Mechanism of Unexpected Viscosity Decrease of Nylon 6 Melts by Low-T_g Inorganic Tin Fluorophosphate Glass during Processing

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Abstract:

We report unprecedented non-Einstein-like viscosity decrease of polymer melts by special low glass transition, T_g, inorganic tin fluorophosphate glass (Pglass) that is remarkably counter to widely accepted dispersions, suspensions, and composites theories. The well dispersed low-T_g Pglass dramatically decrease the polymer melt viscosity while increasing its Young's modulus in the solid state at low loading (<2%) however decreasing with high loading (> 2 %), making the hybrid Pglass/polymer solid material stronger yet easier to process in the liquid state. Disruption of the Nylon 6 melt dynamics, strong physicochemical interactions, and submicrometer nanophase separation (proved by rheometry, FTIR, DSC, SEM, NMR and XRD) are thought to be responsible for this experimental fact. This finding should beneficially impact our ability to prepare lower viscosity, very highly filled Nylon 6 melts from already existing materials and polymer processing methods such as injection molding and extrusion, making the simple strategy potentially widely applicable in a number of applications such as thinner barrier resistant thin films, composites, and membranes for heterogeneous catalysis.

Zusammenfassung:

Wir berichten über eine nicht vorhergesagte nicht-Einsteinartige Viskositätsabnahme von Polymerschmelzen durch einen besonderen Glasübergang (T_g) von anorganischen Zinnfluorphosphatgläsern (P-Glas). Dieser Übergang steht im Gegensatz zu allgemein akzeptierten Theorien für Dispersionen, Suspensionen und Kompositen. Das homogen dispergierte P-Glas mit einem niedrigen T_g reduziert in drastischer Weise die Viskosität der Polymerschmelze, wohingegen der Elastizitätsmodul im festen Zustand bei einer niedrigen Füllstoffkonzentration (< 2 %) zunimmt. Jedoch nimmt der Elastizitätsmodul bei hohen Füllstoffkonzentrationen (> 2%) ab. Auf diese Art und Weise besitzt das Material eine höhere Festigkeit und ist einfacher zu verarbeiten. Die Unterbrechung der Dynamik der PA 6-Schmelze, ausgeprägte physikalisch-chemische Wechselwirkungen und Nanophasenseparation (experimentell bestätigt durch Rheometrie, FT-IR, DSC, SEM, NMR und XRD) werden für dieses experimentelle Ergebnis verantwortlich gemacht. Diese Resultate besitzen eine hohe Bedeutung für die Herstellung niedrigviskoserer, hochgefüllter PA 6-Schmelzen, ausgehend von existierenden Materialien und kunststofftechnischen Verarbeitungsmethoden wie Spritzgießen und Extrusion. Anwendungen sind Dünnschichtsysteme als Barrierematerialien, Komposite und Membranen für heterogene Katalyse.

Résumé:

Nous présentons pour la première fois une chute de la viscosité (comportement non Einsteinien) dans des polymères fondus due à un verre spécial d'étain inorganique fluorophosphaté (Pglass) possédant une transition vitreuse T_g basse, et qui va remarquablement à l'encontre des théories largement acceptées pour les dispersions, les suspensions et les composites. Le verre de basse T_g bien dispersé diminue dramatiquement la viscosité du polymère fondu, tandis qu'il augmente le module de Young à l'état solide pour des charges faibles (< 2 %), mais qu'il le diminue pour de plus grandes charges (> 2 %), rendant cet hybride polymère/Pglass un matériau solide plus fort mais encore plus facile à mettre en œuvre à l'état liquide. La disruption de la dynamique du fondu de Nylon 6, les fortes interactions physico-chimiques et la séparation de nano phases à l'échelle sous micrométrique (démontrées par rhéomètrie, FTIR, DSC, SEM, NMR et XRD) semblent être responsables de ce fait expérimental. Cette découverte devrait avoir un impact bénéfique sur note capacité à préparer des fondus de Nylon 6 moins visqueux et hautement chargés à partir de matériaux et procédés de transformation de polymères déjà existant tels que le moulage-injection et l'extrusion, rendant la stratégie simple potentiellement largement applicable à un nombre d'applications telles que des films barrières plus fins et résistants, des composites et des membranes pour la catalyse hétérogène

1 INTRODUCTION

The physical modification of polymer structure and properties via reactive (polar) and nonreactive (nonpolar) polymer blending and reinforcement is a common practice in the plastics industry and has a large economic advantage over synthesizing new polymeric materials to fulfill new material needs. In this context, a new class of inorganic glass/organic polymer hybrids with enhanced benefits has been recently developed by blending low-T_g phosphate glasses with polymeric materials in the liquid state, to afford new hybrid materials with significant improvements in properties that are impossible to achieve from classical polymer blends and composites [1 – 3] .

As previously reported [1], a dramatic torque reduction has been observed when a small amount of a low glass transition, T_g, tin fluorophosphate glass (Pglass) [4] was melt blended with a high molecular weight commerical Nylon 6 in an internal batch mixer such as a Haake Polydrive® mixing machine. Note that the components of the Pglass/polymer hybrid are both liquid during the blending process in the mixer. The low torque (which scales directly as low viscosity as will be demonstrated later) during melt processing offers a number of advantages including use of relatively lower shear rates and processing temperatures, and higher processing speeds, thus minimizing the adverse effects of thermal and mechanical degradation on the Pglass/polymer hybrid material. Recently, a similar significant torque reduction was also observed in our laboratory during mixing of Pglass with a commerical polyester resin, suggesting that the torque reduction may be universal to reactive (polar) polymers that contain carbonyl (C=O) groups, such as polyamides and polyesters and possibly polyurethane and polyurea. Therefore, it is crucial to explore the underlying fundamental mechanisms responsible for the torque reduction during melt procssing of the Pglass/polymer hybrid system, enabling preparation of new and useful Pglass/polymer materials to prescribed macromolecular structure and performance properties.

