APPLICATION: GRAPHENE NANOCOMPOSITE FOR IMPROVEMENT OF VACCINE TRANSPORTATION COLD CHAIN

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ABSTRACT

Vaccines are biological products that must be kept between 2°C and 8°C. If not, they lose effectiveness to the point of total inactivity. Seeking to enhance the useful life of vaccines when they must be transported to remote locations, the use of a mobile monitored cooling system (SMRM, by its Spanish acronym) using a graphene-reinforced polymer nanocomposite has been proposed. This nanocomposite improves the cooling or heating speed of thermal, electric, and electronic devices. This improvement aims to ensure that SMRM transported vaccines have a reduced exposure to temperatures outside the specified range, allowing for greater efficiency than when they are transported using commercial systems. As a result of this study, a cooling rate of 1.54 (°C/min) and energy consumption of 6.67 W/h were achieved, demonstrating a significant improvement, which, compared to commercial systems, yields a 200% higher cooling rate and 41% less energy consumption.

KEYWORDS: Vaccine, transportation, graphene, energy efficiency, nanocomposite, cold chain, thermoelectric cooling.

APLICACIÓN: NANOCOMPUESTO DE GRAFENO PARA MEJORA DE LA CADENA DE FRÍO EN EL TRANSPORTE DE VACUNAS

RESUMEN

Las vacunas son productos biológicos que se deben conservar entre 2° y 8°C, de lo contrario van perdiendo acción hasta llegar a inactividad total. Buscando mejorar la vida útil de las vacunas cuando requieran transportarse a lugares apartados, se ha propuesto utilizar un sistema móvil de refrigeración monitoreada (SMRM) que usa un nanocompuesto de matriz polimérica reforzado con grafeno. Esto mejora la velocidad de enfriamiento o calentamiento en dispositivos eléctricos, electrónicos y térmicos. Dicha mejora pretende asegurar que las vacunas transportadas en el SMRM tengan menor exposición a temperaturas por fuera de las especificadas, permitiendo que el producto tenga mayor eficacia que...
el transportado con sistemas comerciales. Finalmente, al lograr una velocidad de enfriamiento de 1,54 (˚C/min) y un consumo energético de 6,67 W/h, se evidencia una mejoría importante, que comparándolos con el sistema comercial genera el equivalente a 200 % mayor velocidad de enfriamiento y 41 % menor consumo energético.

PALABRAS CLAVE: transporte de vacunas, grafeno, eficiencia energética, nanocompuesto, cadena de frío, refrigeración termoeléctrica.

APLICACIÓN: NANO COMPÓSITOS DE GRAFENO PARA A MELHORA DA CADEIA DE FRIO NO TRANSPORTE VACINAS

RESUMO

As vacinas são produtos biológicos que devem ser conservados entre 2° e 8° C, se não, elas vão perdendo a eficácia ao ponto de inatividade total. Procurando realçar a vida útil da vacina quando precisem ser transportadas para locais remotos, se tem feito uma proposta de utilização de um sistema móvel de refrigeração monitorizado (SMRM), (por sua sigla em castelhano) que utiliza um nano-compósito de matriz polimérica reforçado com grafeno. Isto melhora a velocidade da refrigeração ou aquecimento dos dispositivos elétricos, eletrônicos e térmicos. Tal melhoria visa assegurar que as vacinas transportadas no SMRM tenham menor exposição a temperaturas aparte das especificadas, permitindo que o produto tenha uma maior eficiência que o transportado com sistemas comerciais. Finalmente, quando alcançou uma velocidade de refrigeração de 1,54 (˚C/min) e um consumo de energia de 6,67 W/h, se observa uma melhoria significativa, que em comparação com o sistema comercial produz a equivalência a 200% maior velocidade refrigeração e 41% menos consumo de energia.

PALAVRAS-CHAVE: Transporte De Vacinas, Grafeno, Eficiência Energética, Nanocompósito, Cadeia Do Frio, Resfriamento Termoeléctrico.

