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Article

Environmentally-friendly graphene conductive ink using graphene powder, polystyrene, and waste oil

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SUMMARY

Waste oil and polystyrene are main sources of pollution that endanger our health. This project proposes an effective, environmentally-friendly method of producing conductive ink using expired waste oil, polystyrene, and graphene. We compared three types of differently-sized graphene powder, two of which are ball-milled. We hypothesized that the ink made with the graphene with the longest milling time will have the best conductivity and the lowest viscosity, thus the easiest to spread. Furthermore, we hypothesized that the film-forming properties would increase with the addition of more polystyrene, regardless of the type of powder. We also determined the microscopic lamellar pattern of the graphene powder. Increased ball-milling time resulted in more polarized powder distribution; smaller pieces of graphene were stacked together as well as larger flakes. We assessed the correlation between the conductivity of graphene powder and its free volume, highlighting how the graphene and waste oil bounded together. We later explored a combination of waste oil with graphene and evaluated the oil absorption of graphene. An ink with a conductive coating film resistance below 100 Ohm was made by altering the proportions of the composition of graphene, polystyrene, and oil. We determined that the best ink recipe consists of mineral oil (baby oil), graphene milled for 2.5 hours, and a polystyrene-to-graphene ratio of 0.5 to 1 because it compromises between low resistance, moderate viscosity, good spreadability, and good film-forming properties. This work has important implications on developing a novel way to recycle waste into applicable conductive ink.

INTRODUCTION

Taiwan is surrounded by oceans, so the marine environment is a major natural asset (1). Taiwan is a major fixture along the busy international shipping lanes of Asia, which together with adverse weather events such as typhoons, has led to a considerable marine pollution problem (1). Of the different forms of marine pollution, waste polystyrene and waste oil pollution are the main sources that endanger our health (1,2).

Oil leakage is another environmental problem: Edible waste oil used in the catering industry cannot be exported from the recycling pipeline, leading to wastewater (2). Recycling these waste edible oils at a low cost is a major issue (3). Additionally, polystyrene is a serious pollution source, occupying a substantial portion (about 30%) of landfill sites (4). Temperature change may further decompose this polystyrene into harmful substances, such as Bisphenol A, which may be harmful to animals' reproductive systems (4). At the same time, polystyrene may flow into the sea, causing serious pollution (4). Both Stewart et al. and Savoldelli et al. provided methods for recycling polystyrene but do not mention polystyrene as a conductive ink material (4, 5).

Searching for effective solutions to reduce these two pollution sources was the main motivation of this research. We found some research and developmental studies of graphene being used in the preparation of conductive inks. Graphene is highly conductive and flexible and, when incorporated into inks, can be printed onto flexible, bendable electronics as electric circuits (6). We should leverage such properties of the graphene conductive ink since Taiwan is a major electronics manufacturer. Taiwan makes electronic products on the market that have become thinner, lighter, and easier to carry over the years (7). The development of highly ductile conductors is a major trend in the technology market, making graphene conductive inks a suitable choice for such technological products (7). These applications of the inks inspired the investigation into the production of environmentally-friendly conductive graphene ink.

The aim of our work was to produce ink from polystyrene and waste oil, reduce costs, and help to solve a pollution problem. Developing environmentally-friendly conductive inks was a promising approach to partially resolve pollution problems, and we could incorporate the resulting ink into toys, teaching materials, and machines in the industry. To determine the best parameters for the graphene conductive ink, we conducted a considerable amount of foundational work.

RESULTS

In this investigation, we tested the different types of powder (Gr00, Gr25, and Gr70, with no ball-milling, 2.5 hours of ball-milling, and 7 hours of ball-milling, respectively). We measured the changes in conductivity, viscosity, spreadability, and film-forming properties of the conductive ink.

We hypothesized that if we made the conductive ink with the Gr70, Gr25, and the Gr00 graphene, then the Gr70 would have the best conductivity, spreadability, and the lowest viscosity because the grounded Gr70 had more connected graphene pieces. Furthermore, film-forming properties would increase with the addition of more polystyrene, regardless of the type of powder because polystyrene and graphene were two independent ingredients.

