

PREPARATION OF CONDUCTIVE FILM CELLULOSE/REDUCED GRAPHENE OXIDES

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ABSTRACT

This work aimed to prepare conductive composite films of cellulose and reduced graphene oxide (RGO), and also to study the effect of RGO contents on electrical properties. The cellulose was extracted by using microwave assisted method from cotton wool. To prepare conductive composite film, cellulose was mixed with 0%, 0.1%, 0.5%, 1.0% and 2.0% (w/w) RGO using toluene diisocyanate (TDI) as a cross-linking agent. According to FT-IR characterization, films exhibited cellulose characteristics without a trace of untreated TDI on cellulose backbones. It was found that the conductivity of films increased as RGO concentration increased. The film exposed to the higher % RH exhibited a lower conductivity.

Keywords : Cellulose, Reduced Graphene Oxide, Cross Linking Agent, Conductivity, Composite Film

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INTRODUCTION

Cellulose is the biopolymer. Compared with synthetic polymer, cellulose has many advantages including biocompatibility, easy modification, eco-friendliness and low price. Cellulose is a carbohydrate polymer containing β -D-glucopyranose units, and consists of three hydroxyl groups per anhydroglucose unit (AGU)¹. The differences between various forms of cellulose are related to the shape, size and degree of crystallinity of their particles (fibrous or agglomerated)².

Graphene has attracted many attentions due to its exceptional thermal, mechanical, and electrical properties. Graphene oxide (GO) sheets have recently attractive as possible intermediates in graphene manufactural³. In GO, there are epoxy and hydroxyl groups on the surface and carboxyl groups on the edges⁴. By using mechanical and chemical reduction techniques, the oxygen containing functional groups were removed. The GO can be converted to reduced graphene oxide (RGO), the other graphene derivative. Because of their single-layered two-dimensional sheets and their excellent mechanical and electrical properties, graphene and its derivatives are promising materials to mix with cellulose for the effective reinforcement and the electrical enhancement of the biopolymeric composites.

Ouyang et al⁵ reported that RGO/cellulose composite could be used as supercapacitor. The composites were prepared by mixing graphene and hydrogel cellulose solution, followed hydrazine addition. It was found that the electrical conductivity of RGO/cellulose composite at 70% by weight of RGO was 15.28 S/m. It was found that the electrical conductivity of RGO/cellulose composite at 70% by weight of RGO was 15.28 S/m.

There is no publication about conductive composite film cellulose and reduced graphene oxide which prepared by microwave assisted machine and to produce cellulose and by using formic acid to produce RGO as the novelty of this study.

EXPERIMENTAL

Material and Methods

A Source of cellulose used in this experiment was cotton wool (brand of Ambulance). Sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were analytical reagent grade, and were supplied by Ajax
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Finechem. To dissolve cellulose, lithium chloride (LiCl) and N,N-dimethylacetamide (DMAc) were used, and both of them were analytical grade.

The raw material of reduced graphene oxide was graphite powder, and was supplied by Thermo Fisher. The others reagents such as sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), ortho-phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), formic acid (HCOOH), ethanol and toluene diisocyanate (TDI), were analytical reagent grade.

General Procedure

Reduction of Graphene Oxide

RGO was prepared as explained by Mitra et al⁶. 30 ml of GO suspension methanol (2.5 mg/cm^3) diluted with de-ionized water to 250 ml. 100 ml of formic acid was added to the suspension. The mixture was kept at 100°C for two days. The color of suspension turned to black. Then, the product was filtered, and dried at 40°C in vacuum oven until the weight was constant (6 hours).

Preparation of Cellulose Solution

To prepare cellulose solution, cellulose was prepared with condition 30°C , 5 min and 55.0 % H_2SO_4 by using microwave assisted machine. N,N-dimethylacetamide (DMAc)/lithium chloride (LiCl) was chosen as solvent for dissolving process. In brief, 0.25 g of cellulose was added with 20 mL of DMAc and heated until 100°C for 30 minutes. 0.40 g LiCl was poured to DMAc and heated for an hour.