1. INTRODUCTION

Few-layer graphene (FLG), a two-dimensional (2-D) nanomaterial in the form of a sheet whose thickness ranges from a single layer of 1.8 nm to FLG from 3.7 to ~20 nm, and which, through its mechanic isolation in 2004 by the Russian physicists Andre Geim and Konstantin Novoselov (Geim, et al., 2004) (Geim & Novoselov, 2007), has become the subject of a great deal of research, patents, and applications in areas ranging from medicine to bioengineering and electronics, and even to athletics. Additionally, it has begun to be utilized in energy storage, automobiles, the aerospace industry, and electric and electronic devices. The most promising applications using graphene are those already developed and about to be developed in radio frequency electronics, flat screens, photovoltaic cells, transparent conductor electrodes, high current density conductors, photodetectors, light modulators, thermoelectricity, thermal sensors, and thermal interface materials (Geim & Novoselov, 2007)(Choi & Lee, 2012) (Avouris & Dimitrakopoulos, 2012) (Shahil & Balandin, 2012). This enthusiastic acceptance is nothing more than the product of the unique characteristics this nanomaterial offers, such as having a null overlap between electric conduction layers in the case of single-layer graphene (Choi & Lee, 2012) (Avouris & Dimitrakopoulos, 2012) (Valencia, 2011), which allows electrons and phonons to move in a different way than three-dimensional (3-D) materials (Geim, et al., 2004) (Fisher, 2013) (Balandin & Nika, 2012). The aforementioned makes a much better electric and heat conductor than silver, gold, and copper. Furthermore, it exhibits a resistance 200 times greater than steel (Valencia, 2011), it is resistant to corrosion, it is physically and chemically stable under normal environmental conditions, and it supports temperatures of more than 1,000 degrees Celsius, and much lower than zero Celsius without altering its properties.

The reception of this 2-D nanomaterial has been such that the European Union, North America, and the East have invested, in just 5 years, more than a billion
Euros in research and development related to the material. In Europe alone the European Commission designated in 2013 and for 10 years thereafter the equivalent of 100 million Euros annually for a total of one billion Euros in a program called the Graphene Flagship, with the goal of bringing graphene from the laboratory to the market (Johnson, 2013). The countries with the highest number of patents related to graphene in the period from 2010 to 2014 are China followed by South Korea, with a growth in the same period of 802% in the global register of patents related to graphene (UK Intellectual Property Office Informatics Team, 2015).

The vast majority of research conducted focuses on methods of graphene fabrication and uses in electronics and photonics. Many of these applications require the use of graphene alone or as reinforcement in a compound material known as nanocomposite, so named because it contains within a matrix of base material such as metal, ceramic, or polymer, one or more materials different from the matrix with the characteristic of being nanometric in size. These nanocomposites are fabricated using techniques that allow a homogenous or fixed dispersion of the sheets, filaments, or particles in nanometric size within the selected support matrix (Salavagione & Martinez, 2011). In the case of this article the application of a nanocomposite with a polymeric matrix reinforced with FLG nanoparticles in cold chain improvement during the transport of vaccines, medications, or other thermolabile products was studied.

Adequate transport and handling of vaccines and/or medications is of the utmost relevance for the protection of agricultural health in Colombia, hence the existence of the organization called the Colombian Institute of Agriculture (Instituto Colombiano Agropecuario or ICA, in Spanish). This organization seeks, through laws and regulation, to coordinate, supervise, and evaluate activities that improve competitiveness, avoid economic loss, avoid harm to human health, limit the commercialization of animals or their products, and promote the prevention and control of sickness in animals through the selection and monitoring of optimal vaccines and medications (ICA, s.f.).

It is known, then, that vaccines are products that must be maintained within a temperature range of 2˚ and 8˚C. If not, they begin to lose their effectiveness until reaching a point of total inactivity (Ministerio de Salud. Dirección General de Promoción y Prevención, 1999). The ICA and other entities indicate that this is a critical point in the care of vaccines, and that transport and conservation conditions must be maintained (Ministerio de Salud. Dirección General de Promoción y Prevención, 1999)(Instituto Colombiano Agropecuario, 2003)(Muñoz & Lorenzana, 1990). In order to increase the competitiveness of the agricultural sector it is necessary to deliver these medications to remote places that are difficult to access, an apt description of the majority of the territory in Colombia.
To wit, the prototype of an SMRM has been designed and fabricated for the agricultural sector. It is easy to transport, with a weight of no more than 3 kg and a load volume of 5 liters. Then, for the purpose of reduction to the maximum size and weight of the system, it became necessary for the consumption of energy to be as low as possible in order to do without the number of batteries required for the system to function autonomously for a minimum of 12 hours. Given the circumstances, and upon utilizing a graphene-based nanocomposite (Patino, 2013) as the Thermal Interface Material (TIM) at the critical points of heat transference, the expectation was to improve the cooling rate and, more directly, the system’s energy consumption to maintain the temperature in the desired range.

