DEVELOPMENT OF HIGHLY THERMALLY CONDUCTIVE NANOCOMPOSITES

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Abstract

We are designing a novel class of polymer composites featuring a significantly increased thermal conductivity. These materials will enhance conduction of heat away from thermally sensitive technological components, such as microelectronics. This is because most thermally conductive materials are also very rigid, thus minimizing contact area and heat conduction. Materials that can conform to surfaces are typically poor thermal conductors and so result in inefficient heat dispersion. Our research is dedicated towards the production of polymer-based nanocomposites that are both highly conductive and surface conforming such that they are hyper efficient heat dissipaters. In the pursuit of this goal, we are investigating the interactions between nanomaterials and differing phases of polymer host matrices of nanocomposites. To this end, we conducted an extensive exploration process to find appropriate host polymers for nanocomposites with optimized thermal conductivity. Following the results of that stage, we are using atomic force microscopy to investigate the dynamics of differing phases of polymer and using those results to optimize processes to alter the phase of polymer host materials. Following the results of that stage, we will use scanning thermal microscopy to investigate how host polymer phase impacts the microscale thermal interactions of nanomaterials and their host polymers.

Introduction

Many industries that utilize electronics face a number of issues pertaining to heat management. Microelectronic components are continually being developed at increasingly small scales. These smaller scale microelectronic components, largely as an ultimate result of their smaller size, have become more thermally sensitive and susceptible to overheating[1,2].

Many higher thermal conductivity materials, however, such as various metals and crystalline substances, diamond, for example, are unsuitable for a wide variety of heat management applications due to a variety of factors. This is largely because these materials tend to lack the ability of surface conformation to the components that they need to be conducting heat away from, as low surface conformation greatly reduces the number of contact points between the component and thermally conductive material and thus results in greatly reduced thermal conduction.[3] This is a widespread issue in highly thermally conductive materials as their high thermal conductivity is largely a result of their rigidity.[3]

Current solutions for heat management in thermal conductivity largely comprise of mounting components on thin layers of polymer or conductive pastes serving as interfaces between component and heat sinks. This is not an optimal solution, however, as these materials still possess relatively low thermal conductivity (k<10 $\frac{W}{mK}$)

Polymers are used as heat management solutions in a variety of applications as they do possess a number of desirable properties for these applications. They are capable of conforming to surfaces and therefore maximizing contact area for optimal thermal performance.[4,5] Further, they are flexible (and therefore very durable) and resistant to corrosion. [4,5] Conventional, amorphous polymers do, however, possess extremely low thermal conductivity, typically between 0.1-0.15 $\frac{W}{mK}$. Thermal conductivity is largely so low due to the disordered nature of the polymer chains. Phonons are hindered in their propagation as these disordered chains cause low phonon mean free paths within amorphous polymers, often on the order of a few nanometers.

A traditional method of increasing the thermal conductivity of polymers is through the addition of thermally conductive materials. In particular, addition of thermally conductive nanoscale fillers for creation of nanocomposites with favorable thermal conductivity could potentially greatly enhance the properties of polymers while allowing composite materials to retain the desired properties of polymers (flexible, lightweight, durable etc.)[6] Nanomaterial fillers often possess high degrees of thermal conductivity. Examples of this are carbon-based nanomaterials, such as carbon nanotubes and graphene which possess thermal conductivity of up to 3000 $\frac{W}{mK}$ for individual nanotubes[7] and graphene. [8,9] Additionally, boron nitride based nanomaterials often possess high thermal conductivity, boron nitride nanotubes possess thermal conductivity of up to 2400 $\frac{W}{mK}$ for vertically aligned nanotubes.[10]

Unfortunately, addition of carbon-based nanomaterials to a polymer matrix only yields moderate amounts of enhancement of thermal conductivity, with the resulting thermal conductivity of nanocomposites being less that one order of magnitude greater than the thermal conductivity of the unmodified matrix polymer.[11,12,13] This is believed to be due to poor connectivity between the thermally conductive filler materials, due to the dispersion of the fillers being poor[14-16] and high thermal resistance at the interfaces between the polymer matrix and the filler materials[17-19].

The crystallization of polymers largely results in a marked increase in the thermal conductivity of polymers.[13,20-22] Extreme crystallization in polymers has resulted in measurements of thermal conductivity k up to 104 $\frac{W}{mK}$ within ultra-drawn polyethylene nanofibers with diameters between 50 and 500 nm[23], while other investigations on the effect of polymer crystallinity on thermal conductivity have yielded measurements of >50 $\frac{W}{mK}$.[24-26] The phase of polymer materials clearly has an outstanding impact on their thermal conductivity.

