

# Rheological Characterization of Liquid Polymers Containing Ceramic Nanopowders for Use in Thermoelectric Devices

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We have determined shear viscosities as a function of temperature for several liquid high temperature polymers (HTPs) as potential coatings for solid state thermoelectric generators (TEGs) as well as for TE coolers (TECs). To each HTP we added in turn several ceramic nanopowders: alumina, silica and multi-wall carbon nanotubes (MWCNTs). The shear rate applied range is from 0.0002 to 60 s<sup>-1</sup>. The results are compared to those for neat HTPs. For a given HTP, we obtain for some nanopowders significant lowering of viscosity, or else a significant increase, or else a small effect only. Possible reasons for such differences in behavior are discussed in terms of the spatial structures of CNTs (random orientations at low temperatures), and the interactions between functional groups on HTPs and atoms in the nanoceramics.

**Keywords:** Thermoelectric Coolers, Thermoelectric Generators, Nanocomposites Rheology, Polymer Melt Viscosity.

## 1. INTRODUCTION

In 1821 the Estonian-German physicist Thomas Johann Seebeck discovered an effect now named after him, the Seebeck Effect. A temperature difference  $\Delta T$  between two dissimilar electrical conductors or semiconductors produces a voltage,  $V$ . The Seebeck Coefficient,  $S$ , is given by  $S = V/\Delta T$ . When the pair is connected through an electrical circuit, direct current flows through that circuit. In 1834 the French physicist Jean Peltier reported the cooling of one junction and the heating of the other when electric current is maintained in a circuit of a system consisting of two dissimilar conductors or semiconductors. The Peltier Effect,  $\Pi$ , is given by  $\Pi = Q/i$  where  $Q$  is the heat absorbed or released and  $i$  is the electric current. In 1855, Lord Kelvin (known earlier as William Thomson), derived from the principles of thermodynamics the relationship between  $S$  and  $\Pi$ , namely  $\Pi = ST$ .<sup>1,2</sup>

Thermoelectric (TE) devices can therefore be used for two purposes: (1) to generate electrical energy or (2) to

cool or heat an environment. In the former case, the device is called a TE generator (TEG) and in the latter a TE cooler (TEC). In TEGs and TECs, material selection is based on materials with a high value for  $S$  at the desired application temperature. A dimensionless figure of Merit,  $ZT$ , is defined as  $ZT = (S^2/\rho\kappa)T$ , where  $\rho$  is the electric resistivity and  $\kappa$  is thermal conductivity.<sup>1</sup> Materials with relatively high  $ZT$  in the desired temperature application range are chosen and include bismuth telluride alloys, silicon, germanium, lead telluride, and skutterudites. Other metals have been considered at various times as candidates for use in TE devices; however, it was found that their figures of merit are much lower, typically by an order of magnitude.

TEG devices could increase the mileage per amount of fuel in cars and in airplanes. The excess heat given off in the form of exhaust could be harvested into recycled electrical energy through the temperature difference between the exhaust and the ambient at opposing ends of a TE device. This could both increase fuel efficiency and reduce the strain on the environment created from

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automobile exhaust pollution. TECs could be applied to create solid-state refrigerators. The current cooling process in refrigerators involves Freon or a similar liquid, a chlorofluorocarbon (CFC), which after service causes ozone layer depletion. Actually, ozone layer depletion comes mainly from two sources: CFCs and car exhausts. Thus, TE devices of both kinds, TEGs and TECs, could alleviate both problems. In the present project we focus on the creation of TEGs with skutterudite TE material.

TEG devices in service necessarily undergo temperature cycling over large  $\Delta T$  intervals. TE materials such as skutterudites undergo thermal degradation at elevated temperatures by processes such as oxidation or sublimation. While in vacuum oxidation is necessarily absent, for instance in  $\text{CoSb}_3$  in the temperature range 600 °C–750 °C antimony undergoes sublimation.<sup>3</sup> Scanning electron microscopy shows that a grain boundary crack that appeared early in the test gradually evolved into a micro-void. Moreover, some bubbles of gasified antimony appeared on the samples. After thermal duration test of 16 days at 750 °C, thermoelectric performance of  $\text{CoSb}_3$  evidently declined and the ZT value at 327 °C decreased from 0.24 to 0.16.<sup>3</sup> For these reasons, the service life of TEG devices is much shorter than desired.

