Abstract: In this work, we demonstrate that dimethylformamide (DMF) leads to better dispersion of graphene nanoplatelets relative to acetone, leading to higher thermal conductivity epoxy-graphene nanocomposites. Uniform dispersion of graphene nanoparticles into epoxy is critical for achieving high thermal conductivity epoxy-graphene nanocomposites. Uniform dispersion of graphene nanoplatelets can improve thermal contact with polymer leading to higher thermal conductivity of the composite. Organic solvents typically lead to efficient dispersion of graphene into the epoxy matrix. In this study, we compare the effect of two organic solvents, dimethylformamide (DMF) and acetone, in terms of their efficiency in dispersing graphene into the epoxy matrix and their effect on enhancing thermal conductivity of the composite. While the effect of solvents on mechanical properties of polymer-graphene nanocomposites has been studied, their effect on thermal conductivity is not well understood. In this study we find that polymer-graphene composites made with DMF show 44% higher thermal conductivity than those made using acetone. Laser scanning confocal microscopy (LSCM) imaging reveals improved dispersion of graphene-nanoplatelets in samples prepared using DMF compared to acetone. These results provide new avenues to achieve higher thermal conductivity graphene-epoxy composites, of key importance for a wide range of thermal management technologies.

1. Introduction: Graphene, since its discovery in 2004(1), has been thoroughly studied for various applications. Properties like extremely high electrical resistivity, high thermal conductivity, high mechanical strength, and modulus are of great interest for various technologies (2). This study focuses on the role of solvents in enabling superior dispersion of graphene in epoxy composites for achieving higher thermal conductivity values. High thermal conductivity of graphene (2000
W/mK – 5000 W/mK) makes it an ideal filler material for obtaining thermally conducting polymer composites (3-7).

Incorporation of graphene nanoplatelets into polymer matrix has been shown to yield significant enhancement in physical properties of polymers (8). Uniform dispersion of graphene into the polymer is of utmost importance to achieve maximum improvement in properties. Uniform dispersion leads to superior thermal contact between graphene nanoplatelets and polymer matrix leading to lower thermal interface resistance between the two, thus enabling higher composite thermal conductivity. Uniform dispersion can also help in forming efficient graphene percolation networks in the polymer matrix by reducing gap between the graphene nanoparticles (8-10).

Stable and uniform dispersion of graphene is thus of utmost importance for achieving large improvement in properties of polymer nanocomposites. Commonly used polymers in engineering applications are mostly soluble in organic solvents. This makes dispersion of graphene sheets into organic-solvents, an important parameter to prepare a homogeneous composite. Graphene also cannot be simply mixed mechanically with the polymer as it tends to reaggregate due to strong Van der Waals forces between graphene sheets. Furthermore, high viscosity of typical polymer melts prevents uniform dispersion of graphene. Therefore, using organic solvents compatible with the common polymers has been widely accepted and regarded as the simplest method for uniformly dispersing graphene sheets (9-11).

Studies have been conducted for the effect of solvents on dispersion of graphene in regards with improvement of mechanical properties (12). However, no results have been reported for the effect of solvents on improvement of thermal conductivity. Acetone, one of the commonly used solvent for preparing graphene-polymer composites has shown short-term stability of graphene dispersions when compared to many other organic solvents like dimethylformamide (DMF), tetrahydrofuran (THF), N-methyl-2-pyrrolidone (NMP) and ethylene glycol, which show long term stability of dispersions (13). The improved dispersion of graphene in solvents such as DMF compared to acetone, has been shown to also lead to improved mechanical properties such as strength. Mishra et al compared the effect of three solvents (ethanol, acetone, and toluene) on the dispersion of polyhedral oligomeric silsequioxane (POSS) in epoxy and the subsequent enhancement of mechanical properties of POSS-epoxy nanocomposite. They found that composite
prepared using ethanol showed increase in elastic modulus and fracture toughness values due to the better dispersion of POSS in epoxy resin in ethanol solvent(14).

While above studies addressed the effect of improved dispersion in certain solvents on mechanical properties like mechanical strength, the present study focuses on the effect of solvents on thermal conductivity. The present investigation addresses comparison between the graphene dispersion capability of two organic solvents- acetone and dimethylformamide (DMF) and also reports the subsequent differences in thermal conductivity of the epoxy-graphene nanocomposites prepared using the two solvents. The study is conducted for three graphene concentrations- 3 weight%, 5 weight% and 7 weight%. The dispersion effect is characterized using confocal laser scanning microscopy which provides optical images of the graphene sheets dispersed in the polymer matrix, enabling a visual comparison of achieved dispersion.

2. Materials and Methodology: Graphene nanoplatelets were purchased from Graphene Supermarket. Epoxy resin used for the study was EPIKOTE RESIN MGS RIMR 135 and the hardener used was EPIKURE CURING AGENT MGS RIMH 137, both purchased from Hexion. The organic solvents N-N, Dimethylformamide (DMF) and Acetone were purchased from University of Oklahoma chemical stock room.

3. Experimental Work

3.1 Preparation of Epoxy/Graphene composite with Acetone: Graphene nanoplatelets (3-7 nm thick and ~5 microns in lateral size) were dispersed in 80 mL Acetone and tip sonicated for one hour in an ice bath to prevent heating and evaporation of acetone. The resin was then added to the solution and tip sonicated in an ice bath for another two hours. After sonication, the solution was heated to 80 °C and stirred continuously using a mechanical mixer to remove the solvent. The mixture of graphene and epoxy was weighed until required weight was reached related to removal of acetone. This mixture was then spread on a PTFE sheet and placed in a vacuum oven at 65 °C for 15 hours to further ensure complete removal of acetone. The composite mixture was then transferred into aluminum molds and cured at 90 °C for 20 hours.