Preparation of Reduced Graphene Oxide (RGO)/Cellulose Composite Film

To prepare a cellulose film, 1.1 % (w/v) cellulose solution was mixed by TDI (toluene diisocyanate). The weight ratio TDI/cellulose was 20.8:1. This ratio was chosen because of the physical property of films. When the ratio of film was less than 20.8:1 brittle property was observed. Then, this mixture was mixed for 5 minutes and casted onto 3cm x 7cm glass substrate by using a laser blade technique (see Figure 3), and let it cure at room temperature for an hour. The obtained film was then rinsed with deionized water to get rid of LiCl. To prepare RGO/cellulose composite films, the cellulose solution was mixed with different amounts of RGO (0%, 0.1%, 0.5%, 1.0% and 2.0%). Each RGO/cellulose mixture was then mixed with TDI, casted on glass substrate, and cured at room temperature as explained above.

Characterization

FT-IR

Samples were mixed with KBr with a ratio of sample to KBr 1:99 (w/w) and were then pelletized in the compression mold. Meanwhile, cellulose film and composite films were characterized by using attenuated total reflection (ATR) method.

The Viscosity Average Molecular Weight Determination

The viscometric measurement was performed at 30°C using a Ubbelohde viscometer. A 1.6 % (w/w) stock solution were prepared. A series of dilution of cellulose solution were made as 0.1, 0.2, 0.4 and 0.8% (w/v) by pipetting the stock solution 1.6, 3.1, 6.3 and 12.5 mL, respectively into 25 mL volumetric flask, and diluted to the mark with 9 % (w/w) LiCl/DMAc.

To obtain the specific the viscometer was clamped to a holder and suspended in a water bath. A 20 mL of sample was pipetted into the viscometer for each determination time to flow from one mark to another was measured. Five flow time measurements were carried out. The average value of time to flow for each sample concentration was calculated and reported.

Conductivity Measurements

Conductivity measurements of composite films at an ambient condition (64% RH) were performed by using Van Der Pauw method⁷. Each film was adhered to the printed circuit board (PCB) by using silver glue before performing the test. The PCB with the attached sample film was put into a socket and the resistivity were measured. The repetitions were carried out for three times. The average values of conductivity, an inversion of recorded resistivity were reported. In this research, the conductivity of samples were also carried out at high percentage of relative humidity (% RH~84). Film samples were

placed in desiccator containing saturated KCl solution and kept overnight. The procedure followed ASTM E104-02. The %RH was reported at 84.2 ± 0.3 at 25°C ⁸. Film were placed at closed system and kept it for overnight. Conductivity was measured at room temperature using the same method as explained previously, except that each sample was soaked in desiccator for 30 minutes after assembling with PCB.

RESULTS AND DISCUSSION

Determination of Viscosity Average Molecular Weight (M_v)

The molecular weight of cellulose was determined using the viscometry technique. The results are shown in Table-1.

Table-1: Flowing Time of Solvent (DMAc) and Cellulose (0.1% (w/w), 0.2% (w/w), 0.4% (w/w) and 0.8% (w/w)).

Concentration	0%	0.1%	0.2%	0.4%	0.8%
Flow Time (s)	10.994	11.277	11.580	12.717	15.410
	10.927	11.156	11.666	12.614	15.493
	10.913	11.207	11.640	12.684	15.461
	10.948	11.226	11.672	12.714	15.518
	10.880	11.252	11.648	12.716	15.466
t average (s)	10.932	11.224	11.641	12.689	15.469
η_{sp}	-	0.027	0.065	0.161	0.415
η_{sp}/C (cm^3/g)	-	26.636	32.417	40.170	51.878

Using the Huggins equation, the reduced viscosity η_{sp}/C was plotted as a function of concentration (Fig.-1).