After the ball-milling process, the individual grains/flakes of the Gr70 graphene powder should break apart even more, resulting in a smaller specific free volume. These tinier spaces in between the powder meant that the flakes of graphene were held even closer together compared to the ungrounded Gr00 graphene. These smaller pieces should be more attached to each other, and since graphene was a conductive material, free electrons could find more pathways through the material (8). Therefore, the ground Gr70 graphene should result in the most conductive ink. As for viscosity, Gr70 had the smallest free volume that could hold the added oil in place. Hence, the oil would fill up these tiny empty spaces and seep out into the surrounding space outside of the powder (9), enhancing the spreadability as well.

Our research established the feasibility of using ball-milled ink through chemical composition and crystalline structure. We also investigated the free volume and oil absorption of diverse types of powders. We then combined the graphene powder, oil, and polystyrene-ethyl-acetate-mixture to form the conductive inks.

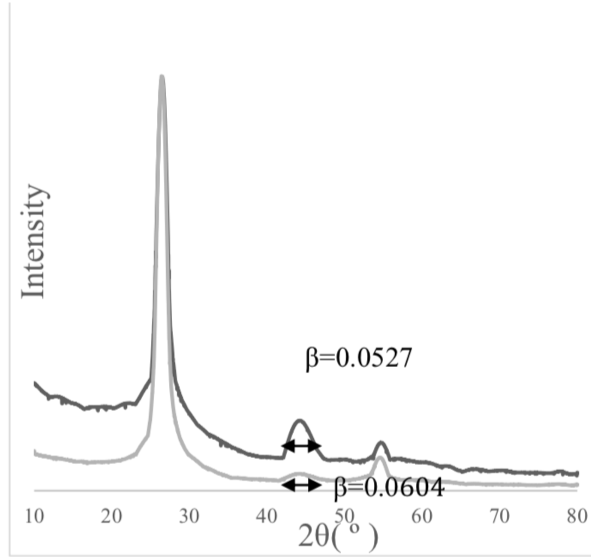

Figure 1: Comparison of Crystalline Properties for Gr00 and Gr70. Comparisons of wide-angle XRD patterns (intensity vs 2θ) of Gr00 (black) and Gr70 (gray) showed similar angles where the highest intensity occurred, implying similar crystalline structures between Gr00 and Gr70.

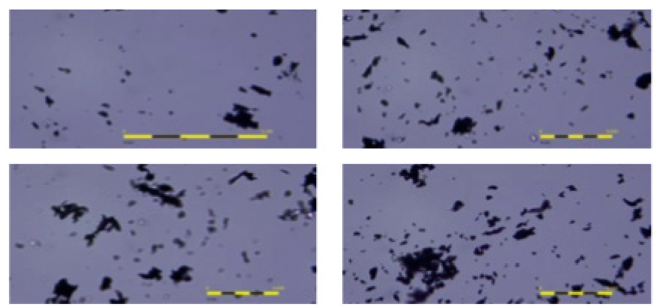

Figure 2: Optical Micrographs for Gr70 (7 Positions). There is a combination of extremely tiny flakes and stacked-up pieces (which results from tiny pieces stacking together to form a much larger piece).

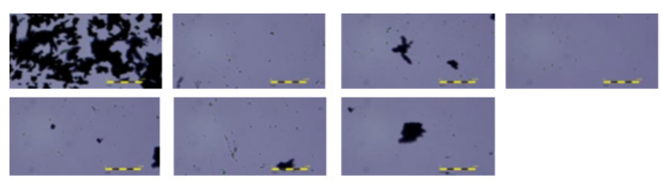

Figure 3: Optical Micrograph for Gr00 (4 Positions). There are pieces of similar sizes, with the least number of areas in large tracts (sizes are more normally distributed).

Ball Milling

We examined the physical properties of the graphene powder following ball milling. We analyzed three samples of graphene powder: Gr00 (the initial graphene powder), Gr25 (Gr00 ball milled for 2.5 hours), and Gr70 (Gr00 ball milled for 7 hours). After 2.5 hours (Gr25) and 7 hours (Gr70) of ball milling of the Gr00 graphene powder, the C, N, H, O element composition of the three powders did not change meaningfully. During the ball milling process, the crystalline form of the graphene powder did not change greatly: the wide-angle XRD patterns showed that the peaks of the curve occurred at similar angles (2θ) (**Figure 1**). These experiments indicated that although the particle sizes of the graphene powders changed after different ball-milling durations, their elemental compositions (chemical) and crystalline properties (physical) did not change noticeably.

