

11-1-2007

Rheology of Tin Fluorophosphate Glass/ Polyamide 12 Hybrids in the Low Concentration Regime

Kevin Urman

University of Southern Mississippi

Thomas Schweizer

ETH Zürich

Joshua U. Otaigbe

University of Southern Mississippi, joshua.otaigbe@usm.edu

Follow this and additional works at: http://aquila.usm.edu/fac_pubs

 Part of the [Chemistry Commons](#)

Recommended Citation

Urman, K., Schweizer, T., Otaigbe, J. U. (2007). Rheology of Tin Fluorophosphate Glass/Polyamide 12 Hybrids in the Low Concentration Regime. *Journal of Rheology*, 51(6), 1171-1187.

Available at: http://aquila.usm.edu/fac_pubs/1890

Rheology of tin fluorophosphate glass/polyamide 12 hybrids in the low concentration regime

Kevin Urman Thomas Schweizer Joshua U. Otaigbe

Citation: *J. Rheol.* **51**, (2007); doi: 10.1122/1.2789954

View online: <http://dx.doi.org/10.1122/1.2789954>

View Table of Contents: <http://sor.scitation.org/toc/jor/51/6>

Published by the [The Society of Rheology](#)

Rheology of tin fluorophosphate glass/polyamide 12 hybrids in the low concentration regime

Kevin Urman

*School of Polymers and High Performance Materials, 118 College Drive No. 10076,
University of Southern Mississippi, Hattiesburg, Mississippi 39406*

Thomas Schweizer

*Department of Materials, Polymer Physics, ETH Zürich,
CH-8093 Zurich, Switzerland*

Joshua U. Otaigbe^{a)}

*School of Polymers and High Performance Materials, 118 College Drive No. 10076,
University of Southern Mississippi, Hattiesburg, Mississippi 39406*

(Received 8 August 2006; final revision received 28 July 2007;
accepted 29 August 2007)

Synopsis

Phosphate glass (Pglass)/polymer hybrids are a unique material class that promises to help fulfill the growing need for new advanced materials. Rheological investigations into Pglass/polyamide 12 hybrids have shown a strong dependence on temperature and composition. Strong negative deviations from the log-additivity rule are also observed for these materials as well as a reduction in the activation energy for viscous flow. Hybrids containing <2 vol. % Pglass are rheologically simple fluids that display temperature independence in plots of storage modulus versus loss modulus. Hybrids containing ≥ 2 vol. % Pglass are rheologically complex and do not obey the time-temperature superposition principle. Through application of Han plots, we identified a structural change that occurs in hybrids containing ≥ 2 vol. % Pglass at temperatures in excess of 220 °C. This microstructural change induces an apparent yield stress in the material at these elevated temperatures. It is believed that the microstructural change is due to enhanced interactions that occur at elevated temperatures between the compatible pure components of the hybrids. © 2007 The Society of Rheology. [DOI: 10.1122/1.2789954]

I. INTRODUCTION

Polymer blends represent a rapidly growing area of polymer technology that is satisfying the material needs for a wide range of applications. This is driven by their cost effectiveness, as compared with synthesizing a new polymer and their ability to be designed via morphology control, pure component selection, and component interactions. Due to these factors, polymer blends are more adaptable than conventional polymer

^{a)} Author to whom correspondence should be addressed; electronic mail: joshua.otaigbe@usm.edu

composites that typically contain rigid, inorganic fillers. However, polymer composites have found a myriad of uses, especially in high stiffness applications.

A relatively new class of materials that combines the advantages of conventional polymer composites and blends without their disadvantages is inorganic/organic hybrids. One such hybrid is phosphate glass/polymer hybrids. These materials are mixtures of an ultralow glass transition (T_g) phosphate glass (Pglass) and an organic polymer. Phosphate glasses that display both water resistance and chemical durability are now readily available [Brow (1999); Sammler *et al.* (1996)]. One such Pglass is tin fluorophosphate glass, which has a T_g of about 125 °C and is known to be extremely resistant to water and chemical degradation [Tick (1983, 1984); Xu and Day (1990); Xu *et al.* (1995)]. Due to their low T_g , this phosphate glass is liquid over a range of temperatures that includes the melt processing temperature of many different polymers. Therefore, it is possible to blend these inorganic glasses with organic polymeric materials, using conventional processing methodologies, to yield hybrid materials containing Pglass loadings of up to 60% by volume or 90% by weight. Because both the organic polymer and inorganic Pglass are fluid during processing, the morphologies of these materials can be controlled, the interactions between components can be tailored, and the intractable viscosity problem inherent to conventional polymer composites at high solid filler (e.g., borosilicate glass) compositions is circumvented [Adalja and Otaigbe (2002); Uрман *et al.* (2006); Uрман and Otaigbe (2006); Uрман *et al.* (2007b)].

The rheological properties of a polymer blend play an important role in determining its final morphology. Rheology is also important in determining the processability of both polymer blends and composites. While these materials and their rheology have been widely studied, Pglass/polymer hybrid rheology has received relatively little attention. A number of researchers used zinc alkali phosphate glasses ($T_g > 272$ °C) as the Pglass for hybrid systems involving engineering thermoplastics with high flow temperatures [Otaigbe *et al.* (1998); Quinn *et al.* (1996); Young *et al.* (2000)]. For example, it has been shown that for the Xydar LCP hybrid system that the viscosity of the system, as compared to that of the pure LCP, increased only slightly at low shear rates and was unchanged at high shear rates [Quinn *et al.* (1996)]. It was also demonstrated that a variety of morphologies could be achieved [Quinn *et al.* (1996)]. The rheology of polyetherimide/Pglass hybrids was qualitatively examined through evaluation of its processing by Young and co-workers (2000). They found that the Pglass modified the flow behavior of the polyetherimide and enhanced the formability of the hybrid and its resultant properties [Young *et al.* (2000)]. Otaigbe and co-workers examined zinc alkali Pglass/LCP hybrids and zinc alkali/poly(ether ether ketone) hybrids. They determined that the thermorheological stability of the material depended on the polymer matrix and that the resultant morphologies depended on the processing history [Otaigbe *et al.* (1998)].

The effect of tin fluorophosphate glasses (TFP glass) on LDPE/Pglass hybrid rheology has also been reported elsewhere [Adalja and Otaigbe (2001, 2002); Adalja *et al.* (2001); Guschl *et al.* (2004); Guschl and Otaigbe (2003a, 2003b)]. Because TFP glasses have a T_g around 125 °C, they are able to be easily mixed with commodity plastics such as polyethylene. Adalja *et al.* (2001) examined the rheology of the pure TFP glass and found that the time-temperature superposition (TTs) principle applies to the glasses [Adalja and Otaigbe (2001)]. Additionally, these glasses display a steep dependence of viscosity on temperature and can crystallize at high shear rates and temperatures [Adalja and Otaigbe (2001)]. Adalja *et al.* also examined TFP/LDPE hybrid rheology and found that while the TTs principle applied to these materials, the Pglass induced strong shear thinning behavior and reduced creep strain in the solid state [Adalja and Otaigbe (2002); Adalja *et al.* (2001)]. They also successfully treated the Pglass with silane coupling agents that re-

sulted in an increase of the complex viscosity [Adalja and Otaigbe (2002); Adalja *et al.* (2001)]. Guschl *et al.* examined hybrids of LDPE, polystyrene (PS), and polypropylene (PP) and TFP glasses [Guschl *et al.* (2004); Guschl and Otaigbe (2003a, 2003b)]. Torque rheometry revealed a trend toward linear additivity for PS/TFP hybrids, and small amplitude oscillatory shear measurements were used to determine the phase inversion point for this hybrid system [Guschl *et al.* (2004)]. Guschl *et al.* also determined the interfacial tension between TFP glass and LDPE, PS, and PP [Guschl and Otaigbe (2003b)]. They compared pendant drop measurements with the Palierne and Choi and Schowalter emulsion models [Graebbling *et al.* (1993); Palierne (1990)]. These models fit the PS/TFP glass and PP/TFP glass hybrids with Pglass loadings up to 10 vol. %. However the models were found to be inadequate for hybrids containing more than 30 vol. % Pglass and for the LDPE hybrids at all TFP glass concentrations studied. Guschl *et al.* also examined steady shear and transient rheology of a ternary Pglass-PS-LDPE hybrid system [Guschl and Otaigbe (2003a)]. The rheological properties of the ternary hybrid depended strongly on Pglass concentration with hybrids at moderate Pglass loadings (>30 vol. %) displaying a flow behavior similar to that of liquid crystal polymers [Guschl and Otaigbe (2003a)].