Viscosity (or torque) reduction during polymer melt processing had been observed when thermotropic liquid crystalline polymers (LCP) were melt blended with thermoplastic polymers as reported in the literature [5 – 14]. For example,

Weiss and coworkers [5,6] reported that addition of main chain LCP into polystyrene and polycarbonate reduced the melt viscosity because the LCP can be oriented to form fibrils that can align the polymer chains near the LCP. Blizard and Baird [7] also showed that adding a polyester-based LCP into polycarbonate and Nylon 6,6 reduced the viscosity during extensional flow. Kim and Denn [8] studied the viscosity-composition relationship of LCP-PET blend over the whole composition range and found that the shear rheology deviates significantly from simple mixing laws and from theoretical predictions of an emulsion model of dispersed blends. Brostow and coworkers [9] showed similar viscosity reduction when blending a LCP with four different thermoplastic polymers. Gao and coworkers [11 – 13] reported a series of articles on the viscosity reduction mechanisms when blending LCP with high molecular mass polyethylene. In the articles just cited, one common explanation for the observed viscosity reduction was attributed to the 'anisotropic' fibril shapes of LCP that are formed at the melt processing temperature of the blend components. This explanation is consistent with the special 3-region rheological behavior of polymer liquid crystals first reported by Onogi and Asada [15] and corroborated by Wissbrun [16].

La Mantia and coworkers [14] studied viscosity reduction and the minimum in viscosity-composition curve for extruded Nylon 6/LCP blend. They showed that fibril formation is responsible for the viscosity reduction, and interfacial slip due to the immiscible nature between LCP and Nylon 6 is responsible for the minimum in viscosity-composition curve. More recently, Mackay and coworkers [17, 18] reported a dramatic viscosity reduction of polystyrene blended with polystyrene nanoparticles. They conjectured that the viscosity reduction is partly due to constraint release and possibly free volume effects both caused by the presence of the nanoparticles. While the observed viscosity reduction in the polystyrene system just mentioned is similar to that reported in the present article, the composition of the current Pglass/polymer hybrid system is remarkably different from that of the polystyrene/LCP blend. Because of their facile synthesis and desirable characteristics, the present Pglass/polymer hybrid materials may be model systems for exploring feasibility of new routes for driving inorganic glasses and

organic polymers to self-assemble into useful materials. Conceptually, it may even be possible to use block copolymers, with one block being miscible with Pglass, to perform self directed assembly of nanostructured hybrids, where the Pglass is confined solely to one phase [1].

In this study, we aim for the first time to find the underlying fundamental mechanisms responsible for the observed dramatic torque reduction of Pglass/Nylon 6 hybrid system which may also explain similar observed phenomena when Pglass is blended with other reactive polymers such as poly(ethylene terephthalate), making the results of the study widely applicable. It is worthy to note that there are two important differences between the Nylon 6/LCP system studied by La Mantia et. al. and the current Pglass/Nylon 6 system. Previous NMR study on 10 % Pglass/Nylon 6 system revealed evidence of nano-scale mixing at the mixing temperature used (250 C) [19]. In addition, there is no minimum in the viscosity-composition curve for the Pglass/Nylon 6 system, a precipitous drop in viscosity is always observed that appears to be insensitive to the Pglass concentration in the hybrid as will be demonstrated later. The low-T_g tin fluorophosphate glass [1, 2 ,20, 21] used in the present study has a low T_g of approximately 115 ± 5°C that significantly makes it easy to be mixed in the liquid state with most organic polymers also in the liquid state. This simple blending strategy is somewhat similar to that employed by Mackay and coworkers [17,18] via co-dissolution in tetrahydrofuran of linear polystyrene and polystyrene nanoparticles but avoids the difficulties of solvent handling and subsequent removal in the final blend or hybrid. This article will explore plausible mechanisms of torque (or viscosity) reduction such as molecular weight reduction, wall slip, shear induced elongation as well as the physcochemical interactions between Pglass and Nylon 6. This will be done via viscosity measurements, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) experiments as described in the following section of the article. Understanding the torque (or viscosity) reduction mechanism will help to elucidate the composition-processing-structure-property relationships so as to assure preparation of Pglass/polymer hybrid materials with enhanced benefits to prescribed macromolecular structure and function during use. In addition, the study may shed light i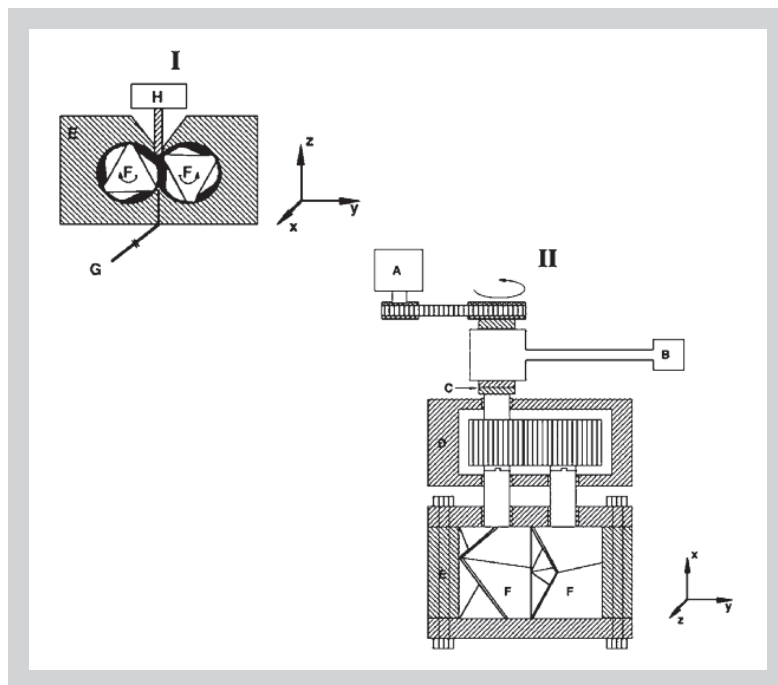nto the feasibility of using the present solid Pglass as a polymer processing aid (e.g., plasticizer) for polymers with obvious enhanced benefits over the traditional low molecular weight compounds (e.g., dioctylphthalate) that are conventionally liquid at ambient conditions and used widely in industry [22].

