Novel Chemistry and Dispersive Techniques for Diverse CNT Applications

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Abstract

Carbon nanotubes (CNTs) do not disperse very easily in organic media or at low viscosities. Thus, to produce a nanomaterial coating that can be applied by various methods, such as screen printing or ink-jet printing, the dispersed material must have the appropriate chemical properties and the dispersion method must be carefully selected. Moreover, the dispersion medium's chemistry must allow for formulation of non-viscous and viscous materials alike and possibly function as a fugitive material to avoid interfering with the properties of the deposited nanomaterials. Most electronic nanomaterials have properties such that any surfactant or polymer used in the dispersion medium to disperse the nanomaterials, stabilize the dispersion, or increase its viscosity hinders the electronic nature of the nanomaterial and therefore must be removed. The nanomaterial's chemistry must also allow for adjustments to the formulation that make the coating thermally stable at up to 300ºC or the give it the ability to be fugitive as low as 130ºC but still stable enough at room temperature to maintain its form or function. In other words, dispersing CNTs poses many challenges. In this work, we have devised a polymer-based system for dispersing CNTs that addresses these issues.

Introduction

Carbon nanotubes (CNTs) occur inherently in a bundled form due to their unique properties (Figure 1). To be able to effectively deposit them in a usable form, they have to be dispersed and then remain dispersed. Most of the typical dispersion methods use surfactants, polymers, or other chemical means to disperse particles. These additives tend to hinder the electrical properties of the CNTs.
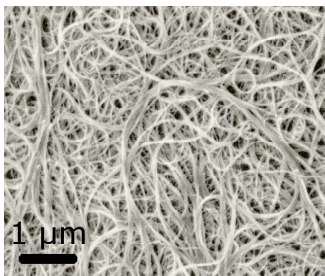

Figure 1: Scanning electron microscope (SEM) image of bundled CNTs

To take full advantage of the properties of the CNTs, the additives have to keep the CNT ink stable and be fugitive upon either the printing process or the drying process.

Most of the additives such as surfactants and solvents will leave the system at temperatures below 200ºC. Systems that require a higher viscosity for the application process typically require a polymeric additive. Most polymeric additives do not decompose below 250ºC. This property is not an issue when substrates such as glass, ceramics, and most metals are processed. It only becomes problematic when flexible substrates, which typically start to have dimensional stability issues at 150ºC, are processed. This paper will focus on development of a polymer chemistry to allow standard printing techniques such as flexographic or screen printing and allow lower-temperature processing for temperature-sensitive substrates.

Experimental

The CNTs used in this work were all single-walled carbon nanotubes (SWCNTs) having different dimensions. The dimensions of the SWCNTs affect the dispersion properties, viscosity, and the printing process even when they are used at the same concentration. The effects that the CNT dimensions have on the ink, play a role in the printing process and the amount of ink deposited onto the substrate.

Polymers that were selected for the dispersion media were a polyether, a polycarbonate, a polyaldehyde, a cellulosic polymer, and several different polyolefins. Different molecular weights of the various polymer types were also investigated to understand the effect molecular weight has on the degradation of the polymer. The polymer degradation process was examined using a thermogravimetric analyzer (TGA) from TA instruments. The ramp speed was set at 2ºC/min. For this paper, the onset of degradation is defined as the temperature at which a $\geq 10\%$ weight loss occurs. Final CNT films were made using an Exakt three-roll mill to disperse the CNTs into the polymer mixture and an ATMA semiautomatic screen printer using a 390-mesh screen.

Results and Discussion

The first step of this investigation was to understand the degradation of the different polymers that were selected. We used a method for the TGA that included a heating rate of 2ºC/min. This slow heating rate was selected because understanding the onset of degradation was an important

aspect for post-processing of the final printed film. Also, such a rate provided an indication of the minimum processing time required for the final film. Figure 2 shows results from the initial polymer study.
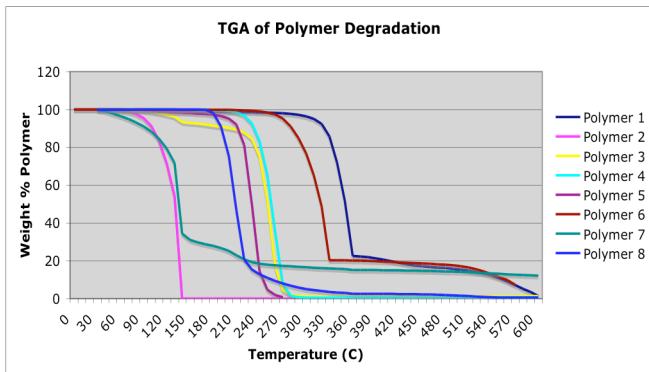