Unfortunately, the high values of k in these high-crystallinity and ordered-chain conditions are particular to those configurations and manufacturing conditions which do not permit usage in a wide variety of applications. A wider approach is necessary to create materials that are both thermally conductive and in possession of the desirable properties of polymers, encompassing a more broad investigation of both polymer phase and nanomaterial fillers.

The objective of this project is to investigate how the thermal conductivity of polymer-based nanocomposites varies across different phases of polymer matrices. Ultimately, we hope to develop a set of techniques to optimize the thermal conductivity of polymer-based nanocomposites across a variety of polymers and nanoscale fillers, thus allowing thermally conductive nanocomposites to be created with a high degree of specificity for many applications.

Methods

A multi-stage approach is being taken towards the ultimate objective of investigating the thermal conductivity of nanocomposites with varying phases of polymer matrices.

Selection of Optimal Matrix Polymers

A prerequisite for studying the phases of polymer matrices and its impact on thermal conductivity within nanocomposites is the selection of an appropriate matrix polymer.

We have a set of optimal properties for polymers that may be useful for our investigative purposes.

The first and primary concern is that the polymer matrix must be able to exist in phases that are not simply amorphous. There are many considerations that go into this concern, such as the properties of individual batches of polymer used, such as molecular weight, or whether or not a particular polymer is isotactic or atactic. For our initial studies, the primary criteria was for semi-crystalline polymers, as crystallization is a type of polymer phase that we are investigating the interactions of various nanomaterials with. For this purpose, molecular weight, and side-chain orientation were primary concerns as they significantly impact the amount of crystallinity achievable.[27]

The next criteria we had for an optimal matrix polymer was that it needed to be able to be spin-coated onto a substrate in order to generate a thin film. The primary form which we will be investigating the thermal conductivity of polymer-based nanocomposites will be in very thin films due to the use of atomic force microscopy and a need to eliminate confounding variables that may arise with large masses of polymer. A feasible way of achieving this is via the use of spin-coating. As such, a polymer needs to be easily spin coated onto a choice substrate, such as mica. Factors that go into this consideration are that it be easily soluble in some solvent, and that the solution created with the prospective matrix polymer and its solvent does not require significantly elevated temperatures in order to remain a solution.

Additionally, the need for the polymer to be soluble at low temperatures could have implications for dispersion of nanomaterials, as elevated temperatures in solvents increases the likelihood of unwanted structural or chemical modification to the dispersed nanomaterials.[28] However, this is not a strict requirement, as the scope of polymer processing for this project is not strictly limited to solvent-based methods.

As our investigation into the effect of polymer phase on the thermal conductivity of polymer-based nanocomposites began with an investigation into the matrix polymer crystallinity's effect on the thermal conductivity of the nanocomposite, a number of semi-crystalline polymers have been and are being continuously evaluated over the course of this project.

Polyethylene was the first semi-crystalline polymer investigated. We selected it as the first potential candidate for investigation as it is able to achieve high degrees of crystallinity due to it being simply extremely long alkane chains.[23]

A number of solvents and cosolvent mixtures were used in attempts to dissolve polyethylene to prepare it for spin coating. Toluene at just below its boiling point of 111 °C[29] was found to dissolve ultra-high molecular weight polyethylene. However, small fluctuations in temperature were found to result in its complete precipitation from solution. Further, this tendency to precipitate with even small drops in temperature made spin coating exceedingly difficult. Lower molecular weight polyethylene-toluene solutions were additionally evaluated but possessed the same tendency to completely precipitate out of solution with minor drops in temperature. Significant efforts were made to overcome these issues, but ultimately work on toluene-polyethylene solutions was suspended. A xylene and carbon disulfide cosolvent mixture at a ratio of approximately 4:1 respectively, based on previously existing data, was evaluated as a potentially optimal way to dissolve polyethylene at approximately room temperature[30] without the undesirable high-temperature and precipitative effects that toluene-polyethylene solutions created. Our attempts to replicate that method did not succeed in dissolving polyethylene samples of varying molecular weights, at room temperature or up to 40 °C. 40 °C was not exceeded due to elevated safety concerns as carbon disulfide vapor is extremely flammable in air.[31]

Considering the consistent temperature issues related to dissolution, work on polyethylene as a candidate for a matrix polymer for thermally conductive nanocomposites has been suspended, pending newly found methods for creating thin films of it.

