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Ceramics International 28 (2002) 507–514

CERAMICS
INTERNATIONAL

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Effect of ethylene–vinyl acetate copolymer on the rheological behaviour of alumino-silicate/polyethylene wax suspensions

M. Attarian[a], E. Taheri-Nassaj[a,*], P. Davami[b]

[a]*Department of Materials Science and Engineering, Tarbiat Modarres University, Tehran, Iran*
[b]*Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran*

Received 23 April 2001; received in revised form 1 December 2001; accepted 19 December 2001

Abstract

Ceramic suspensions were prepared from an alumino-silicate powder, polyethylene wax (PE-wax) as binder with additions of stearic acid (SA). The ceramic powder consisted of mullite, corundum and tridymite phases. The organic binders contained 3 to 8 wt.% ethylene–vinyl acetate (EVA) and were filled with various volume fractions of ceramic powder. The yield stresses of suspensions were estimated using shear stress-shear rate data measured at 90–120 °C. The addition level of EVA was shown to have a considerable effect on the yield stress of suspensions. The effect of EVA on the flow parameters was also investigated over the temperature range of 90 to 120 °C. It was shown that the addition of 5 wt.% EVA in organic binder causes a decrease of viscosity at a temperature of 90 °C and the higher the volume fraction of ceramic powder, the higher the efficiency of EVA in reducing the viscosity. But at higher temperature, EVA acts as a flow modifier rather than increasing the wettability of polymer blend. In fact at this temperature the polymer–particle interaction weakens with EVA content. Moreover, it was found that the required amount of EVA depends on the degree of powder agglomeration.

Keywords: A. Injection moulding; Alumino-silicate; Polyethylene wax; Rheology; Ethylene vinyl acetate

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1. Introduction

The injection moulding of ceramic shapes is based on the application of external forces to a suspension of ceramic powder in an organic vehicle. The plastic suspension deforms and flows under applied stresses. The external forces cause the plastic mix to be adjusted to any die or mould which dictates the eventual shape [1].

To confer fluidity, ceramic particles are dispersed in a molten polymer or wax vehicle. After solidification in cavity, the organic binder is removed by pyrolysis prior to sintering. A highly concentrated suspension exhibits complex flow behaviour. Such a suspension with good homogeneity, a low viscosity at low temperature, a low shear rate and temperature sensitivity and a yield stress value in acceptable range was found to exhibit good injection moulding and debinding behaviour [2].

Wax-based binder consisting of a major fraction of various waxes and a minor fraction of a polymer and other additives, are used widely in powder injection moulding. They are easy to handle and thermally stable. However, the powder mixtures made of wax-based binders tend to have a "binder separation problem" during moulding and a "slumping problem" during thermal debinding [3]. Different polymers are used to formulate various wax-based binders. Nishimura et al. [4] have indicated that ceramic powders with near-hydrophilic surfaces wet very poorly with hydrophobic binders such as polyethylene (PE), polypropylene (PP), and polystyrene (PS). The suspension becomes highly viscous and exhibits poor mouldability, if it contains agglomerates, which are not wetted with the binder. One approach to increase wettability of ceramic powders with binders can be implemented by introducing wetting agents with functional groups into the binder [4].

The ethylene–vinyl acetate (EVA) copolymer has polar functional groups and is highly miscible with sinterable powders, hence this resin is extensively used as a component of injection moulding binder systems [5].

In the present work, three types of alumino-silicate powder with different particle size distribution and degree of agglomeration have been used to prepare suspensions containing PE-wax as major binder, varying

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* Corresponding author.
E-mail address: taheri@modares.ac.ir (E. Taheri-Nassaj).

0272-8842/02/$22.00
PII: S0272-8842(02)00003-2

amount of EVA as minor binder and stearic acid as a constant component. Using a capillary rheometer, the rheological properties of formulations were characterized as suggested by Edirisinghe and Evans [6]. The yield stress of formulations was estimated and the influence of EVA content of organic binder on flow parameters such as shear rate dependence of viscosity, fluidity at a shear rate of 100 s^{-1} and the temperature dependence of viscosity over temperature range of 90 to 120 °C were determined.

2. Experimental details

2.1. Materials

Alumino-silicate powders suitable for the fabrication of refractory articles were used as the ceramic powders. Three powders used in this investigation, IR1, IR2 and IR3 mainly consisted of mullite, corundum and tridymite phases and have approximately similar chemical compositions (except for Fe content, which took up during ball milling). The particle size distribution and particle morphology of each powder are given in Figs. 1 and 2 respectively. Stearic acid was used as the processing aid in all formulations. The major binder used was polyethylene wax. All formulations contained different proportions of EVA as a minor binder. Data on the ceramic powders and binders are given in Tables 1 and 2 respectively. Details of the formulations and binder systems used are shown in Table 3.

