



# The evolution of the network structure in tin-fluoro-phosphate glass with increasing temperature

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## ABSTRACT

The interfacial interaction between tin-fluoride-phosphate glass (TFP-glass) and polar polymers is enhanced with increasing temperature, however, the mechanism is still unclear. In this work, the evolution of the network structure in TFP-glass with increasing temperature is investigated to explore the plausible mechanism. The dissociation of the network structure in TFP-glass, which can be observed in all TFP-glass samples synthesized at different conditions, is believed to be the reason for the temperature-dependency of the interfacial interaction. The mechanism for the dissociation has been thoroughly investigated via two-dimensional infrared spectroscopy (2D-IR), dynamic rheological analysis and XRD. The almost disappeared dissociation of TFP-glass extracted from Poly (ethylene terephthalate) (PET)/TFP-glass composite validates our inference. The conclusion would help us to deeply understand the interfacial interaction in polar polymer/TFP-glass composites and ultimately provide a guideline for the preparation of polar polymer/TFP-glass composites with strong interfacial interaction.

## 1. Introduction

Tin-fluoro-phosphate glass (TFP-glass), which is composed of cross-linked network structure based on phosphate anion tetrahedron [PO<sub>4</sub>] and coordinated with metal cation, has attracted considerable attentions of polymer researchers in the past decades [1,2]. Compared with traditional inorganic fillers, TFP-glass exhibits a relatively low glass transition temperature (T<sub>g</sub>), which allows them to be melt blended with polymer matrix using traditional polymer processing methods [3,4]. The fluidity of TFP-glass during processing makes it possible to prepare composites containing up to 90 vol% TFP-glass without the intractable viscosity problems [5], and also makes it possible to regulate its morphology to fulfill some special requirements [6,7]. More importantly, the hydroxyl groups (-OH) and activated sites on the surface of TFP-glass [8,9] are the structural basis for the formation of strong interfacial interaction in polar polymer/TFP-glass composites [10,11].

Many works have been done to investigate the interfacial interaction between TFP-glass and polar polymers [12–14]. The chi interaction parameter ( $\chi$ ) for polyamide 6 (PA6)/TFP-glass [14] and Poly (ethylene terephthalate) (PET)/TFP-glass [2] composites are calculated to be -0.067 and -0.075, respectively, indicating that the two components in each composite are indeed miscible in melt state. The miscibility is attributed to the hydrogen bonds (H-bonds) formation between the functional groups in polymer and -OH in TFP-glass. It is worthy to note that the interfacial interaction between polymer and TFP-glass exhibits

a strong temperature-dependency. The miscibility between the components in PA6/TFP-glass [14,15] and PET/TFP-glass [2] composites is reduced to be partial as temperature decreases to room temperature. As temperature increases from 190 °C to 250 °C, the morphology and rheological behavior of polyamide 12 (PA12)/TFP-glass [16] composite are changed greatly and the reason is attributed to the enhancement of the interfacial interaction. Although the positive correlation between temperature and the interfacial interaction in polar polymer/TFP-glass composites has been observed, the mechanism is still unclear.

Generally, the interfacial interaction between the components in polymer/filler composites is strongly dependent on the structure of the filler and the functional groups on its surface [17–19]. For example, the interfacial interaction between graphene oxide (GO) and nylon matrix is enhanced by Roy and his co-workers via introducing amine groups on GO surface [20]. It is well known that the dimension of the network in phosphate glass, which can be reflected by T<sub>g</sub>, and the number of -OH groups on its surface are very sensitive to its thermal histories (temperature, melting time, annealing time et.). Ehrhart [21] finds that tin-phosphate glass prepared at a lower temperature (450–550 °C) shows a T<sub>g</sub> of 150–200 °C and higher -OH content, while TFP-glass prepared at a higher temperature (800–1200 °C) has a T<sub>g</sub> of 250–300 °C and lower -OH content. Gupta et al. [6] proposes a preparation procedure for synthesizing TFP-glass, which results in a TFP-glass with a T<sub>g</sub> of 118 °C. Liu et al. [9] shortens the melting time from 70 min to 60 min but prolongs the annealing time from 90 min to 180 min, resulting in the

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**Table 1**

The synthesizing conditions for TFP-glass samples.

Sample	Composition in molar ratio SnF <sub>2</sub> : SnO: NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	Melting temperature/ °C	Melting time/ min
TFP-glass-1	5:2:6	420	20
TFP-glass-2		430	20
TFP-glass-3		440	20
TFP-glass-4		440	30

increment of  $T_g$  to 137 °C. The thermal-induced changes in the dimension of the network in TFP-glass and –OH content on its surface should have a great influence on the interfacial interaction between TFP-glass and polar polymers and therefore provide the plausible mechanism for the temperature-dependency of the interfacial interaction in polar polymer/TFP-glass composites.

Understanding the evolution of the network in TFP-glass with increasing temperature will help us elucidate the mechanism for the positive correlation between temperature and the interfacial interaction in polar polymer/TFP-glass composites and fundamentally understand the strong interfacial interaction between them, and thus provide guidance to prepare polar polymer/TFP-glass composites with strong interfacial interaction. The improvement of interfacial interaction is facilitate us to tune the morphology of TFP-glass dispersed in polar polymer matrix and eventually enhance the performances of the composite. Therefore, in this work, four kinds of TFP-glass samples with different dimensions of network and –OH content on its surface are synthesized by changing preparation condition. The thermal behavior of these four TFP-glass samples is investigated. And then taking one of them as an example, the chemical structure of the network is studied by FT-IR and XPS tests. The evolution of the network structure with increasing temperature is explored via two-dimensional infrared spectroscopy (2D-IR) and rheological test. Additionally, in order to verify the contribution of the evolution of the network structure in TFP-glass to the interfacial interaction in Poly (ethylene terephthalate) (PET)/TFP-glass composite, which has been reported most recently to be enhanced at elevated temperatures, the structure and the thermal behavior of TFP-glass extracted from PET/TFP-glass composite were investigated.