Polyvinyl alcohol was then evaluated as a potential matrix polymer for our investigations. Polyvinyl alcohol is semi-crystalline, and capable of reaching large degrees of crystallinity due to its small side groups and high degrees of hydrogen bonding within the structure.[32] From this ability to achieve high degrees of crystallization, its feasibility as a matrix polymer for our investigations was evaluated.

Polyvinyl alcohol (PVA) was found to completely dissolve into water at approximately 90 °C over approximately 30 minutes at a concentration of 2%wt PVA. Further, these solutions are stable at room temperature, with the PVA largely remaining in solutions over long periods of time, with only small amounts of PVA precipitating on the scale of weeks-months. Due to its desirable chemical properties, structural properties, and the practical feasibility of working with it, PVA was selected as a candidate for our investigation into the thermal conductivity of variable-phase polymer-based nanocomposites.

Other potential candidate polymers with properties of interest, particularly related to the phases that they can exist in, will be continually evaluated over the course of the project, in conjunction with later stage thermal conductivity investigations.

Generation of Thin Films of Polymer Matrix

The most feasible method for the creation of thin films of polymer matrix for our thermal investigations was found to be spin coating, wherein drops of polymer solution are deposited onto a substrate rotating at high speed.

Through several trials, we developed our procedure for generating a thin film of PVA polymer matrix using spin coating to be as follows: Set the rotation speed of the spin coater chuck, with the desired substrate mounted upon it (usually either mica or silicon wafer), to 1200 rpm. Using a variable volume pipette, deposit 2 25 μL drops of PVA onto the spinning substrate. Allow the substrate with the polymer solution deposited onto it to continue spinning for 2 minutes to ensure maximum solvent water removal is achieved.

Evaluation of polymer melts as a potential means of generating thin films of polymer matrix is ongoing.

Investigation of Properties of Differing Phases of Polymer

In order to gain an experimental understanding of the properties of the different phases of polymer we will be working with in our thermal investigations, we must acquire an understanding of the physical and chemical properties of differing phases of polymer. Additionally, we must develop means by which different phases of polymer can be created and then characterized.

The primary means by which this is currently being accomplished is via tapping-mode atomic force microscopy (AFM), which allows for the topography of a sample to be imaged to a high degree of precision, while additionally creating a dataset displaying the phase of the AFM tip that is vibrating at a high frequency at each point along the surface of the materials. This allows for data pertaining to the composition of the surface of a material to be acquired on the basis of the surface stiffness of a material[33], presenting potential for characterization of different phases in polymers.[34]

As it is the currently the sole candidate nanocomposite polymer matrix for the purpose our investigations that has been selected, these tests and measurements have largely been performed on PVA.

A number of treatment methods to vary the phase of the matrix polymer are in development. One that is of primary interest to us is developing a thermal annealing process that will facilitate crystallization of a polymer under an inert atmosphere. An additional method that has been successfully used to crystallize our PVA samples, spin coated from solutions of 2%wt, 0.4%wt, and 0.08%wt, has been an aging process within an isolated environment.

These crystallized samples were then scanned using tapping-mode AFM in order to acquire topographical height and phase-imaging data in order to understand both the structure and morphology of matrix polymer samples.

Further, we are beginning scanning thermal microscopy (SThM) investigations of PVA samples in order to gain a firm understanding of how structures on the surface of the PVA, corresponding with different phases of the PVA, correspond with differing values of thermal conductivity k. SThM, a derivative of AFM which places a thermopile inside of an AFM tip, allows for microscale measurements of thermal conductivity along the surface of a sample, which can then be correlated with direct topographical measurements of the sample to gain precise understanding of how the morphology and structure of a sample correspond with thermal conductivity. This technique will comprise the bulk of our investigations into the thermal properties of the interactions between variable-phase matrix polymers and nanomaterial fillers.

Results

The results that have been produced so far are largely the development of the procedures mentioned in the Methods section of this paper, as this project is in progress. In particular, the entire first phase of the project was dedicated to the search for ideal candidates for a polymer matrix for our investigation of thermal conductivity in nanomaterials, and, as an extension, the development of procedures for the production of thin films of candidate polymer matrices.

Investigations into the topographical structure and morphological properties of the surfaces of spin-coated PVA using tapping-mode AFM has yielded clear evidence of crystallization through processing.