2.2. Mixing and compounding

Each ceramic powder was treated by surface adsorption of different amounts of EVA in toluene for 2 h through hot ball milling followed by compounding with stearic acid and PE-wax in desired proportions via the same ball milling operation for another 2 h. Suspensions were dried at 45 °C for a week. A sample of each

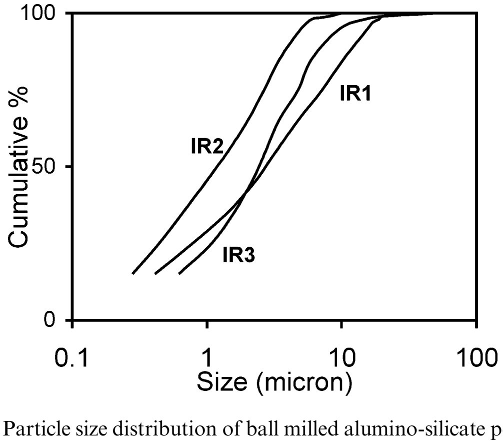

Fig. 1. Particle size distribution of ball milled alumino-silicate powders.

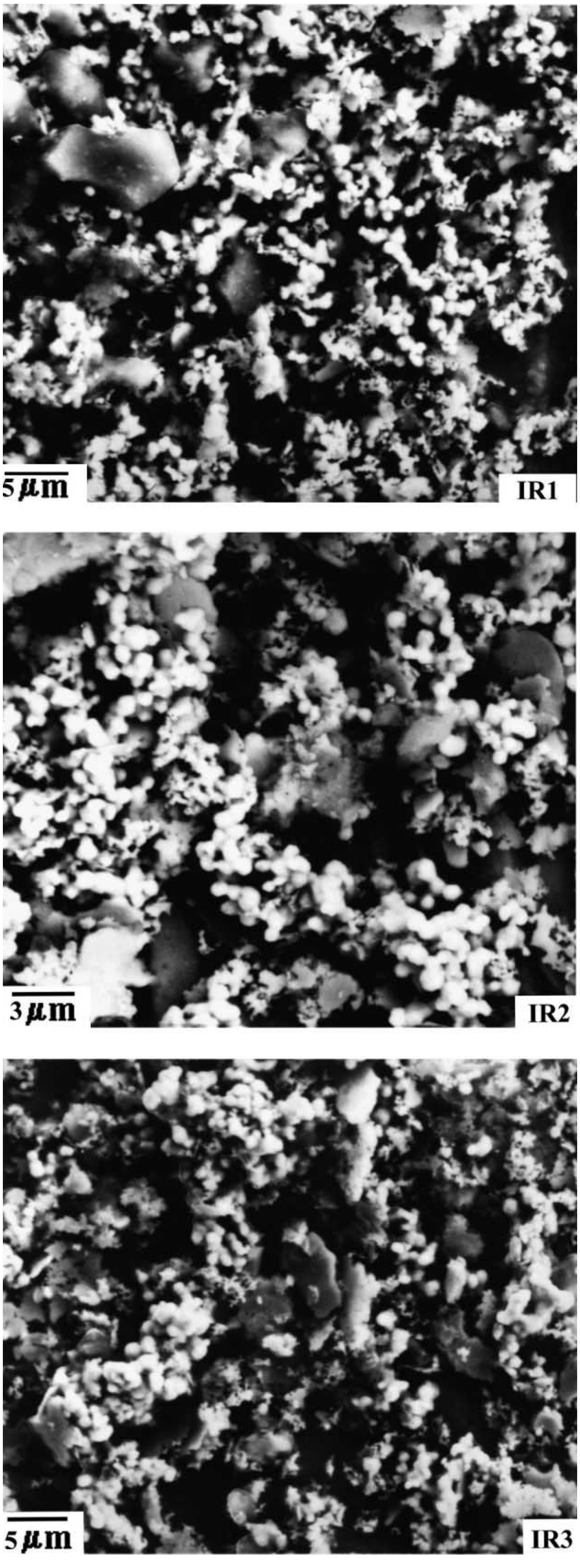

Fig. 2. Scanning electron micrographs of ball milled alumino-silicate powders.

formulation was ashed at 600 °C to estimate the actual filler loading.