2 EXPERIMENTAL METHODS

2.1 MATERIALS

The low-T_g tin fluorophosphate glass (Pglass) was prepared in our laboratory following the procedures previously reported [1, 2, 20]. The Pglass has a typical composition of 50 % SnF_2, 20 % SnO, and 30 % P_2O_5 (in mole %) The glass transition temperature was determined by DSC during heating and found to be approximately 115 ± 5°C. The Pglass density at room temperature is 3.75 g/cm [3]. The Nylon 6 (Capron® 8270 HS) used was supplied by Allied Signal. Because both Nylon 6 and Pglass like to absorb water, both the Pglass and Nylon 6 were dried in a vacuum oven maintained at 85 °C for 24 hours prior to mixing as described in the following section.

2.2 MIXING AND GRINDING

Pure Nylon 6 pellets and hybrids of different volume concentrations (i.e., 0, 1, 5, 10%) were mixed in a Thermo-Haake Polydrive® melt mixer & torque rheometer equipped with roller blades (see Figure 1). For each composition, the total added volume of Nylon 6 and Pglass was kept constant at 48.3 cm³. The Polydrive® mixer was preheated to 250°C and allowed to equilibrate at this temperature for 30 minutes. The dried Nylon

6 pellets were first added into the mixer operating at a rotor speed of 75 rpm (revolutions per minute) and mixed for 5 minutes. The dried Pglass was then added and mixed for another 10 minutes. To determine the processing effects on the pure Nylon 6 introduced in the Pglass/Nylon 6 hybrid, the pure components (pure Nylon 6 and pure Pglass) were mixed independently under the same conditions used for the hybrids. The resulting pure components were used as controls for this study.

The Nylon 6 and Pglass/Nylon 6 hybrids samples were collected in chunks after mixing. The chunks were cryogenically ground into powders in liquid nitrogen using a IKA A11 basic analysis mill. The pure Pglass powders were sieved through a mesh of size 0.589 μm and the Pglass/Nylon 6 hybrids containing 0, 1, and 5 % Pglass could only be ground into small particles with sizes greater than 1 mm instead of the fine powder obtained from the pure Pglass and 10 % Pglass/Nylon 6 hybrid. These powders were used as is or molded into desired shapes for subsequent measurements described below.

2.3 PREPARATION OF 5% PGLASS/95% NYLON 6 HYBRID FOR SEM

A sample containing 5 % Pglass and 95 % Nylon 6 (by volume) in powder form was injection molded at 250°C into a standard dog bone shape mold (at 50°C mold temperature) using a MicroInjector® machine (DACA Instruments Company). The resulting molded sample was quenched in liquid nitrogen for about 30 seconds and then broken with a plier in the melt flow direction of injection in order to preserve the morphology which was originally formed at 250°C and quenched to 50°C.

2.4 INTRINSIC VISCOSITY MEASUREMENTS

Pure Nylon 6 (original as-received pellets and processed Nylon 6 (at 250°C, 75 rpm for 10 minutes)) and the extracted Nylon 6 portions in the Pglass/Nylon 6 hybrids were dissolved in an effective solvent mixture (at room temperature) which contains 55 % phenol and 45 % xylene (by volume) [23]. The Intrinsic viscosities of the processed pure Nylon 6 and the Nylon 6 extracted from the hybrids were measured using a Cannon-Ubbelohde dilution type (#75) capillary viscometer (Cannon Intrument Co., State College, PA). All the measurements were made at 25°C by sub-

merging the capillary viscometer into a custom built constant temperature bath. The temperature of the bath was controlled to within ± 0.01°C during the measurements. A stop watch with an accuracy of 0.01 second was used to record the flow times that were used to calculate the intrinsic viscosity as described later.