The prior work on TFP glass/polymer hybrids has concentrated on nonpolar, noninteracting commodity resins. By extending this field into highly interacting commodity resins, such as nylons, new hybrids with very unique and interesting properties can be generated. This is due to the expected strong physiochemical interactions between the hybrid components. It has been shown that ammonia will adsorb to the surface of phosphate glasses [Hersh *et al.* (1995)]. This classical interaction facilitates a high degree of interaction between polyamide 6 and TFP glass, thereby encouraging both good compatibility in the melt and polymer/glass adhesion in the solid state [Urman and Otaigbe (2006)]. By using polyamide 12 instead of polyamide 6 in the hybrid system, the interactions between the Pglass and the functional groups along the polyamide backbone will be halved. This should lead to a material with good compatibility and interesting melt properties that reflect either an immiscible or a partially miscible system. To our knowledge, this is the first rheological study of TFP glass/polymer hybrids that display good and desirable interactions that are beneficial in a number of applications.

II. EXPERIMENTAL

A. Materials preparation

The low T_g TFP glass used in this study has a molar composition of 50% SnF₂ + 20% SnO + 30% P₂O₅. This results in a glass with a density of 3.75 g/cc and a T_g of 125.7 °C. The glass was synthesized in our laboratory using procedures reported elsewhere [Tick (1983)]. The tin fluoride and tin oxide were supplied by Cerac Inc., and the ammonium phosphate was supplied by Sigma-Aldrich. The polyamide 12 (Vestamid L1700) was supplied by Creanova Inc. The hybrids were prepared using a Thermo-Haake Polydrive Melt Mixer equipped with roller blades. Hybrids containing 1%, 2%, 5%, and 10% Pglass by volume were mixed at 220 °C with a rotor speed of 75 rpm for testing. The melt-mixed hybrid materials were collected in “chunks” from the Polydrive. The “chunks” were subsequently compression molded into plaques at 220 °C in a rectangular mold (126 mm × 63 mm × 3 mm) using a Tetrahedron compression molder.

B. Rheological measurements and SEM

Small disks (9 mm radius) were punched from the rectangular plaques for shear rheological measurements that were performed on a Paar-Physica UDS 200 at temperatures

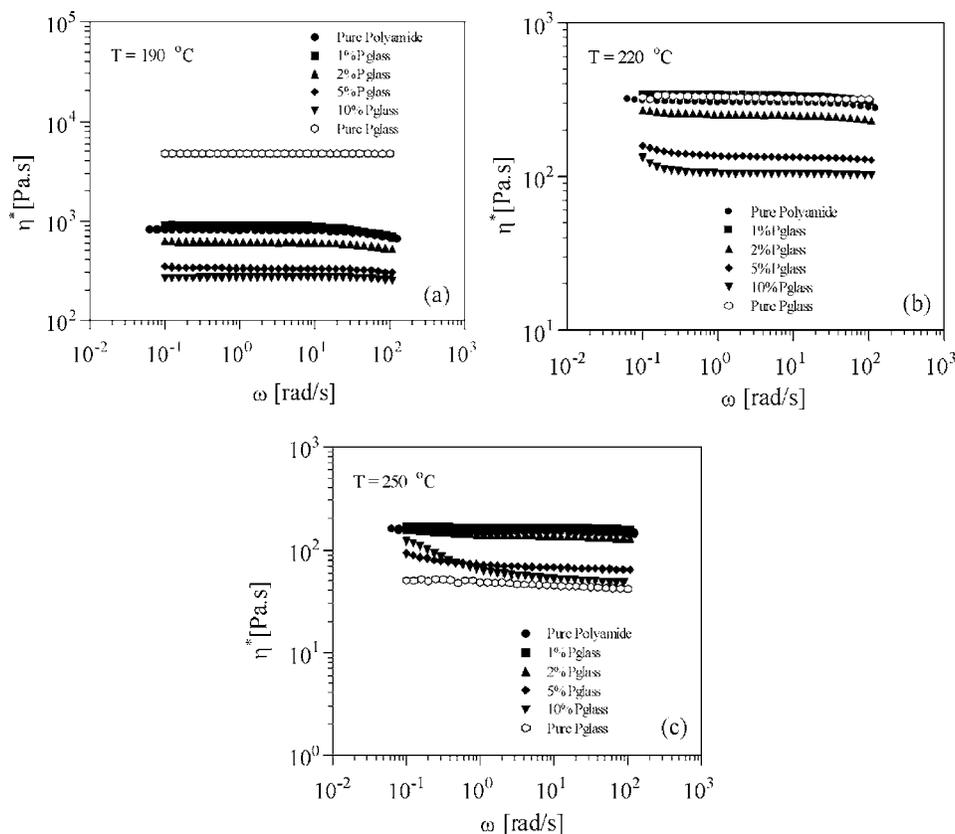


FIG. 1. Frequency dependence of the complex viscosity of polyamide 12 hybrids at (a) 190 °C, (b) 220 °C, and (c) 250 °C.

ranging from 190 °C to 250 °C using a cone and plate geometry according to standard procedures. Strain sweep tests were performed on the hybrids to determine the linear viscoelastic region, and a linear strain of 10% was used for all small amplitude oscillatory shear tests. A TA Instruments ARES equipped with cone and plate tools was used to measure the complex viscosity of the Pglass under small amplitude oscillatory shear flow at 190 °C, 220 °C, and 250 °C. A strain of 2%, which is well within the linear viscoelastic region, was used to perform the frequency sweeps on the pure Pglass. The rheology of the pure TFP glass has been previously reported [Adalja and Otaigbe (2001)] and is not the focus of this article. The morphology of the hybrids was examined using a FEI Quanta 200 SEM. Samples of the compression molded plaques were cryotomed and subsequently gold sputtered prior to microscopy.

III. RESULTS AND DISCUSSION

A. Complex viscosity and yield stress behavior

Figure 1 displays the frequency dependence of the complex viscosity for the hybrid materials at 190 °C, 220 °C, and 250 °C. Over the whole range of temperatures studied, the pure Pglass behaves as a Newtonian fluid. Due to rheometer limitations, the extremely low viscosity of the pure Pglass at 250 °C causes some scatter in the observed data. At 190 °C, the pure polyamide 12 and all of the hybrids display a long Newtonian

region with some slight shear thinning behavior at high frequency. Additionally, despite the high viscosity of the pure Pglass, at this temperature, hybrids containing ≥ 2 vol. % Pglass show a dramatic decrease in viscosity, suggesting a plausible constraint release or disruption of the polymer chain entanglements caused by the addition of Pglass. This finding is somewhat similar to the non-Einstein-like decrease in viscosity of polystyrene filled with nanoscale particles reported by Mackay and co-workers [Mackay *et al.* (2003); Tuteja *et al.* (2005)]. This behavior changes as the testing temperature is increased to 220 °C. Hybrids containing >5 vol. % Pglass begin to show an increase in complex viscosity at low frequencies at this temperature. The increase of the complex viscosity becomes more pronounced as the temperature is further increased. An increase in complex viscosity at low frequencies is often attributed to interfacial effects and yield stress behavior [Gramespacher and Meissner (1992); Moan *et al.* (2000); Nandan *et al.* (2004)]. Above a critical composition of 2 vol. % Pglass, a dramatic change in the interfacial characteristics of the hybrid occurs at elevated temperatures.