2.3. Rheology

Viscosity of suspensions was measured in an Instron capillary rheometer with temperature control accuracy of ±1 °C and allowing 10 min to reach thermal equilibrium after charging the barrel. A die with 1.5 mm diameter and 38 mm length was used. The end correction was ignored, but the results were corrected for non-newtonian flow effects using Rabinowitsch correction. Rheology of suspensions was studied at 90 and 120 °C.

3. Results and discussion

3.1. Powder characteristics

The particle size distributions were determined by the laser diffraction technique. Powders IR1 and IR2 have multimodal particle size distributions. Powder IR2 has relatively wider particle size distribution and contains the highest proportion of sub-micrometer particles compared to the other two. Both IR1 and IR2 have almost an equiaxed particle shape (Fig. 2) and are much

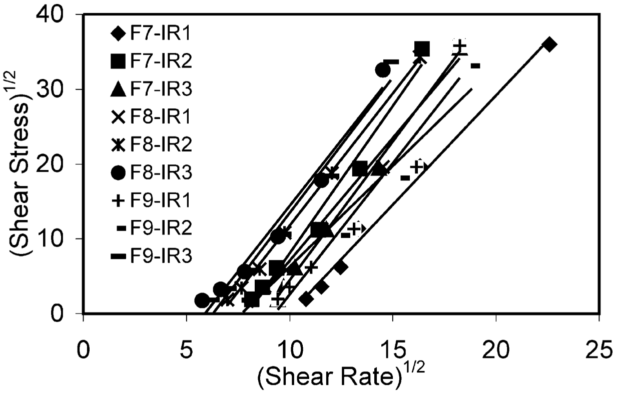

Fig. 3. (Shear rate) $^{1/2}$ versus (shear stress)$^{1/2}$ graphs of formulations with 59 vol.% filler at 90 °C.

Table 1
Details and sources of ceramic powders used

Type	Source	Particle shape	Density (gr cm^{-3})	Chemical composition (wt.%)						
				Al_2O_3	SiO_2	CaO	MgO	TiO_2	Fe_2O_3	Alkalies
IR1	Iran	Equiaxed, sharp edges	2.97	Balance	38	4.8	0.2	1.6	1.1	0.4
IR2	Refractories	Equiaxed, sharp edges	2.97	Balance	38	4.8	0.2	1.6	1.2	0.4
IR3	Co.	Round agglomerates	2.97	Balance	38	4.8	0.2	1.6	1.3	0.4

Table 2
Details and sources of binders used

Type	Source	Density (kg m^{-3})	T_m °C (from DSC peaks)
Polyethylene wax	Arak Petrochemical Co.	920	115.3
Ethylene vinyl acetate	Grade ELVAX 250, ex. Du Pont, UK	950	−25 (Tg)
Stearic acid	BDH Chemicals	941	—

Table 3
Formulations and ashing results

Formulation	Organic binder (wt.%)			Ceramic powder (vol.%)	Calculated powder (vol.%) (ashing results)		
	PE-wax	EVA	SA		IR1	IR2	IR3
F4	87	3	10	55	55.2	54.8	55.5
F5	85	5	10	55	55.5	54.6	55.3
F6	82	8	10	55	55.4	54.5	54.7
F7	87	3	10	59	59.5	58.9	59.2
F8	85	5	10	59	58.9	58.6	58.4
F9	82	8	10	59	59.5	58.4	58.4
F10	87	3	10	63	63.6	62.4	63.4
F11	85	5	10	63	63.7	62.6	62.7
F12	82	8	10	63	62.7	62.9	62.6

less agglomerated compared to IR3. IR3 has a monomodal particle size distribution and highest degree of agglomeration. As shown in Fig. 2, it seems that the particle size distribution of the IR3 powder corresponds to both the agglomerates and the primary particles.

3.2. Suspensions

Ashing results are given in Table 3. Maximum variability of powder volume fraction for all formulations was 0.6%.

