

# MELT RHEOLOGY OF TIN PHOSPHATE GLASSES

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## ABSTRACT:

The melt rheology of a low  $T_g$  tin phosphate glass [Pglass] has been studied with oscillatory shear flow experiments to accelerate efforts to melt process the glass with different organic polymers. The  $\omega$  dependence of the complex viscosity  $\eta^*$  of the Pglass is easily predicted by a modified Rouse model with two relaxation times. The complex viscosity of the glass at different temperatures and frequencies can be superposed and described by the Arrhenius equation. At higher temperatures, the melt viscosity of the Pglass increased monotonically with time. This viscosity rise is thought to be due to sample crystallization. The Pglass was melt-mixed with two different thermoplastic polymers (low-density polyethylene and polystyrene) to produce unique hybrid materials with interesting microstructures.

## ZUSAMMENFASSUNG:

Die Schmelzrheologie eines niedrig-Tg Zinnphosphatglases wurde mittels oszillatorischen Scherströmungsexperimenten untersucht, um die Anstrengungen zum Schmelzprozessieren von Glas mit verschiedenen organischen Polymeren zu beschleunigen. Die Frequenzabhängigkeit der komplexen Viskosität  $\eta^*$  des Zinnphosphatglases kann leicht anhand eines modifizierten Rousemodells mit zwei Relaxationszeiten vorausgesagt werden. Die komplexe Viskosität des Glases bei verschiedenen Temperaturen und Frequenzen kann überlagert und durch eine Arrhenius-Gleichung beschrieben werden. Bei höheren Temperaturen steigt die Viskosität der Schmelze aus Zinnphosphatglas monoton mit der Zeit an. Dieser Anstieg der Viskosität ist vermutlich auf Kristallisation in der Probe zurückzuführen. Das Zinnphosphatglas wurde mit zwei verschiedenen, thermoplastischen Polymeren (LDPE und PS) schmelzvermischt um einzigartige Hybridmaterialien mit interessanten Mikrostrukturen herzustellen.

## RÉSUMÉ:

La rhéologie à l'état fondu d'un verre de phosphate [verreP] de basse Tg a été étudiée au moyen d'expériences d'écoulement en cisaillement oscillatoire, afin d'accélérer les efforts entrepris pour mettre en oeuvre le fondu de verre avec différents polymères organiques. La dépendance en fréquence de la viscosité complexe  $h^*$  du verreP est aisément prédite par un modèle de Rouse modifié avec deux temps de relaxation. La viscosité complexe du verre à différentes températures et fréquences peut être superposée et est décrite par une équation de type Arrhenius. A plus hautes températures, la viscosité du fondu de verreP augmente avec le temps de manière monotone. Cette montée en viscosité est attribuée à la cristallisation de l'échantillon. Le verreP a été mélangé à l'état fondu avec deux polymères thermoplastiques différents (polyéthylène basse densité et polystyrène) pour produire des matériaux hybrides uniques possédant des microstructures intéressantes.

**KEY WORDS:** Rheology, phosphate glasses, processing, modeling, organic-inorganic polymer hybrids, glass-polymer melt blends

## 1 INTRODUCTION

Recent successes [1-9] in developing low- $T_g$  inorganic glasses based on phosphate glass chemistry have spurred interest in the relationship among processing, properties, and microstructure of organic-inorganic polymer hybrids. The low  $T_g$  [ $\cong 100^\circ\text{C}$ ] of the inorganic glass phase permits its loading at a very high content [up to 50 vol.% or 85 wt.%] in the hybrid. By contrast, such high glass loading levels are impossible to process by using conventional inorganic fillers

such as borosilicate [E-glass] glasses and conventional polymer processing method because of high intractable viscosity of the composite melt.

Phosphate glasses [1-4, 7, 10-13] offer many advantages over the more traditional inorganic fillers such as silicate glasses [14]. One key advantage of the former is their  $T_g$  that is low enough to permit melt processing with engineering thermoplastics to afford composite hybrid systems

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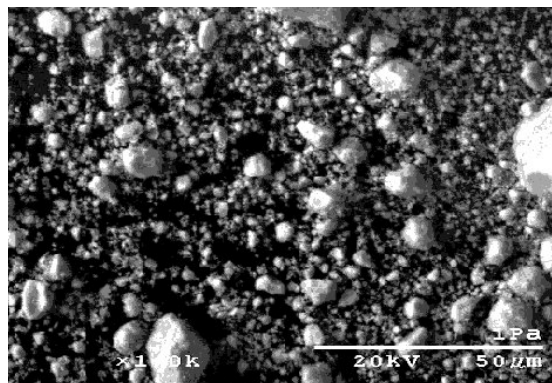


Fig. 9: SEM micrograph of the pure Pglass powder used in making the hybrids with organic polymers.

accounted for in the Palierne model and are expected to play a significant role in the viscoelastic behavior of the polymer-Pglass hybrid system. The Palierne model can be used to predict the linear viscoelastic behavior of polymer emulsions, taking into account the size of the viscoelastic droplets dispersed in a viscoelastic polymer matrix and the interfacial tension between the components. The model reduces to the Oldroyd model if the components are Newtonian liquids and the droplets are of a unique size [30].

### CONCLUSION

The melt rheology of a low  $T_g$  tin phosphate glass was studied and used to guide the selection of optimum processing temperatures with different thermoplastic polymers. The complex viscosity of the Pglass can be modeled by a modified Rouse model with two relaxation times. The frequency and temperature dependence of complex viscosity of the glass can be superposed and described by the Arrhenius-type relation. An Arrhenius flow activation energy of 87.08 kJ/mol was estimated for the Pglass. This value is consistent with the values reported for inorganic glass melts. The superpositioning of the experimental data enables the estimation of the viscosity for any frequency and temperature relevant to the processing of the Pglass. Thermal instabilities in the melt viscosity of the Pglass were observed at longer times, and these were accelerated at elevated temperatures.

Special organic-inorganic hybrid materials were developed by melt-mixing the Pglass with LDPE and PS to yield materials showing evolution of a unique and interesting microstructure of the Pglass phase in the organic-inorganic polymer hybrids. These microstructures may be beneficially exploited in applications requiring the desirable properties of the hybrid components such as high stiffness and strength, excellent flame resistance, gas/liquid barrier properties, ease of processing, and low cost. The dynamics of the microstructure evolution in these hybrid materials is one critical area for additional study because it will afford the knowledge needed to

tailor the final properties of these interesting materials to specific applications.

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