



*Letter*

## Understanding the influence of graphene and nanoclay on the microcracks developed at cryogenic temperature

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**Abstract:** This research examines reduction of microcracks in polyurea by addition of graphene and nanoclay on account of potential improvement in barrier properties. Graphene and nanoclay were added in different wt. fractions to polyurea followed by thin film preparation. The prepared thin film samples were characterized using scanning electron microscopy. Surface images before and after exposure to cryogenic temperature indicate that controlled addition of graphene and nanoclay to polyurea thin film can lead to a reduction in microcracking caused by thermal shocks.

**Keywords:** graphene; polyurea; nanoclay; microcracks; cryogenic

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### 1. Introduction

Polymers play a vital role in all industrial applications because of their high specific strength and flexibility. However, factors like low absolute strength and poor fracture toughness limit their applications, especially in the case of rubbers and thermoset resins. To address these limitations, polymers are often reinforced with a variety of fillers including carbon black, carbon nanotubes, silica, and polymeric particles. Previous studies have demonstrated that addition of carbon nanotubes to polymer matrices can lead to dramatic improvement in mechanical, electrical and thermal properties [1,2]. Nonetheless, the high manufacturing costs, high viscosity and high anisotropic functionality of carbon nanotubes renders it be a not so ideal reinforcing agent. In contrast, graphene nanoplatelets which are fillers that consist of one or more layers of a graphene plane offer very exceptional functionalities like high mechanical strength and chemical stability. Furthermore, its

notable features such as availability in nature, cost-effectiveness, high specific surface area leading to higher levels of stress transfer across interface, makes it a strong choice as reinforcement [3] than carbon nanotubes. Additionally, it possesses isotropic electrical/thermal conductivities on the graphene plane, low viscosity, and non-toxicity when compounded with the polymer. These appealing characteristics of graphene over carbon nanotubes has encouraged researchers to widen their field of study by using them as reinforcing agents.

Previous studies have also explored the use of organoclays formed from montmorillonite to fabricate polymer nanocomposites [4]. Addition of nanoclay have resulted in significant changes in the gas barrier properties of polymer nanocomposites [5]. The primary consideration to improve the barrier properties is through the homogenous dispersion of nanoclay into the polymer matrix to create a tortuous diffusion pathway [6].

Polyurea (PU) is a very widely used polymer material and exhibits unique properties due its phase-separated morphology. It is a copolymer formed by the rapid interaction of an isocyanate and an amine component which yields a urea linkage. Theoretically, the isocyanate component and amine component must be mixed in a stoichiometric ratio of 1:1, i.e., the total number of isocyanate functional ends must equal the total number of amine functional sites [7–9]. PU self-assembles into a continuous rubbery matrix with dispersed rigid domains that are well-connected to the rubbery phase and have nanoscale dimensions representing an ideal filler–polymer composite. The hydrogen bonding within the soft phase providing additional toughness [10]. It has attracted significant attention with its use as a protective coating or inserted layer for enhanced blast protection and penetration resistance of structures and buildings [11]. Recently, efforts are underway to improve the mechanical properties of polyurea by optimal micro-structural modifications through the addition of fibers [12] and nanoparticles [13,14]. In our previous work, we have used filler to understand the influence of filler at cryogenic condition, where we observed that material properties at cryogenic condition is govern by filler architecture in the host polymer [15].

A combination of nano-additives involving graphene and Cloisite 30B, a type of nanoclay in PU is considered to provide potential improvements in the overall thermal and barriers properties of the nanocomposites. In this regard, the study examines the use of controlled addition of the nano-additives in reducing the formation of microcracks in the nanocomposites due to thermal shocks. There is not much research done on using two different kinds of nano-additives with the polymer to gain the distinct characteristics of both the fillers.