Numerous attempts to solve the thermal degradation problem are summarized in.<sup>4</sup> For example, thin metallic films such as tantalum, titanium, molybdenum, antimony, cobalt and/or vanadium were coated over TE materials to suppress Sb sublimation. Slight progress was achieved, but insufficient to provide stability to TE devices subjected to thermal cycling. A new solution was also proposed in,<sup>4</sup> coating TE materials and devices with polymers that are stable at unusually high temperatures. We will refer to these as high temperature polymers (HTPs). Typical polymers degrade or melt at much lower temperatures than those needed for TEGs, which is likely the reason it has not been attempted before. For example, polyethylenes melt in the temperature range from 70° to 130 °C. This while thermal stability of TE devices can be achieved only if the polymeric coatings melt or degrade at no less than 400 °C, with 600 °C preferred.

HTP coatings require good adhesion to TE materials substrates, evaluated by measuring wetting angles as a function of temperature when an HTP is in the liquid state. There is also another requirement for an HTP used as a TE device coating: its thermal expansivity  $\alpha$  should be comparable to that of TE materials and other components of the TE device. Isobaric expansivity  $\alpha$  is defined as  $V^{-1}(\partial V/\partial T)_P$ , where  $V$  is volume,  $T$  is temperature and  $P$  is pressure. In practice, instead of the volumetric expansivity one most often determines the linear isobaric expansivity,  $\alpha_L = L^{-1}(\partial L/\partial T)_P$ , where  $L$  is length (or height) of two parallel surfaces. For an isotropic material the knowledge of  $\alpha_L$  is sufficient for calculation of  $\alpha$ ; for an anisotropic material one has to determine  $\alpha_L$  along the

three Cartesian coordinates so as to be able to calculate  $\alpha$ .<sup>5</sup> Lowering  $\alpha$  of HTPs can be achieved by fillers with low expansivity, and here we enter the field of nanotechnology.

The HTP systems should also have low thermal conductivity for minimal thermal conduction effects on TE device performance. Thermal conductivity measurements, however, are outside the scope of this paper.

The final requirement is the ease of processing that is influenced by pressure, temperature, time, shear rate, and nanotechnology filler properties—as reflected in rheological properties;<sup>6</sup> here nanotechnology can also be helpful.<sup>7,8</sup>

Polymer-based nanocomposites have been created for a variety of reasons: for enhancement of Raman scattering,<sup>9</sup> reinforcement of elastomers,<sup>10,11</sup> reinforcement of polyesters,<sup>12,13</sup> improvement of scratch and wear resistance,<sup>14–16</sup> making of polymer-based photovoltaic devices,<sup>17,18</sup> or for electrogeneration of platinum nanoparticles in the presence of carbon nanotubes (CNTs).<sup>19</sup> Somehow less effort has been invested into rheology of polymer-based nanocomposites, with the exception of systems containing CNTs<sup>7</sup> combined with layered silicates,<sup>20</sup> and our own work on rheology of Boehmite containing polymer melts,<sup>21</sup> preceded by chemical modification of Boehmite.<sup>22</sup> While normally ceramic particles in a liquid polymer increase the viscosity, we have demonstrated that viscosity of polyethylene can be lowered by addition of Boehmite. We note that in multiphase polymer-based systems the system properties are determined to a large extent by the interfaces.<sup>23,24</sup> This problem is related to self-organization of materials structures discussed in a book by Desai and Kapral.<sup>24</sup> Modification of polymer properties by additives has been discussed in a book by Rabello<sup>25</sup> while modification by nanosize materials is covered in a book by Michler and Balta-Calleja.<sup>26</sup>

Given these facts, we have determined shear viscosities of several HTPs, neat as well as containing several nanopowders as fillers, for each such material for a number of shear rates. The results are reported below.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

We prepared samples for five high temperature materials in the laboratory. HTP2 and HTP5 are polyamic acids that cure into polyimides while HTP4 is a highly viscous cyanate ester resin. HTP5 contains stiff aromatic backbones. HTP7 is a phenol formaldehyde resin. Somewhat more details on these polymers have been provided before.<sup>4</sup> We also include HTP9, an advanced polyamic acid with many properties similar to HTP2. The key difference between HTP2 and HTP9 is that the latter requires a higher-temperature curing procedure and that the cured system exhibits more robust thermal properties. Each of these polymers is characterized by high heat resistance, high glass transition temperature and relatively high dielectric strength upon forming a thermoset.

