I-BIM-P-066-16

PREPARATION OF CONDUCTIVE INKS FROM EPOXIDIZED - SOYBEAN OIL AND EPOXIDIZED NATURAL RUBBER CONTAINING CONDUCTIVE CARBONS

Pinyalak Wisetraksakun*, and Pathavuth Monvisade

Polymer Synthesis and Functional Materials Research Unit, Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand
Phone: +66-2329-8400, Fax: +66-2329-8428

*Corresponding author's e-mail address: eve.pinyalak@gmail.com

Abstract

The conductive inks were prepared by the mixing of the recipe including epoxidized soybean oil (ESO), epoxidized natural rubber (ENR), drying oil (linseed oil and tung oil), and conductive carbon (graphite and graphene). The prepared ink was printed on the paper substrate with subsequently exposed to UV radiation to allow the crosslinking reaction. The electrical resistivity was determined by using 4-point probe method. The results showed that the formula G8 gained the lowest sheet resistance at 1898.35 Ω /sq. Moreover, the sheet resistance was decreased when the higher content of RGO was applied. The circuit including LED and the prepared conductive print was set up to confirm the electrical conductivity.

Keywords: Conductive carbon, Conductive ink, Drying oil, Epoxidized natural rubber, Epoxidized soybean oil

Introduction

Printed electronics are a combination of new technology and conventional printing to create the electronic circuit and electric equipment with inkjet printing, gravure printing, and screen printing.[5,6] The application of this process is to create the electronic circuit on the flexible surface which uses as the components of electric appliances and sensors [1-3,7]. In printing, the conductive ink was required due to its distinctive properties such as electrical conductivity, durability, and printability.[6] After printing, the ink was exposed to the light or subjected to heat to form a thin film on the various substrate.[9] The printed electronics are more popular in the electronic applications than the conventional electronics due to the printability of flexible and large area substrates to get the lightweight electric equipment, simple production, and cost reduction.[10,11] The conductive particles are the main part of conductive ink. The good electrical conductive particles such as silver, copper, gold, and aluminum [7] are high cost and some types undergo rapid oxidation in the air resulting in loss of electrical conductivity.[1] To lowering the cost, conductive carbons such as carbon black, graphite, or graphene have been exploited as a recipe in conductive ink.[9, 15]

Up to now, kinds of solvents such as N-Methyl-2-pyrrolidone (NMP), Dimethylformamide (DMF), and Dimethyl sulfoxide (DMSO) are used in the conductive inks and these solvents are allowed to dry by evaporation during use of causing hazardous to the environment and toxic to human. [4,6] Therefore, alternative solvents such as water and non-toxic solvent have been developed for conductive ink.[4] Although the water-based ink can conquer the environment and toxic issues, the problem of the water-based ink is the rapid evaporation of water. This causes the dried ink easily stuck in printing mesh.

Soy-based ink has been developing to replace the regular ink [12] in the printing industry. The soybean oil is used as the active solvent which is binder after curing. The using soy-based ink was satisfied due to reduction of hazardous volatile and, thus, safety for workers and users. For more efficacy of film forming, the drying oils were added into the ink formula [14].

In this work, the conductive ink was prepared by the mixing of epoxidized soybean oil and epoxidized natural rubber together with the conductive carbon. Tung oil and linseed oil were also used to enhance film forming of the ink. The electrical properties of the conductive ink were studied. The obtained conductive ink could be useful for creating electric circuits in the print electronics industry.

Materials and methods

Materials

Epoxidized soybean oil (ESO) (VIKOFLEX® Series 7170) was purchased from SRITHEPTHAI CHEMICAL CO.,LTD. Epoxyprene 25 (ENR) was purchased from Muang Mai Guthrie PCL CO.,LTD. Linseed oil and Tung oil was purchased from UNION CHEMICAL 1986 CO.,LTD. Graphite powder (< 20 µm) was purchased from Aldrich Chemical Company. Sulfuric acid 98% (H_2SO_4) was purchased from S.D. Fine Chem Ltd. Potassium permanganate ($KMnO_4$) was purchased from Ajax Finechem Pty Ltd. Hydrogen peroxide solution 40%m/m in water (H_2O_2) was purchased from CARLO ERBA Reagents. DI water