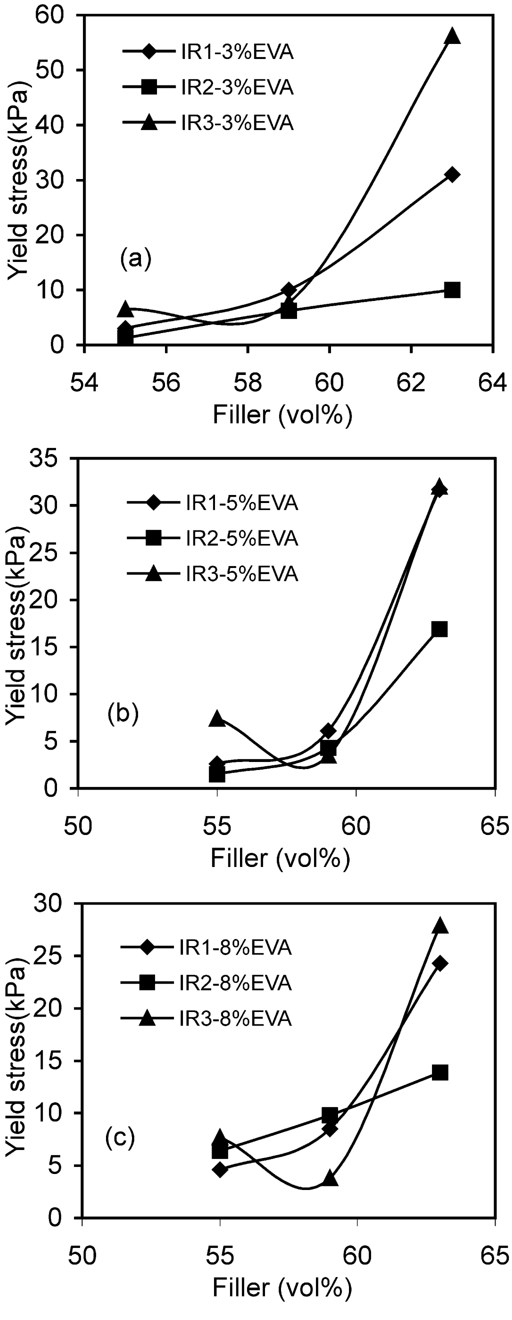

Fig. 4. Yield stress versus filler (vol.%) graphs of: (a) 3 wt.% EVA, (b) 5 wt.% EVA, and (c) 8 wt.% EVA formulations at 90 °C.

3.3. Yield stress

By replotting the graphs of shear rate ($\dot{\gamma}$) against shear stress (τ) in the form of $\dot{\gamma}^{1/2}$ versus $\tau^{1/2}$ (Fig. 3 for formulations with 59 vol.% filler) linear relationship should result according to the Casson equation [7]:

$$\tau^{1/2} = \left(\tau_y\right)^{1/2} + (\mu)^{1/2}(\dot{\gamma})^{1/2} \tag{1}$$

where μ and τ_y are high shear rate viscosity and yield stress of suspension respectively. Yield stress variation versus powder volume fraction and EVA content in organic vehicle at 90 °C is shown in Fig. 4.

The acceptable level of yield stress for these suspensions was estimated to be about 5–8 kPa from the injection moulding and debinding experiments [8]. This is in agreement with the value suggested by Edirisinghe et al. [7]. The yield stress in the lower limit of this region permits laminar flow of suspensions into the mould and in the upper limit enough strength to prevent deformation during the binder removal stage. Fig. 4 shows that suspensions with 55–59 vol.% ceramic filler look most favourable in terms of having an acceptable level of yield stress. For all formulations the yield stress values became larger with increasing ceramic volume fraction. The exceptions were IR3 suspensions that contained 5 and 8 wt.% EVA as minor binder, whose yield stress values suddenly dropped at 59 vol.% ceramic filler.

The positive gradient of yield stress with filler loading decreased with EVA weight percent. This behaviour is more pronounced in a higher powder volume fraction range. It was also shown that the presence of 8 wt.% EVA in organic binder formulation caused reduction of the maximum yield stress of IR1 and IR3 suspensions significantly but not to an acceptable range.

It was observed during rheological measurements that the F10–IR1 and F10–IR3 formulations containing 3 wt.% EVA as minor binder showed very low fluidity at low shear rates. The high τ_y values and ribbon injection behaviour in injection experiments confirms this. The presence of EVA up to 5 wt.% in organic vehicle caused

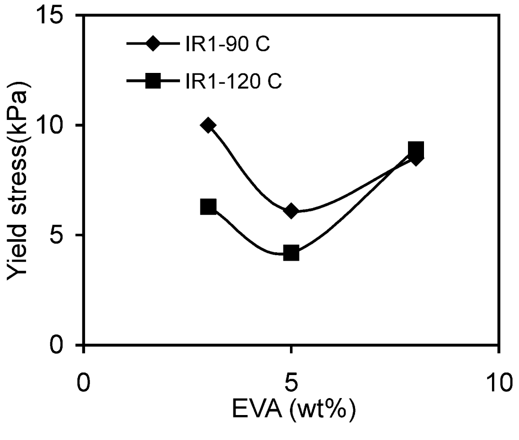

Fig. 5. Yield stress versus EVA (wt.%) graphs of IR1 suspensions with 59 vol.% ceramic filler at 90 and 120 °C.

the reduction of the yield stress of IR1 suspensions in the lower region of filler loading over the temperature range of 90 to 120 °C (Fig. 5). In this region, 8 wt.% EVA could be used to adjust the yield stress of IR2 suspensions in the desirable range for debinding stage.