**Table I.** Description of specimens for testing: HTPs and corresponding nanocomposites.

Nanoparticle fillers (0.1 wt%)	High temperature polymers (HTPs)				
	HTP2	HTP4	HTP5	HTP7	HTP9
None	neat HTP2	neat HTP4	neat HTP5	neat HTP7	neat HTP9
Alumina	HTP2 + alumina	HTP4 + alumina	HTP5 + alumina	HTP7 + alumina	HTP9 + alumina
Silica	HTP2 + silica	HTP4 + silica	HTP5 + silica	HTP7 + silica	HTP9 + silica
Carbon nanotubes	HTP2 + CNT	HTP4 + CNT	HTP5 + CNT	HTP7 + CNT	HTP9 + CNT

Alumina and silica nanoparticles were purchased from US Research Nanomaterials, Inc., Houston, TX. We also applied as a filler multi-walled carbon nanotubes received from the Technical University of Hamburg,<sup>8,10</sup> used before by other groups as well.<sup>13</sup> Made by Nanocyl, these are multi-walled CNTs, with the length of  $\approx 40 \mu\text{m}$  and the diameter of  $\approx 10 \text{ nm}$ ; thus the length/diameter ratio of approximately 4,000. Each of these nanomaterials was incorporated into the HTPs for investigation of rheological behavior.

## 2.2. Mixing

Composites containing 0.01 wt% filler were developed for each polymer + nanomaterial pair. Mixtures were then ultra-sonicated in a Bransonic<sup>®</sup> Ultrasonic Bath for one hour, with the bath temperature at  $\approx 40 \text{ }^\circ\text{C}$ . Table I describes the compositions of prepared specimens.

## 2.3. Equipment

We used a Rheologica Viscoanalyzer parallel-plate rheometer to determine the flow behavior of the HTPs. With the rheometer applying a shear stress upon a thin layer of liquid polymer (or polymer composite) via the upper rotating plate, the shear rate was varied and the corresponding shear stress measured as the response. Viscosity is derived from dividing the shear stress by the shear rate at each point. The gap distance between the parallel plates was set at 0.25 mm for all experiments, and the temperature of the experiments was selected as 25, 35, or 45  $^\circ\text{C}$ .

## 3. RESULTS AND DISCUSSION

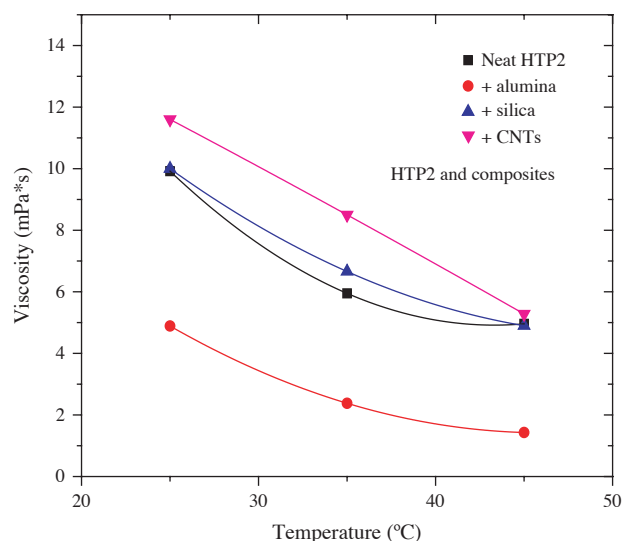
Results of our viscosity measurements for HTP2 and HTP2-based nanocomposites are shown in Figure 1. For brevity these results are averaged over the frequency range studied,  $0.0002 \text{ s}^{-1}$  to  $60 \text{ s}^{-1}$ , otherwise our set of results would be very large. Results for the remaining high temperature polymers (HTPs) and their corresponding nanocomposites are displayed in Figures 2–5.

The results displayed in Figure 1 are extraordinary. Consider for example the middle temperature of 35  $^\circ\text{C}$ . The shear viscosity value for the composite containing the alumina particles is less than half of the value for the neat polymer. In the case when carbon nanotubes (CNTs) are the filler, viscosity higher by some 50% than that of the

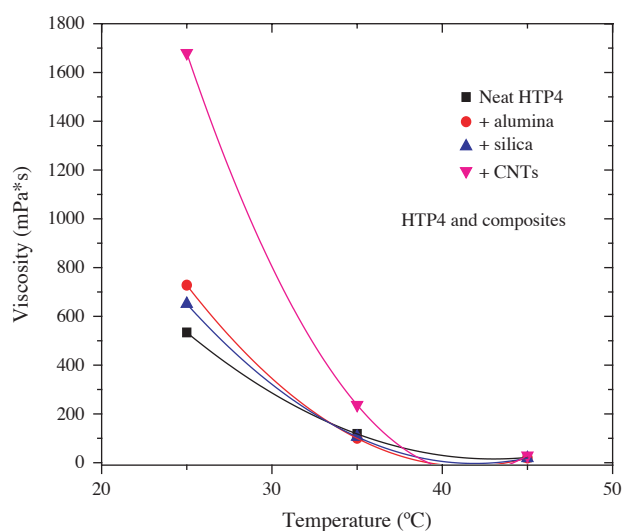
neat HTP is seen. For silica, we see the value close to that of the neat polymer. Thus, all possible types of behavior are represented.