Methods

1. The preparation of reduced graphene (RGO)

The graphene oxide was synthesized by the oxidation of graphite powder adapted from Hummers method.[8] In detail, the graphite 3.0 g was added into concentrated H_2SO_4 70 ml under stirring at 15˚C and subsequently $KMnO_4$ 9.0 g was added. The reaction temperature was raised to 40˚C with further stirred for about 30 minutes. Then, 150 mL water was added, and the solution was stirred for 15 min at 95˚C. After that, 500 mL water was added and followed by a slow addition of 15 mL H_2O_2. The solution was filtered to yield the solid form of graphite oxide with further aqueous dispersion by diluted to 600 mL water. This solution was purified by using a dialysis membrane with a molecular weight cut off of 8000 - 14,000 gmol^{-1} for 7 days. The result was diluted to 1.2 L, stirred for 3 h and sonicated for 60 min to exfoliate it to graphene oxide (GO). The GO dispersion was centrifuged at 4000 rpm for 20 min to remove the unexfoliated graphite. The result GO was reduced following the method of Loryuenyong et.al.[13], by heating GO solution at 95˚C for 4 days and freeze drying to yield RGO.

2. The preparation of ink and printed pattern

The ink was prepared by mixed the solution of 20 w/w% ENR in ESO with tung and linseed oils. Graphite at 0, 20, 40, 60, 80 and 100 pph was then added into the solution and mixed well using mechanical stirrer at 600 rpm for 30 min. In term of applying RGO, RGO was applied into the formula at given weight ratio of Graphite: RGO at 7.5:0.5 and 7.0:1.0 using the same procedure. The recipes of all formula are summarized in Table 1. The prepared ink was printed on the paper followed by an exposure to UV radiation to form film. The thickness of the film was measured by micrometer before testing.

Table 1 The weight ratio of oil in the ink formula

Formula	ENR solution	Tung oil	Linseed oil	Graphite	RGO
G0	5.0	2.5	2.5	-	-
G2	5.0	2.5	2.5	2.0	-
G4	5.0	2.5	2.5	4.0	-
G6	5.0	2.5	2.5	6.0	-
G8	5.0	2.5	2.5	8.0	-
G10	5.0	2.5	2.5	10.0	-
G7.5+0.5	5.0	2.5	2.5	7.5	0.5
G7.0+1.0	5.0	2.5	2.5	7.0	1.0

3. The testing of ink

The drying time of printed pattern was counted and used the eligible time for curing the ink. The surface of dried ink was observed by Dino-Lite Digital Microscope PRO 60x and 500x. The electrical efficacy of dried ink was studied by 4-point probe tester: signatone SP4-50045TRS. The electrical resistance (R) of the patterns was calculated from the slope of the graph that showed the relativity between applied electric current (I) and the voltage (V). Each sample was tested for five times. The sheet resistance (R_s) is calculated by equation. (1). Finally, the conductivity of the pattern was inspected by the circuit including LED.

$$R_s = \frac{\pi}{\ln 2}\left(\frac{V}{I}\right) \qquad (1)$$

By $R = \left(\frac{V}{I}\right)$

Results and discussion

1. Printability and drying

The viscosity of prepared conductive ink increased as relatively high content of graphite was applied. All formula (except G10) are convenient viscosity to print easily. The ink was dried by UV curing at which the crosslinking reaction was occurred at double bonds belonging to ESO, tung oil, and linseed oil. The propose mechanism is shown in Figure 1. The presence of tung and linseed oils can enhance the performance of curing of ink by generating free radicals on the chain of the oils both stimulated by UV radiation and oxidation by oxygen in the air, with subsequently initiated the crosslinking point. From the result, the optimum exposure time to UV radiation for drying ink is approximately 10 min.

2. Surface

Optical microscope was used to study the surface of the printing ink on the paper as shown in Figure 2. At 60x magnification, the image showed the wrinkle on the surface pattern of G2 and G4 (Figure 2a and 2b) and showed the smoother on the surface of G6 and G8 (Figure 2c and 2d). However, at 500x magnification, the surface of G6 presented a very tiny wrinkle (Figure 2g) which cannot be seen by naked eye. The shrinkage of the film during crosslinking reaction resulted in wrinkle on the surface of dried ink. The high content of graphite in the ink can impede the shrinkage resulting from crosslinking reaction, thus, lowering the wrinkle on the surface of dried ink. The obvious wrinkle on the surface of G2 and G4 are impractical to use.