3.4. Fluidity

The log viscosity against log shear rate of all formulations fitted an almost straight-line relationship, (Figs. 6–8). Fig. 6 shows graphs of log viscosity against log shear rate for formulations F4, F5 and F6 which contain 55 vol.% ceramic filler and 3, 5 and 8 wt.% EVA as minor binder, respectively. In this group, IR2 suspensions show the lowest and IR3 suspensions show the highest viscosity values at all shear rates. The exception is F6–IR3 formulation whose viscosity shows lower values compared to F6–IR1.

With some higher powder loading (59 vol.% ceramic filler, formulations F7, F8 and F9), the reducing behaviour of EVA is observed in IR3 suspensions and F8–IR1 and IR2 formulations (Fig. 7).

With further powder loading (63 vol.% ceramic filler, formulations F10, F11 and F12), the above observations

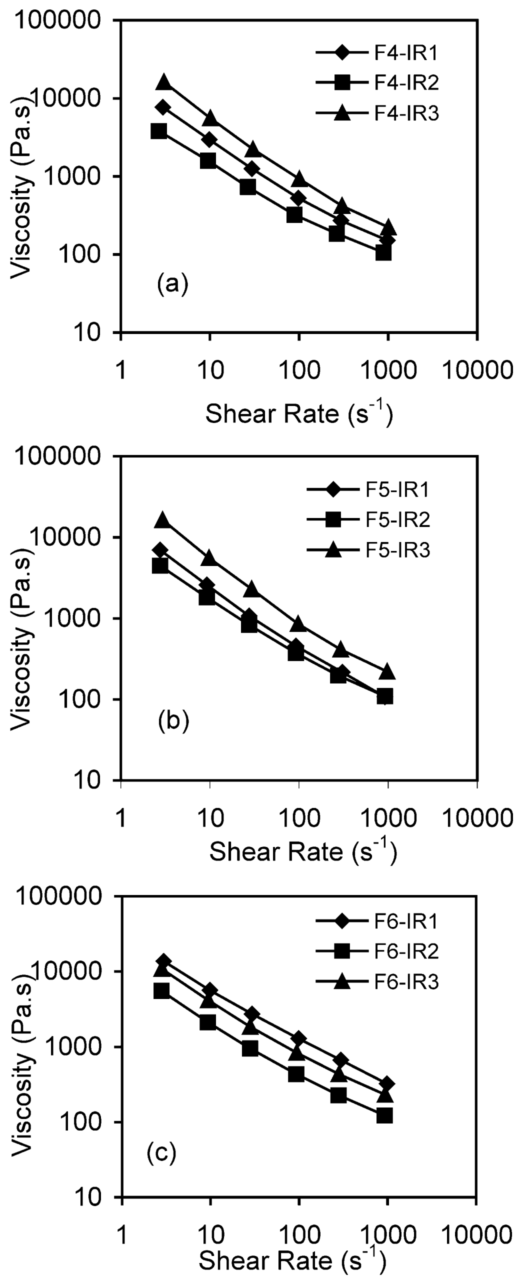

Fig. 6. Viscosity versus shear rate graphs of: (a) F4, (b) F5 and (c) F6 formulations at 90 °C.