2.5 STEADY SHEAR VISCOSITY MEASUREMENTS

Steady shear viscosities of the hybrids at the mixing temperature (250°C) was measured using an Advanced Rheometrics Expansion System (ARES®, TA instruments) in the parallel plates configuration operating under TA Orchestrator 7.0 software for automatic equipment control and data acquisition. Due to the difficulties in cleaning the test fixtures, especially the cone of cone/plate fixture, stainless steel parallel plates were used instead for measuring the steady shear viscosity. Steady shear viscosities of different hybrids and pure Nylon 6 were measured at different shear rates and a gap size of 1.4 ± 0.1 mm. Heating control was realized by using the convection oven that was continuously blanketed with nitrogen throughout the measurements; and the nitrogen temperature was used to control the sample temperature. The sample temperature was sensed by the thermocouple inside the oven. It is worthy to note that wall slip during the rheological measurements was tested by making measurements with varying gaps between the parallel plates of the test fixture. Within the accuracy of ARES® measurements the effect of the varying gap on the obtained results was found to be negligibly small under the conditions of testing used. The powder samples were first loaded between the parallel plates that were equilibrated at 250°C. Subsequently, the gap size was decreased to squeeze out and consolidate the melted powders into shape, the edges trimmed, and the sample was allowed to equilibrate at 250°C prior to making the measurements. Note that great care was taken to avoid entrapped air in the samples and the hybrid sample preparation method just described gave reproducible results that were similar to that obtained from premolded sample disks. In addition the sample preparation method was facilitated by the relatively low viscosity of the hybrids. The Pglass disk was heated at 250°C into a completely homogeneous liquid that was
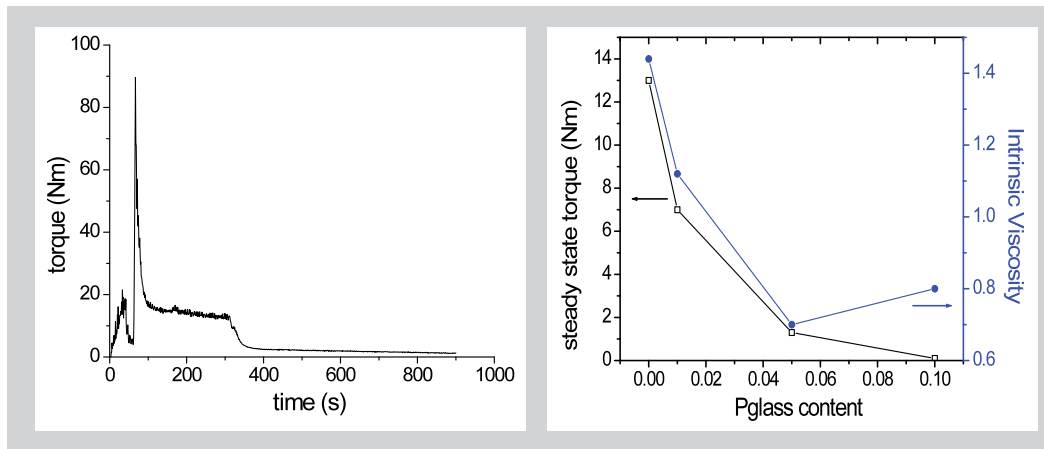
sqeezed out to fill the gap and subsequently allowed to thermally equilibrate at 250°C before making measurements.

### 2.6 FOURIER TRANSFORM INFRARED SPEC-TROSCOPY (FTIR)

FTIR measurements were performed using a Nicolet 6700 FT-IR spectrometer (Thermo Scientific) in the reflective mode. Dried powders of the samples at each concentration were used in the test with a resolution of 2 cm^{-1} and at least 128 scans.

2.7 SEM

A Quanta 200 scanning electron microscope (FEI company) was used to observe the morpholgy of the sample under high vacuum and at room temperature. The surface of the injection molded hybrid sample that was broken in liquid nitrogen as already mentioned was sputtered with gold to enhance contrast prior to SEM examination.

3 RESULTS AND DISCUSSION

The torque evolution as a function of time observed during the melt mixing of 5 % Pglass/Nylon 6 hybrid (by volume) in the Polydrive® mixer is shown in Figure 2. Immediately after the addition of the Nylon 6 pellets into the mixer maintained at 250°C (i.e., after 60 s), the initial torque first increased and then subsequently decreased to a plateau value corresponding to a completely and homogeneously melted Nylon 6. The Pglass powder was then added to the homogeous melt of Nylon 6 and a spontaneous dramatic reduction in the torque value from about 13 ± 1 Nm to a final steady state torque value (SSTV) of 1.4 Nm. The final SSTV as a function of the Pglass concentration for all the materials of this study is shown in Figure 3. Also shown on the right y-axis of this figure is the intrinsic viscosity, which will be discussed later, for easy comparision. The figure shows that the SSTVs decrease with increasing Pglass concentration. The final SSTV observed for the 10% Pglass/Nylon
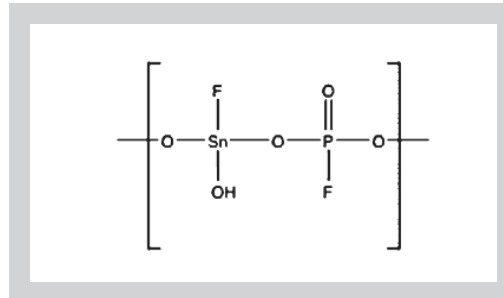
6 hybrid was found to be about 0.1 Nm, a value that was similar to that obtained when the pure Pglass was subjected to the same mixing conditions in the Polydrive® mixer. At higher Pglass content (i.e., 10 % < Pglass content ≤ 90 %), the final SSTVs observed were always found to be about 0.1 Nm and appear to be independent of the Pglass concentration. Note that 0.1 Nm is near the limit of the sensitivity of the Polydrive® mixer used.