3. Resistivity

The average voltage was received from the 5 electric currents (10, 12, 15, 20, and 25 µA) applied through the samples. The resistance (R) of the pattern was calculated from the slope of the graph demonstrated in Figure 3. The sheet resistances (R_s) calculated from equation (1) of the patterns of G6 and G8 are 2242.95 and 1898.35 Ω/sq., respectively. The sheet resistance of the pattern was decreased when the graphite content in the ink was increased. Moreover, the surface roughness of the pattern related to electrical properties. The high surface roughness, the high sheet resistance was obtained. As relatively low content of graphite and high surface roughness of G6, it gained higher sheet resistivity than G8.

In term of applying RGO, the sheet resistances of G7.5+0.5 and G7.0+1.0, calculated from the slopes presenting in Figure 3 and further calculation by equation (1), were at 1610.04 and 1350.06 Ω/sq., respectively. From the results, the better electrical properties could be obtained when the higher content of graphene was applied in the ink.

Finally, the simple circuit including LED and the prepared conductive print was set up to confirm the electrical conductivity as shown in Figure 4.

Conclusion

The soy-based conductive inks were successfully prepared by the mixing of the recipe including epoxidized soybean oil (ESO), epoxidized natural rubber (ENR), tung and linseed oils, and conductive carbon, i.e. graphite and graphene. The ink was printed and dried by exposure to UV radiation for 10 min. The surface roughness and sheet resistance of dried conductive patterns were studied. The results showed that the formula G8 gained the lowest sheet resistance at 1898.35 Ω/sq. Moreover, the sheet resistance was decreased when RGO was added to the ink. It can be suggested that these soy-based conductive inks are the good choice to avoid drying by evaporation of toxic solvent

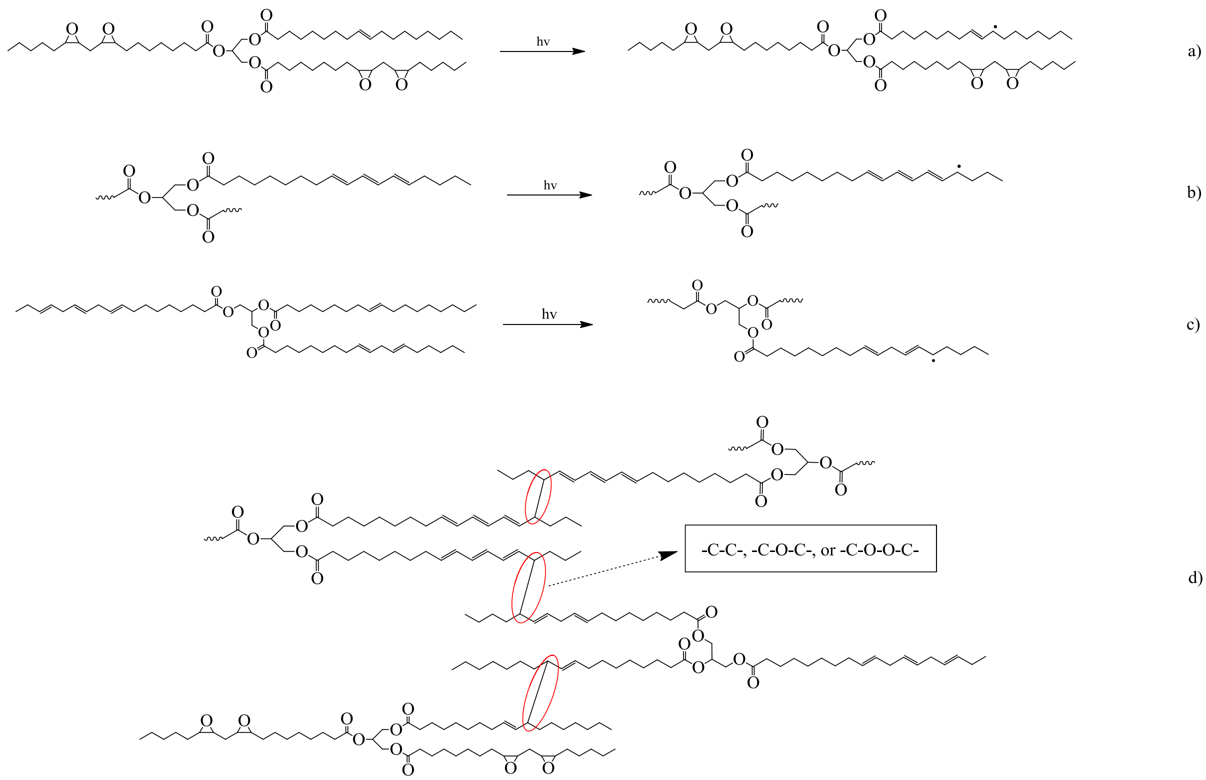


Figure 1 Radical initiation by UV radiation of a) ESO, b) tung oil, and c) linseed oil. d) the propose model of crosslinking among tung oil, linseed oil, and ESO