Using the complex viscosity data, the activation energy of flow can be determined for the pure components and the hybrids using an Arrhenius type equation:

$$\eta = A \exp\left(\frac{-E_a}{RT}\right). \quad (1)$$

In this equation, η is the steady shear viscosity at a given shear rate, A is a pre-exponential constant, E_a is the activation energy for viscous flow, R is the universal gas constant, and T is the absolute temperature. E_a can be calculated from the slope of a plot of the $\log(\eta)$ versus $(1/T)$. This equation strictly requires a steady shear viscosity, but it is possible to use the complex viscosity if it is assumed that the Cox–Merz rule applies to these materials [Cox and Merz (1958); Nandan *et al.* (2004)]. It has been shown by other researchers that the Cox–Merz rule is applicable to pure nylon 12, and it is assumed that it will apply to the hybrids at the low concentrations studied as well [Huitric *et al.* (1998)]. The E_a was calculated at two different frequencies, 0.5 and 50 rad/s, and the results of this calculation are shown in Fig. 2. Similar results were found at both frequencies, indicating that despite the high flow activation energy of the pure Pglass, the hybrids generally displayed lower activation energy of flow as compared with the pure polyamide 12. While E_a is not often reported in the literature as a function of composition and its full significance in hybrid rheology is not yet clear, we hypothesize that the lowering of flow activation energy in the hybrids is due to good compatibility between the components [Ausin *et al.* (1987); Schmidt (1979); Utracki and Kamal (1982)]. Future proposed studies will test this hypothesis via dielectric spectroscopy and NMR [Urman and Otaigbe (2007); Urman *et al.* (2007a); Rawal *et al.* (2006)].

Further evidence of compatibility of the hybrid systems in the melt can be seen when the logarithm of the complex viscosity is plotted as a function of Pglass concentration (Fig. 3). The lines shown in Fig. 3 represent attempts to fit the viscosity of the hybrids using the log-additivity rule:

$$\log \eta_h = \phi \log \eta_p + (1 - \phi) \log \eta_g. \quad (2)$$

In Eq. (2), η_h is the calculated hybrid viscosity, ϕ is the volume fraction of polyamide 12 in the hybrid, η_p is the viscosity of the pure polyamide 12, and η_g is the viscosity of the pure Pglass. The log-additivity rule is often used to classify immiscible blends, but the full significance of this rule is still under debate [Fang *et al.* (2005); Nandan *et al.* (2004); O'Conner and Orlor (1988); Supaphol *et al.* (2004)]. Adherence to the log-additivity rule is sometimes taken to indicate miscibility between phases in the melt state,

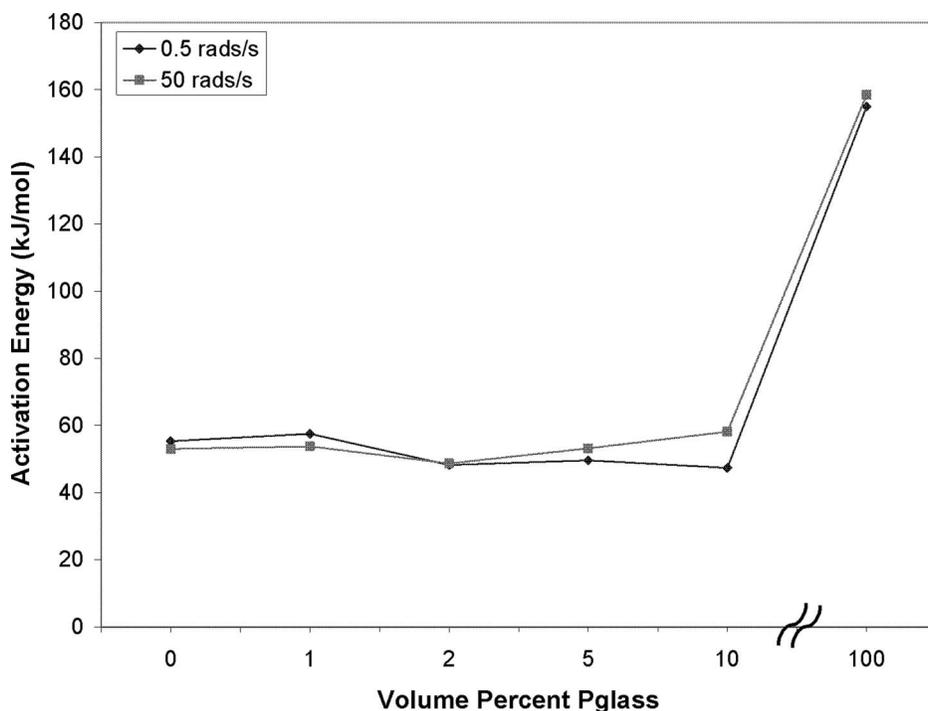


FIG. 2. Activation energy of viscous flow as a function of composition for polyamide 12 hybrids (lines are guides for the eyes).

while positive deviation is usually associated with immiscible polymers, and negative deviation is expected for compatible polymers. From Fig. 3, it is seen that the log-additivity rule fits the hybrid viscosities up to 1 vol. % Pglass for both frequencies. Higher concentrations of Pglass led to negative deviation from the log-additivity rule. However, the magnitude of the negative deviation decreases as the temperature is increased, which is indicative of enhanced interactions between the components.

The previously discussed rise in the complex viscosity at low frequencies observed for the 5 and 10 vol. % Pglass hybrids has been related to the appearance of an apparent yield stress in the material [Jafari *et al.* (2002)]. Early attempts to describe a yield stress did not allow any elastic behavior below the yield stress, but this was found to be an oversimplification for many material systems [Doraiswamy *et al.* (1991)]. It has been shown that plotting complex viscosity versus complex modulus indicates an apparent yield stress in a material system by an upturn in the graph at low complex modulus values [Nandan *et al.* (2004); Yoshikawa *et al.* (1994)]. Figure 4 displays such plots for the hybrid systems at 190 °C and 250 °C. At 190 °C, all of the hybrids tend to approach constant $\eta^*(\omega)$ at low $G^*(\omega)$, implying that these hybrids display Newtonian behavior at low frequencies with no evidence of the possible existence of a yield stress. However, as the temperature is increased, a sharp upturn of the graph is observed for hybrids containing ≥ 5 vol. % Pglass, suggesting that these hybrid compositions have a yield stress for viscous flow. Apparent yield stresses have been reported in the literature for some immiscible polymer blends and are usually attributed to strong interactions between the components [Feldstein *et al.* (2006); Nandan *et al.* (2004); Pavlinek and Saha (1999); Yoshikawa *et al.* (1994)].

