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The rheological behavior of ceramic/polymer mixtures for coextrusion processing

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Abstact Coextrusion is a novel fabrication method for ceramic processing. However, the rheological behavior of ceramic/polymer blends during batching and extrusion in a coextrusion process is not well understood. In this study, the rheological properties of $BaTiO_3$/polymer mixtures during batching in a high-shear rate mixer (C.W. Brabender) were investigated and several models were evaluated. The $BaTiO_3$/polymer mixtures exhibited shear thinning behavior with a yield stress. The power-law model still fit for the data obtained from the high-shear rate mixer in the tested shear rate range. The results also showed that Bousmina's model only fits well for the pure polymer melts. For the ceramic/polymer mixtures, large deviations from Bousmina's model were observed.

Introduction

Successful coextrusion of plastic-plastic, ceramic-ceramic or ceramic-metal systems requires a close viscosity match for each component during extrusion [1–3]. The components are usually batched in a high-shear roller-cone mixer and then laminated or organized in a die for coextrusion. Roller-cone mixers are widely used in the plastic industry to control the rheological properties of polymer melts and also in a variety of thermoplastic processing procedures in the ceramics industry [4–9]. The fundamental problem with the process is that data received from the torque rheometer is torque–roller rotational speed dependent while the data from the extruder is load-velocity dependent. The torque reading obtained from the Brabender is a qualitative indication of the melt viscosity, as well as a measure of the viscosity-temperature dependence. But the torque–roller speed dependence does not provide direct viscosity data. This makes viscosity matching of the components difficult to control, especially when mixing and coextrusion may occur at different temperatures. Since Brabender-type high shear mixers are used for ceramic thermoplastic processing in labs and industries more often than in the past, a study of the relation between the data obtained from a torque-rheometer and the data obtained from a viscometer for ceramic/polymer mixtures is necessary [3, 5, 10].

Some modeling work has been performed in the past 40 years on converting the torque–roller speed data directly to viscosity data. Goodrich and Porter first presented an approximate method for converting torque rheometer data into fundamental rheological units for polymer melts by assuming the torque rheometer acts as a concentric-cylinder viscometer [11]. Blyer and Danne extended this work to non-Newtonian fluids, and derived the equation [12]: $M = \mathrm{C}(n)KN^{\mathrm{n}}$, where M is torque, $\mathrm{C}(n)$ is a constant, N is the roller speed in Revolutions Per Minute (RPM). K and n are parameters similar to a power law equation: $\tau = K\gamma^{\mathrm{n}}$, where K is a constant, γ is the shear rate, τ is the shear stress, and n is the power law index. They concluded that the slope of the log(torque)–log(roller speed) of a polymer melt should be identical to the slope of the log(τ)-log(γ) curve obtained from a capillary rheometer at constant temperature and that

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the flow activation energies obtained from the Brabender and capillary data should be equivalent.

Lee and Purdon derived another power law equation, which is in the same format as Blyer's but from a different point of view [13]. Marquez et al., calibrated Lee's equation by introducing a geometrical parameter α (which is defined as the ratio of the outside radius to the equivalent radius of the roller) [14]. However, the calibration parameter α in their equation is not only related to the geometrical characteristic of the roller but also to the polymer intrinsic properties.

More recently, Bousmina et al., provided a more general analysis allowing the determination of shear rate and viscosity from batch mixer roller speed and torque data [15]. They introduced an effective equivalent internal radius R_i. For Newtonian fluids, the R_i is defined as:

$$R_i = \frac{R_c}{\left[1 + \frac{4\pi N}{n}\left(2\pi \cdot mLR_c^2 \frac{1+g^{n+1}}{M}\right)^{1/n}\right]^{n/2}} \tag{1}$$

where R_c is the radius of the mixing chamber, M is the torque exerted on the roller shaft, g is the gear ratio, N is the roller rotational speed per second, n is the power law index, m is the melt consistency index, and L is the roller length. The shear rate is then given by:

$$\dot{\gamma} \approx 2\pi N / \ln(R_c/R_i) \tag{2}$$

and the viscosity can be described as:

$$\eta = \frac{M}{N} \frac{((R_c/R_i)^2 - 1)}{8\pi^2 LR_c^2(1+g^2)} \tag{3}$$

Their most important result is that R_i is a universal quantity that is practically insensitive to the nature and rheological behavior of the fluid under mixing. It depends only on the geometrical dimensions of the mixer and the gear ratio. Equations 1–3 were also found to work well for non-Newtonian fluids in their report. This latter modeling and experimental work demonstrated the feasibility of evaluating the power law index (n) and the melt consistency index (m) for the torque rheometer data. However, it was based on pure polymer melts. Ceramic/polymer mixtures have never been investigated using similar models. Additionally, the influence of solids loading in these mixtures is also unknown. This paper is aimed at evaluating these models using ceramic powder/polymer mixtures and obtaining a direct indication of viscosity data for rheological control in the coextrusion process.

Experimental procedure

In this study, a Brabender high shear, roller-cone mixer (EPL-/5501 Mixer, C.W. Brabender Instrument Inc., South Hackensack, NJ) was used. A schematic of the torque rheometer portion of a Brabender roller-cone mixer is shown in Fig. 1 and its geometric data is listed in Table 1.

The samples used in this study are listed in Table 2. The ceramic powders ($BaTiO_3$, Ferro Corp., APS 1 μm) were blended with several organic thermoplastics and plasticizers including EEA (poly[ethylene-co-ethyl acrylate], Union Carbide Corp.), PEBA-7 (poly[ethylene-co-butyl acrylate], 7 wt% butyl acrylate, Aldrich Chemical Co.), wax (MobilWax 2305, ExxonMobil), and HMO (heavy mineral oil, Aldrich Chemical Co.). The EEA and PEBA-7 are common polymers being used in the coextrusion process [3, 5,

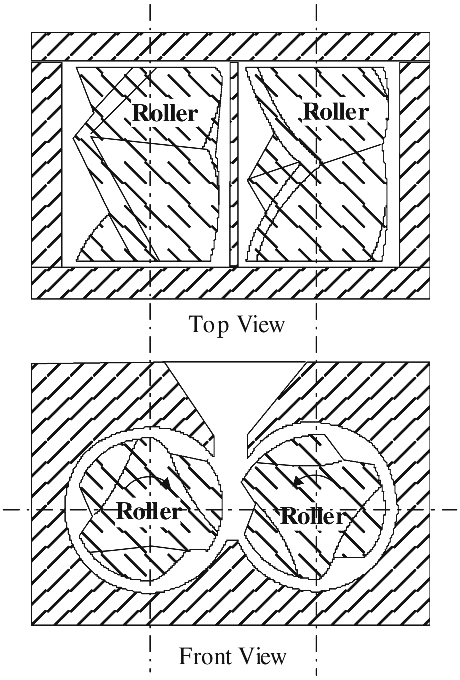


Fig. 1 Schematic view of the torque rheometer

Table 1 The geometric data for the torque rheometer

Items	Size
Sample chamber size	60,000 mm^3
Radius of chamber (R_c)	19.65 mm
Chamber length (L_c)	48.10 mm
Gear ratio (g)	3:2
Roller length (L)	46.90 mm
Radius of roller (Max)	19.47 mm
Radius of roller (Min)	10.5 mm

Table 2 Polymer and ceramic/polymer samples used in this study

Sample #	Composition	Ceramic solids loading (vol%)
1	Pure PEBA-7	0
2	Pure EEA	0
3	$BaTiO_3$+EEA+HMO+Wax	49
4	$BaTiO_3$+EEA+HMO+Wax	52
5	$BaTiO_3$+EEA+HMO+Wax	55

10, 16]. Wax and HMO were used as a lubricant for better mixing of ceramic powders with the polymer. The same amount of wax and HMO were added for samples 3 through 5 (Table 2).