Figure 2: TGA results showing degradation of the different polymers tested

Figure 2 shows results for the eight different polymers that were examined. Polymers 4 and 5 are the same chemically but have different molecular weights. Note that the molecular weight difference in the polymer causes a shift in the onset and completion of polymer degradation. Polymer 5 has a molecular weight of ~ 70,000, whereas Polymer 4 has a molecular weight of ~ 270,000.

Polymer 2 degrades the fastest and cleanest. Upon further experimentation, we found that Polymer 2 is not readily soluble in many solvents without degrading, which makes processing the CNTs with it nearly impossible and makes its shelf life very short.

Polymer 7 decomposes at a low temperature and has about 20% of residual by-products that do not leave the system. Making inks with this polymer and then processing the inks to remove the polymer without removing the CNTs resulted in a browning of the film. Because the application for these inks is to make flexible transparent conductive films, we eliminated this polymer from consideration. The browning of the by-products would hinder the transparency of the film even if it does not hinder the conductivity of the film.

Polymers 1 and 6 start to degrade above 300ºC. The ideal post-processing temperature is below 150ºC. This gap is relatively large and indicates that these polymers are very thermally stable; thus, it might be difficult to initiate their degradation. Therefore, we decided to focus on Polymers 4 and 8 for two reasons. The first is that the onset temperature of degradation for each of the polymers is roughly 200ºC. The second is that both of these polymers degrade very cleanly and leave no residual by-products to hinder the conductivity or color the film after processing.

In most cases, one would look to additives to enhance the thermal stability of the system. In contrast, in this case, we wanted to accelerate the degradation process. Figure 3 shows TGA results for Polymer 8 with different additives.

From Figure 2, the onset of degradation for Polymer 8 was at ~ 200ºC. In Figure 3, the onset of degradation has shifted to a lower temperature for each of the additives. Not all of the additives were equally effective.
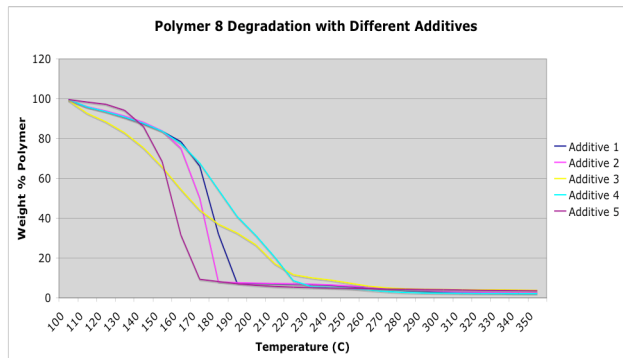

Figure 3: Polymer 8 with different additives

From Figure 3, Additive 5 provided the most enhancement. It accelerated the onset of degradation from 200ºC to 130ºC, which allows for processing below the required temperature for the thermal stability of the flexible substrate that we are printing.

We did the same experiment with Polymer 4 (Figure 4). The TGA results show that Additive 2 was more effective at accelerating the degradation. The onset was shifted from 225ºC to 150ºC. In these results, Polymer 4 was in a solvent, which caused the initial weight loss.
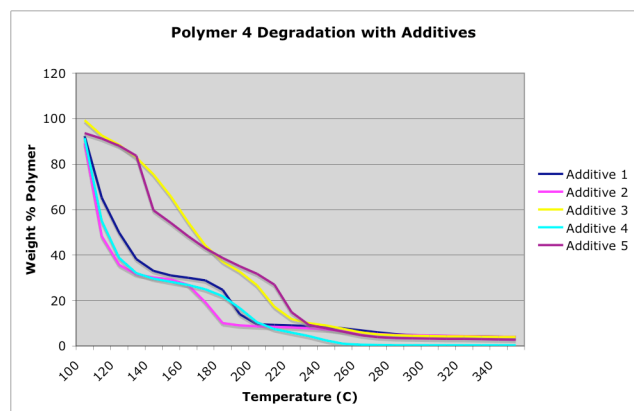

Figure 4: Polymer 4 with additives.