2. MATERIALS AND METHODS

The conception of the design and fabrication of the SMRM prototype was developed by a team of leaders in the areas of electronics, telecommunications, virtual technology, and engineering and design from the Medellín node of the SENA Technopark Network (La Red Tecnoparque SENA nodo Medellín, in Spanish) and at their facilities. Tecnoparque, as it is known, is a public entity connected to SENA, and is charged with accelerating research projects as well as supporting development and innovation. The design and fabrication of the graphene-based TIM were completed in the laboratory of MAsertivos (Patino, 2013), a private sector business dedicated to research, development, and innovation in the area of heat and energy conduction materials. The SMRM prototype (Figure 1) fulfills the task as a test bed for the simulation of the transport conditions that come closest to reality. The computer equipment and laboratory at Tecnoparque were used to determine the energy, temperature, and time values. The TIM was used at the critical heat transference points for the SMRM. Below is a list of the characteristics and components of the system, the equipment, and the composition.

2.1. Mobile Monitored Refrigeration System

This system consists in a series of components selected to comply with the function of having compact equipment that is easy to transport: storage space, refrigeration, energy supply, power control, data collection and interpretation, and a searchable database. For the purpose of precision in energy consumption measurements, the energy supply component was exchanged for a power source from the laboratory. In addition, the power control, as well as the data interpretation and searchable database components were removed, all with the goal of minimizing the number of variables to take into account at the moment of temperature data collection and calculation of consumption. Listed below are all of the components used.

2.1.1. Container. This is the portable refrigerator-type structure with a capacity to hold 5 liters, made of expanded polystyrene. It served as support and coupling for the different units that composed the complete system, as well as a compartment for the product stored to be refrigerated and as a storage temperature measurement zone.

2.1.2. Refrigeration system. This is a thermoelectric refrigeration kit with a Peltier 6A cell, measuring 40 mm x 40 mm x 3.5 mm, reference number TEC1-12706. It requires a 12 V electrical supply with a maximum Qc refrigeration power of 50 to 60 W. The kit also contains a refrigeration radiator with a 40 mm x 40 mm fan and a 90 mm x 90 mm heating fan, see Figure 2.

2.1.3. Data collection system. Arduino Due AT91SAM3X8E programmable microcontroller card equipped with two relative temperature and humidity sensors. USB output for data interpretation. Power input that requires 12 V.

A TKC Cooler-box TK034OT77GJELCO commercial mobile refrigeration system. This was also used for purely benchmark tests, given that this system lacks the portability and network monitoring necessary for the ultimate research aims.
2.2. Data interpretation equipment

This refers to a personal computer with a USB input where the data collection system can be connected. The equipment has LabVIEW MyRIO 2014 software installed, which makes it possible for the Arduino Due microcontroller to be programmed, capture the signals the coupled sensors emit, and graph the data obtained over time. The software recognizes and installs Arduino automatically and opens a programming interface of the fields it has available. The fields occupied by the sensors are selected and the variables are defined, which in this case would be temperature and relative humidity. It was programmed to collect data in cycles of 1.6 seconds during 34 minutes or 1,270 cycles. Figure 3 shows a screenshot of the software as Arduino’s data are collected.

2.3. Power source

As the laboratory power source providing a direct current, a Gw Instek GPC-30300 was used to supply the refrigeration system with a measurable current controlled at every moment. This was thanks to the screens it has where the power consumption of the devices connected to it can be displayed. It is programmed to deliver 3 amperes (A) to the refrigeration system and 0.25 A to the fans. In Figure 4 we can see the power source already configured.

2.4. Thermal interface materials

Two different dissipator gels were selected. The first is the most commonly used commercial gel under the brand name HC-151 Heatsink Compound, available in an amount of 30 g. The graphene-based nanocomposite for heat dissipation is a gel with a PDS polymer matrix reinforced with FLG nano-platelets and other ceramic materials (Patino, 2013) that allow for an efficient flow of heat between the generating contact surfaces and heat and cold dissipators. This last item is specially formulated so it does not conduct electricity, and so it avoids undesirable short circuits in the electronic components. It carries the brand name Fres-1 and is available in a quantity of 9 grams. The thermal gel can be seen in Figure 5.
2.5. Procedure

The SMRM was taken with the components chosen for the current study (numbers 2.1.1 to 2.1.3) which were previously verified regarding functionality, and installed. Like the data collection system, it has two coupled sensors, one of which was placed inside of the container in a specially chosen location away from the escaping cold from the refrigeration system. The other sensor was placed on the outside to measure the external temperature and humidity during the test, but only as reference data. The thermoelectric refrigeration system is what was modified in the critical points of heat and cold transfer with the goal of measuring its effect on the consumption of energy upon changing from TIM by the capacity they would have for transferring heat and cold. Therefore, it was important to facilitate the assembly and disassembly for each test without compromising the internal environment of the container with the loss of cold air.