Yield stresses have been observed for many different polymer composites and nano-

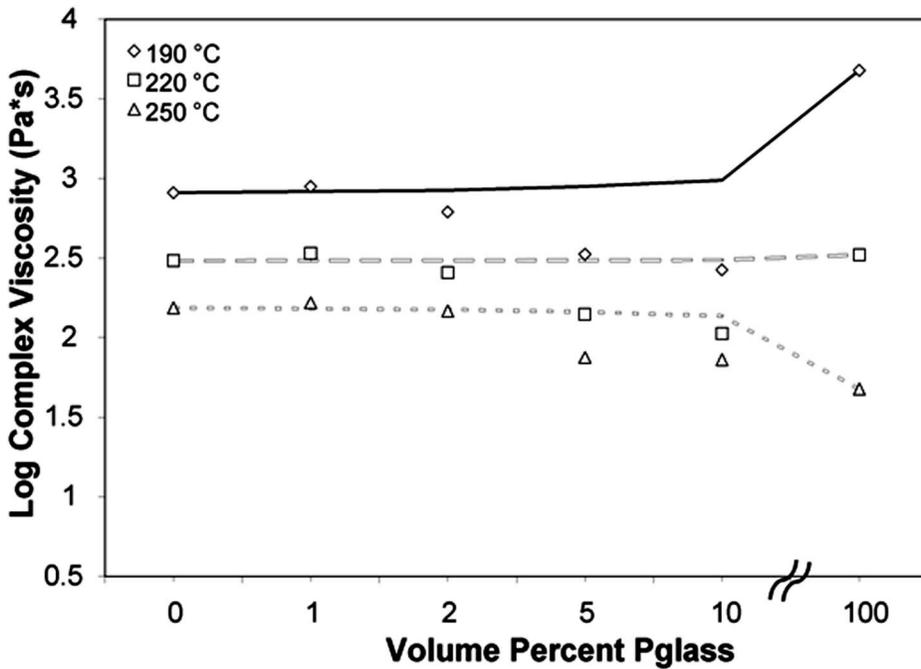


FIG. 3. Log of the complex viscosity as a function of composition at select temperatures (lines show fits of the log-additivity rule).

composite systems at high concentrations of filler and are typically ascribed to the formation of some filler network or aggregates in the polymer melt [Aubry *et al.* (2005); Osman and Atalah (2004); Park and Kyu (1989)]. Evidence of such a yield stress can be observed by examining the change in slope of the storage or loss modulus as a function of frequency. A reduction of the slope in the terminal region has been observed for polyamide 12/clay nanocomposites and was related to the tendency of the silicate platelets to form a superstructure and display a yield stress [Hoffmann *et al.* (2000)]. Figure 5 displays the loss modulus of the studied materials at 250 °C and Table I lists the slopes of the linear portion of the curves at both 190 °C and 250 °C. The slopes displayed by the materials at 190 °C are typical for polydisperse polymers and do not indicate any yield stress behavior [Eckstein *et al.* (1997); Hoffmann *et al.* (2000)]. As the temperature is increased to 250 °C, hybrids containing ≥ 5 vol. % Pglass show a dramatic decrease in the slope, similar to that observed for the polyamide 12/clay nanocomposite. Unlike the silicate nanofillers, the Pglass is fluid at these temperatures. However, it is still likely that dispersed Pglass can interact with itself to form some kind of superstructure that leads to yield stress behavior as will be shown later. The yield stress behavior observed for the hybrids is consistent with the previously discussed rheological data, which indicates that increasing temperature causes a morphological change in the higher Pglass concentration hybrids and an associated enhancement of the interactions between the polyamide 12 and the Pglass.

B. Viscoelastic moduli as a function of temperature and composition

The effect of temperature on the rheological behavior of the hybrids can be further probed using plots of storage modulus (G') versus loss modulus (G''). These plots were

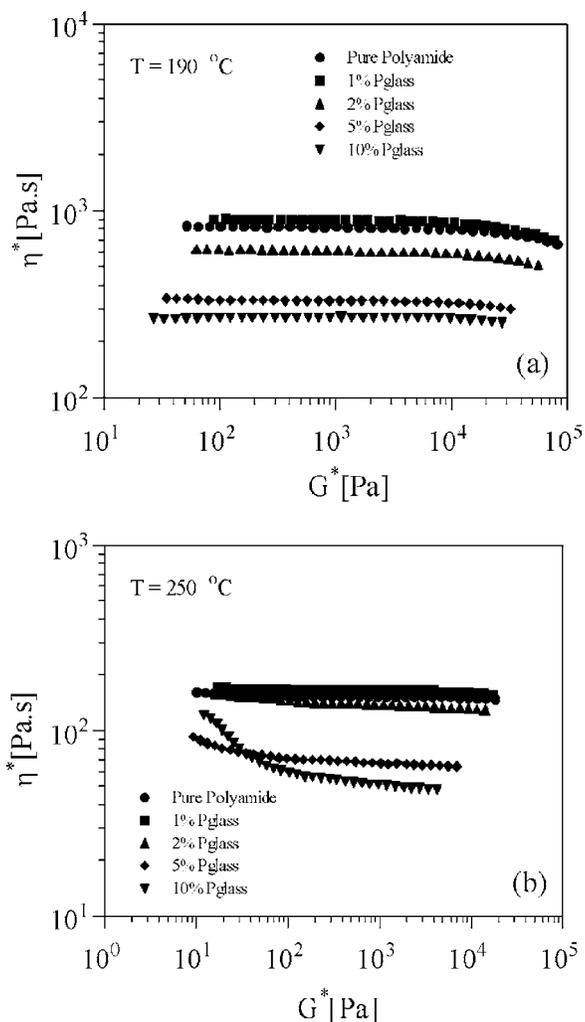


FIG. 4. Complex viscosity vs complex modulus for pure polyamide 12 and studied hybrids at (a) 190 °C and (b) 250 °C.

first developed by Han and co-workers and have been widely used in the literature to investigate the compatibility, morphological development, and temperature dependence (or independence) of polymer blends [Han and Chuang (1985); Jafari *et al.* (2002); Khonakdar *et al.* (2005); Nandan *et al.* (2004); Zarraga *et al.* (2000)]. The temperature independence of a Han plot is a necessary condition for time-temperature superposition to apply to a material. However, materials that display temperature-independent Han plots do not necessarily have to superimpose. Figure 6 displays the Han plots for pure polyamide 12 and the hybrids over a range of temperatures. Temperature independence is observed for the pure polyamide 12 and the hybrid containing 1 vol. % Pglass. A small amount of scatter is seen at low moduli values and is attributed to rheometer limitations. Temperature independence for immiscible blends has been reported in the literature and for the 1 vol. % hybrid indicates good compatibility between the phases and a microstructure that is unaffected by temperature [Jafari *et al.* (2002); Khonakdar *et al.* (2005); Zarraga *et al.* (2000)]. As the volume percent of Pglass is increased in the system, the

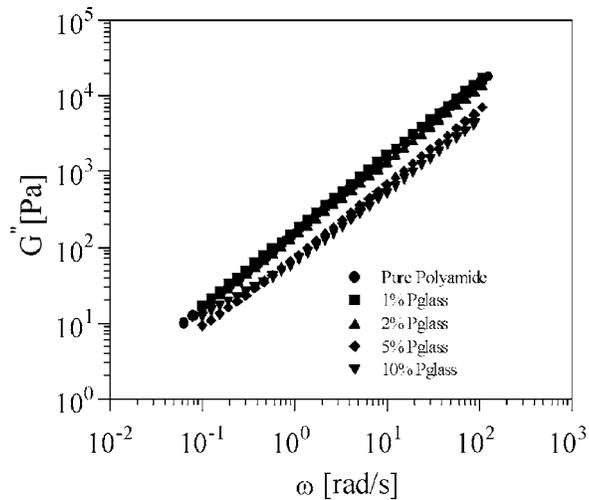


FIG. 5. Loss modulus of pure polyamide 12 and studied hybrid materials at 250 °C.

temperature independence of the Han plots breaks down. Upon closer examination, it can be seen that the breakdown occurs at 220 °C, and the deviation from temperature independence increases with increasing Pglass content. Some microstructural change must be occurring at this temperature, which results in a change in the rheological behavior of hybrids containing >2 vol. % Pglass. Time-temperature superposition was attempted for all of the studied materials (Fig. 7) and it was found that hybrids containing ≤ 1 vol. % Pglass superimpose very well and behave as rheologically simple fluids. For hybrids containing >1 vol. % Pglass, time-temperature superposition failed, and therefore these materials are rheologically complex. The onset of rheological complexity at a certain temperature has been related to changes in the phase behavior of polymer blends, which is accompanied by morphological changes due to coalescence or the formation of a single phase [Sharma and Clarke (2004)].