The measuring head of the Brabender mixer was loaded to 70% of its total volume for each batch, i.e. a total of 42,000 mm^3 of the compositions indicated in Table 2. Two pure polymer samples EEA and PEBA-7 were also used to evaluate the models and for comparison to the ceramic powder/polymer blends. A solids loading of up to 55 vol% was selected for this study since it would provide a fired density which was near theoretical while providing a viscosity that was within a reasonable working range.

All of the ceramic/polymer mixtures were initially mixed at 20 RPM and 150 °C for 25 min, until the torque reading was stable. This is a qualitative indication that all of the soft agglomerates in the ceramic have been dispersed and the ceramic powder is uniformly distributed in the polymer binders. Torque values for these mixtures were then taken at temperatures of 125 °C, 135 °C and 145 °C, and at roller speeds ranging from 10 RPM to 60 RPM. The roller speed was increased successively to selected speeds, and each measurement was taken after at least 1 min (after the torque value had stabilized). The actual viscosity data for all five samples was also measured on a RDA-III Rheometer (Rheometric Scientific Co., parallel plate diameter 25 mm, gap distance 1.5 mm) at 125 °C, 135 °C and 145 °C. A low shear rate range (less than 10 s^{-1}) was used for measurements on the parallel plate rheometer for all samples. This is due to the limitation of parallel plate viscometers for measuring high viscosity melts.

Results and discussion

The pure polymers

According to the rheology models, the torque and roller speed should fit a power law relation, i.e. $M = C{\cdot}N^n$. The torque–roller speed data for both sample 1 (PEBA-7) and sample 2 (EEA) do exhibit a power law relation. The torque measured for sample 2, at different roller speeds and temperatures, is plotted in Fig. 2 and shows a linear relation between the log(Torque) and log(N) at each temperature. Samples 1 and 2 both exhibited shear thinning or pseudoplastic behavior for the test temperatures and speed ranges tested, as the power law indices n are both less than 1. However, the power law index n, which indicates the departure from Newtonian behavior, increases with increasing temperature. This effect can be attributed to the chain entanglement. At higher temperatures, the chains in the random polymers have a higher thermal energy that leads to a more entangled state and increases the resistance to shear [17].

The torque and shear rate data from the parallel plate rheometer for EEA and PEBA-7 at 145 °C are plotted in Fig. 3. For PEBA-7, when the shear rate was less than 0.15 s^{-1}, the melt exhibited shear thinning behavior with n = 0.70, and when the shear rate was

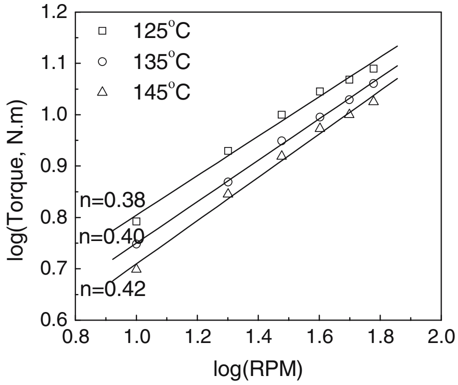


Fig. 2 log(Torque)-log(RPM) dependence at different temperatures for EEA measured on the Brabender torque rheometer

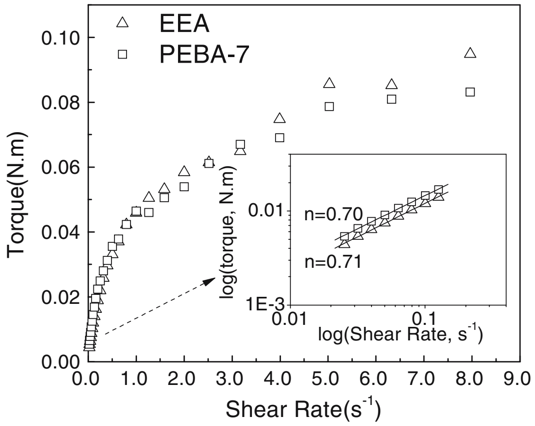


Fig. 3 The torque and shear rate dependence for EEA and PEBA-7 at 145 °C measured on parallel plate rheometer