## 2. Experimental methods

### 2.1. Materials

The tin oxide (SnO, 99.9%) and ammonium dihydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, 98%) were purchased from Bailingwei Co. and the tin fluoride (SnF<sub>2</sub>, 97.5%) was obtained from Alfa Co.

### 2.2. Preparation of TFP-glass samples

TFP-glass samples with the composition in molar ratio of 50% SnF<sub>2</sub> + 20%SnO + 30%P<sub>2</sub>O<sub>5</sub> were prepared using SnF<sub>2</sub>, SnO, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> as the starting materials. The ingredients were accurately weighted and added into a mortar to mix. The uniform mixture was then transferred into a corundum crucible. The crucible was placed into a muffle furnace and melted for 20 or 30 min. The melting temperature was 420, 430 and 440 °C, respectively. Before the raw material mixture put in, muffle furnace is pre-heated to the corresponding melting temperature and allowed to equilibrate for at least 30 min. The glass melt was then poured onto a stainless steel plate and cooled down to room temperature. The obtained block solid glass was at last ground into powder with diameters smaller than 25 μm for characterizations. TFP-glass samples prepared at different conditions have been marked with Arabic numerals as shown in Table 1.

### 2.3. Extraction of TFP-glass from PET/TFP-glass composite

In order to verify the contribution of the evolution of the network structure in TFP-glass to the interfacial interaction in Poly (ethylene terephthalate) (PET)/TFP-glass composite, the structure and the thermal behavior of TFP-glass extracted from PET/TFP-glass composite were investigated. Firstly, PET/TFP-glass composite containing 10 vol% TFP-glass was melt blended using a Hapro Rheometer (RM-200C) equipped with roller rotors at a temperature of 270 °C with a rotor speed of 60 rpm for 8 min. Secondly, the PET/TFP-glass composite was dissolved at room temperature in a mixed solution of phenol and tetrachloroethane (1:1 mass ratio), in which PET was soluble but TFP-glass was insoluble. The solution was stirred for 72 h and then let stand for 72 h to separate into layers. The TFP-glass settled at the bottom of the container is obtained after repeated washing and centrifugation.

### 2.4. Characterizations

Differential scanning calorimetry (DSC) was performed using TA Q20 to determine the glass transition temperature ( $T_g$ ) of the TFP-glass samples. The TFP-glass powders was encapsulated in an aluminum pan and first heated from 40 °C to 280 °C with a heating rate of 10 °C/min and then maintained for 5 min to eliminate the heat history. Then they were cooled to 40 °C at 10 °C/min and reheated under the same condition. The test was carried under nitrogen atmosphere and the second heating was recorded.

Fourier transform infrared spectra (FT-IR) were recorded with a Thermo Nicolet Smart IS10 FT-IR spectrometer in the frequency range 400–4000 cm<sup>-1</sup> at room temperature. Sample pallets were prepared by

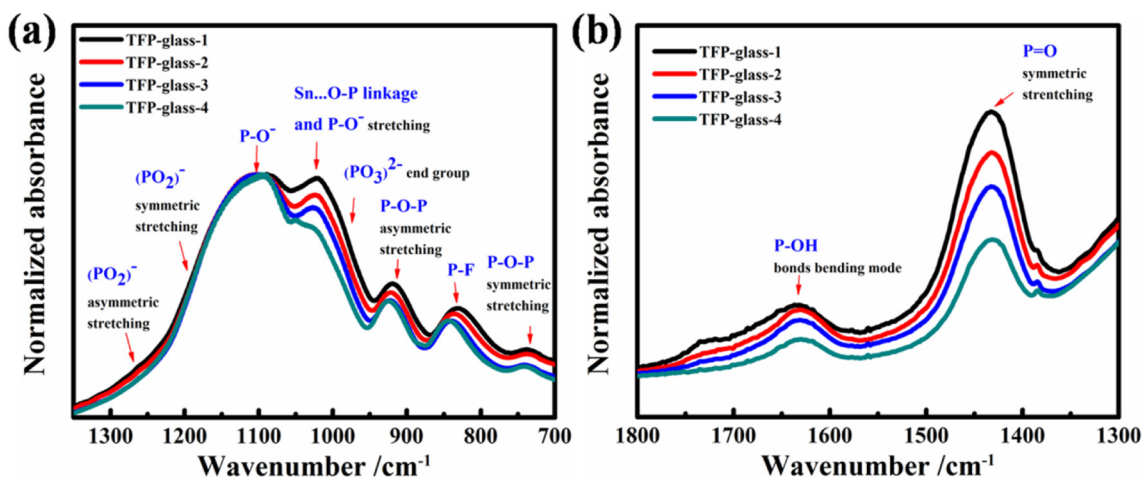


Fig. 1. Normalized FT-IR spectra of TFP-glass samples prepared at different synthesizing conditions in the region (a) 1350–700 cm<sup>-1</sup> and (b) 1800–1300 cm<sup>-1</sup>.

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