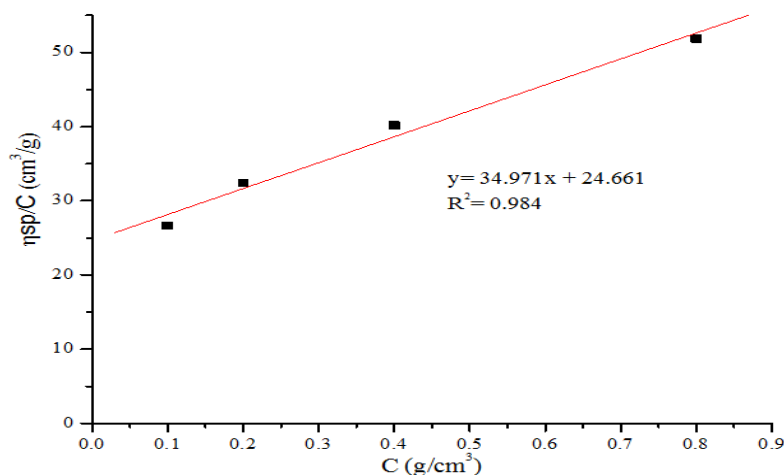


Fig.-1: Plot of % Cellulose vs η_{sp}/C

The intrinsic viscosity $[\eta]$ was obtained as a y-intercept. By entering the value of $[\eta]$ in the Mark-Houwink-Sakurada's equation $[\eta] = KM_v^a$ where K and a values proposed by McCormick⁹ are $1.278 \times 10^{-4} \text{ cm}^3/\text{g}$ and 1.19 respectively, the viscosity average molecular weight (M_v) of cellulose was obtained as $2.76 \times 10^4 \text{ g/mol}$. This value was relatively low as compared to that cotton linter.

Silva et al¹⁰ determined the average molecular weight of cellulose from cotton linter by using size exclusion chromatography (SEC) and viscometry. They found that average molecular weight determined by SEC and viscometry were 3.61×10^5 and $3.64 \times 10^5 \text{ g/mol}$ respectively.

Preparation of RGO/Cellulose Composite Films

The film was prepared using the method adapted from Qiu et al¹¹. In this method, cellulose solution was prepared using DMAc/LiCl as a solvent, and toluene diisocyanate (TDI) was added to form gel. It should be noted that the cellulose film was firstly prepared by solution casting without cross-linking agent (TDI). However, due to the low viscosity average molecular weight of the cellulose, the cellulose film formation was not possible.

Toluene diisocyanate (TDI) is bi-functional group organic, which can easily react with compounds -OH, epoxy, -COOH, -NH₂, etc¹². In addition, the activities of TDI to oxygen functional group were determined by position of isocyanate group at para and ortho¹³.

Meanwhile, the physical appearance of TDI/cellulose can be seen in Fig.-2. As we can observe that, without any cross-linking agent, film could not be formed. The best film was obtained when weight ratio TDI/cellulose was at 20.8:1 (w/w). This ratio was used as a fixed parameter to prepare RGO/cellulose composite films.

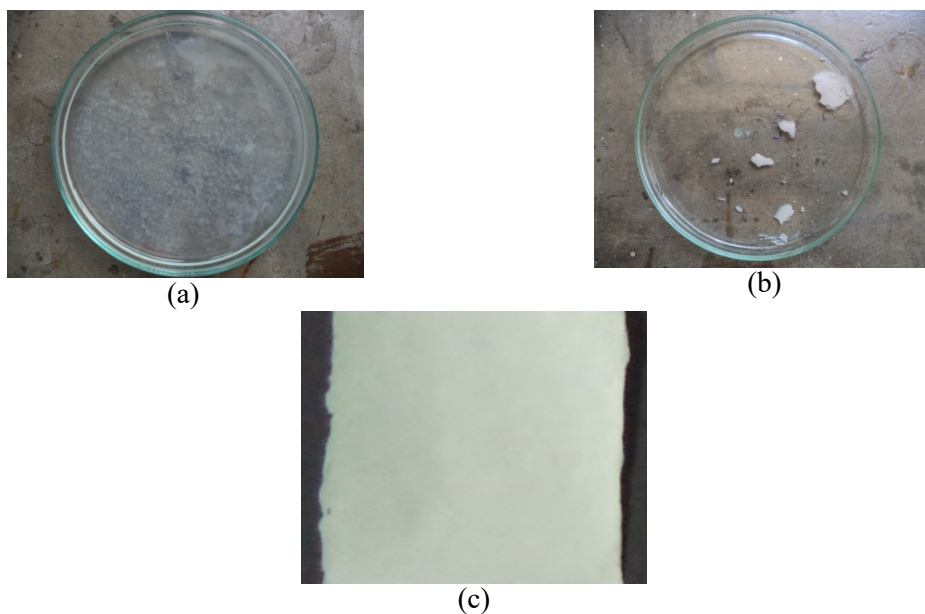


Fig.-2: Physical Appearance of (a) Product without adding TDI (b) Film with weight ratio 10.4:1 TDI/Cellulose (w/w) and (c) Film with weight ratio 20.8:1 TDI/Cellulose (w/w).