A fluorine-containing polymer has been reported to be able to reduce melt viscosity of high density polyethylene system through wall slip mechanism [24]. A typical structure proposed by Xu and Day [25, 26] for the tin fluorophosphate glass composition used in the current study is shown in Figure 4. The presence of fluorine atoms in the structure depicted in Figure 4 suggests that wall slip may be contributing to the observed torque reduction as mentioned above for fluorine-containing polymers. If wall slip is playing a key role in the observed torque reduction in the current Pglass/Nylon 6 hybrid system, then it is reasonable to expect significant reduction in torque when Pglass is mixed in the liquid state with other relatively nonreactive (nonpolar) polymers such as polypropylene. However, no torque reduction was observed when Pglass was melt mixed with polypropylene at 200°C. Consequently, it is clear that wall slip, if present, is unlikely to be responsible for the observed huge torque reduction. Clearly, the observed dramatic reduction in torque is an interesting and complicated phenomenon that is
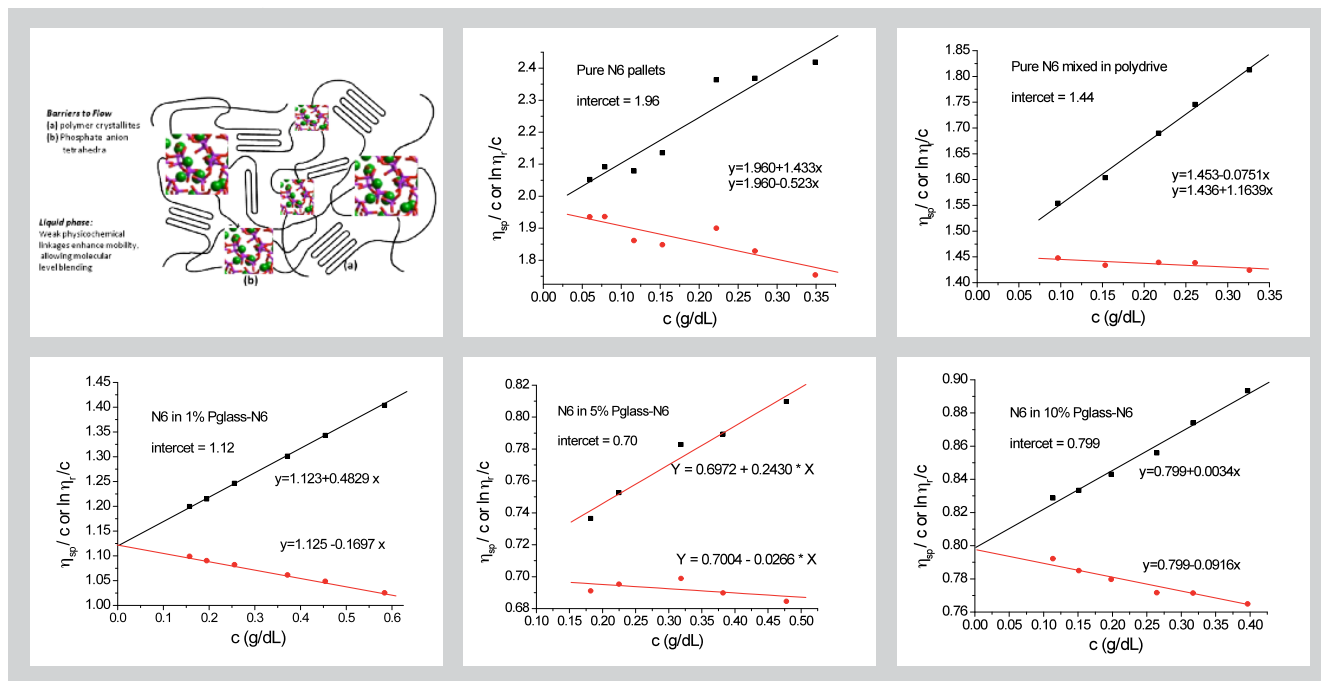
likely to be due to a number of independent mechanisms operating in concert to exhibit the dramatic flow property modification. It is worthy to note that the observed dramatic viscosity reduction cannot be explained by the glass liquid migrating to the walls of the Polydrive® mixing chamber and of ARES® rheometer test fixture because the hybrid components are miscible in the liquid state [1]. This fact is supported by the observed excessive dripping (runny) nature of the hybrids when the Polydrive batch mixing machine was opened at elevated temparatures.

Another plausible explanation for the torque reduction may be ascribed to a decrease in the polymer molecular weight during mixing caused by mechanochemical interactions and thermal degredation. Because the observed torque after about 15 minutes when only the pure Nylon 6 is present in the mixer is still above 10 Nm, it is reasonable not to expect the usually observed polymer degradation mechanisms due to the presence of oxygen or the transamidation reactions [27,28] in presence of water which breaks the polymer chains to be responsible for the observed flow modification behavior introduced by the presence of the Pglass.

It is worthy to note that the Pglass used can form a network structure [1,2] that is relatively rigid compared to the flexible and highly mobile structure of the linear polymer as conceptually depicted in Figure 5. It may be conjectured that the relatively stiff Pglass structure may lead to Nylon 6 polymer chain scission during mixing of the Pglass and the polymer at elevated temperatures, resulting in a decrease of the molecular weight of the Nylon 6. In order to test this hypothesis, we performed intrinsic viscosity measurements were performed to determine the viscosity-average molecular weight of the extracted Nylon 6 component in the Pglass/polymer hybrids. The intrinsic viscosity was determined by plotting the logarithmic normalized reduced viscosity, $\ln(\eta_r/c)$, and normalized specific viscosity, η_{sp}/c, against concentration following standard procedures. The common intercept value when c is approaching zero was taken to be the intrinsic viscosity. The intrinsic viscosities of processed Nylon 6, the extracted Nylon 6 component obtained from 1, 5, and 10% Pglass/Nylon 6 hybrid materials are shown in Figure 6a-e. The intrinsic viscosity as a function of Pglass concentration was shown earlier in Figure 3. This Figure shows clearly that the SSTV and intrinsic viscosity data seem to follow the same trend and the observed reductions in both SSTV and intrinsic viscosity are nearly comparable in magnitude. However, the intrinsic viscosity of the extracted Nylon 6 in the 10 % Pglass/Nylon 6 hybrid is higher than that observed for the 5 % Pglass/Nylon 6 hybrid. In contrast, the SSTV for the 10 % Pglass/Nylon 6 hybrid shows a reverse trend to the one just mentioned (see Figure 3). To understand and interpret the observed results, a more detailed analysis of the data at hand follows.