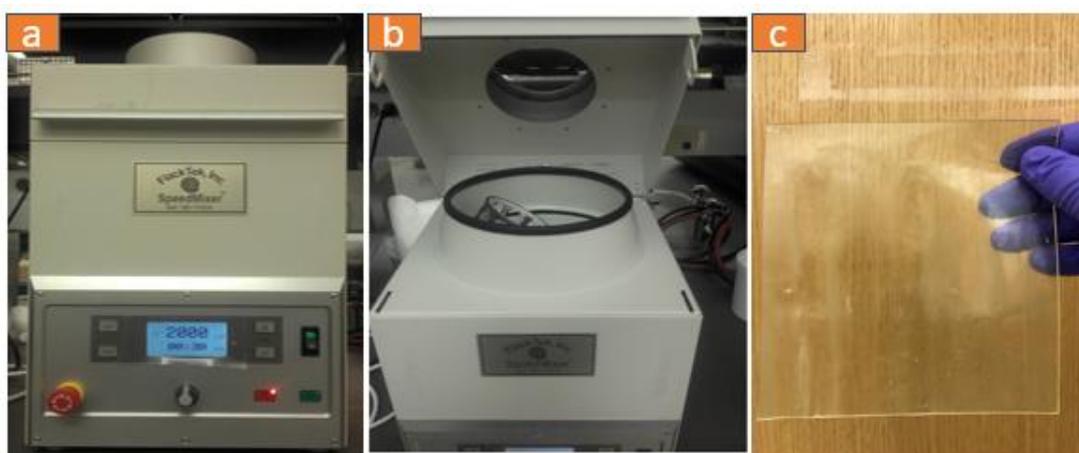
## **2. Materials and method**

### *2.1. Raw materials*

Graphene nanoplatelets with an average size of 5  $\mu\text{m}$  were purchased from XG Sciences, USA. Nanoclay Cloisite 30B was supplied from Southern Clay Products, Texas, USA. The two-part monomer mixture of polyurea containing isocyanate and amine groups was purchased from BJB Enterprises, USA.

## 2.2. Preparation of nanocomposites

The nanocomposites were prepared by solution mixing method. A high speed mixer (shown in Figure 1a) and vacuum degasser (shown in Figure 1b) were used in the fabrication process. A stoichiometric ratio of 1:1 isocyanate to amine ratio was used as recommended by the manufacturer. The two components were degassed under vacuum before use to remove the presence of excess air bubbles. Initially, nanoclay was added to the isocyanate component and mixed at 1000 rpm in a high-speed mixer for 10 minutes. Thereafter, graphene nanoplatelets which were ground using mortar and pestle were added to the above mixture and thoroughly mixed using the speed mixer at 1000 rpm for 10 minutes. Finally, the amine component was added to the blend, and due to the short gelation time of polyurea it was mixed only for 5 minutes at 1000 rpm, and then poured into the silicon molds and was set to cure for 24 hours at room temperature. The nanoparticles were added in different wt% varying up to 1 wt% as a combination of graphene and Cloisite 30B. Pure PU sample developed in this study is shown in Figure 1c.



**Figure 1.** Preparation of PU nanocomposites.

## 2.3. Characterization

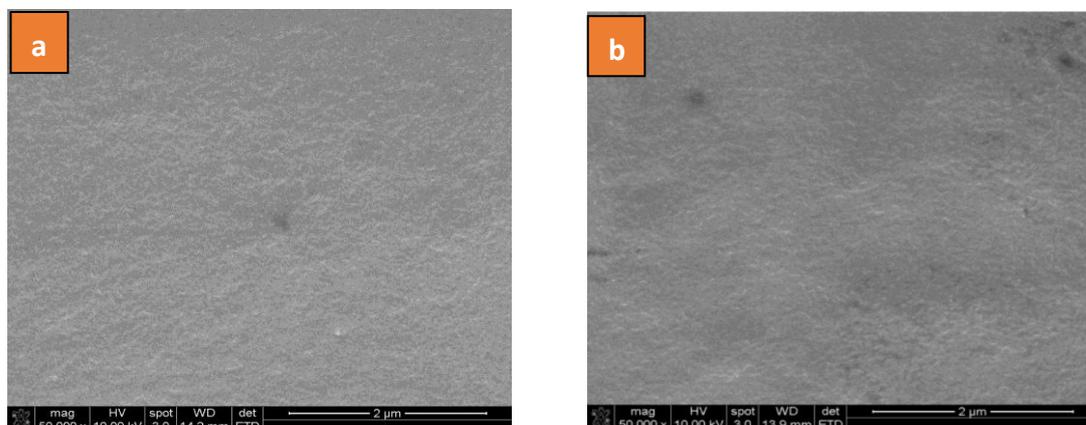
A Hitachi S-4800 (Dallas, Texas, USA) Scanning Electron Microscope (SEM) was used to investigate the microcracks that may develop due to the exposure to cryogenic temperatures. All the samples were sputter coated with a thin layer of platinum for 30 seconds. Before examining the sample for low-temperature condition, samples were dipped inside the liquid nitrogen at 77 K for a soaking time of 5 minutes.

