Modification of Thermal Conductivity of Cotton Fabric Using Graphene

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***Abstract*—This paper investigates the possibility to use Graphene coated fabric for thermal conductive purposes. Existing methods of thermal conductivity improvement of textiles require extrusion facilities and the end products are heavy due to insertion of metal wires. By using Graphene Oxide application, these disadvantages can be eliminated. Graphene Oxide was applied onto the fabric using a simple dip and dry method and an exhaustion dyeing method. Then the coated fabric was allowed to react with an aqueous solution of reducing agents. The test results showed that the most suitable method to obtain a significant improvement in thermal conductivity of textiles is to follow an exhaustion dyeing method with reducing agents. The reduction process should be maintained at 70^{0}C for 30min duration with the addition of Sodium Hydrosulphide. Exhaust dyed fabric which was treated with reducing agents showed an improvement of 55% in thermal conductivity compared to the uncoated fabric, which is a significant improvement in the thermal conductivity of textiles. In addition to the thermal conductivity values, few related textile properties were tested to evaluate the effect of the Graphene coating on the fabric characteristics.**

Keywords*— Graphene, Graphene Oxide, Thermal conductive, Textile, Cotton, Reduction, Exhaustion Dyeing

I. INTRODUCTION

With the development of the technology and lifestyles, the field of textiles has attracted attention for their use in a range of products due to their technical performance rather than aesthetic and comfort properties. There is a growing focus on thermal conductive fabric which can provide a cooling sensation, especially for people living in the hot climates. Body heat generation is a common incident and if the clothes worn produce a cooling effect, this would be beneficial. Effective thermal conductivity should be facilitated from the intermediary fabric. Generally, heat transfer occurs from the high temperature region to the low temperature region. Body temperature of the human being is 37^{0}C (98.6 F) [1]. But due to clothing and physical activities, high levels of energy can be generated and, as a result temperature increases. Thermal conductive fabric will be important not only as wearable products, but also for technical and in domestic applications.

The most well-known method is heat management through moisture management. But in situations where moisture is not involved, this concept will not be valid. Generally textile fabric is considered as thermal insulators or having a very poor thermal conductivity values. Cotton fabric has a higher thermal conductivity value of 0.026–0.065$Wm^{-1}K^{-1}$ compared to synthetic fibers [2]. Coating technique with another material would affect the heat conduction depending on the thermal conductivity of the coating material and application conditions. The general methods of improving thermal transfer are to adjust fabric thickness, porosity, fabric structure and density but better results would be gained through coating techniques. Thermal conductive fabric can be developed by inserting conductive wires into the fabric structure. Thermal conductive gloves are produced by introducing a metallic wire into the Polyester fabric [3]. The disadvantage of currently used methods is the effect on handling and comfort properties of the final product. There is also a tendency to add Carbon and Silver Nano tubes by normal processing methods and fiber spinning techniques [4]. But in order to perform this, fiber extrusion and spinning facilities are required.

Graphite is the more stable form of Carbon at atmospheric pressure. Graphite structure consists of a succession of layers parallel to the base plane of hexagonally linked Carbon atoms [5]. Graphene is a flat mono layer of Carbon atoms which is tightly packed into a two-dimensional honeycomb lattice [6]. At room temperature, thermal conductivity of a single layer Graphene is found to be 5300$Wm^{-1}K^{-1}$ [7]. The aqueous dispersion of Graphene can be easily produced without any polymeric or surfactant stabilizers as it contains Carboxylic and Hydroxyl groups. It can be applied on textiles through simple dip-pad or dyeing assembly [8]. This would be commercially viable in producing thermal conductive fabric compared to other existing method.

In this paper, fabrication of thermal conductive fabric was performed using Graphene. Application of Graphene was done using dip and dry and exhaustion dyeing method. Different

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reducing agents were used to obtain reduced Graphene Oxide loaded fabric and the most suitable agents are selected at the end. The fabric to be developed is recommended to use within a certain range of temperatures. The outside temperature ranges aimed in this project is from 18^0C to 36^0C. This range is specified because this type of product would not be much suited for a very cold climate or a hot climate because in a cold climate, it will further cool the body and it is not required. In a very hot climate, heat transferring from body to outside would not happen in the required way.

II. EXPERIMENTAL APPROACH

A. Tested Fabric

Scoured and bleached 100% Cotton, Single Jersey knitted fabric was used as the testing material in this research. The specifications of the fabric are 150gsm value with 40 wales per inch and 52 courses per inch.