above 0.15 s^{-1}, the melt exhibited shear thinning behavior with $n = 0.39$. For EEA, a similar transition exists. This transition is also due to the polymer's molecular structure. At very low shear rates, the thermal motion of the polymer chains dominate and the molecules are in a random and highly entangled state. They have relatively greater resistance to flow. As the shear rate is increased, the polymer chains begin to untangle and align. The alignment reduces the resistance to shear, and results in laminar flow [17]. The yield stress of these two polymers does exist, but is small.

The high shear rate portion (i.e., PEBA-7 at 145 °C, shear rate above 0.15 s^{-1}.) of the data from the parallel plate rheometer was used to calculate the power law index n and flow consistency index m. The power law index n was found to be close to the power law index n obtained from the Brabender torque rheometer, as shown in Table 3. Furthermore, using the n, m data from the parallel plate rheometer and N, M data from the torque rheometer, the effective radius R_i for the torque rheometer can be calculated from Eq. 1. Then using Eqs. 2 and 3, the viscosity and shear rate data can be obtained at each roller speed. From this log(viscosity)–log(shear rate) dependence, the power law index n and consistency index m for Bousmina's model could also be calculated. These latter results are also listed in Table 3 for comparison. For both the PEBA-7 and EEA samples, the modeling flow consistency index m data from the torque rheometer are close to the parallel plate rheometer data. It is interesting to note that the effective radius for these two polymers is quite close to Bousmina's result of 17.6 mm, although somewhat smaller. This could be due to the slight wear that has occurred in the chamber and rollers of this Brabender mixer after years of use. The measured viscosity from the parallel plate rheometer and the Brabender modeling viscosity is plotted in Fig. 4 (a) and (b) for EEA and PEBA-7, respectively. Due to the close value of m and n from parallel plate rheometer and Bousmina model, Bousmina's model fit well for pure polymer melts.

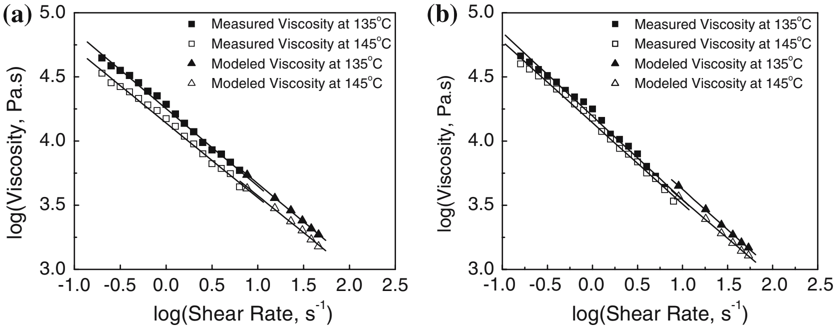
The ceramic/polymer mixtures

The torque measured for sample 5 at different roller rotation speeds and different temperatures is plotted in Fig. 5 and also shows a linear relation between log(Torque) and log(N) at any given temperature, much like the pure polymer samples. Figure 6 shows the torque at 145 °C for different solids loadings. The data from all three ceramic/polymer mixtures confirms the power law relation reported by Beeaff [3].