Researchers have also found it useful to compare different compositions of a blend at a single temperature using a Han plot [Khonakdar *et al.* (2005); Nandan *et al.* (2004)]. Figure 8 displays the Han plots of the pure polyamide 12 and the hybrids at 190 °C, 220 °C, and 250 °C. At 190 °C, all of the hybrids show a compositional independence, which has been shown to indicate a similar morphological state and good compatibility between the phases [Khonakdar *et al.* (2005)]. When the temperature is increased to 220 °C, compositional independence over the studied range no longer exists. However, a closer examination of Fig. 8(b) reveals that hybrids containing ≤ 2 vol. % Pglass still

TABLE I. Slope of the loss modulus in the terminal region.

Volume Percent Pglass	Slope of G'' at 190 °C	Slope of G'' at 250 °C
0	0.99	1.00
1	0.99	0.97
2	1.00	0.97
5	0.99	0.89
10	1.00	0.68

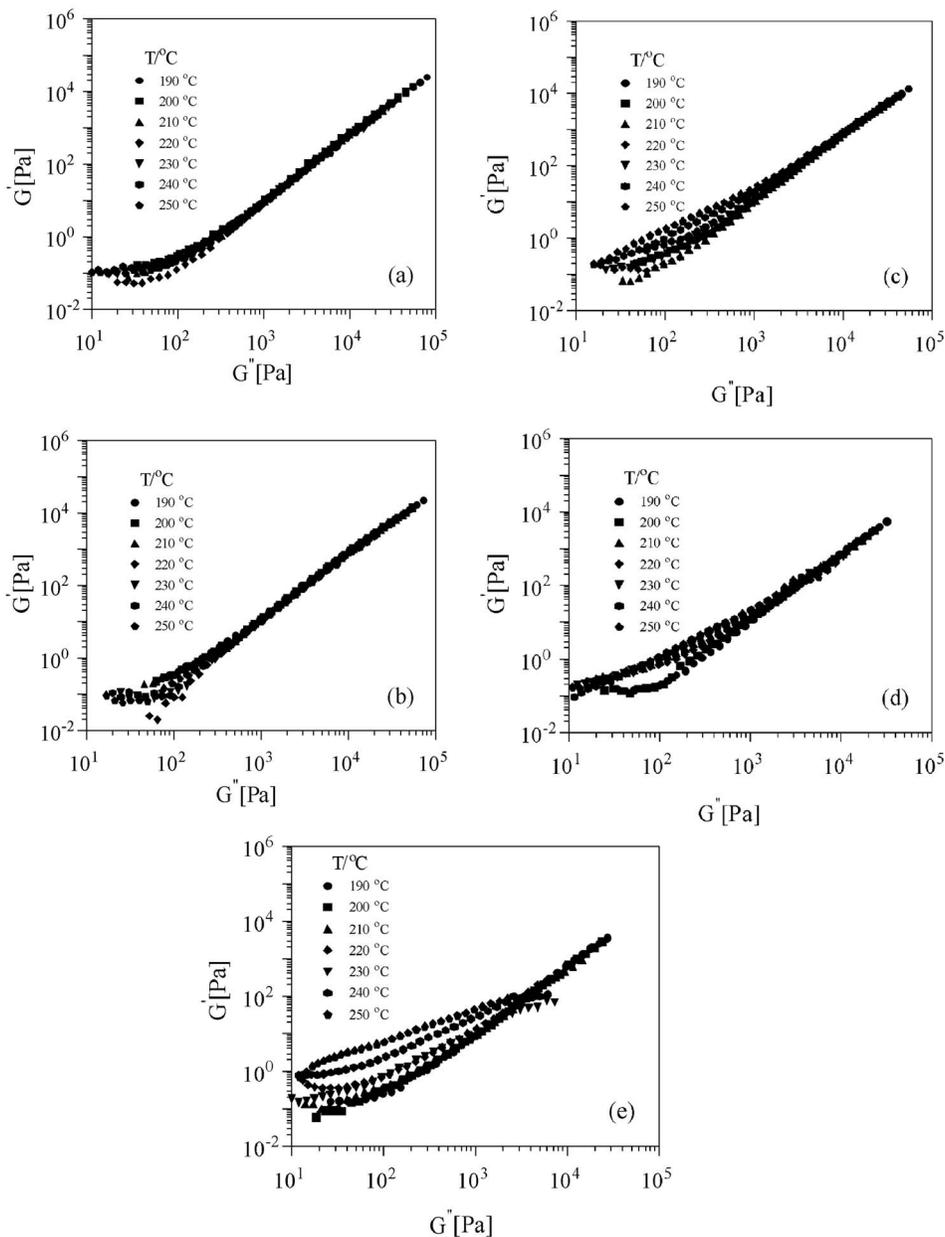


FIG. 6. Storage modulus vs loss modulus at various temperatures for (a) pure polyamide 12 and hybrids containing (b) 1, (c) 2, (d) 5, and (e) 10 vol. % Pglass.

display a compositional independence with each other. Additionally, hybrids with >2 vol. % Pglass display compositional independence. When the temperature is further increased to 250 °C, compositional independence is completely eliminated. This break in the compositional independence is believed to be due to a morphological change caused by the increasing temperature. We conjecture that elevated temperatures increase the compatibility of the phases, leading to a partially miscible material in the melt state and a change in the overall morphology of the material.

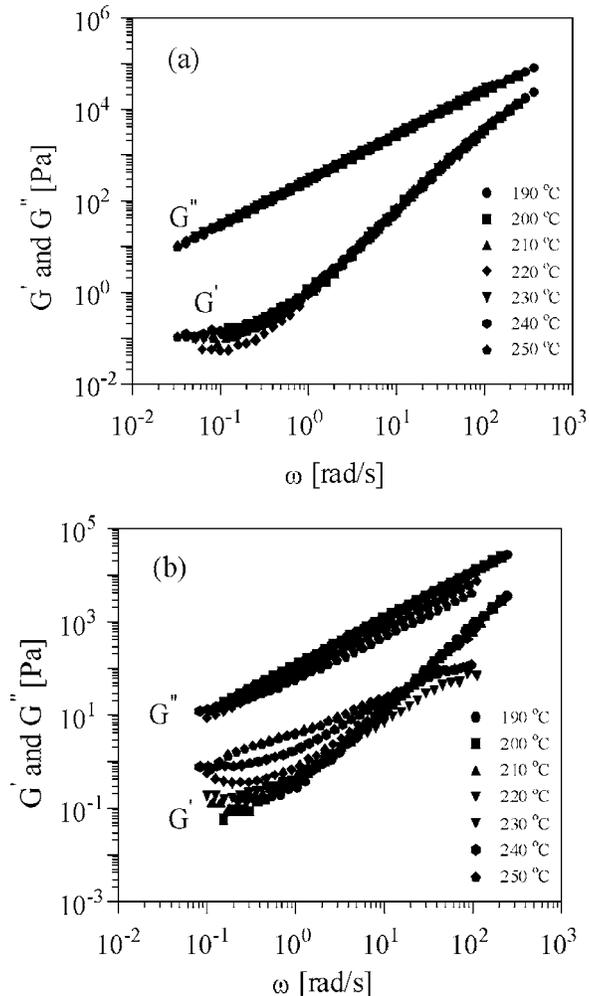


FIG. 7. Time-temperature superposition for (a) pure polyamide 12 and (b) hybrid containing 10 vol. % Pglass (data for other compositions available but not shown).

C. Morphological analysis and comparison of experimental data with an emulsion model

Figure 9 displays SEM micrographs of the hybrids taken before rheological measurements were performed. The Pglass is dispersed as small droplets within the polyamide 12 matrix and the average diameter of the particles is given in Table II. Attempts were made to freeze in the morphology of the hybrids immediately after rheological testing for post testing morphological analysis, but due to the low viscosity of the materials and fast relaxation times, such pictures (not shown) were featureless and showed no effect of shear. Using the droplet size calculated from Fig. 9, the applicability of the Palierne emulsion model to this system can be determined and an interfacial tension estimated [Graebling *et al.* (1993); Palierne (1990)]. The Palierne emulsion model has been used extensively in the literature by many different researchers on many different systems to estimate either the size of a dispersed phase or the interfacial tension between components [Choi *et al.* (2002); Fang *et al.* (2005); Graebling *et al.* (1993); Jafari *et al.* (2005)].