By comparing Figures 6a and b, it is evident that the intrinsic viscosity of Nylon 6 decreases from 1.96 (as-received and unprocessed) to 1.44 (processed). Intrinsic viscosity can be related to viscosity-average molecular weight by the following Mark-Houwink relation:

$$[\eta] = KM_\eta^\alpha$$

(1)

where $[\eta]$ is intrinsic viscosity, M_η is the viscosity-average molecular weight, α is an exponential factor which generally ranges from 0.5 to 0.8 for flexible polymers in good solvents. In general, the viscosity-average molecular weight is close to the weight-average molecular weight, M_w [29]. For monodispersed linear polymers above the critical molecular weight, it has been established that the zero-shear rate viscosity, η_o, varies with molecular weight to the 3.4 power. For polydispersed linear flexible polymers, the zero-shear rate viscosity varies with weight-average molecular weight to the 3.5 ± 0.2 according to the following equation [30]

$$\eta_o = K M_w^{3.5}$$

$\qquad(2)$

The Nylon 6 used here is a very high molecular weight grade and is above its critical molecular weight. Therefore, the Nylon 6 component of the Pglass/Nylon 6 hybrid materials with different Pglass concentration can be safely assumed to be above the critical molecular weight even after the melt processing stage. As Figure 2 shows, when 5 % Pglass was added to the Nylon 6 in the mixer, the final SSTV decreased from 13 ± 1 Nm to 1.4 Nm, a 90 % torque reduction. Bousmina et. al. [31] based on an earlier work reported by Goodrich and Porter [32] showed unambiguously that the torque in an internal batch mixer such as the current Polydrive® mixer is directly proportional to the torque and inversely proportional to the rotor speed. Note that a constant rotor speed (75 rpm) was used for all the materials used in the current study. Therefore, the apparent viscosity must also decrease by 90 % when 5 % Pglass is added into Nylon 6 in the Polydrive® mixer.

If we assume that the shear thinning effect on the viscosity of pure Nylon 6 and the extracted Nylon 6 from the Pglass/Nylon 6 hybrids with different Pglass concentrations is similar, and considering the 3.5 power relation between viscosity and molecular weight, the huge viscosity reduction can not simply be explained entirely by the molecular weight reduction. In reality, different degrees of shear shinning effect was observed for the hybrids as depicted in Figure 7 showing the shear rate dependencies of steady shear viscosity for the pure Nylon 6 and the Pglass/Nylon 6 hybrids measured at 250°C as already described. This is believed to be a consequence of the rela-
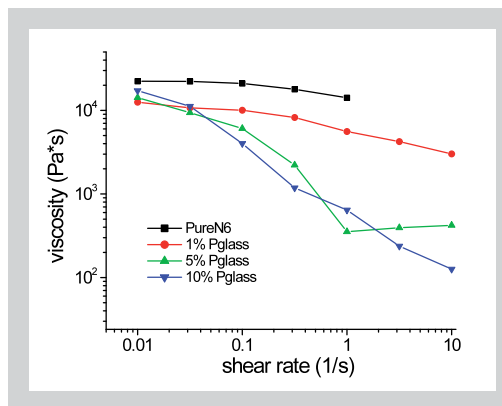
tively favorable strong physicochemical interactions between the Nylon 6 and Pglass in the hybrids [1, 19]. It is noteworthy that viscosity data outside the reported shear rate range (i.e., 0.01 - 10 s^{-1}) are not shown because they were found to be strongly sensitive to sample loading history (time and squeezing procedure) as well as residual moisture content especially for the values obtained at shear rates < 0.01 s^{-1} while at high shear rates > 10 s^{-1} the viscosity data were sensitive to edge effects. Despite the experimental difficulties just mentioned certain interesting trends in the data are discernable. At the lowest shear rate of 0.01 s^{-1} the pure Nylon 6 has the highest viscosity. In contrast, at a shear rate of 0.01 s^{-1}, the viscosity of the 10 % Pglass/Nylon 6 hybrid is higher than that of the hybrid containing 5 % Pglass. The viscosity of the 5 % Pglass/Nylon 6 was found to be higher than that of the 1 % Pglass/Nylon 6 hybrid. This last observation is in contradiction with the trend in intrinsic viscosity and SSTV data during mixing already discussed. However, the viscosity of the hybrids at the high shear rate of 10 s^{-1} appear to be consistent with that of the SSTV data which is also obtained at equivalent shear rates. We used Equations 3 and 4 to estimate the operating shear rate and viscosity of the materials during mixing [29]:

$$\dot{\gamma} \approx \frac{2\pi N}{\ln\beta}$$

$\qquad(3)$

$$\eta = \frac{\Gamma\left(\beta^2 - 1\right)}{8\pi N L R_e^2 \left(1 + g^2\right)}$$