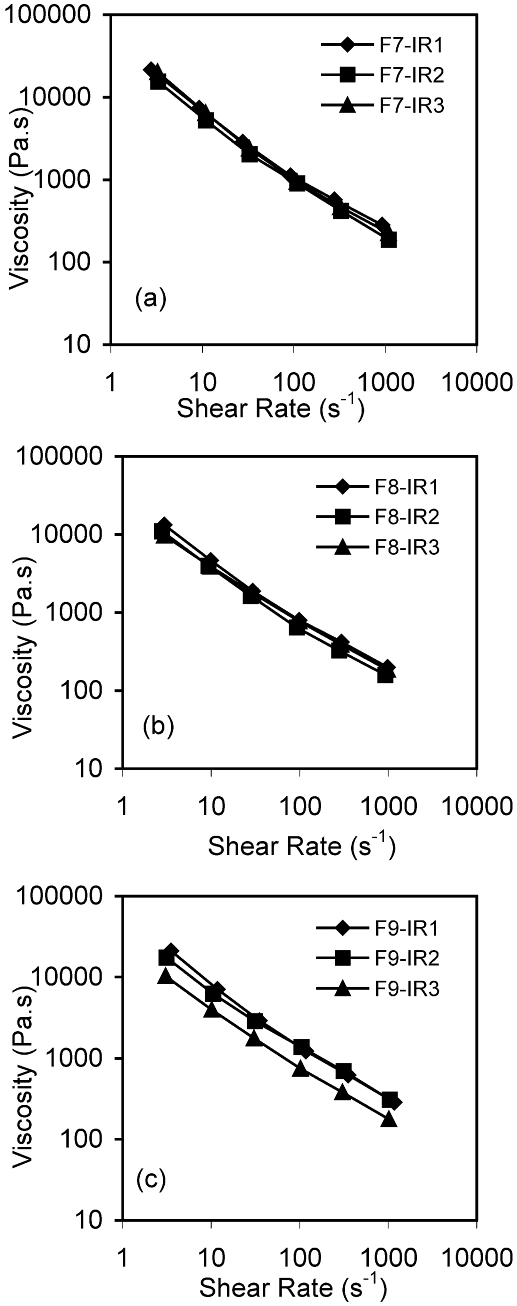

Fig. 7. Viscosity versus shear rate graphs of: (a) F7, (b) F8 and (c) F9 formulations at 90 °C.

do not change except that the influence of EVA in reduction of viscosity is diminished again for IR2 suspensions. The behaviour of IR1 and IR2 suspensions is very close in such high filler loading especially at lower shear rates region (Fig. 8).

The variation of viscosity with ceramic filler and EVA content at shear rate of 100 s^{-1} and temperature of 90 °C is shown in Fig. 9.

According to Mutsuddy criteria a binder system which produces a viscosity of less than 1000 Pa s within the shear rate range for 100 to 1000 s^{-1} when the ceramic powder is added can be regarded as a usable formulation [1].

Fig. 9 shows that at lower ceramic volume fraction, substitution of 8 wt.% EVA for PE-wax reduced the viscosity of F9–IR3 formulation by 23%. The reducing effect of EVA increased with vol.% ceramic up to 42% for F12–IR3 formulation.

There is especially an interest in the reduction of viscosity and improving the mouldability of IR1 suspensions because their favorable behaviour in the debinding stage has already been demonstrated. It is clear that the presence of large particles in these suspensions have an adverse effect on their rheological properties. On the other hand the worst behaviour of

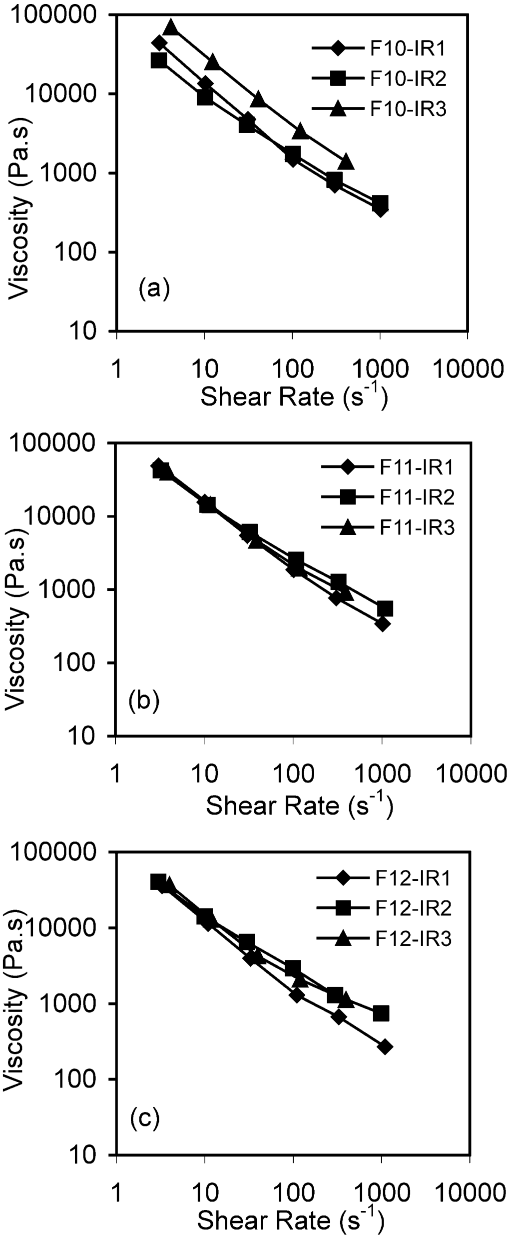

Fig. 8. Viscosity versus shear rate graphs of: (a) F10, (b) F11 and (c) F12 formulations at 90 °C.