Because the additives worked differently for the different polymers, we looked at trying to create a synergistic effect with the different additives. Essentially, we took the additive that worked the best in the respective polymer system and added a small amount of the other additives, up

to 1%, to see if we could enhance the degradation further. Figure 5 shows a slight enhancement of the degradation temperature; however, the major improvement is in how fast the degradation happens.
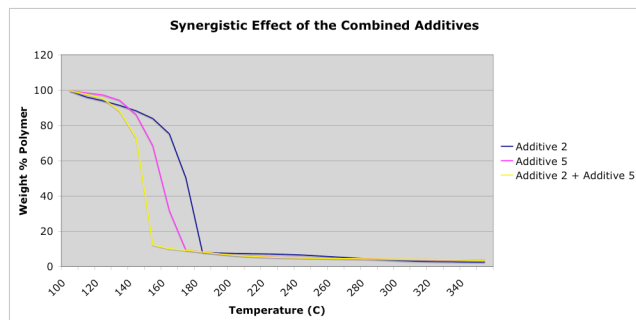

Figure 5: Polymer 8 with Additives 2 and 5

In the best case, the polymer had been fully degraded by 170ºC with the best additive. When 1% of Additive 2 was added with Additive 5, the degradation was complete by 150ºC. We also examined this effect with Polymer 4. There was no improvement over what was achieved with the best additive alone for that polymer.

Based on these results, we made ink systems with Polymer 8 and Additives 5 and 2 containing 0.5% or 1% SWCNTs. These inks were three-roll milled to disperse the CNTs into the polymer carrier. The inks were then screen printed using a 390-mesh screen. This screen mesh printed about a 25-µm wet film. The resulting film thickness after processing was approximately 100 nm, as determined by transmission electron microscopy (Figure 6). Thus most, if not all, of the polymer carrier was removed in the post-processing of the films.
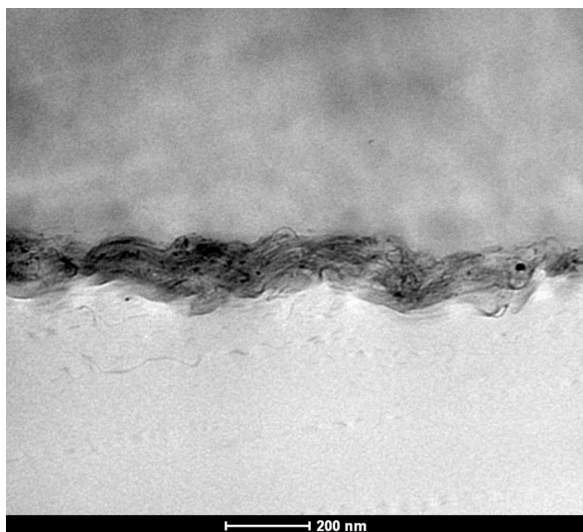

Figure 6: TEM of post-processed screen-printed film

We also looked at the films using SEM and could see the residual polymer (Figure 7).
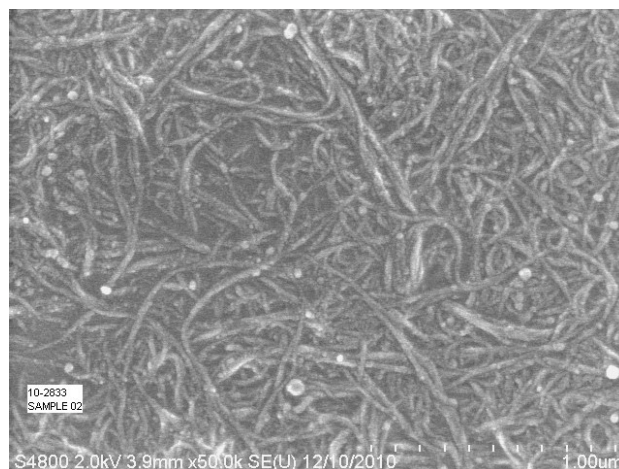

Figure 7: Top-down SEM of screen-printed film

In Figure 7, we can clearly see the CNT layer. The white balls that speckle the film are the residual polymer, which could cause reduced conductivity or transparency.

Conclusions

We have been able to devise a polymer system into which we can disperse CNTs. This system is stable chemically at room temperature and enables low-temperature processing for flexible substrates that cannot handle high-temperature processing.