters of the Outer Paste in Table I

	Yield strength parameters			Wall shear stress parameters		
Sample	**σ_0 (kPa)**	**α (kPa/s/mm)^m**	***m***	**τ_0 (kPa)**	**β (kPa/s/mm)^n**	***n***
Outer paste	73.71	19.06	0.36	4.48	2.45	0.40

Fig. 10. Tangling of two layers due to unmatched rheology. Diameter = 12 mm.

lower extrudate velocity generating a shorter die entry region.

At low extrusion speed, the rheology of the pastes in different layers still needs to be matched to avoid turbulence between layers in the die entry region where the paste is highly sheared. It has been recommended for some ceramic materials that to minimize the velocity difference between layers, the inner layer should have higher viscosity.[21,22] Our experience for the cementitious materials in this study was quite different. Figure 10 shows an example of tangling of two layers in which the inner layer had a higher shear viscosity. For successful co-extrusion of cementitious pastes, we find that the inner layers must have a lower shear viscosity than the outer layer. The rheology of a paste depends on several factors, including the solid particle shape and size distribution, plasticizer type and amount, and water content. The water content was the most convenient parameter to change to adjust the rheology. The water content for each layer in Table I was adjusted by trial and error to match rheology, thereby giving adequate co-extrusion behavior. Using this approach, we have successfully co-extruded mixtures with three and five layers at extrudate velocity of 1.67 mm/s and $L/D = 8$.

Structure and Micro-Structure Examination of the Extrudates

The cross sections perpendicular and parallel to the extrusion direction of a three-layered extrudate and a five-layered extrudate are shown at low magnification in Figs. 11 and 12, respectively. Artificial colors were used to highlight the different layers in the extrudates. The photographs indicate that the roundness perpendicular to the extrusion direction and the straightness parallel to the extrusion direction were well preserved in all layers during extrusion.

The interfaces between layers for the five-layered extrudate were further examined using a scanning electronic microscope (SEM, JSM-6060LV, JEOL, Tokyo, Japan). Results are shown in Fig. 13. As seen in these pictures, the transition between layers is seamless, as is desired for functionally graded materials. Qualitatively, the interfacial bonding characteristics between layers (Fig. 13) translates into material properties which are appropriate to engineering applications.[27]

Conclusions

Rheology control is vital for co-extrusion. For successful co-extrusion of layered cement-based materials,

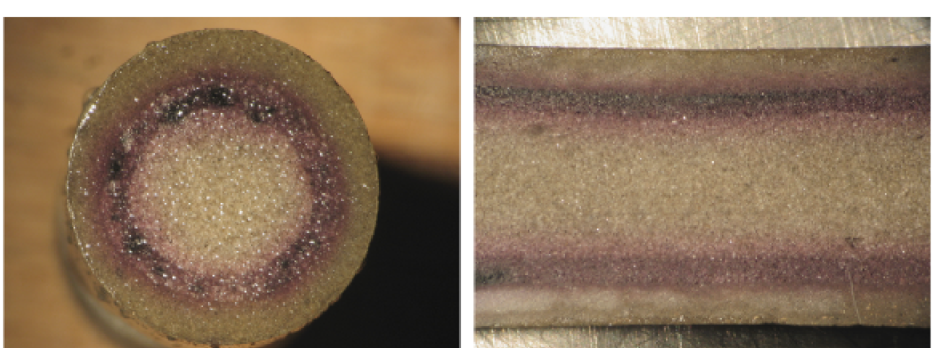

Fig. 11. A three-layered extrudate. Left, cross section perpendicular to extrusion direction; Right, cross section parallel to extrusion direction. Diameter = 12 mm.

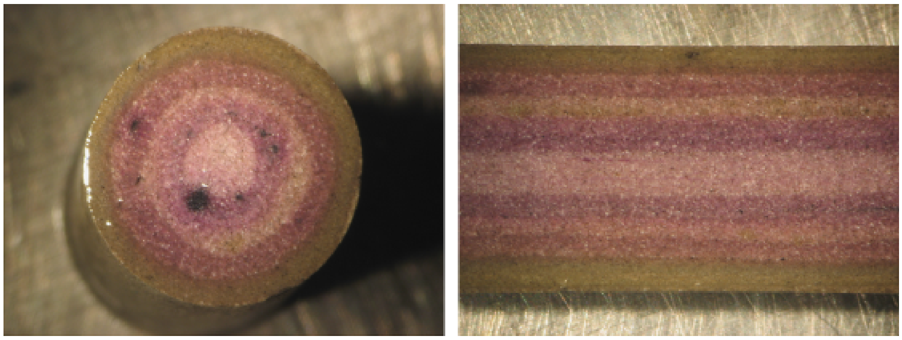

Fig. 12. A five-layered extrudate. Left, cross section perpendicular to extrusion direction; Right, cross section parallel to extrusion direction. Diameter = 12 mm.