$\qquad(4)$

In Equation 3, N is the rotation speed, β is the ratio of the effective radius of the chamber to the rotor; and in Equation 4, Γ is torque, L is the length of chamber, g is 1 in this case. Using these equations and the geometry of the rotors used, an effective shear rate of 130 rad/s and a viscosity of 1485 Pa.s equivalent to the SSTV of 13 Nm at 250°C and 75 rpm were obtained for the pure Nylon 6. Note that the above rad/s unit is basically equiv-
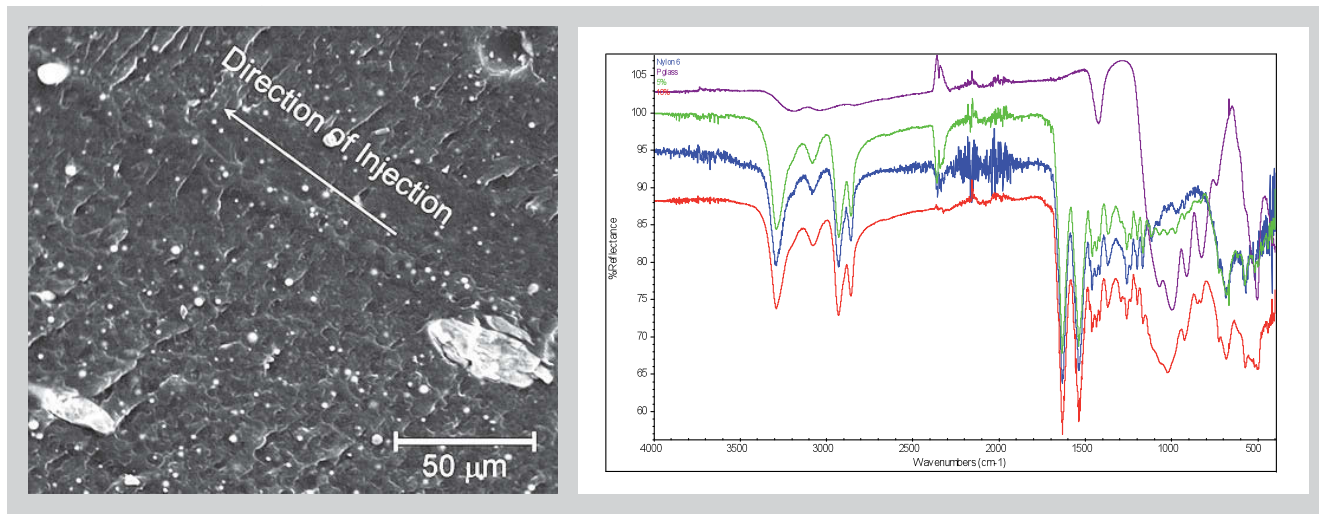
alant to the 1/s unit in Figure 7. From the shear thinning trend of Nylon 6 in Figure 7, the above calculated viscosity is in good agreement with the experimental viscosity data. This finding suggests that shear induced effects (which is exacerbated by the inherent shear thinning behavior of the hybrid components) also plays a key role compared to that of the molecular weight in the observed curious and interesting phenomenon of dramatic viscosity reduction introduced by the presence of the Pglass.

As mentioned in the introduction, viscosity reduction has been observed when liquid crystalline polymers (LCP) is melt mixed with certain linear polymers, and the elongation of the LCP phase has been shown to be responsible for the viscosity reduction in these LCP/polymer blends [5 - 14]. The possibility of a similar mechanism just mentioned playing a role in the viscosity reduction of the Pglass/Nylon 6 hybrids was tested. During the mixing of pure Pglass and pure Nylon 6 (at 250°C and 75 rpm), the pure Pglass has a SSTV < 0.1 Nm, a value that is significantly lower than that of the pure Nylon 6 which is 13 Nm, giving a low viscosity ratio of the dispersed Pglass phase to the continuous Nylon 6 phase in a typical Pglass/polymer hybrid composition. The low viscosity ratio just mentioned is further supported by the relatively steep viscosity versus temperature relationship of the pure Pglass reported previously [1, 33]. The low viscosity ratio of the Pglass/Nylon 6 hybrids should cause the Pglass phase to deform and align in the continuous Nylon 6 melt phase under the shear flow conditions. Evidence for the formation of Pglass fibrils in an LDPE matrix under uniaxial melt elongation conditions has been previously reported [34]. Unfortunately the current Pglass/Nylon 6 can not be tested under uniaxial melt elongation flow condtion due to its low melt strength and viscosity. Because it is practically impossible to

freeze the morphology after mixing Pglass with Nylon 6 directly in the Polydrive mixer, we examined under a SEM the morphology of a 5 % Pglass/Nylon 6 hybrid that was injection molded as already described. The final preserved morphology in the molded sample, although complicated by the high crystallinity of Nylon 6, is shown in Figures 8 (the Pglass phase is the light color and the Nylon 6 phase is the dark color). A particle size distribution of the dispersed Pglass phase is evident in the figure, and only some of the larger Pglass particles show evidence of elongation introduced into the sample during injection molding. This is because the larger Pglass particles are more sensitive to shear deformation and should therefore deform more easily. The interfacial tension effects should play a more significant role in the case of the smaller Pglass particles in maintaining their spherical shape, showing relatively less or no elongation under shear flow conditions. In addition, the complicated interplay between the crystallization process of Nylon 6 may also contribute to the size distribution of Pglass phase.

Infrared spectroscopy measurements on the hybrids containing different Pglass concentrations confirmed our expectation of strong interactions between Pglass and Nylon 6 as shown in Figure 9. The FTIR spectra did not reveal any new peaks after addition of Pglass (despite the very tiny peak at 851 and 832 cm^{-1} which are hard to justify). However, based on the FTIR study of similar Pglass system [25], the peaks assignments are as follows: the characteristic band of P-O stretching peak in pure Pglass (located at 1073 cm^{-1}) is shifted to 1063 cm^{-1}; P-F vibration in pure Pglass (located at 1000 cm^{-1}) is shifted to 1026 cm^{-1} in the hybrid containing 10 % Pglass. The two peaks at 913 and 827 cm^{-1}, which are for P-O-P stretching and P-F vibration, respectively, exhibited by the pure Pglass were also observed to be shifted to
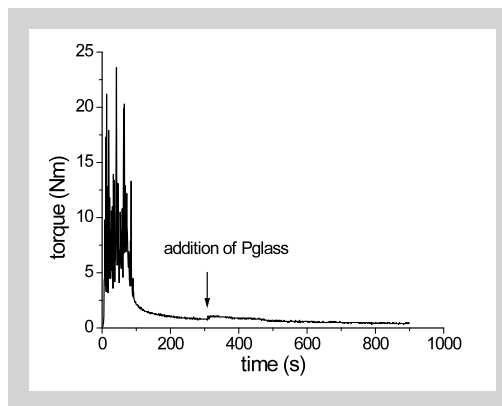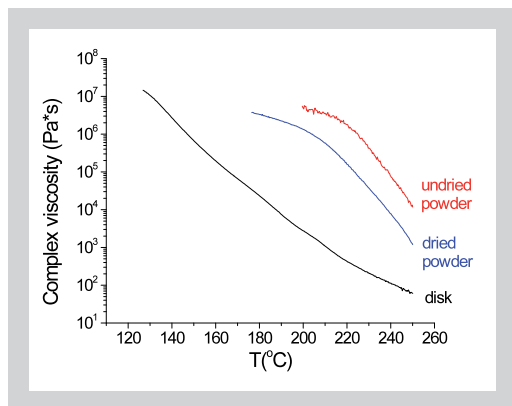
926 and 851 cm^{-1}, respectively. The above peak shifts are ascribed to the strong interactions between the Pglass and Nylon 6. Unlike the Nylon 6 and LCP system studied by La Mantia and coworkers [14], the strong interaction in our system facilitates the alignment of the Nylon 6 chains that are in very close proximity to the Pglass particles thereby lowering the entanglement of Nylon 6 chains, as well as, the torque (or viscosity) during mixing.