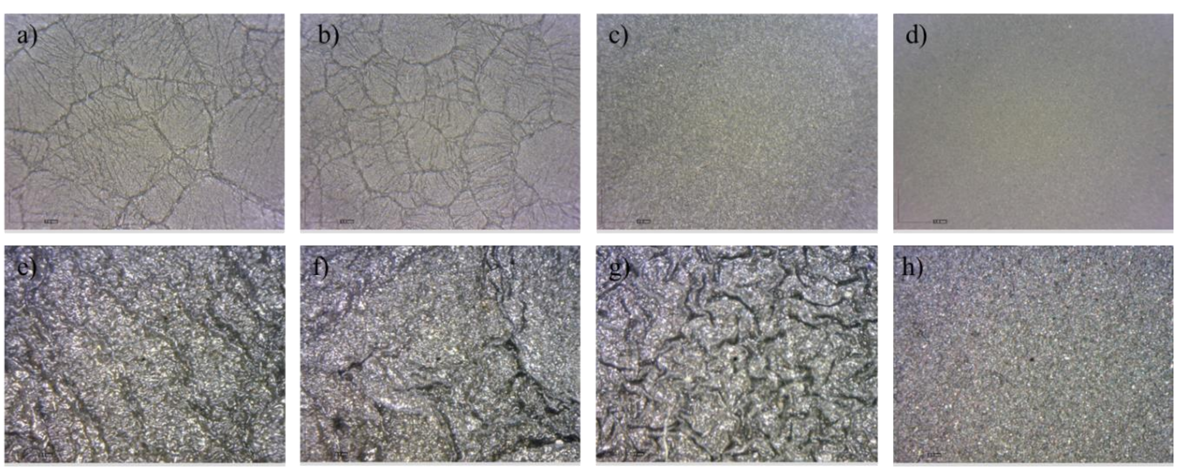


Figure 2 OM image of the surface of the pattern with x60 for a) G2, b) G4, c) G6, and d) G8. e) - h) show x500 of the surface of G2, G4, G6, and G8, respectively

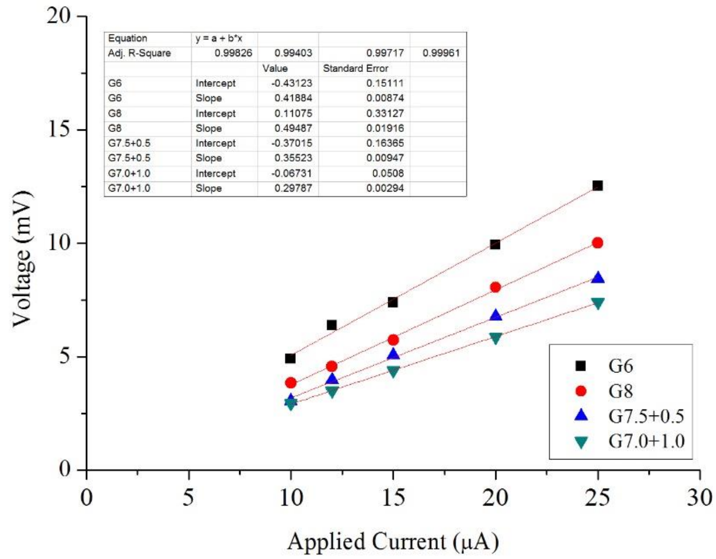
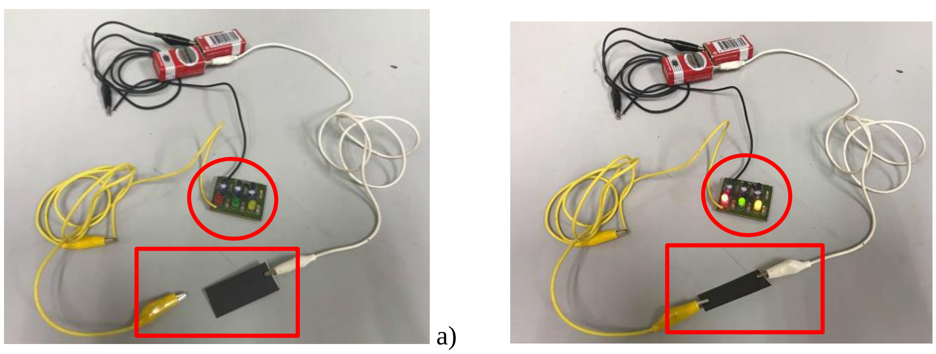