the flow in the barrel and die land should be plug-like, while the paste should be uniformly elongated in the die entry region. Rheology among different layers should be matched to obtain good co-extruded products. Inner layers must have lower shear viscosity than outer layer for cementitious pastes. The extrudate velocity is also important. Too high velocity generates laminar or even turbulent flow, which is not desired in co-extrusion. The plug flow of paste in the barrel was achieved by maintaining a low extrudate velocity. The shear stress applied to the paste by the die-land wall was smaller than its yield stress, thereby ensuring plug flow of paste

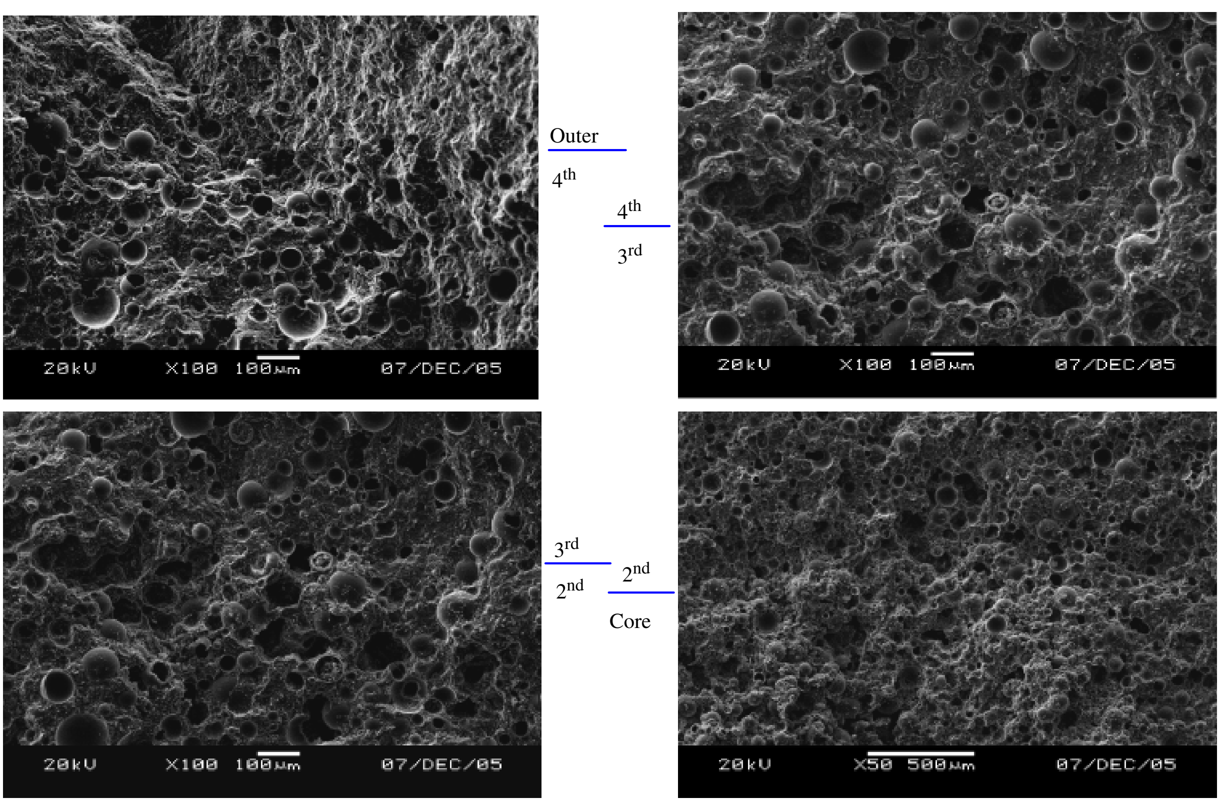

Fig. 13. Interfaces between layers of a five-layered extrudate by scattered electron microscope using secondary electrons.

in the die land. A simple experimental method using thin-walled tubes was effective to prepare a layered feed-rod of cementitious paste. Functionally cellular-graded cement-based extrudates were successfully fabricated by co-extrusion at a low extrudate velocity. Inspection showed that the roundness perpendicular to the extrusion direction and the straightness parallel to the extrusion direction between layers were well preserved after extrusion and that the transition between layers was gradual.

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