To prepare the composite films, RGO was added to the cellulose solution at concentration 0.5% (w/w), 1.0% (w/w), and 2.0% (w/w). It was worth nothing that when the RGO concentration was larger than 2% (w/w) the agglomeration of RGO was found and the composite was too brittle to be handled. The physical appearance of RGO/cellulose composite films can be seen in Fig.-3.

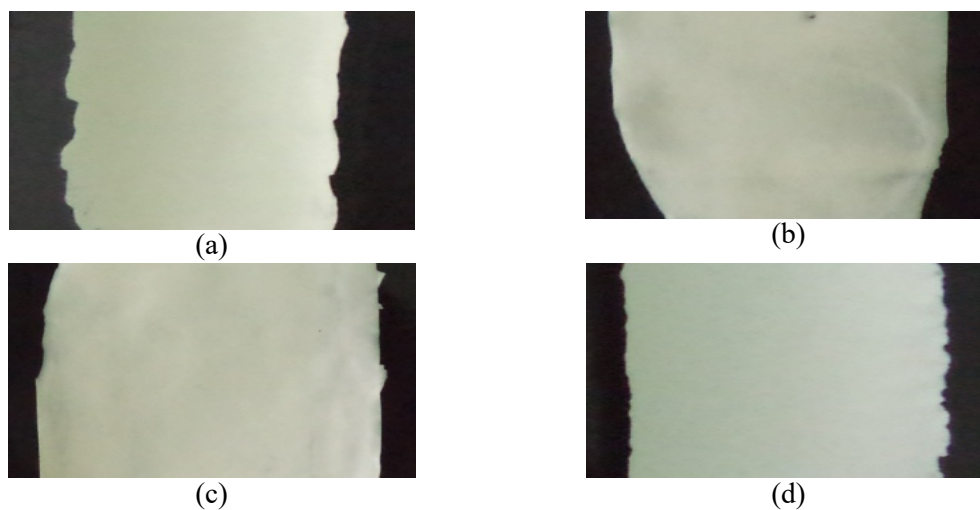


Fig.-3: Physical Appearance of RGO/Cellulose Composite Films containing RGO ratio (a) 0.1% (w/w) (b) 0.5% (w/w) (c) 1.0% (w/w) and (d) 2.0%.

FT-IR Analysis of RGO/Cellulose Composite Films

FT-IR characterization was used to investigate cellulose and cellulose composite films. In Fig.-4 the typical absorptions peaks of a cellulose film were observed at 3400 cm^{-1} (O-H), 2890 cm^{-1} ($-\text{CH}_2$) and 1060 cm^{-1} (C-O of secondary alcohol), which were similar to those of cellulose powder¹⁴⁻¹⁶. However, the reduction of OH peak was observed in case of cellulose film. This result indicated the disappearance of OH groups due to the reaction with TDI.