Figure 3 The graph of the relativity between applied electric current (μA) and the voltage (mV)



a) b)

Figure 4 The simple circuit including LED (in circle) and the prepared conductive print (in square blanket) a) open circuit and b) closed circuit

Acknowledgements

This research was financially supported by KMITL Research Fund and Polymer Synthesis and Functional Materials Research Unit, Department of Chemistry, Faculty of Science, KMITL.

References

[1] Kamyshny, A., & Magdassi, S. (2014). Conductive nanomaterials for printed electronics. *Small*. *10*: 3515-3535.

[2] Arapov, K., Rubingh, E., Abbel, R., Laven, J., de With, G., & Friedrich, H. (2016). Conductive screen printing inks by gelation of graphene dispersions. *Advanced Functional Materials*, *26(4)*, 586-593.

[3] Badri, M. A. S., Salleh, M. M., Noor, N. F. A. M., Rahman, M. Y. A., & Umar, A. A. (2017). Green synthesis of few-layered graphene from aqueous processed graphite exfoliation for graphene thin film preparation. *Materials Chemistry and Physics*, *193*, 212-219.

[4] Capasso, A., Castillo, A. D. R., Sun, H., Ansaldo, A., Pellegrini, V., & Bonaccorso, F. (2015). Ink-jet printing of graphene for flexible electronics: an environmentally-friendly approach. *Solid State Communications*, *224*, 53-63.

[5] Overgaard, M. H., Kühnel, M., Hvidsten, R., Petersen, S. V., Vosch, T., Nørgaard, K., & Laursen, B. W. (2017). Highly conductive semitransparent graphene circuits screen-printed from water-based graphene oxide ink. *Advanced Materials Technologies, 2(7)*, 1700011.

[6] Majee, S., Liu, C., Wu, B., Zhang, S. L., & Zhang, Z. B. (2017). Ink-jet printed highly conductive pristine graphene patterns achieved with water-based ink and aqueous doping processing. *Carbon, 114,* 77-83.

[7] Kamyshny, A., Steinke, J., & Magdassi, S. (2011). Metal-based inkjet inks for printed electronics. *The Open Applied Physics Journal*, *4*. 19-36.

[8] Chen, J., Yao, B., Li, C., & Shi, G. (2013). An improved Hummers method for eco-friendly synthesis of graphene oxide. *Carbon, 64*, 225-229.

[9] Patil, B. H. (2015). Formulation and evaluation of soy polymer based, gravure printed resistive inks for applications in printed electronics.

[10] Arias, A. C., MacKenzie, J. D., McCulloch, I., Rivnay, J., & Salleo, A. (2010). Materials and applications for large area electronics: solution-based approaches. *Chemical reviews, 110(1),* 3-24.

[11] Sun, J., Zhang, B., & Katz, H. E. (2011). Materials for printable, transparent, and low-voltage transistors. *Advanced Functional Materials, 21(1)*, 29-45.

[12] Tutak, D., Husovska, V., Pekarovicova, A., & Fleming, P. D. (2017). Deinkability of soy inkjet ink print by modified ingede method using soy oleic acid. *Cellulose Chem. Technol, 51,* 333-340.

[13] Loryuenyong, V., Totepvimarn, K., Eimburanapravat, P., Boonchompoo, W., & Buasri, A. (2013). Preparation and characterization of reduced graphene oxide sheets via water-based exfoliation and reduction methods. *Advances in Materials Science and Engineering, 2013*.

[14] Oyman, Z. O., Ming, W., & Van der Linde, R. (2005). Oxidation of drying oils containing non-conjugated and conjugated double bonds catalyzed by a cobalt catalyst. *Progress in organic coatings, 54(3),* 198-204.

[15] Movlaee, K., Ganjali, M. R., Norouzi, P., & Neri, G. (2017). Iron-based nanomaterials/graphene composites for advanced electrochemical sensors. *Nanomaterials, 7(12),* 406.