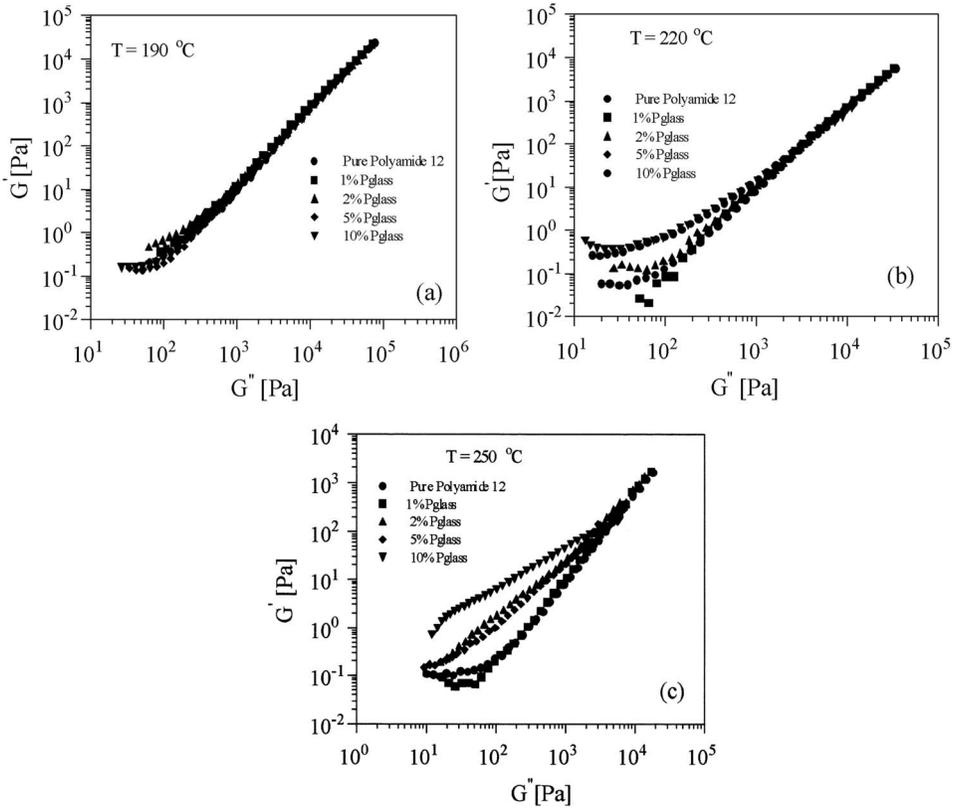


FIG. 8. Storage modulus vs loss modulus for pure polyamide 12 and studied hybrids at (a) 190 °C, (b) 220 °C, and (c) 250 °C.

The Palierne model [Eq. (3)] expresses the complex modulus of an emulsion where the dispersed phase is spherical in terms of the phases, interfacial tension, volume fraction, and radius of the dispersed phase:

$$G^* = G_c^* \left(\frac{1 + 3\phi H}{1 - 2\phi H} \right). \tag{3}$$

In Eq. (3) G^* is the complex modulus of the emulsion, G_c^* is the complex modulus of the continuous phase, ϕ is the volume fraction of the dispersed phase, and H is defined as follows:

$$H = \frac{(G_d^* - G_c^*)(19G_d^* + 16G_c^*) + \frac{4\gamma_{12}}{r_d}(2G_d^* + 5G_c^*)}{(2G_d^* + 3G_c^*)(19G_d^* + 16G_c^*) + \frac{40\gamma_{12}}{r_d}(G_d^* + G_c^*)}. \tag{4}$$

In Eq. (4), G_d^* is the complex modulus of the dispersed phase, r_d is the radius of the dispersed droplets, and γ_{12} is the interfacial tension between the phases. From the small amplitude oscillatory shear tests that were performed on the samples and from the micrographs, all of the variables in Eqs. (3) and (4) are experimentally determined except for the interfacial tension. Therefore, if the model provides a good fit to the data, an

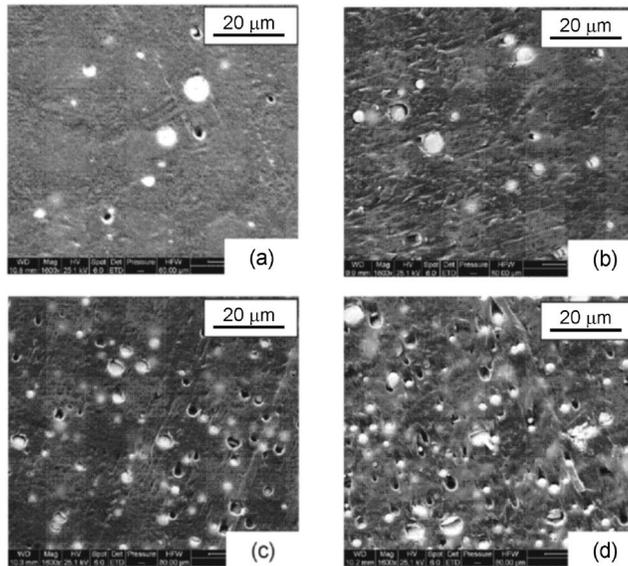


FIG. 9. Micrographs of (a) 1 vol. % P-glass, (b) 2 vol. % P-glass, (c) 5 vol. % P-glass, and (d) 10 vol. % P-glass hybrids.

estimation of the interfacial tension can be made. Figure 10 displays attempts to fit the Palierne model to the storage modulus of the hybrid containing 10 vol. % P-glass at 190 °C and 250 °C. The model does not provide an adequate fit of the data at 190 °C. This is most likely due to the strong negative deviations from the log-additivity rule at this temperature as already discussed. Since the hybrids display a much lower complex viscosity than either of the pure components, the model is unable to successfully predict the viscoelastic behavior of the hybrid. However, the model accurately predicts the storage modulus behavior at 250 °C using a value of 0.002 for the quantity of γ_{12}/r_d . Using the average radius of a P-glass droplet found in the 10 vol. % hybrid, an interfacial tension of 1.69 nNm is calculated. This extraordinarily small value indicates the very favorable interaction that take place in this material at elevated temperatures. It also gives further support for the argument that the polyamide 12 and the P-glass phases display improved compatibility at higher temperatures.

IV. CONCLUSIONS

P-glass/polymer hybrids are a unique class of materials that continue to intrigue researchers with their interesting and often counterintuitive behaviors such as the remark-

TABLE II. Average size of P-glass droplets in the polyamide matrix.