Lamellar Distribution

After comparing physical properties through ball-milling, we compared the lamellar distributions of the three powders. Using the optical microscope to characterize the graphene powder samples, we observed differences in the lamellar area distributions of the three graphene powders. Gr70 had the greatest number of small graphene sheets but also stacks of large-area graphene sheets (**Figure 2**). Gr00 had the smallest number of large graphene sheets, and the lamellar area distribution was more normal (**Figure 3**). Gr25 had larger graphene sheets than Gr00, but Gr70 still had the largest graphene sheets.

Ink Formulations

Using Gr00 and Gr25 mixed with two waste oils (baby oil and sunflower), we produced four graphene cakes. We then mixed them with polystyrene/ethyl acetate solution to create six types of conductive ink (**Table 1**). Compared with Gr00-baby oil ink and Gr00-sunflower oil ink, Gr00-baby oil (Dilute) ink and Gr00-sunflower oil (Dilute) ink had more polystyrene/ethyl acetate solution.

Figure 4: Comparison of Gr00 and Gr25 Conductive Inks' Physical Properties. Photograph of the Gr00-Baby oil conductive ink (left) and Gr25-Baby oil conductive ink (right). Gr00 shows a more viscous nature than does Gr25, so Gr25 was chosen as a more suitable candidate for further experiments.

Figure 5: Inks A to F. Photos of inks A to F from Table 2, after spreading the inks onto a piece of cardboard.

Figure 6: Physical Properties of Ink B. Photograph of ink B showing the sticky nature of the ink, with more improved spreadability relative to those of Figure 4.

We fixed the ratio of polystyrene (g) to graphene (g) at 0.15; the amount of polystyrene in the coating film was exceedingly small, so the adhesion and film formation of the coating film was poor (**Table 1**). Further, we compared the viscosity and spreadability of the conductive inks. We measured viscosity in qualitative terms, and from the highest to lowest viscosity, the terms we used were as follows: "viscous," "sticky," "slightly sticky," and "dilute." We measured spreadability, from most spreadable to least spreadable, as "excellent," "good," "fair," and "poor." We classified the inks' film-forming properties with "good," "fair," and "poor."

Inks made of Gr00 had high viscosity ("viscous" or "sticky") and bad spreading properties ("poor" or "fair"). The Gr25 inks were less viscous ("sticky") and more spreadable ("good" spreadability) compared to the inks made of Gr00 (Table 1). The graphene powders' oil absorption levels decreased after ball-milling. The prepared conductive ink had a moderate viscosity and good spreadability (**Figure 4**).

All the inks made in this first attempt exhibited poor film-forming properties. Therefore, we needed to change the ink's compositions. In our next attempt, we selected the Gr25/baby oil mixture as the base of our ink. We mixed in polystyrene/ethyl acetate solutions and adjusted the polystyrene (g) / graphene powder (g) ratio to 0.5, 1.0, and 1.5. We made six conductive inks (A, B, C, D, E, F).
We then spread the resulting inks onto cardboard surfaces to determine their viscosity and spreadability (**Figure 5, 6**). The viscosity of the conductive ink decreased as the ratio of (polystyrene/graphene powder) increased (**Table 2**). The inks made of Gr25 were generally more spreadable than those made of Gr00. The Gr25 inks also exhibited more film-forming properties ("fair" or "good") compared to the Gr00 inks ("poor").

We compared the resistance values of inks A, B, C (lower ethyl acetate content, so less dilute) and D, E, and F (greater ethyl acetate content, so more dilute). Inks A & D had a polystyrene (g) / graphene (g) ratio of 0.5, B & E with a ratio of 1.0, C & F with a ratio of 1.5. When the ratio of polystyrene (g) / graphene powder (g) increased, the resistance value of the conductive ink increased because the graphene content was relatively small. The conductivity of the coating film decreased, and the resistance value increased. With more ethyl acetate, the group of ink D, E, and F had a lower ink viscosity, making the graphene dispersion better. This in turn created a coating film with higher conductivity (lower resistance).