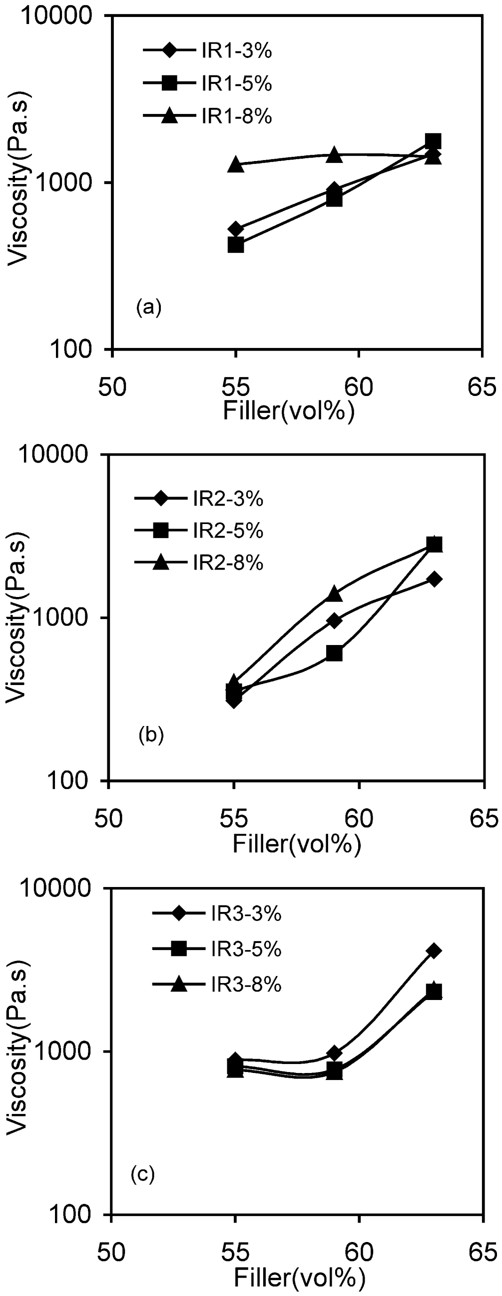

Fig. 9. Viscosity versus ceramic filler loading graphs of: (a) IR1, (b) IR2 and (c) IR3 suspensions at shear rate 100 s^{-1} and 90 °C.

Table 4
Flow parameter

Formulation	$n-1$ (Pa s^2) temp. °C		Fluidity, $1/\eta$ (Pa s °C) 10^{-3} $\dot{\gamma}=100$ s^{-1} temp. °C		$\mathrm{d}\log\eta/\mathrm{d}T$ (Pa s °C) 10^{-3} $\dot{\gamma}=100$ s^{-1}	Activation energy for viscous flow (kJ/mol) $\dot{\gamma}=100$ s^{-1}
	90	120	90	120		
F7–IR1	−0.54	−0.59	1.1	1.6	−5.4	14.6
F7–IR2	−0.68		1.0			
F7–IR3	−0.62		1.0			
F8–IR1	−0.60	−0.53	1.2	1.5	−3.0	8.2
F8–IR2	−0.55		1.65			
F8–IR3	−0.62		1.3			
F9–IR1	−0.71	[a]	0.7	0.8	−2.5	6.8
F9–IR2	−0.62		0.7			
F9–IR3	−0.63		1.3			

[a] Became dilatant at shear rates lower than 100 s^{-1}

IR3 suspensions show greater importance of degree of agglomeration in imparting rheological behaviour. Fig. 9 also shows that substitution of 5 wt.% EVA for PE-wax reduced the viscosity of F8–IR1 formulation by 12%. Further addition of EVA caused an increase in the viscosity of F9–IR1 formulation. According to fluidity criteria, 63 vol.% filled suspensions were not suitable for injection moulding at a temperature of 90 °C.

3.5. Temperature dependence of viscosity

At temperature appreciably higher than $T_g + 100$ the temperature dependence of viscosity is no longer strongly affected by the increase of free volume. Instead, the energy barriers to motion become limiting. In that case the viscosity is expressed in familiar Arrhenius form with constant activation energy whose value depends upon the chemical structure of the polymer blend.