As mentioned, HTP2 is a polyamic acid. It contains phenyl rings, three nitrogen atoms containing six member rings, one nitrogen atom containing five member rings, and carbonyl groups  $=\text{C}=\text{O}$ . Alumina is amphoteric, capable to react with both acids and bases. In the carbonyl groups, oxygen is more electronegative than carbon, and thus draws electron density away from carbon to increase the bond polarity. Thus, a possible explanation of the low viscosity of alumina containing HTP2 is strong interaction of carbonyl groups on HTP2 with aluminum atoms in alumina. Such an interaction can lead to more alignment of the macromolecules along the flow direction. High viscosity values for the CNTs containing melts can be explained by the preparation procedure we use, resulting in random orientation of the nanotubes, and thus increased resistance to flow. We recall that the length/diameter ratio for our MWCNTs is approximately 4,000. No surprises are seen for the silica containing composite, with the viscosity values close to those for the neat polymer, and practically equal to those for the neat HTP2 at 25 and at 45  $^\circ\text{C}$ .

For HTP4 containing nanocomposites the situation is partly different. We still have higher values of viscosity for CNT-containing composites, particularly so at the lowest



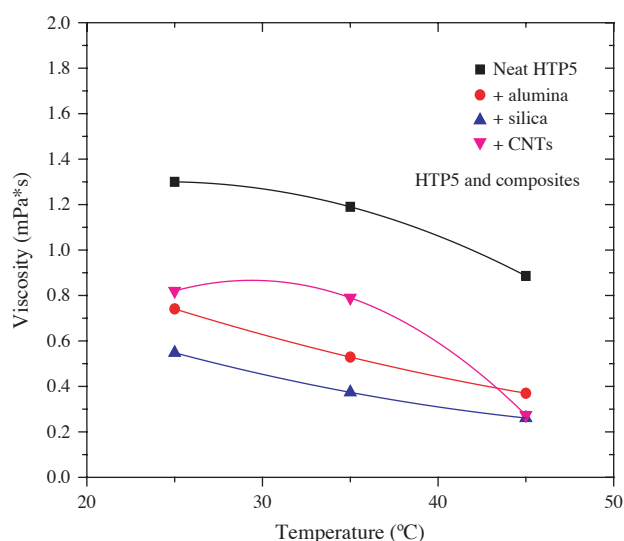
**Figure 1.** Viscosity of HTP2 and nanocomposites based on HTP2, averaged over a range of shear rates and at selected temperatures.



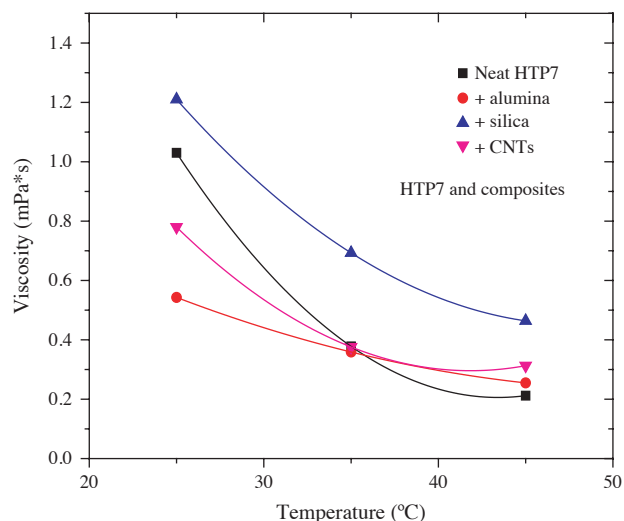
**Figure 2.** Viscosity of HTP4 and nanocomposites based on HTP4, averaged over a range of shear rates and at selected temperatures.

temperature. At 25 °C the shear viscosity of the HTP4 composite with CNTs is more than twice the value for the neat polymer. With temperature increase this difference decreases, and almost disappears at 45 °C. The present results reinforce the conclusion reached analyzing Figure 2: at the lowest temperature we have random orientation of the nanotubes, and thus CNTs offer resistance to flow. Consecutive temperature increases provide more free volume, more mobility to the nanotubes, thus enhanced orientation along the flow direction and lower viscosity. As for alumina and silica containing nanocomposites, the differences in viscosity between them and the neat polymer are small at 25 °C and practically absent at higher temperatures.