The tensile experiments were carried out as per ASTM D638, the samples were prepared inside the mold and machined as per ASTM standard.

## 3. Results

SEM images taken at 2 microns' magnification were used to determine the surface morphology of neat polyurea (Figure 2a), graphene and nanoclay reinforced polyurea nanocomposites before and

after exposure to the cryogenic condition. It can be observed from the Figure 2b that graphene and clay have dispersed uniformly in the polyurea matrix as no phase separation has occurred. The images are noticeably featureless before the exposure to very low temperatures.

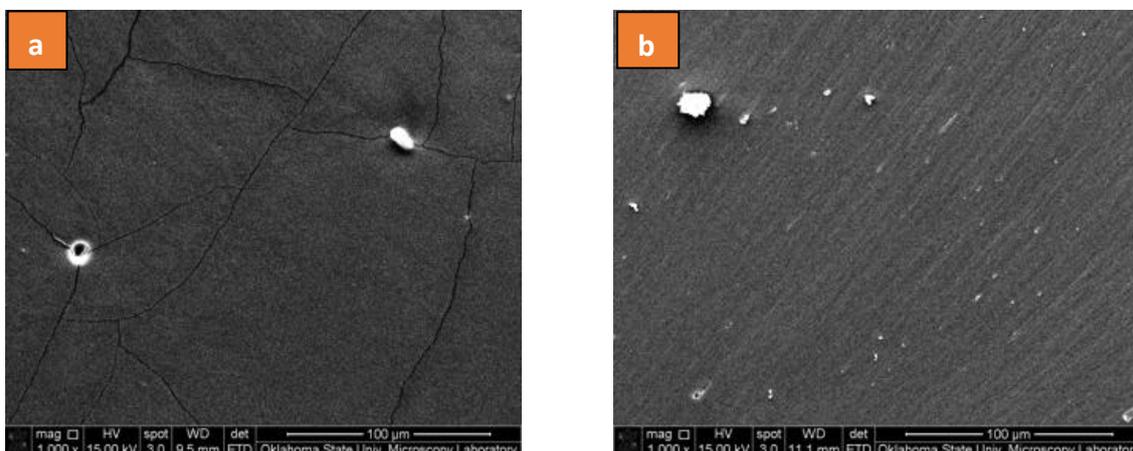


**Figure 2.** Surface images of (a) Neat PU, (b) PU + 0.50 wt% G + 0.50 wt% C taken before exposure to cryogenic conditions (C: Clay and G: Graphene).

Figure 3 shows the SEM images of the surface of the different types of nanocomposites included in this study after exposure to cryogenic condition. The formation of micro-cracks in the neat polyurethane sample can be seen in Figure 3a. This could be due to the brittleness developed at liquid nitrogen temperature. At low temperatures, the matrix becomes stiffer and stronger but less ductile. The internal stresses generated due to thermal contraction could lead to matrix failure by creating cracks. When the sample is exposed to liquid nitrogen, the external surface of the material starts to shrink while the internal core remains at room temperature with no contraction. The outer layers become rigid by the time internal core begins to contract leading to residual thermal stresses. This residual stress occurs twice in the same sample due to sudden changes in the temperature from room temperature to cryogenic temperature and vice versa. When these stresses in the material become considerable, they are relieved through physical processes such as microcracking seen in Figure 3a.