The flow parameters of 59 vol.% filled suspensions over a temperature range of 90 to 120 °C are given in Table 4. It was shown that the temperature dependence of viscosity expressed as $\mathrm{d}\log\eta/\mathrm{d}T$ and activation energy for viscous flow decreased with EVA content. The low activation energy value (6.8 kJ mol^{-1}) probably arises because the polymer fraction F9 contains 8 wt.% EVA that may be in good compatibility with PE wax melt and may act as a flow modifier.

3.6. Shear rate dependence of viscosity

The pseudoplasticity criterion requires that the slope of log viscosity–shear rate graph ($n-1$) be negative, where n is a power low index. The negative values of ($n-1$) in Table 4 indicate that all formulations show pseudoplastic flow characteristics and indeed the value of the parameter ($n-1$) is generally in the range of −0.54 to −0.71 Pa s^2 at temperature of 90 °C.

Values in Table 4 also show that the pseudoplasticity increases with EVA content in the organic binder. The exception is F7–IR1 formulation which has a strong pseudoplasticity and an intermediate fluidity. Conversely at a temperature of 120 °C the pseudoplasticity decreased with EVA content. However, all formulations satisfy the condition, as proposed by Mutsuddy [1], for pseudoplasticity at shear rates higher than 100 s^{-1}. Therefore, they deserve full investigation as potentially usable moulding compositions.

4. Conclusion

The shear stress–shear rate relationship of aluminosilicate/polyethylene wax suspensions gave a good fit to Casson's equation. These suspensions with 55–59 vol.% ceramic filler had the yield stress values lower than 10 kPa at 90 °C.

The yield stress and viscosity of IR3 suspensions decreased with EVA content in organic binder significantly. The worst behaviour of IR3 suspensions with 3 wt.% EVA as minor binder could be related to its high degree of agglomeration. However, this characteristic caused the increase of effective particle size and decrease the required EVA to wet particle surfaces. On the other hand, extrusion force breaks loosely agglomerates to discrete particles and thus the larger amount of EVA needs to wet new surfaces.

Using 5 wt.% EVA as minor binder (F8 formulation) results in an effective reduction of yield stress value and fluidity improvement of IR1 suspensions. This formulation also showed low values of $\mathrm{d}\log\eta/\mathrm{d}T$ and activation energy.

The yield stress and viscosity values of IR2 suspensions increased with EVA content in organic binder. It seems that because of the high proportion of submicrometer particles these suspensions need a larger amount of EVA (>8 wt.%) to wet surfaces. At 120 °C, the loss of pseudoplasticity and the reduction of activation energy for viscous flow with EVA content probably arise because EVA may act as a flow modifier rather than increasing the wettability of the polymer blend. In fact at this temperature the polymer–particle interaction weakens with EVA content.

Acknowledgements

The authors are grateful to the Razi Metallurgical Research Center (RMRC), Iran, for supporting this work; Professor H. Assadi and Professor N. Varahram for useful discussion and Mr. S. Nasiri, Mr. H. Ashrafi for technical help and Mrs. K.E. Tatler for the review the manuscript.

References

[1] B.C. Mutsuddy, Rheology and mixing of ceramics mixtures used in plastic molding, in: B.I. Lee, E.J.A. Pope (Eds.), Chemical processing of ceramics, Marcel Dekker Inc, New York, 1994, pp. 239–261.

[2] M.Y. Cao, B.O. Rhee, C.I. Chung, Usefulness of viscosity measurement of feedstock in powder injection molding, in: Advances in powder metallurgy. Vol. 2, Metal Powder Industries Federation, USA, 1991.

[3] B.O. Rhee, M.Y. Cao, H.R. Zhang, E, Streicher, C.I. Chung, Improved wax-based binder formulations for powder injection moulding, in: Advances in powder metallurgy, Vol. 2, Metal Powder Industries Federation, USA, 1991.

[4] Nishimura, Kimihiro, Yshino, Kenji, US patent 5,380,179, 10 January 1995.

[5] Kato, Shigeki, Inoue, Katsushiro, US patent 5,087,594, 11 February 1992.

[6] M.J. Edirisinghe, J.R.G. Evans, Properties of ceramic injection moulding formulations, part 2, melt rheology, Journal of Materials Science 22 (1987) 269–277.

[7] M.J. Edirisinghe, H.M. Show, K.L. Tomkins, Flow behaviour of ceramic injection moulding suspension, Ceramics International 18 (1992) 193–200.

[8] M. Attarian, E. Taheri-Nassaj, in preparation.