Volume Percent P-glass	Average Diameter (μm)
1	5.06 ± 2.553
2	3.18 ± 1.303
5	2.09 ± 0.658
10	1.69 ± 0.236

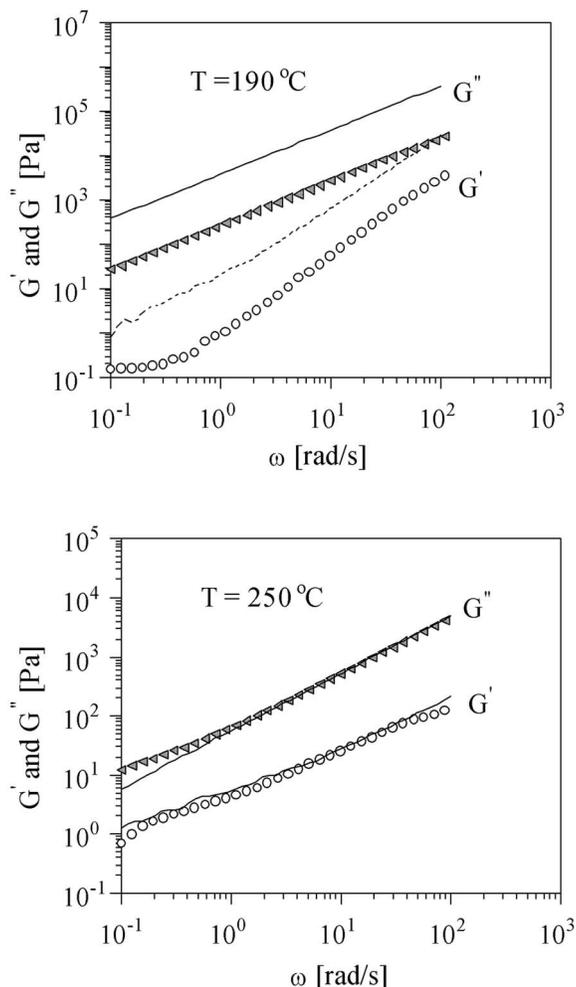


FIG. 10. Fit of the Paliérne model to the storage modulus of the hybrid containing 10 vol. % Pglass at 190 °C (top) and 250 °C (bottom). The lines are the Paliérne model fits to the experimental data (symbols).

able viscosity decrease of the polymer caused by the addition of Pglass. The combination of a melt-processable, inorganic glass with an organic polymer allows for the creation of a material with “tunable” morphologies and extraordinary properties, which are due to favorable interaction between the phases and molecular-level (i.e., single phase) mixing that occurs during processing. Rheological investigations into Pglass/polyamide 12 hybrids have shown a strong dependence on temperature and composition. The addition of Pglass to the polyamide 12 matrix results in an activation energy of flow that is less than that of both of the pure components. Strong negative deviations from the log-additivity rule are also observed for these materials. Hybrids containing <2 vol. % Pglass are rheologically simple fluids that obey the time-temperature superposition principle and display temperature independence in plots of storage modulus versus loss modulus. Hybrids containing ≥ 2 vol. % Pglass are rheologically complex and do not obey the time-temperature superposition principle. Through application of Han plots, we were able to conclude that the hybrid materials were very compatible, and we identified a structural

change that occurs in hybrids containing ≥ 2 vol. % Pglass at temperatures in excess of 220 °C. This microstructural change has a further impact on the hybrid rheology in that it induces an apparent yield stress in the material at these elevated temperatures. It is believed that the microstructural change is due to enhanced interactions between the pure components. Future and ongoing research into these materials continues to uncover the unique properties and potential of Pglass/polymer hybrids. The results presented in this article both extend the small body of work on Pglass/polymer hybrid rheology and provide the basis for further experimental and theoretical work that will help hybrid materials reach their full potential. Further, the results point to a facile strategy and the versatile route to new polymeric materials that may be ideal model systems for a better understanding of the effects of particle size and interactions between the components on the rheological behavior of multicomponent polymeric materials.

ACKNOWLEDGMENTS

This work was primarily supported by the Office of International Science and Engineering and the Division of Materials Research Programs of the U.S. National Science Foundation under Award Nos. OISE 0436384 and DMR 0309115, respectively, and by the Hearin Foundation for graduate student fellowship support to K. Urman. The authors thank Professor Hans Christian Öttinger's research group at ETH, Zurich for their support during K. Urman's extended visiting graduate research assistantship at ETH. The research work of J. Otaigbe's former graduate students and postdocs is gratefully acknowledged.

References

- Adalja, S. B., and J. U. Otaigbe, "Creep and recovery behavior of novel organic-inorganic polymer hybrids," *Polym. Compos.* **23**, 171–181 (2002).
- Adalja, S. B., and J. U. Otaigbe, "Melt rheology of tin phosphate glasses," *Appl. Rheol.* **11**, 10–18 (2001).
- Adalja, S. B., J. U. Otaigbe, and J. Thalacker, "Glass-polymer melt hybrids. I: Viscoelastic properties of novel affordable organic-inorganic polymer hybrids," *Polym. Eng. Sci.* **41**, 1055–1067 (2001).
- Aubry, T., T. Razafinimaro, and P. Mederic, "Rheological investigation of the melt state elastic and yield properties of a polyamide-12 layered silicate nanocomposite," *J. Rheol.* **49**, 425–440 (2005).
- Ausin, A., I. Eguiazabal, M. E. Munoz, J. J. Pena, and A. Santamaria, "Melt rheology of polyarylate/polybutylene terephthalate blends," *Polym. Eng. Sci.* **27**, 529–534 (1987).
- Brow, R. K., Review: The structure of simple phosphate glasses, in *Structure, Properties and Applications of Phosphate and Phosphate-Containing Glasses* (Elsevier, Danvers, Massachusetts, 1997).
- Choi, G.-Y., H.-G. Kim, Y.-H. Kim, C.-W. Seo, J.-H. Choi, D.-H. Han, D.-H. Oh, and K.-E. Min, "The rheological behavior of immiscible polymer-blends," *J. Appl. Polym. Sci.* **86**, 917–924 (2002).
- Cox, W. P., and E. H. Merz, "Correlation of dynamic and steady flow viscosities," *J. Polym. Sci.* **28**, 619–622 (1958).
- Doraiswamy, D., A. N. Mujumdar, I. Tsao, A. N. Beris, S. C. Danforth, and A. B. Metzner, "The Cox–Merz rule extended: A rheological model for concentrated suspensions and other materials with a yield stress," *J. Rheol.* **35**, 647–685 (1991).
- Eckstein, A., C. Friedrich, A. Lobbrecht, R. Spitz, and R. Muelhaupt, "Comparison of the viscoelastic properties of syndio- and isotactic polypropylenes," *Acta Polym.* **48**, 41–46 (1997).
- Fang, Y., J. Carreau, and P. G. Lafleur, "Thermal and rheological properties of mLLDPE/LDPE blends," *Polym. Eng. Sci.* **45**, 1254–1264 (2005).
- Feldstein, M. M., V. G. Kulichikhin, S. V. Kotomin, T. A. Borodulina, M. B. Novikov, A. Roos, and C. Creton, "Rheology of Poly(N-vinyl pyrrolidone)-Poly(ethylene glycol) adhesive blends under shear flow," *J. Appl. Polym. Sci.* **100**, 522–537 (2006).