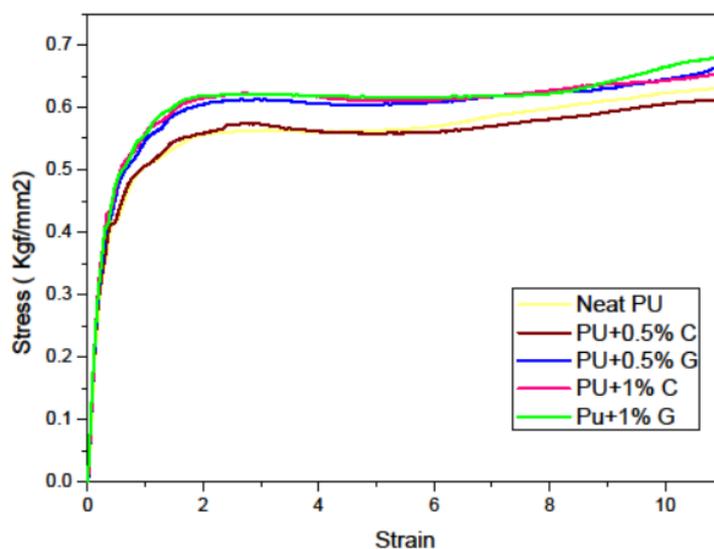
This effect of thermal shock can be minimized by toughening the material with nanoadditives. It can be observed from Figure 3b that the addition of graphene and nanoclay significantly reduces the microcracking on the surface caused by exposure to cryogenic temperature. This phenomenon indicates that nanofillers used in this study behaves as bridges by creating the strong interface in the polymer hence hindering possible crack propagation. It is important to note that excellent dispersion of the nanoadditives in the polymer is a critical aspect to achieve resistance to crack propagation. At high loading of nanoadditives, agglomeration can be detrimental in achieving good toughness properties. In this study, it can be noted that the samples with graphene and clay at loadings of 1 wt% of combination of nanoadditives have been very well dispersed and hence there is significant reduction of any microcracks from thermal shocks. This can be explained for graphene and clay as the embedment of the PU matrix within the layers and acting as stacking agents in crack propagation. Thus, thermal shock mitigation can be achieved by controlled addition of nanofillers in the PU matrix, which act as bridges to crack initiation and propagation due to abrupt changes in temperature.

Additionally, it can be learnt from further study that combination of the two nanoadditives is useful in enhancing the effectiveness of graphene in improving the overall behavior of the modified nanocomposites. The striations on the surface of the modified nanocomposites after exposure to cryogenic conditions also indicate the effectiveness of the nanoadditives in the resistance to microcracking from sudden thermal changes.



**Figure 3.** Surface images (a) Neat PU, (b) PU + 0.50 wt% G + 0.50 wt% C after exposure to cryogenic conditions (C: Clay and G: Graphene).

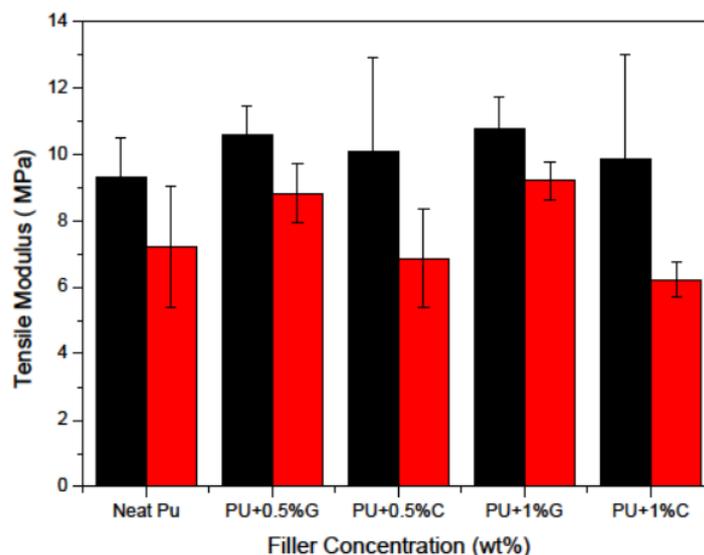
The tensile modulus of all the samples was calculated from the slope of the stress–strain curve as shown in Figures 4 for neat PU and filler reinforced PU tested at room temperature.