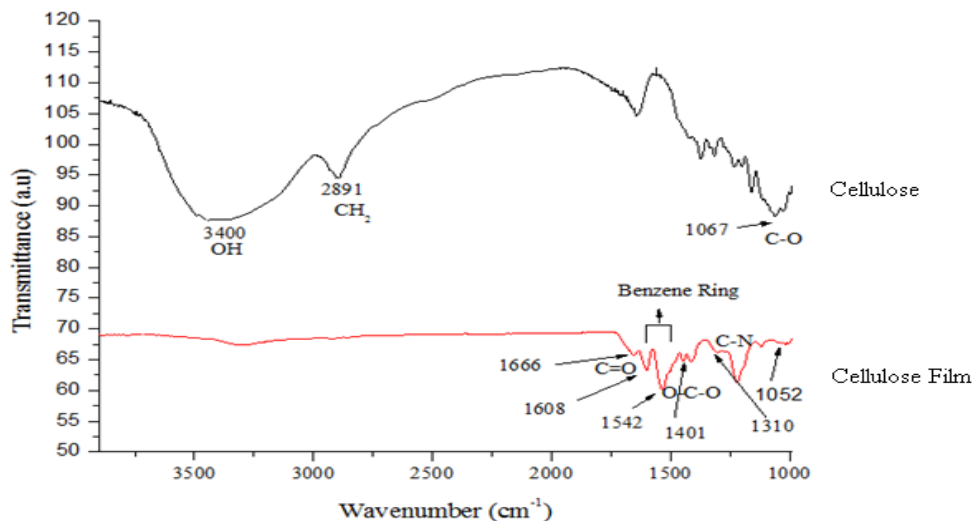


Fig.-4: FT-IR Spectra of Cellulose (30°C , 5 min, 55.0 % H_2SO_4) and a Film Cellulose

Characteristic peaks of amide (NHCO) at 1608 cm^{-1} and 1542 cm^{-1} correlated to benzene ring of TDI structure were observed. Besides, peaks at 1666 cm^{-1} , 1401 cm^{-1} and 1310 cm^{-1} assigned to $\text{C}=\text{O}$ stretching (amide: NHCOO), O-C-O stretching, and C-N stretching respectively were found.

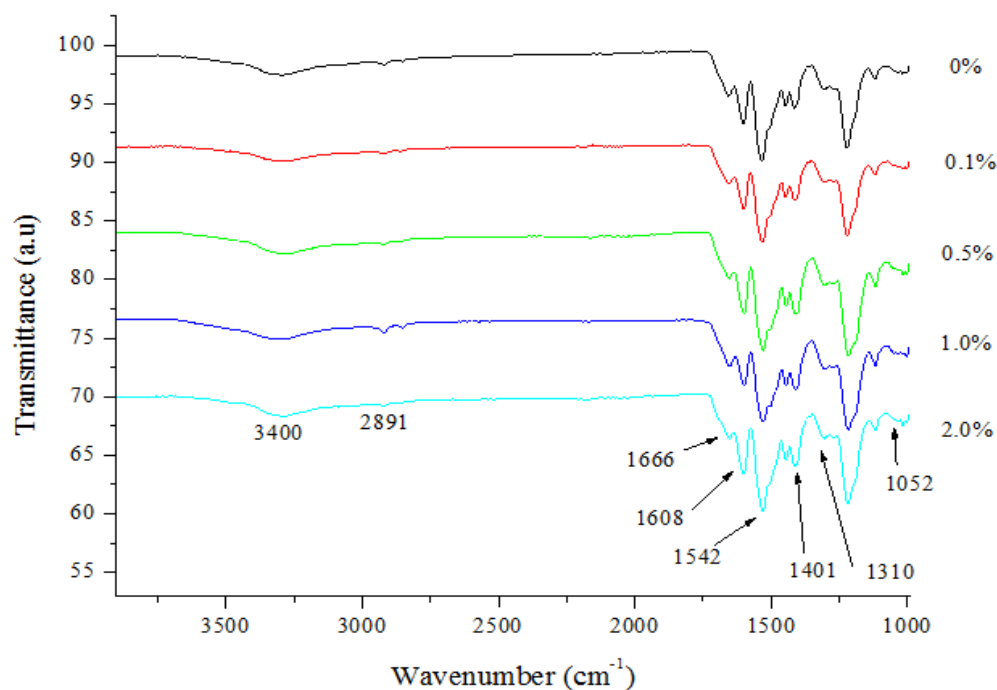


Fig.-5: FT-IR Spectra of RGO/Cellulose Composite Film containing RGO Concentration of 0%, 0.1%, 0.5%, 1.0%, and 2.0% (w/w)

Figure-5 shows the FT-IR spectra of RGO/cellulose composite films containing RGO of 0.1 0.5, 1.0 and 2.0 % (w/w). It was found that FT-IR spectra of all composite films are similar to that of the cellulose film. No characteristic peak of RGO could be detected due to the overlapping of peaks. There is no an

excessive isocyanate observing, can be detected peak at 2265 cm^{-1} . This information indicating that no unreacted isocyanate group remained.¹⁷

