Thermal performance of hybrid thermal interface graphene nanocomposites

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Abstract: This research examines thermal performance of hybrid thermal interface graphene nanocomposites. Graphene nanoflakes were added in different wt. fractions to thermoplastic polymeric materials (polyacrylate and other polymers) followed by thin film preparation. The prepared thin film samples were characterized using optical and scanning electron microscopy. The fabricated samples of polymer-graphene composites were studied to determine the contact angles at different temperatures and the droplet evaporation rates from the surfaces of such materials.

1. Introduction
Currently, there is growing interest in new thermal functional materials (TFM), which are widely used for thermal stabilization and thermal management of electronic and energy devices [1-3]. Thermal functional materials are important for the removal of heat from various energy and electronic devices and other applications: thermal interfaces materials (TIM), thermal management nanofluids (TMNF) for heat removal, phase-change materials (PCM) and thermal conductive plastics (TCP). In addition to the bulk properties, such materials should also have special surface properties - surface electric and thermal conductivity, wetting and spreading of droplets, evaporation and condensation modes on the surface of such materials, and controlled modes of pool, transition and film boiling [1-3]. In [4-9], new hybrid graphene nanocomposites were studied, which can be very effectively used as a new generation TFM. In this work, we continue the study of these materials, in particular, their thermal properties and the possibilities of using them for thermal stabilization.

In many tasks of thermal, solar and nuclear power, it is necessary to have special surfaces for efficient heat and mass transfer. However, often good wettability and contact angle dynamics as well as thermal conductivity cannot coexist on functional surfaces. Under these conditions, it is necessary to search for new surfaces made of functional materials. In recent years, materials based on graphene, its components added to polymers or hybrid graphene materials with the addition of other nanoparticles, have been actively studied. In this work, we experimentally studied graphene nanocomposites based on a thermoplastic polymer polyacrylate and graphene flakes of various concentrations: pure polyacrylate, polyacrylate with the addition of 10-15%, 30-35% and 60-70% graphene nanoflakes.

2. Materials and method
Graphene nanoflakes with an average size of 15-30 μm (thickness - 3.5 - 5 nm) were received from Graphene Star Ltd, UK. Polyacrylate and other polymers was supplied from RusHIM, Moscow, Russia. The graphene nanocomposites were prepared by solution mixing method. A high speed mixer (3500-9000 rpm) and vacuum degasser were used in the fabrication process. Various thermoplastic...
polymers were mixed with graphene nanoflakes (GNF) in specific weight ratios: 10-15 wt%, 30-35 wt% and 60-70 wt%. The components were degassed under vacuum before use to remove the presence of excess air bubbles. Examples of such samples are shown in Figure. 1. Figure 1 in the center and on the right also shows images of the surface of PA+ GNF 30-35% and PA+ GNF 60-70%.

![Figure 1](image1.png)

Figure 1. Functional PA+GNF samples: A - pure polyacrylate (PA), B – PA+ GNF 10-15%, C - PA+ GNF 30-35% and D - PA+ GNF 60-70%.

For all types of samples, contact angles and evaporation rates were studied. For measurement the contact angle and evaporation rates of drops on the graphene nanocomposite surface was using the system Kruss EasyDrop (Figure. 2). The Kruss EasyDrop measuring system was used with a special heater and temperature control system. Graphene nanocomposites were applied in a thin layer on a glass substrate, which was placed on a heater (Figure 2). First, contact angles were studied as a function of temperature for different samples of graphene substrates. Second, the evaporation rate was also measured by determining the volume of the evaporating droplet.

![Figure 2](image2.png)

Figure 2. Method for measuring the contact angle of evaporating droplets.

3. **Contact angles for graphene nanocomposites**

Problems of wettability and spreading of droplets of operating thermo-fluids are often found in heat exchangers for various purposes. Similar problems occur in the systems of purification and desalination of water or its splitting. In recent years, the problems of wetting and spreading drops of various liquids on the surfaces of functional materials have been actively investigated. Serious prospects are outlined in the use graphene materials and hybrid graphene nanocomposites are often used to solve these problems [1,10].