**Figure 4.** Stress–strain plot of single-additive PU composites.

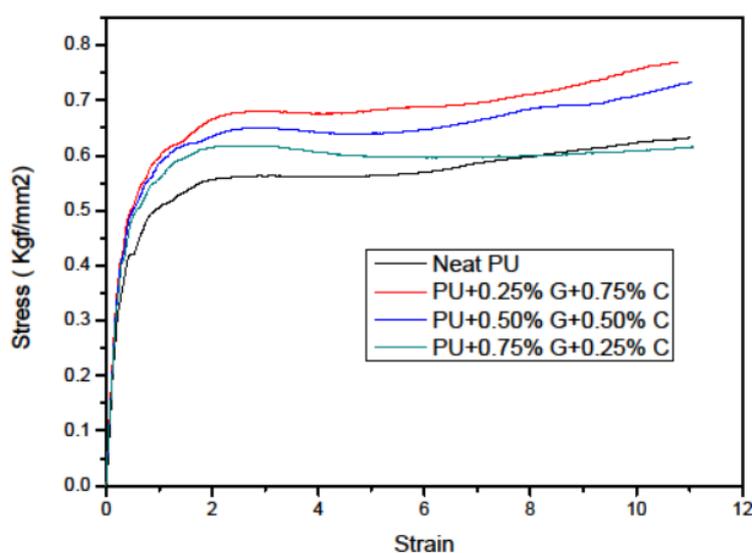
We observed that, for sample before cryogenic temperature exposure, inclusion of the filler at 0.5 wt% increases tensile modulus by 30% and 35% of PU as shown in Figure 5. However, with increase of filler percentage in PU the tensile modulus decreases. This decrease in the modulus is due

to formation of agglomerates at higher filler loading that deteriorates the PU–filler system. For the sample after cryogenic exposure, the tensile modulus of the neat PU increases by 30% compared to PU before exposure. This increase in the tensile modulus after cryogenic exposure is due to shrinkage of polymer chain that results in increase in intermolecular force. The inclusion of filler does not show any modification in the tensile modulus for the samples exposed to cryogenic condition considering the scatter in the data.



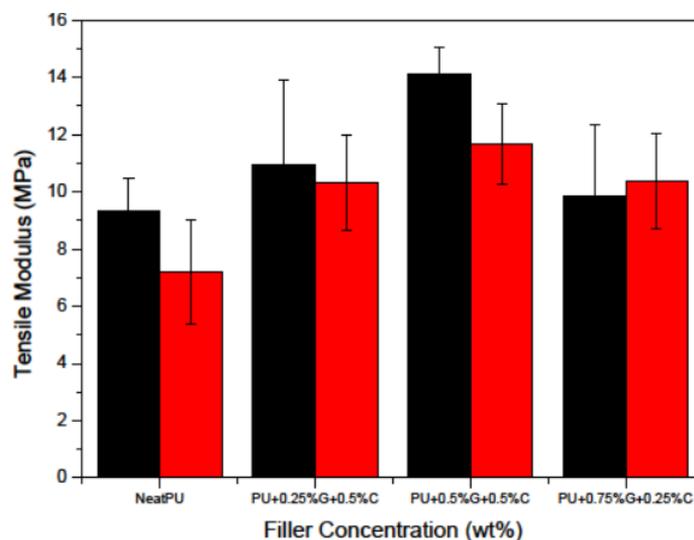
**Figure 5.** Tensile modulus of neat PU and 0.5 and 1 wt% filler reinforced PU. Red color represents modulus before and black color represents modulus after cryogenic exposure.

Tensile modulus for hybrid (clay + nanocomposites) was obtained from stress–strain graph as shown in Figure 6.



**Figure 6.** Stress–strain plot of dual-additive PU composites at 1 wt%.

Figure 7 shows that inclusion of 1% filler as dual additive in the PU increases the tensile modulus. In particular 0.5% clay and 0.5% graphene increase the tensile modulus by 60%. For the sample exposed to cryogenic condition the tensile modulus increases by 65% for 1% filler in particular 0.5% clay and 0.5% graphene.



**Figure 7.** Tensile modulus variation in dual-additive PU composites at 1 wt%. Red color represents modulus before, and black color represents modulus after cryogenic exposure.

#### 4. Conclusions

In this work, polyurea nanocomposites are prepared by using the solution mixing method by adding graphene, and nanoclay within 1 wt%. SEM images of the modified nanocomposites indicate uniform dispersion of the nanoparticles with the PU matrix. Surface images after exposure to cryogenic conditions with a soaking time of 5 minutes indicates the presence of microcracks in neat PU. But the modified nanocomposites with the addition of nanofillers have attributed to significant reduction in generation of micro-cracks when exposed to very low temperatures. We have also observed that inclusion of solo filler increases the tensile modulus before cryogenic exposure, however, no modification was observed in the tensile modulus after cryogenic exposure. Dual additive in PU increases the tensile modulus for both before and after cryogenic exposure. This is a major benefit from the use of graphene and nanoclay as a reinforcement in PU, which in addition is expected to improve the thermal and barrier properties of the polymer resin system.

#### Conflict of interest

The authors declare no conflict of interest.

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