- Graebing, D., R. Muller, and J. F. Palierne, "Linear viscoelastic behavior of some incompatible polymer blends in the melt. Interpretation of data with a model of emulsion of viscoelastic liquids," *Macromolecules* **26**, 320–329 (1993).
- Gramespacher, H., and J. Meissner, "Interfacial tension between polymer melts measured by shear oscillations of their blends," *J. Rheol.* **36**, 1127–1141 (1992).
- Guschl, P., J. U. Otaigbe, and C.-K. Loong, "Investigation of phase behavior during melt processing of novel inorganic-organic polymer hybrid material," *Polym. Eng. Sci.* **44**, 1692–1701 (2004).
- Guschl, P. C., and J. Otaigbe, "An experimental study of morphology and rheology of ternary Pglass-PS-LDPE hybrids," *Polym. Eng. Sci.* **43**, 1180–1196 (2003a).
- Guschl, P. C., and J. U. Otaigbe, "Experimental observation and prediction of interfacial tension and viscoelastic emulsion model behavior in novel phosphate glass-polymer hybrids," *J. Colloid Interface Sci.* **266**, 82–92 (2003b).
- Han, C. D., and H. Chuang, "Criteria for rheological compatibility of polymer blends," *J. Appl. Polym. Sci.* **30**, 4431–4454 (1985).
- Hersh, L. S., E. C. Onyiriuka, and W. Hertl, "Amine-reactive surface chemistry of zinc phosphate glasses," *J. Mater. Res.* **10**, 2120–2127 (1995).
- Hoffmann, B., J. Kressler, G. Stoppelmann, C. Friedrich, and G.-M. Kim, "Rheology of nanocomposites based on layered silicates and polyamide 12," *Colloid Polym. Sci.* **278**, 629–636 (2000).
- Huitric, J., P. Mederic, M. Moan, and J. Jarrin, "Influence of composition and morphology on rheological properties of polyethylene/polyamide blends," *Polymer* **39**, 4849–4856 (1998).
- Jafari, S. H., P. Potschke, M. Stephan, H. Warth, and H. Alberts, "Multicomponent blends based on polyamide 6 and styrenic polymers: Morphology and melt rheology," *Polymer* **43**, 6985–6992 (2002).
- Jafari, S. H., A. Yavari, A. Asadinezhad, H. A. Khonakdar, and F. Bohme, "Correlation of morphology and rheological response of interfacially modified PTT/m-LLDPE blends with varying extent of modification," *Polymer* **46**, 5082–5093 (2005).
- Khonakdar, H. A., S. H. Jafari, A. Yavari, A. Asadinezhad, and U. Wagenknecht, "Rheology, morphology, and estimation of interfacial tension of LDPE/EVA and HDPE/EVA blends," *Polym. Bull. (Berlin)* **54**, 75–84 (2005).
- Mackay, M. E., T. T. Dao, A. Tuteja, D. L. Ho, B. Van Horn, H.-C. Kim, and C. J. Hawker, "Nanoscale effects leading to non-Einstein-like decrease in viscosity," *Nat. Mater.* **2**, 762–766 (2003).
- Moan, M., J. Huitric, M. Mederic, and J. Jarrin, "Rheological properties and reactive compatibilization of immiscible polymer blends," *J. Rheol.* **44**, 1227–1245 (2000).
- Nandan, B., L. D. Kandpal, and G. N. Mathur, "Poly(ether ether ketone)/Poly(aryl ether sulfone) blends: Melt rheological behavior," *J. Polym. Sci., Part B: Polym. Phys.* **42**, 1548–1563 (2004).
- O'Conner, K. M., and E. B. Orlor, "Thermal, dynamic mechanical, and rheological behavior of linear low-density Polyethylene/Poly(Octadecene-Co-Maleic Anhydride) blends," *Polym. Eng. Sci.* **28**, 1132–1141 (1988).
- Osman, M. A., and A. Atallah, "High-density Polyethylene Micro- and Nanocomposites: Effect of particle shape, size and surface treatment on polymer crystallinity and gas permeability," *Macromol. Rapid Commun.* **25**, 1540–1544 (2004).
- Otaigbe, J. U., C. J. Quinn, and G. H. Beall, "Processability and properties of novel glass-polymer melt blends," *Polym. Compos.* **19**, 18–22 (1998).
- Palierne, J. F., "Linear rheology of viscoelastic emulsions with interfacial tension," *Rheol. Acta* **29**, 204–214 (1990).
- Park, H.-S., and T. Kyu, "Rheological and mechanical characteristics of Poly-P-Phenylene Terephthalamide/nylon molecular and particulate composites," *Polym. Compos.* **10**, 429–438 (1989).
- Pavlinek, V., and P. Saha, "Rheological behavior of poly(methyl methacrylate) dispersions stabilized by a diblock copolymer: An anomalous viscosity-partical concentration dependence," *J. Rheol.* **43**, 1547–1554 (1999).
- Quinn, C. J., P. Frayer, and G. Beall, "Glass-polymer melt blends," *Polymeric Materials Encyclopedia*, edited by J. C. Salamone (CRC Press, New York, 1996), Vol. 4, pp. 2766–2777.
- Rawal, A., K. Urman, J. U. Otaigbe, and K. Schmidt-Rohr, "Detection of nanometer-scale mixing in phosphate-

- glass/polyamide-6 hybrids by ^1H - ^{31}P NMR," *Chem. Mater.* **18**, 6333–6338 (2006).
- Sammiler, R. L., J. U. Otaigbe, M. L. Lapham, N. L. Bradley, B. C. Monahan, and C. J. Quinn, "Melt rheology of zinc alkali phosphate glasses," *J. Rheol.* **40**, 285–302 (1996).
- Schmidt, L. R., "Viscoelastic melt behavior of Poly(2,6-dimethyl-1,4-phenylene oxide), high impact polystyrene, and A 35-65 blend," *J. Appl. Polym. Sci.* **23**, 2463–2479 (1979).
- Sharma, J., and N. Clarke, "Miscibility determination of a lower critical solution temperature polymer blend by rheology," *J. Phys. Chem. B* **108**, 13220–13230 (2004).
- Supaphol, P., N. Dangseeyun, P. Thanomkiat, and M. Nithitanakul, "Thermal, crystallization, mechanical, and rheological characteristics of Poly(trimethylene terephthalate)/Poly(ethylene terephthalate) blends," *J. Polym. Sci., Part B: Polym. Phys.* **42**, 676–686 (2004).
- Tick, P. A. (1983), U.S. Patent 4,379,070.
- Tick, P. A., "Water duable glasses with ultra low melting temperatures," *Phys. Chem. Glasses* **25**(6), 149–154 (1984).
- Tuteja, A., M. E. Mackay, C. J. Hawker, and B. Van Horn, "Effect of ideal, organic nanoparticles on the flow properties of linear polymers: Non-Einstein-like behavior," *Macromolecules* **38**, 8000–8011 (2005).
- Urman, K., D. Iverson, and J. U. Otaigbe, "Study of the effects of processing conditions on the structure and properties of phosphate glass/polyamide 12 hybrid materials," *J. Appl. Polym. Sci.* **105**, 1297–1308 (2006).
- Urman, K., and J. U. Otaigbe, "Novel phosphate glass/polyamide 6 hybrids: Miscibility, crystallization kinetics, and mechanical properties," *J. Polym. Sci., Part B: Polym. Phys.* **44**, 441–450 (2006).
- Urman, K., and J. U. Otaigbe, "New phosphate glass/polymer hybrids—Current status and future prospects," *Prog. Polym. Sci.*, doi:10.1016/j.progpolymsci.2007.07.006 (2007).
- Urman, K., S. Madbouly, and J. U. Otaigbe, "Unusual accelerated molecular relaxations of a tin fluorophosphate glass/polyamide 6 hybrid studied by broadband dielectric spectroscopy," *Polymer* **48**, 1659–1666 (2007a).
- Urman, K., T. Schweizer, and J. Otaigbe, "Uniaxial elongation flow effects and morphology development in LDPE/phosphate glass hybrids," *Rheol. Acta* **46**, 989–1001 (2007b).
- Utracki, L. A., and M. R. Kamal, "Melt rheology of polymer blends," *Polym. Eng. Sci.* **22**, 96–114 (1982).
- Xu, X. J., and D. E. Day, "Properties and structure of Sn-P-O-F glasses," *Phys. Chem. Glasses* **31**, 183–187 (1990).
- Xu, X. J., D. E. Day, R. K. Brow, and P. M. Callahan, "Structure of tin fluorophosphate glasses containing PbO or B₂O₃," *Phys. Chem. Glasses* **36**, 264–271 (1995).
- Yoshikawa, K., A. Molnar, and A. Eisenberg, "Rheological properties of blends of lithium- or sodium-sulfonated polystyrene ionomers with polyamide 6," *Polym. Eng. Sci.* **34**, 1056–1064 (1994).
- Young, R. T., M. A. McLeod, and D. G. Baird, "Extensional processing behavior of thermoplastics reinforced with a melt processable glass," *Polym. Compos.* **21**, 900–917 (2000).
- Zarraga, A., J. J. Pena, M. E. Munoz, and A. Santamaria, "Thermorheological analysis of PVC blends," *J. Polym. Sci., Part B: Polym. Phys.* **38**, 469–477 (2000).