DISCUSSION

This research used waste oil and polystyrene, combined with secondary graphene powder, to modulate environmentally-friendly conductive ink. Initially, we speculated whether the ball-milling process might play a role in the ink's quality and properties. But after observing that the three powders' elemental compositions and crystalline structures were similar, we concluded that we could use the ball-milled graphene in further experiments without much concern for property changes.

We used three main factors to determine whether our ink mixtures were a good formulation: conductivity, spreadability, and film-forming properties. Although conductivity was a crucial factor in the ink, it did not indicate that the ink had a good formulation. For example, the resistance of the formula using Gr00 was lower, but the viscosity was too high to evenly coat it on the cardboard's surface. The processability was also

Ink Codename/ Composition	Gr25 (g)	Gr00 (g)	Baby Oil (ml)	Sunflower Oil (ml)	Polystyrene (g)	Ethyl Acetate (ml)	Polystyrene (g) / Graphene (g)	Resistance (ohm)	Viscosity	Spreadability	Film-forming properties
Gr25- Baby Oil Ink	10		17		1.5	10	1.5/10 = 0.15	100	Sticky	Good	Poor
Gr25- Sunflower Oil Ink	10			18	1.5	10	1.5/10 = 0.15	320	Sticky	Good	Poor
Gr00- Baby Oil Ink		5	16.5		0.75	5	0.75/5 = 0.15	45	Viscous	Poor	Poor
Gr00- Sunflower Oil Ink		5		17	0.75	5	0.75/5 = 0.15	120	Viscous	Poor	Poor
Gr00- Baby Oil (Dilute) Ink		5	16.5		0.75	6	0.75/5 = 0.15	40	Sticky	Fair	Poor
Gr00- Sunflower Oil (Dilute) Ink		5		17	0.75	6	0.75/5 = 0.15	110	Sticky	Fair	Poor

Table 1: Composition and film properties of conductive ink

Ink Codename/Composition	Gr25 (g)	Baby oil (ml)	Polystyrene(g)	Ethyl Acetate (ml)	Polystyrene (g) /Graphene (g)	Resistance (ohm)	Viscosity	Spreadability	Film-forming properties
A	2	3.4	1	3.33	1/2 = 0.5	95	Viscous	Poor	Fair
B	2	3.4	2	6.66	2/2 = 1.0	420	Sticky	Good	Good
C	2	3.4	3	10	3/2 = 1.5	1000	Sticky	Good	Good
D	1	1.7	0.5	3.33	0.5/1 = 0.5	110	Slightly sticky	Excellent	Good
E	1	1.7	1	6.66	1/1 = 1.0	290	Slightly sticky	Excellent	Good
F	1	1.7	1.5	10	1.5/1 = 1.5	410	Dilute	Fair	Good

Table 2: Revised composition and film properties of conductive inks A- F.

poor. The free volume was the greatest in Gr00; most of the oil seeped into the free volume while the graphene surface did not have excess oil. The resulting ink was therefore more viscous and stickier than the inks made of Gr25 or Gr70. The free volume of Gr25 was smaller compared to Gr00. As the oil filled all the available space of Gr25's free volume, excess oil seeped out to the surface of the graphene, thus giving it a slippery surface. The resulting ink made of Gr25 was less viscous and more spreadable than the ink made of Gr00.

When choosing graphene, we should consider the resulting ink's spreadability. In this study, the ink prepared with Gr25 powder exhibited the most appropriate spreadability and an excellent conductivity. Its viscosity was also lower than that of the Gr00 ink, with excellent uniformity. The conductivity of its coating film was slightly lower (100~320Ω) than that of the Gr00 ink (40~120Ω), but its resistance was still low enough for the ink to be conductive. In addition, Gr70 powder was not suitable for making ink; this powder had poor connectivity (thus poor conductivity) and low oil absorption. The ink produced was too thin and difficult to spread evenly, with sagging, thick, frayed edges.

Adding more polystyrene to the inks increased the resistance value, but polystyrene could provide a film on the ink's surface to prevent graphene powder from flaking off. Increasing polystyrene while keeping the amount of graphene unchanged decreased the concentration of graphene per gram of ink. Since graphene was the only ingredient that showed conductivity, decreasing graphene concentration led to an increase in the resistance value. Polystyrene also had film properties that were absent in graphene, so increasing polystyrene enhanced film-forming properties of the ink. If we only considered the conductivity, the ink would be unusable due to poor film-forming properties; graphene powder peeled off easily from the surface after the ethyl acetate volatilized. Therefore, it was necessary to choose and compromise among these three main factors in order to formulate an ink with low resistance, moderate viscosity, good spreadability, and good film-forming properties.