For the first test the refrigeration system was assembled in the container without any applied composite; in this case the TIM is the air. The test was conducted with three repetitions. First, the data interpretation software was initialized. Then, the data collection system was connected to the refrigeration system at the power source with the currents established (number 2.3). Next, data collection was booted up in interpretation equipment. Once the established cycles were completed (1,270 cycles) the test was stopped and the data obtained was exported to a spreadsheet and graphed. In the second test the refrigeration system was dismantled and a maximum 0.5 mm layer of commercial TIM was applied to the two active surfaces of the Peltier cell, meaning on the cooling side and on the heating side. The refrigeration system was reassembled in the container, the container was closed, and the second test was conducted following the same steps as before. For the third test the procedure was the same as the second test except that the graphene-based nanocomposite was applied. It is important to note that we had to wait between each test until the interior temperature of the container was the same as the exterior.

A fourth test was conducted with a different mobile refrigeration system than that developed by the research team, without physically altering it. To conduct the benchmark test with the commercial equipment, sensors were placed on the data collection system inside the system’s container. The system was turned on, and at the same time data collection and interpretation were initiated.

The limitations for the method developed for this study in particular are outlined in the following points: the tightening of the assembly screws for the container of the refrigeration system can alter the contact area of thermal transfer between the Peltier cell and the heat/cold dissipator, making for varied results in the cooling rate from one test to another. As the best countermeasure for this effect, the tightening was done by the same person in the nine tests conducted. Furthermore, if a test resulted in values with a considerable deviation from the other two repetitions, it was discarded and repeated one more time. Another limitation of the method used is that one must begin each test at the same or nearly the same temperature; however, certain materials, in particular the nanocomposite, have a percolation threshold (Sadasivuni, et al., 2015) (Lin, et al., 2014) within which their thermal conductivity is altered, which then alters the temperature.

3. RESULTS

Assembly of the SMRM. Withdrawing from the energy supply, storage, and control complied with the mission to simplify the control of the variables, and it was then possible to obtain test reproducibility when wanting to conduct later tests with a different TIM
than those analyzed in this article. The power sources in the laboratory also have good reproducibility of the test conditions due to having a visual register of the current that the connected system consumes, such as precision in adjusting the voltage entered in the event that it would not be reliable upon connecting it to the batteries, a socket, or an autonomous energy generator.

**Cooling of the vaccine container.** Once the data series from each test and its repetitions have been downloaded, they are organized into a spreadsheet and, taking as a variable of the abscissa the time in seconds and as the ordinate the temperature in °C, the average values for each cooling test are graphed. The graphs can be viewed in Figure 6 and show the results of the first three tests that are completely comparable. It can be observed that the graphene-based nanocomposite allows for better cooling than the commercial gel and even more so than air. The lowest temperature reached was with the graphene-based nanocomposite at 16.3 °C, while the standard commercial composite reached 18.2 °C and without a composite it reached 19.1 °C. It should be noted that the Peltier cell at its full cooling capacity (6 amps) would easily reach 2 °C. It can be observed in Figure 4 that it was configured at less than half its capacity.

**Cooling rate.** For each of the four tests conducted a data range of displayed numbers between 25 and 288 was selected. This range corresponds to the time they have in common when there are higher cooling kinetics. With the help of the spreadsheet’s software the trend line was taken out of each test and from that its slope. Because the curvature is smallest in the selected range, the slope of the trend line gives us a very close idea of the cooling rate of the system for each test. The graph of this range and its respective slopes can be viewed in Figure 7. Upon multiplying each slope by 60 s, which equals one minute, we convert the rate from °C/s to °C/min. The system without a composite reached a cooling rate of -1.11 °C/min, the system with the commercial composite reached a cooling rate of -1.21 °C/min, and the system with the graphene-based nanocomposite reached a cooling rate of -1.54 °C/min. Alternately, the commercial refrigerator or commercial mobile refrigeration system measured a rate of -0.52 °C/min. For the latter the same methodology for data collection was used but they are not comparable because they are different systems; they were only taken as baseline data.