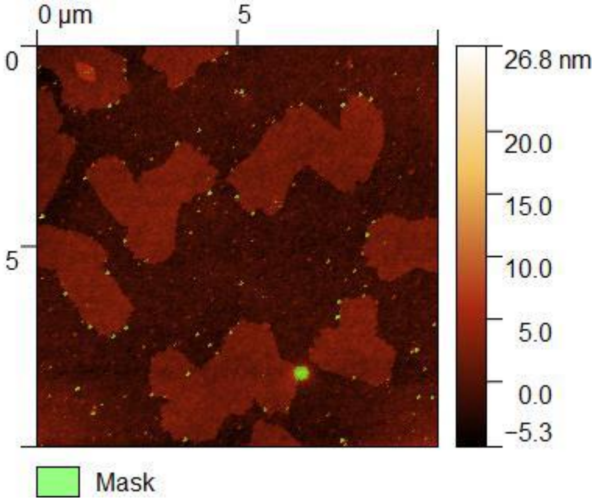

Figure 1: Topographical height image of spin-coated PVA on mica substrate acquired via tapping-mode AFM. Vertical scale ranges from -5.3 to 26.8 nm Sample was generated by spin-coating a 2%wt solution of PVA and aging it in an isolated environment for 5 months. A masking color, green, has been used to mark areas of significant noise and scars not representative of the surface

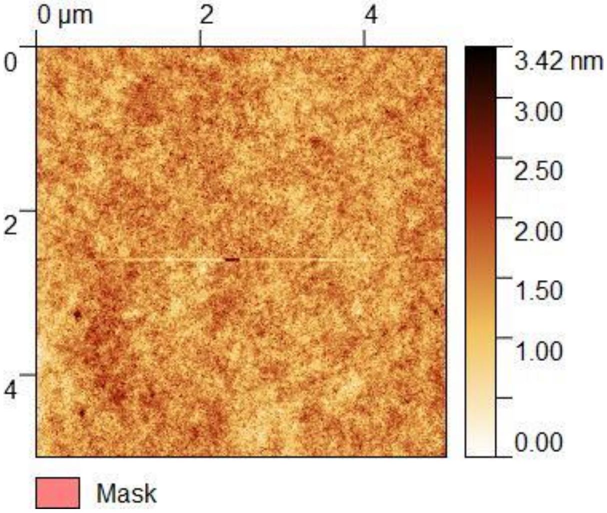

Figure 2: Topographical height image of spin-coated PVA on silicon wafer substrate acquired via tapping-mode AFM. Vertical scale ranges from 0-3.42 nm Sample was generated by spin-coating a 2%wt solution of PVA. Scan was taken immediately following spin-coating process

Figures 1 and 2, when compared, display the efficacy of aging as a processing method for generating crystallinity within semi-crystalline polymers. There are features resembling "plateaus" that are of an extremely consistent height of approximately 4 nm on the aged sample, while the freshly spin-coated sample contains no such features. The discrepancies between the topographies of these samples, along with the extremely consistent height of the "plateaus" in the aged sample demonstrates that the aging process has resulted in significant amounts of crystallization.

Discussion

We have developed a number of techniques that, while on their own have not yielded significant results towards the ultimate objective of the project, are important foundational work for the stages of the project that will be worked upon very soon.

The next stage of our project is to start creating polymer-based nanocomposites from the polymers that exhibit differing phases and then investigating their thermal properties at the microscale. The creation of the nanocomposites will largely happen through the embedding, via various means, of various nanomaterial fillers into our chosen polymer matrices. We will begin by embedding copper nanowires due to their relative chemical simplicity. This will allow us to gain a generalizable understanding of the interactions between polymers of varying phases and a prototypical nanomaterial filler by eliminating many of the confounding variables that may arise by using other nanomaterials that each have their own chemical and physical interactions with a given polymer matrix.

Once there are nanocomposite samples that we have generated, with specific polymer matrices and filler materials, we will proceed to use SThM to take thermal conductivity scans of the surfaces of the nanocomposites in order to gain a microscale understanding of the dynamics of thermal interactions between matrix polymers of varying phases and nanomaterial fillers. These results will allow us to optimize nanocomposites that we create later for even greater thermal conductivity at the microscale.

The stage following that will be to scale the thermal conductivity dynamics involving the thermal interactions between polymer matrices of various phases and nanomaterials that we have observed on the microscale to the macroscale and create larger scale films of nanocomposites that we will be able to perform macroscale thermal measurements on. This is largely a speculative phase as the focus is currently on the microscale. There is a direct path from this phase to application, as the larger scale nanocomposite films could potentially be integrated into technologies.

Conclusion

Polymer phase has great potential to enable nanocomposites to harness the incredible thermal properties of nanomaterials. This would enable the desirable properties of polymers to be used in conjunction with high degrees of thermal conductivity in a great many applications. Understanding the thermal dynamics of polymers of various phases and nanomaterial fillers, dynamics that can be observed via scanning thermal microscopy, will enable us to optimize nanocomposites for a myriad of applications.

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