Of particular interest are micro- and nanorough surfaces, the influence of a regular or irregular surface structure on the behavior of contact three-phase lines, the dynamics of the contact angle and contact line when heating or cooling the surface [1,5].

The wettability and spreading of droplets on the surface of graphene (monoatomic or polyatomic thickness) is still of interest, since there is no final clarity here. In particular, recently it has been
possible to find out that the contact angle of water on graphene-coated substrates and the contact angle of water on the same substrates without graphene are almost identical, which indicates the transparency of graphene wetting [11]. If the thinnest layers of graphene flakes do not adsorb water, regardless of relative humidity, on the other hand, thicker graphene nanoflakes an increasing amount of water with increasing humidity. This allows us to evaluate their wettability, which is the result of competition between adhesive interactions of water and graphene and cohesive interactions of water.

At the same time, the number of works devoted to these problems in the study of graphene-polymer and hybrid graphene composites is relatively small. There is some data available on the dynamics of contact angles at different surface temperatures of graphene nanocomposites, the evaporation rate of droplet, and the effect on the evaporation rate of surface morphology, the behavior of the drop-substrate contact interface of a graphene nanocomposite in bubble nucleation, transition, or film boiling modes (near the Leidenfrost point). Studies on these surfaces showed the behavior of contact angles and contact lines, and some of the detected effects have not yet been clearly explained. Of particular interest are the effects of the active influence of contact lines on the surface of the material, which is manifested in the possibility of partial destruction of hybrid graphene-polymer surfaces. The latter circumstance is extremely important in the development and creation of heat transfer surfaces, for thermal and electric energy.

It is of particular interest to study the dynamics of the contact angle during droplet evaporation on the surface of graphene nanocomposites. It is well known that on smooth and partially rough surfaces, droplet evaporation can occur in the regimes of a constant contact angle, constant contact line, or in a mixed regime. We have studied such modes, and the results have shown that for graphene composites, very complex modes of behavior of the contact angle and contact line can be observed. It should be noted that such a strong dependence of the contact angle on the fraction of graphene in the nanocomposite has not yet been explained. It is possible that an increase in the concentration of graphene nanoflakes changes the surface morphology - at their high concentration, the surface becomes nanorough, since graphene particles can be partially located vertically on the surface of the polymer. This leads to an increase in the contact angle, i.e. to superhydrophobicity.

In particular, in the Figure 3 and Figure 4 show the dependences of the contact angles for different samples at two temperatures $T_{\text{surf}}=24^\circ\text{C}$ and $T_{\text{surf}}=40^\circ\text{C}$. The most significant change in the contact angle is observed for PA$+$Graphene (60-70%) nanocomposite. At the same time, at a temperature close to room temperature, the contact angle decreases continuously, but at higher temperatures, first a mode of approximately constant contact angle is observed, and then, its rapid decrease. The latter means that there is a transition to the constant contact line mode. The average contact angle on the
PA+ GNF nanocomposite over a wide temperature range is shown in Figure 5. Linear correlation 
\[ \alpha = b + ac = \alpha = 73.82 + 0.71c \] and degree of uncertainty are also presented here. Function obtained with linear approximation - coefficient errors: \( b = 73.82 \pm 1.57; a = 0.71 \pm 0.04 \).

Even when using evacuation of samples of PA+ GNF nanocomposites, microscopic pores remain inside, which can have a noticeable effect on the dynamics of contact angles and the evaporation rate drops on the surface. However, this problem needs additional research, since there is no clear understanding of the dynamics of contact angles and the features of evaporation of liquid droplets on such surfaces. At the same time, for the use of such surfaces as functional materials for thermal stabilization, these data are necessary.

**Figure 5.** Average contact angle during droplets evaporation for PA+GNF nanocomposites at various mass loading of GNF.

**Figure 6.** Evaporation time of water droplets for PA+GNF nanocomposites at different surface temperatures.

4. **Drop evaporation rates on the PA+GNF nanocomposite surfaces**

As mentioned earlier, there is very little research on measuring the evaporation rate on the graphene nanocomposite surfaces. There are still no experimental data on the features of the evaporation rates in thermoplastic polymers with different graphene concentrations. Despite the importance of this problem, in particular, for the development and creation of light polymer heat exchangers with high thermal conductivity, in fact, we do not know such works, except for some of the solutions noted in [8,9].