In this study, conductive ink composed of Gr25 graphene powder, polystyrene, baby oil, and ethyl acetate with a polystyrene-to-graphene ratio of 0.5-to-1 and an ethyl acetate-to-baby-oil ratio of 3.33-to-1.7 resulted in optimal characteristics. Resistance measurements indicated a high of 110 ohms, and lows of 40 ohms after subsequent drying. Sufficient repetitions of the experiment led to more thorough drying of the ink and thus accounted for this variance.

This research was still in the development stage, so it may be prone to measurement errors such as imprecise ratios of polystyrene to graphene. Measuring resistance with multimeters may be another major source of error. The tip of the multimeter is spaced unevenly for each measurement, so the resistance of the ink may not be accurate, although we already took the mean of five measurements, each at different locations of the ink. Furthermore, the polystyrene we used may be different from other sources, so the quality of our ink may not reflect the general quality of conductive inks. Future experiments could implement more accurate resistance measurement devices, along with testing different types of polystyrene to optimize the film-forming properties. Possible expansions included malleable conductive inks, conductive masterbatches, water-based conductive inks, antistatic materials, and heat sinks.

The experiment investigated different aspects of three graphene powders with different ball-milling time: microscopic lamellar pattern, chemical composition, correlation between the conductivity of graphene and its free volume, and oil absorption. After conducting these preliminary research, we combined expired waste oil, polystyrene, and graphene to produce an environmentally friendly conductive ink, with a resistance below 100 Ohm. We determined the best recipe to be that of mineral oil, 2.5 hours milled graphene, and a polystyrene-to-graphene ratio of 0.5 to 1 as it compromises between three factors: low resistance, moderate viscosity, and good film-forming properties. This experiment illustrates possible methods to recycle waste into useful materials, such as conductive ink. The findings of this experiment can be used to optimize eco-friendly conductive ink that can be applied to multiple industries, most notably printed electronics.

MATERIALS AND METHODS

Two (polystyrene/ethyl acetate) solutions were prepared. Solution 1 had a polystyrene-to-ethyl-acetate ratio of 6 (grams) to 20 (milliliters), and Solution 2 had a polystyrene-to-ethyl-acetate ratio of 9 (grams) to 60 (milliliters). Solution 1 was more viscous because it contained a higher proportion of polystyrene. Four graphene powder/waste oil cakes with a composition mix were prepared in beakers as described:

10 grams of Gr00 with 33mL of baby oil, 10 grams of Gr00 with 34 mL of sunflower oil, 10 grams of Gr25 with 17 mL of baby oil, and 10 grams of Gr25 with 18 mL of sunflower oil. The graphene/waste oil cake with the polystyrene/ethyl acetate solution was mixed. The composition of the formula was modified to identify optimal final characteristics of the ink, and various conductive inks were prepared. Next, the conductive ink was applied on thick cardboard to evaluate ink viscosity and spreadability. The coating film was then dried with hot air from a hairdryer, and the adhesion film formation was evaluated. Lastly, a multimeter was used to measure the resistance value (1 cm distance on the cardboard) of the coating film of various ink formulations.

Control variables included baby oil (mineral oil), beaker, dropper (measurement tools), polystyrene-to-graphene ratio, type of polystyrene, resistance tester, environment (room temperature), and ethyl acetate.

During this multifaceted experiment, we identified the risk assessment for each component and the safety protocols followed for the handling, storage, and disposal of chemicals and materials. Due to the chemicals and the laboratory equipment required, standard laboratory safety measures were adopted. Safety glasses, gloves, and a lab coat were worn at all times. No open fire source was utilized. The laboratory bench was kept clean at all times. Graphene powder yielded no known significant risk (10), and ethyl acetate was considered a flammable liquid and vapor that caused eye irritation (11). Similarly, acetone was an extremely flammable liquid and vapor that caused eye irritation (12). As for the oils, baby oil was not considered hazardous (13), sunflower oil might cause some irritation to the eyes and mucus if smoking occurs and was combustible if a cloth soaked in oil was near a fire source (14).

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