The power law indices n of samples 3, 4 and 5 at different temperatures are shown in Table 4. The three ceramic/polymer mixtures all exhibited shear thinning behavior as expected. The power law index n obtained from the samples is in the range of 0.30 ~ 0.38, and n increases with increasing temperature for the same solids loading, just like the pure polymers. Compared

Table 3 The measured n, m and modeling results for the pure polymer samples

Samples	Temp. (°C)	Parallel plate rheometer		Torque rheometer	R_i (mm)	Modeling data	
		n	log(m)	n		n	log(m)
#1 PEBA-7	135	0.37	4.188	0.37	17.64	0.37	4.243
	145	0.39	4.135	0.40	17.23	0.40	4.132
#2 EEA	135	0.39	4.234	0.40	17.01	0.40	4.238
	145	0.42	4.141	0.42	17.27	0.42	4.181



EEA PEBA-7

Fig. 4 log(viscosity)-log(shear rate) dependence with both measured data and calculated data

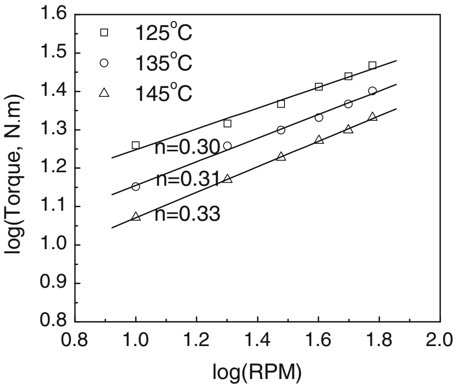


Fig. 5 log(Torque)-log(RPM) dependence at different temperatures for sample 5 measured on Brabender torque rheometer

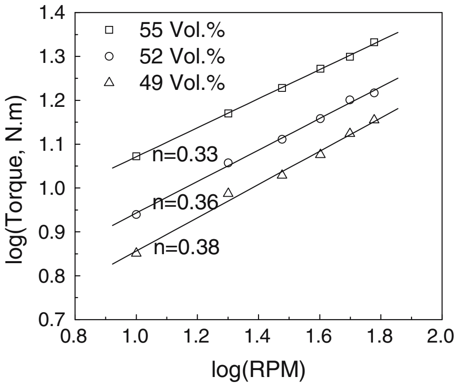


Fig. 6 log(Torque)-log(RPM) dependence for different solids loading at 145 °C measured on Brabender torque rheometer

to the pure EEA polymer, the power law index *n* of the ceramic/polymer mixtures is smaller at the same temperature and decreases with increasing solids loading at the same temperature. This effect could be due to two factors. First, the wax and HMO addition can act as an internal lubricant for the polymers during mixing. Second, it is easier to achieve laminar flow with the presence of the ceramic particles in the ceramic/polymer mixtures. When the particles are oriented by the laminar flow, the resistance to shear is known to be reduced [18].

Figure 7 shows the torque-shear rate dependence obtained from the parallel plate rheometer for sample 4 at 125 °C and 145 °C. Due to the presence of the ceramic particles in the polymers, the thermal motion of the polymer chains is no longer dominant. Sliding between the particles will occur with increasing shear rate and finally laminar flow will be in effect when the yield stress is overcome. Because of the mechanical interactions between the particles, all of the ceramic/polymer mixtures must overcome a yield stress to initiate flow. Thus, the yield stress increases with increasing solids loading, as shown in Fig. 8.

Table 4 Brabender measured *n* for samples 3, 4, and 5

Samples	125 °C	135 °C	145 °C
#3 (49 vol%)	0.34	0.36	0.38
#4 (52 vol%)	0.32	0.35	0.36
#5 (55 vol%)	0.30	0.31	0.33

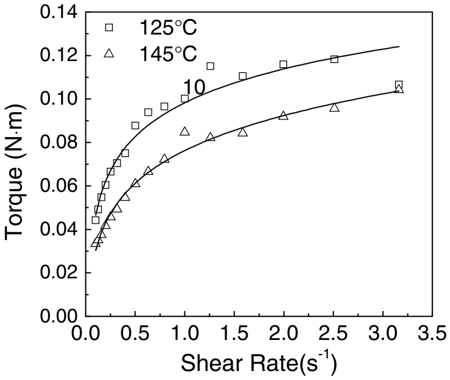


Fig. 7 Torque-shear rate dependence for sample 4 measured on parallel plate rheometer