4. **CONCLUSIONS**

The application of the graphene-based nanocomposite during the assembly of an SMRM was helpful because it was fabricated with easily accessible commercial parts; even the graphene-based nanocomposite can currently be obtained commercially. In addition to commercial access, the application of the nanocomposite to evaluate the decrease in energy consumption was aided by a good SMRM design. This also made it possible to easily conduct the tests according to the planned design of the experiment with good repeatability and reproducibility. Having easily accessible commercial parts makes it possible for people with minimal technical knowledge to fabricate...
an SMRM. Regarding the elements used to do so, it was noted that the Peltier cell requires a supply current of 6 A, which is high for a portable system and to be able to reach the optimal temperature for vaccine storage. One can opt then to place two Peltier cells next to each other in order to reach the desired temperature. For the object of demonstrating that energy consumption can be decreased with the use of a graphene-based nanocomposite, the conclusions follow below.

During the cooling tests (Figure 6) the graphene-based nanocomposite had the capacity to lower the internal temperature of the SMRM more than the air alone and the other composites, this due to the heat being transmitted much more quickly when it comes in contact with each of the layers of FLG (Shahil & Balandin, 2012) dispersed in the composite. That is, the excitement of the particles travels at a faster velocity due to the confinement the acoustic phonons suffer, which are what play the most important part in the transference of heat in the graphene and two-dimensional materials (Fisher, 2013) (Balandin & Nika, 2012). These acoustic phonons have a phononic state density lower than that of the three-dimensional materials (Fisher, 2013), which reduces the opportunity for an acoustic vector wave to deviate within the atomic net in which it travels. For this reason, when we upgrade the quality of the FLG to single layer graphene, both thermal and electric conductivity increase (Balandin & Nika, 2012). Regarding electron movement, which for some bulk materials also contributes significantly to heat conduction (Callister & Rethwisch, 2010), for two-dimensional materials its contribution to the double spin that doubles the density of the states will always be secondary (Fisher, 2013); therefore, this is not the principal mode. The polymer matrix in which the FLG layers are dispersed in the nanocomposite utilized operates, then, as a non-conducting or isolating electric material because the matrix doesn’t have free electron conduction bands. But it does have a molecular structure of long chains separated from each other that liken themselves to a one-dimensional material as long as it is not cross-linked. This means that heat conduction by acoustic phonons, which continue traveling after contact with the layers of FLG, takes precedence. In the air heat conduction is very low because of the large distance between molecules and atoms, and it only occurs when they collide with each other at random. In composites where the particles are all three-dimensional the state densities are already phononic or electronic, so it is higher.

In the same way that the nanocomposite could lower the temperature of the SMRM’s internal enclosure more, the cooling rate was more pronounced when the graphene-based TIM was applied to the parts

| Table 1. Performance comparison with different composites and the commercial system. |
|--------------------------------|-------------|--------|--------|--------|----------------|
| TEST                        | RATE (˚C/min) | VOLTAGE (V) | CURRENT (A) | POWER (W) | CONSUMPTION* (W.h) |
| STANDARD COMMERCIAL REFRIGERATOR | -0.516       | 12      | 4.12   | 49.44   | 11.29          |
| SMRM WITHOUT COMPOSITE      | -1.110       | 12      | 3.13   | 37.56   | 3.99           |
| SMRM WITH COMPOSITE HC151   | -1.110       | 12      | 3.13   | 37.56   | 3.99           |
| SMRM WITH NANOCOMPOSITE FRES-1 | -1.540      | 12      | 3.13   | 37.56   | 2.87           |

*This consumption corresponds to the time each test took below 26.5˚ to 19.5˚C.
that were critical to heat conduction. The cooling rate is important in this case in order to ensure that the SMRM’s energy consumption, and any other system with a graphene-based TIM, has a considerably lower time. This occurs because the temperature reaches the desired level in a shorter period of time, making the energy control system turn off sooner. The energy control system was not included in the studies for this article, but knowledge about it already exists from our own tests in which, when the system began functioning on and off during long periods of time, it consumed less energy because it cooled more rapidly. In this way, when using the complete SMRM, one should make sure that the cold chain, extremely important for the transport of vaccines and medications, is more efficient, thus ensuring the medicine can arrive at more remote zones of the country in excellent condition. In future publications an in-depth demonstration will be made on the phenomenon of cooling rate effects over time. In Table 1, below, the comparison between the sought values and the actual values for energy consumption can be found.

REFERENCES