3.2 Preparation of Epoxy/Graphene composite with DMF: Graphene nanoplatelets (3-7 nm thick and ~5 microns in lateral size) were dispersed in 80 mL DMF and bath sonicated in an ice bath for 30 minutes. Epoxy resin was then added to the solution and bath sonicated for another one hour.
After sonication, the solution was heated and stirred at 150 ºC to remove the solvent. The graphene-epoxy mixture was then spread on a PTFE sheet and placed in a vacuum oven at 140 ºC for 15 hours to ensure complete removal of the solvent. The mixture was then transferred into aluminum molds and cured at 90 ºC for 20 hours. Optical image of the prepared composite samples is shown in figure 1.

Figure 1 Optical images of epoxy/graphene composite samples.

3.3 Measurements and Characterizations: The thermal diffusivity of the prepared composite samples was measured using LFA 467 HyperFlash from NETZsch. The dispersion effect of the two solvents was characterized using confocal microscopy imaging.

4. Results and Discussion:

4.1 Characterization of graphene:

Graphene nanoplatelets were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Raman spectra is taken from the graphene supermarket website (23). The SEM and TEM image shown in figure 2a and c shows lateral size and thickness of approximately 5 microns and 6 nm respectively. Chemical composition of the graphene nanoplatelet was characterized using X-ray Photoelectron Spectroscopy which shows approximately 96% carbon content and 3% oxygen content. The XPS
spectra (fig. 2b) shows the peaks of C1s at ~285eV and O1s at ~533V respectively (15). Raman spectra (fig. 2d) of graphene nanoplatelet reveals G peak ~1585 cm\(^{-1}\), G\(^{*}\) band at ~2450 cm\(^{-1}\) and 2D band at ~ 2700cm\(^{-1}\) (16). Absence of D band indicates the high quality of these commercial GNP. The intensity of G band presents due to in-plane or out-of-plane atomic vibration of sp\(^{2}\) carbon and the position refers multilayer structure (17). The G\(^{*}\) band occurs due to is second order phonon scattering. Asymmetric peak shape and position relates to multilayer structure with respect to monolayer graphene (18, 19).

Figure 2a) SEM image, b)XPS spectra, c)TEM image, d)Raman Spectra

4.2 Thermal Conductivity Measurements: 
Figure 3. Thermal conductivity variation with increasing graphene concentration

Figure 3 shows the thermal conductivity values of the graphene-epoxy composites with 3wt%, 5wt% and 7wt% concentration for the two organic solvents - acetone and DMF. Thermal conductivity of 0wt% sample (corresponding to pure epoxy sample), is measured to be 0.169 Wm\(^{-1}\)K\(^{-1}\). At 3wt%, DMF and acetone samples show thermal conductivity values of 0.313 Wm\(^{-1}\)K\(^{-1}\) and 0.377 Wm\(^{-1}\)K\(^{-1}\) respectively. However, at higher concentrations, DMF-based composite samples show approximately 40% and 44% higher thermal conductivity than acetone-based samples for 5wt% and 7wt% graphene content respectively.

The solvent thus has a clear effect on thermal conductivity of epoxy-graphene nanocomposites. This enhancement in thermal conductivity at higher concentrations can be explained in terms of improved dispersion of graphene at higher concentrations in the epoxy composite prepared with DMF (discussed in section 4.3).
4.3 Confocal Microscopy Imaging for Dispersion Characterization:

Laser Scanning Confocal Microscopy (LSCM) is used to provide an optical image visualization of the graphene dispersion in the composite samples and compare the effect of the two solvents (acetone and DMF) on dispersion of graphene within the composites. LSCM generate images with lesser haze and better contrast than a conventional microscope and can be focused on a thin cross-section of a sample (20-22). It can also be used to generate a three-dimensional image of the sample. This makes LSCM an effective tool to visualize the dispersion of graphene within the composite samples.

Figure 4 shows the LSCM images of the graphene-epoxy composites with 3 wt%, 5 wt% and 7 wt%. There is clear visible difference in the dispersion of graphene in the epoxy composites prepared using DMF and acetone solvents. Acetone based samples (fig. 4 a,b,c) show larger gaps between graphene nanoparticles indicating poor dispersion. Composites prepared using DMF, however, show relatively more uniform distribution of graphene sheets leading to higher thermal conductivity (fig. 4 d,e,f).
5. Conclusion:
Dispersion of graphene into epoxy matrix and its effect on the thermal conductivity of the graphene-epoxy composite was investigated for two organic solvents - acetone and DMF. Laser Scanning Confocal Microscopy was used to obtain optical images of the composite samples to visualize the dispersion of graphene in the epoxy matrix. In comparison to the DMF-based samples, acetone-based samples showed poor dispersion with agglomeration of graphene visible at various locations. Improved dispersion of graphene in composites prepared with DMF as solvent was found to lead to 40% and 44% higher thermal conductivity in DMF based samples than the acetone-based samples at 5wt% and 7wt% respectively. These results provide new pathways for developing graphene-epoxy nanocomposites with high thermal conductivity.

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