The shear stress–shear rate dependence of a shear thinning fluid with yield stress can be expressed as:

$$\tau = \tau_0 + K \cdot \gamma^n \tag{4}$$

where τ_0 is the yield stress, K is a constant, γ is the shear rate, and n is the power law index. At the measuring temperatures, the yield stresses for all three samples were small, as shown in Fig. 8. Thus, these

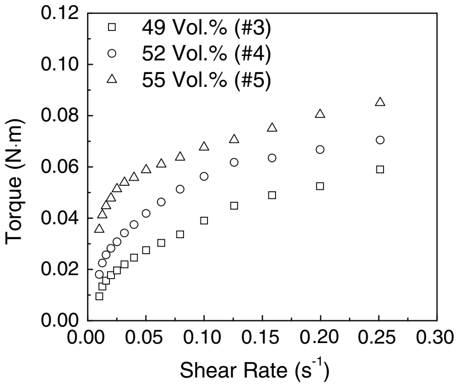


Fig. 8 Torque-shear rate dependence for samples measured on parallel plate rheometer at 125 °C

Table 5 The measured *n*, *m* and modeling results for samples 3, 4, and 5

Samples	Temp. (°C)	Parallel plate rheometer		Torque rheometer	R_i (mm)	$\overline{R}_i$ (mm)	Modeling data	
		n	log(*m*)	*n*			*n*	log(*m*)
#3 (49 vol%)	125	0.41	4.466	0.34	16.67	16.68	0.34	4.625
	145	0.46	4.269	0.38	16.68		0.38	4.448
#4 (52 vol%)	125	0.31	4.511	0.32	18.27	18.05	0.32	4.574
	145	0.35	4.384	0.36	17.82		0.36	4.371
#5 (55 vol%)	125	0.19	4.675	0.30	19.01	18.83	0.30	4.616
	145	0.20	4.467	0.33	18.65		0.33	4.411

samples were still treated as power law fluids for the remainder of the study. Using similar calculation methods as for the pure polymers (using the high shear rate portion of the parallel plate rheometer data), the power law index *n*, the melt consistency index *m*, and the effective equivalent internal radius R_i of the Brabender for each sample were calculated and are listed in Table 5. Using R_i, the modeled shear rates and viscosities were calculated from the Brabender's torque–roller rotational speed data using Bousmina's Eqs. 2 and 3. The power law indices *n* obtained from the model are no longer close to those obtained from the parallel plate rheometer, but the melt consistency indices still show good agreement. In addition, the effective radius again deviated from Bousmina's universal value of 17.6 mm.

Based on our results, we believe that the reason for the deviation is that Bousmina's model is based on Newtonian fluids although it fits for some pure polymers, which are non-Newtonian fluids without an apparent yield stress. However, for the ceramic/polymer mixtures presented in this study, exhibiting a yield stress, the log(torque)–log(shear rate) relation is not linear over the entire shear rate range, thus *n* and *m* are not constant. Only in the high shear rate range will the curve become close to linear. Even with the yield stress, all three ceramic/polymer mixtures exhibited the power law relations as shown in Fig. 6, because the torques were measured at the high shear rate range in the Brabender mixer.

Conclusions

The rheological behavior of pure polymer melts, and ceramic/polymer mixtures consisting of a 49 to 55 vol% solids loading of $BaTiO_3$ in polyehthylene-based block copolymers, was measured using a Brabender high shear mixer and a parallel plate rheometer. The mixtures were found to exhibit shear-thinning behavior with a yield stress. A power-law model was used to fit the data consistently for the Brabender mixer (torque rheometer) in the tested shear rate range. However, the torque–roller speed relation from the Brabender was found to be no longer equivalent to the shear stress–shear rate relation. The results also showed that Bousmina's model only fit well for the pure polymer melts. For the ceramic/polymer mixtures, large deviations from Bousmina's model were observed. Based on current studies, this is likely due to the mechanical interactions between the particles. For ceramic/polymer mixtures, a calibration would need to be developed in order to obtain the actual viscosities.

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