It is worthy to note that the pure Pglass viscosity is very sensitive to temperature as previously reported. Figure 10 shows a typical temperature dependence of complex viscosity as measured under small amplitude oscillatory shear flow conditions using an ARES rheometer following standard conditions. To illustrate the effect of sample preparation, data obtained from Pglass samples in the form of a disk (25 mm diameter and 4 mm thick) and in the form of powder (mesh size 0.589 μm) are shown in Figure 10 for comparison. The strong temperature dependence of the pure Pglass is evident in this figure and the magnitude of complex viscosities are different for the three types of samples tested (i.e., disk, dried powder and undried powder). The reason for the latter discrepancy is due to sensitivity of the Pglass powder to absorb water from the atmosphere as well as the differences in the exact sample preparation and loading method used. Pglass powders, which have been processed at 250°C for 10 minutes, showed very similar complex viscosity versus temperature profile (not shown). However, in all cases, it is clear from Figure 10 that the complex viscosity of pure Pglass increased by two orders of magnitude from 250 to 200°C in both cases. This viscosity increase just mentioned suggests that the lack of torque reduction when polypropylene (PP) is melt blended with Pglass at 200°C (as already mentioned) may be due to the relatively large viscosity ratio of Pglass to PP phases. In addition, the relatively poor interaction between the Pglass and PP (even if Pglass can deform at 200°C) may not permit the PP chains to align and follow the Pglass.

In order to account for the role of the proprietary additives in the commercial Nylon 6 grade used in the observed torque (or viscosity) reduction phenomenon, a sample of as-synthesized Nylon 6 was prepared in our laboratory via the fast anionic polymerization of ϵ-caprolactam. Note that the molecular weight of the as-synthesized Nylon 6 (not shown) is lower than that of the commercial Nylon 6 used. Details of the Nylon 6 polymerization is previously reported elsewhere [35 – 37]. The torque during mixing as a function of mixing time of 5% Pglass with the as-synthesized pure Nylon 6 is shown in Figure 11. The figure shows that the steady state torque value (SSTV) after mixing Nylon 6 for 5.5 minutes drops to about 1 Nm which is ten times lower than that of the commerical Nylon 6 used in this study. After addition of Pglass, the torque only drops slowly over time and decreased to about 0.5 Nm, indicating a similar viscosity reduction effect introduced by the addition of Pglass as before. All the experimental observations of this study show that the curious and remarkable dramatic viscosity reduction introduced by the addition of Pglass into Nylon 6 is a complicated phenomenon that cannot be explained by current theories in the literature. It is hoped that this article may stimulate additional studies that will lead to a better understanding of the behavior of these interesting materials with enhanced benefits.

4   CONCLUSIONS

We have systematically studied for the first time the role of possible mechanisms that may be responsible for the remarkable and unique viscosity reduction observed when Pglass is melt mixed with Nylon 6 at 250°C by using a number of analytical techniques including intrinsic viscosity, rheometry, FTIR and SEM. This peculiar behavior is also observed for other polar polymers such as poly(ethylene terephthalate) but not observed for nonpolar polymers such as polypropylene, suggesting that the torque (or viscosity) reduction may be universal to reactive polymers that contain carbonyl (C=O) groups,

such as polyamides and polyesters and possibly polyurethane and polyurea as already mentioned. All the plausible underlying mechanisms examined in the current study are certain to contribute in concert to the flow property modification with the strong interaction between the Pglass and Nylon 6, the polymer molecular weight reduction, and viscosity ratio of the hybrid components playing a major role.

In our previous study [38], we used advanced solid-state nuclear magnetic resonance spectroscopy to demonstrate that the addition of the Pglass even at relatively low concentrations in Nylon 6 has a significant effect on the crystallization behavior of Nylon 6, producing a remarkably large fraction of γ-phase crystals. This is consistent with our previous finding of intimate mixing (or interaction) of the hybrid components on a 10-nm scale [19]. Due to the wide range of size scales (i.e., from nanometer to micrometer) available to the Pglass phase of the hybrids through carefully controlled processing parameters and hybrid compositions, a large amount of surface area is available for interaction between the Pglass and the polymer phases. By controlling the interactions between the inorganic Pglass and the organic polymer phases, new materials with unprecedented properties can be achieved as previously reported by us [1] and more recently by others [39].

The unexpected, counterintuitive phenomenon discussed in this article is thought to be remarkable and will provide useful guidelines to future experimental studies and theory development that explicitly takes into account the special Pglass/polymer interactions, miscibility, and microstructure evolution of the little-studied Pglass/polymer hybrid materials. Because of their facile synthesis and desirable characteristics, the current hybrid systems are expected to be excellent model systems for exploring feasibility of new routes for driving inorganic glasses and organic polymers to self-assemble into useful materials

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