Conductivity of RGO/Cellulose Composite Films

The RGO/cellulose composite films with various RGO contents were exposed to two different relative humidity namely, 64% RH (ambient condition) and 84% RH (saturated KCl solution). The conductivity of the composite films was measured and the result is shown in Fig.-6. It was found that the conductivity of composite films exposed to both of the conditions increased steadily with the increase of RGO contents. However, the conductivity of composite films after exposing to the higher humidity (84% RH) reduced significantly. The values of conductivity decreased almost two orders of magnitude as compared to those at 64% RH. The result could be explained by the fact that the RGO showed the inherent p-type semiconducting behavior where the electrical conduction was dominated by the holes¹⁸. When the relative humidity was further increased, water molecules, which behave as electron donors, were absorbed more on the sensing layer surface. Thus, the hole concentration reduced, leading to a reduction in conductivity. Ouyang et al⁵ found that RGO(x)/cellulose composite increased rapidly $1.9 \times 10^{-5}\text{ S/cm}$ for $x=5$,

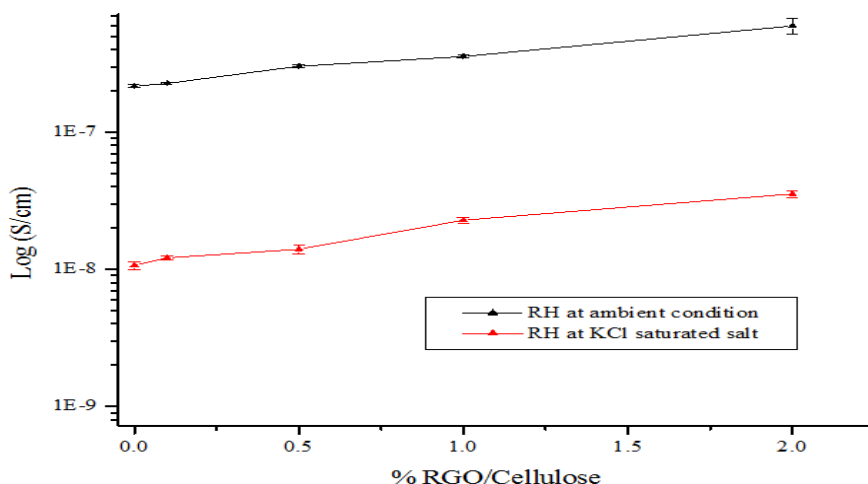


Fig.-6: The Conductivity of RGO/Cellulose with Different RH (Relative Humidity) at Room Condition and KCl Saturated Salt (0% (w/w), 0.1% (w/w), 0.5% (w/w), 1.0% (w/w) and 2.0% (w/w)).

Ouyang et al⁵ found that RGO(x)/cellulose composite increased rapidly $1.9 \times 10^{-5}\text{ S/cm}$ for $x=5$, $3.4 \times 10^{-4}\text{ S/cm}$ for $x=10$ and $15.28 \times 10^{-2}\text{ S/cm}$ at ambient condition. This result indicated that our RGO/cellulose composite had much lower conductivity than their composites (by considering curve trend). It might be explained by the difference of a reducing agent used in RGO production. Ouyang et al⁵ used hydrazine which is stronger reducing agent than formic acid that we used.

CONCLUSION

FT-IR analysis of RGO/cellulose composite films showed the typical absorption peaks of a cellulose film. The presence of TDI was confirmed by the reduction of intensity OH peak in case of cellulose film. In addition, there were no excessive isocyanate groups present in the films. The existence of RGO could not be detected due to the overlapping of peaks. The conductive behaviors of cellulose composite films were monitored under two different relative humidity condition (%RH) namely, at ambient (64 %RH) and high humidity (84% RH) conditions. It was found that the conductivity of composite films after exposing to the higher humidity (84% RH) reduced significantly almost two orders of magnitude as compared with those at the ambient condition. However, the conductivity of cellulose composite films exposed to both of the conditions increased steadily with the increase of RGO contents. Based on their sensitive conductivity to the humidity change, cellulose composite film has a potential as a humidity sensor candidate.

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