Figure 3 for HTP5 presents a different situation than the previous figures. All nanopowders provide viscosity



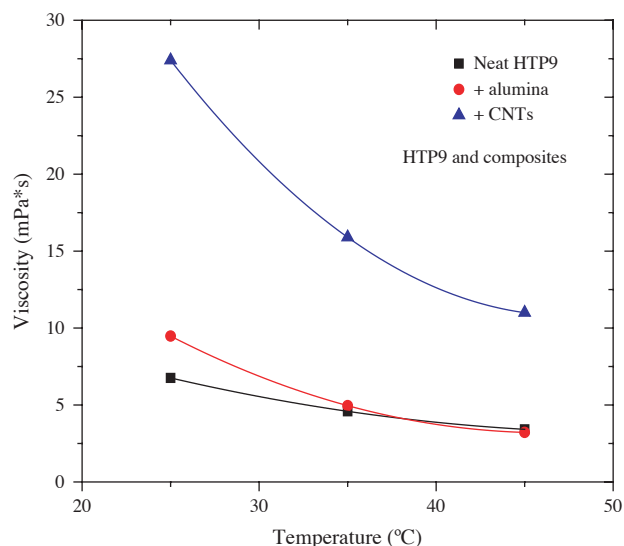
**Figure 3.** Viscosity of HTP5 and nanocomposites based on HTP5, averaged over a range of shear rates and at selected temperatures.



**Figure 4.** Viscosity of HTP7 and composites based on it, averaged over a range of shear rates and at selected temperatures.

lowering. Moreover, the values are much lower than in the previous figures. Apparently stiff aromatic backbones in HTP5 are already oriented in the flow direction. Addition of any of our ceramic nanopowders seems to provide a little more space between the flat phenyl groups, and thus facilitates the flow. Recall that for two HTPs we have concluded above that the CNTs are randomly oriented at lower temperatures but more oriented along the flow at higher temperatures; this is the case also when HTP5 is the matrix, with the same consequences for the viscosity.

We now consider results for HTP7 and nanocomposites based on it. We see here viscosity values both higher and lower than for the neat polymer, similarly as for HTP2. Now, however, the highest values are for the composite containing silica. It seems that silica ‘does not like’



**Figure 5.** Viscosity of HTP9 and composites based on it, averaged over a range of shear rates and at selected temperatures.

the phenyl formaldehyde resin and makes the flow more difficult. Effects of the presence of alumina and carbon nanotubes are small, while they are manifested only at the lowest temperature.

Finally, we consider results for HTP9 and nanocomposites with HTP9 as the matrix. Here alumina produces an insignificant increase of viscosity, this only at the lowest temperature; apparently the macromolecular structure here does not lend itself to the alignment in flow by alumina particles. Carbon nanotubes provide a large viscosity increase, the effect going down with the temperature increase. The explanation is the same as before for HTP2 and HTP4: random orientation of the nanotubes, the randomness decreasing with increasing temperature, hence the viscosity going down, but at all temperatures still higher than that of the neat polymer.

#### 4. GENERAL DISCUSSION

As noted in the beginning, research on thermoelectric materials and their applications has a very long history. We have located an 1886 article by Pilleur and Jannetaz<sup>27</sup> in which several TE materials were studied to evaluate magnitudes of the Seebeck effect. Grain orientation was evaluated in relation to the magnitude of the effect, and a conclusion reached that “the strongest currents were shown by zinc and the feeblest by copper.”

We find that ceramic nanoparticles can significantly affect the shear viscosity of the high temperature polymers; there is a capability to either increase or decrease the viscosity by appropriate choices of the ceramic.

We also find large differences between the HTPs in terms of viscosity. High values of viscosity are seen for HTP4, low for HTP5 and HTP7. HTP5 has an interesting property that any of the nanopowder additions results in viscosity lowering.

Our present results fit well with the earlier results for polyethylene and Boehmite<sup>20</sup> where lowering of viscosity was achieved using the nanopowder filler.

Finally, we recall that the concentration of the nanopowder ceramic filler was in each case only 0.01 wt%. Thus, large effects can be obtained using only small amounts of the filler.

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