

# 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 rhéométrie, FTIR, DSC, SEM, NMR et XRD) semblent être responsables de ce fait expérimental. Cette découverte devrait avoir un impact bénéfique sur notre 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

**KEY WORDS:** inorganic/organic polymer hybrid, phosphate glass, rheology, processing, structure and properties

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  $\gamma$ -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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