We have investigated the characteristic modes of evaporation of water droplets on various surfaces of PA+Graphene composites - Figure 7 shows these modes in the initial time period and after 45-55 seconds of the evaporation process \( T_{\text{surf}}=80^\circ\text{C} \).

**Figure 7.** Drop evaporation on the graphene nanocomposites surface.
At temperatures of 120 °C and above, a small drop-shaped rim is formed on a sample of pure polyacrylate and some structures grow after the end of the evaporation process (for example, Figures 8a and Figure 8b). When graphene nanoflakes are added to polyacryl, the noted inhomogeneities practically disappear and the evaporation process has no peculiarities up to the mass fraction of graphene flakes of 70%. All these features can be associated not only with the nano-roughness of the nanocomposite surface or the presence of microbubbles inside the structure, but also with the partial thermal destruction of the matrix material – polyacryl (destruction temperature is close to 150 °C).

Figure 8. Inhomogeneous structures on the surface after evaporation.

We also investigated nanocomposites polyurethane + metal microspheres + graphene nanoflakes (PU+MMS+GNF). The rates of evaporation of water droplets on such surfaces and the contact angles in the process of evaporation are studied. The results of such studies are shown in Figure 9. It is clearly seen that the processes of evaporation of droplets have many features: first, the evaporation rates are non-monotonic, and secondly, in contrast to polyacrylic nanocomposites, the relationship between contact angles and evaporation rates is ambiguous. So far, we have not been able to establish the mechanisms of the features of such evaporation, but our results indicate a nontrivial behavior of interfacial contact lines during the evaporation of drops on polyurethane composites with graphene flakes and metal microspheres.

Figure 9. Evaporation rate of water droplets for PU+MMS+GNF nanocomposites.

5. Results and discussions
The thermal performance of hybrid thermal interface graphene nanocomposites play an important role in various applications, in particular, in power engineering and electronics, for thermal stabilization and cooling of various devices. Some important properties necessary for solving such problems are studied in this work. In particular, results were obtained for graphene nanocomposite surface based on polymers that are important for manufacture thermal functional materials. A study has been carried out and new experimental data have been obtained on the contact angles, the dynamics of the contact line of liquid drops on the surface of such composites in a wide temperature range (from 24 to 150 °C). The main attention in this work is paid to graphene composites based on thermoplastic polymer
(polyacrylate) and graphene flakes of various concentrations: 10-15wt%, 30-35wt% and 60-70wt% and polyurethane+GNF, since they are the most common polymers in practice functional materials.

The influence of the graphene flakes fraction and the surface temperature on the dynamics of the contact line and the contact angle of the sessile drops on the surface, as well as the evaporation rate of the drops, depending on various factors, was studied. As a result of the research, the following conclusions can be drawn:

1. It is shown that even at temperatures below the boiling point of water, a complex behavior of the contact angle and the contact line is observed, which are not consistent with existing models, within which the evaporation regime must be accompanied in certain evaporation ranges by either a constant contact angle (CCA) or a constant contact line (CCL).

2. Experimental data indicate a more complex behavior of the contact angle and contact line, in particular, practically no regimes with a constant contact angle were found, especially in the region of high surface temperatures.

3. Standard models for describing the evaporation regimes of sessile droplets on rough (superhydrophobic) surfaces cannot describe the evaporation regimes observed in this study. Apparently, the reason lies in the presence of microvoids (cavities) inside nanocomposites with graphene flakes, inside which vapor can form. In this regard, it is necessary to develop new models of evaporation on graphene-polymer surfaces, since the physical properties of the latter can reversibly or irreversibly change during heating.

4. When heated above 120-150, unstable regimes are observed, associated with both nucleate boiling inside the droplets and thermal instability of the polymers themselves.

5. Small overheating of the surface of the composites relative to the saturation temperature leads to different mechanisms of nucleation of bubbles inside the droplets. It remains unclear why boiling behaves so differently on samples of similar types.

These data clearly show the importance and the effect of surface properties on sessile drop evaporation. They can be used for new functional materials, including thermal interface materials, as well as thermal management materials in power engineering, electronics and optoelectronics.

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