B. Thermal Conductive Measuring Equipment

Lee's disc method is used to determine the thermal conductivity of a weak conductor, such as textiles and glass at steady state [9]. Ignoring the heat losses from the edge of the disk, the amount of heat transfer "Q" across the thickness of the sample is given by Fourier's Law of Conductivity, Q = KA (T2-T1) / X where K - Thermal conductivity of the sample, A – Cross sectional area, T2-T1- Temperature difference across the sample thickness, X –Thickness

Temperature gradient, dT/dt at T1, steady state temperature of the top plate, can be obtained by drawing a tangent line at T1 on the Cooling graph. This is applied to Newton's Law of Cooling, dQ/dt = m C (dT/dt) where M - Mass of the refractory plate, C- Specific heat capacity of the Refractory material [10].

Equation (1) is used to obtain the K value of the fabric samples.

$$\frac{K \times A \times (T2-T1)}{X} = m \times C \times \frac{dT}{dt} \tag{1}$$

III. EXPERIMENTAL PROCEDURE

A. Preparation of dispersion of Graphene Oxide

Synthesis of Graphene Oxide was done by Modified Hummer's Method and it was used to prepare the dispersion. Graphene Oxide solid which is 5% on the weight of fabric samples was obtained to prepare the dispersion. Material to Liquor Ratio was maintained at 1:30 and water was added to the above Graphene Oxide amount. This dispersion was stirred at 800rpm for 30min using high speed stirring machine [11]. The output, Graphene Oxide dispersion was divided into several parts in order to be applied on the fabric by using several methods.

B. Application of Graphene Oxide dispersion on to the fabric samples

Method 1 – Dip and Dry Method. The fabric samples were dipped in the Graphene Oxide dispersion for 12h & 24h time durations at room temperature.

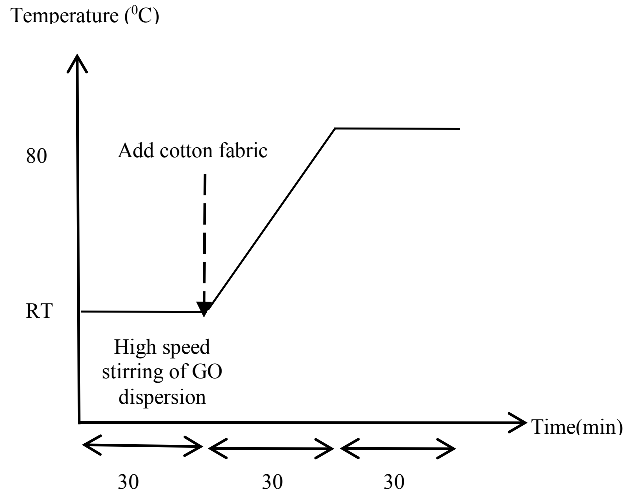

Fig. 1. Exhaustion dyeing cycle

Method 2 – Exhaustion dyeing cycle was followed in this method. After dipping the fabric in the dispersion, it was heated for 1h until the temperature reached up to 80^0C [12]. The exhaustion dyeing cycle is shown in Fig. 1.

Then, the samples obtained from above methods were sent through the padding mangle to squeeze off the excess dispersion and to obtain a uniform application throughout the fabric surface. The samples were dried in the oven at 60^0C for 24h time period. Then they were treated with reducing agent, Sodium HydroSulphide (NaHS), in order to reduce the applied Graphene Oxide coating on the fabric.

Chemical Reduction Technique –The dried samples obtained from above methods were put into a water bath at 70^0C temperature. Then NaHS was added at 4% on the weight of fabric. Material to Liquor Ratio was maintained at 1:50. Then the aqueous solution with the fabric samples was kept to be heated at 70^0C temperature for 30min time duration [13]. Fig. 2 shows the chemical reduction process.

Samples were again sent through the padding mangle and oven dried for 24h after reduction. The dried samples were kept in the conditioning room for 24h time duration with the conditions of 20°C ±2°C, RH 65% ±4%. The conditioned fabric samples were used for testing of thermal conductivity and other textile properties.

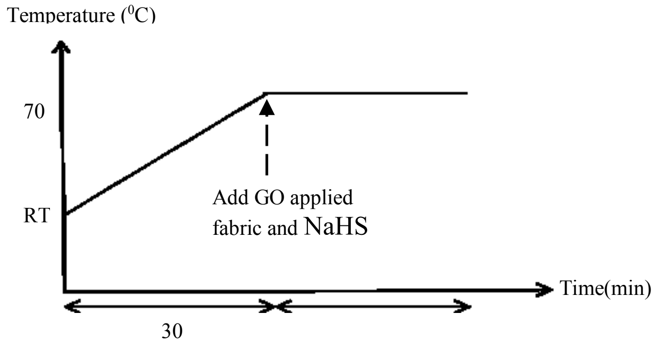

Fig. 2. Chemical reduction process

The Graphene Oxide coated samples were sent through washing cycle in order to check their fastness to washing properties. A washing cycle was carried out with ECE Reference detergent under the standard of ISO 105C01. The pilling level was tested using BS EN ISO 12945-1 standard. This test was done for untreated control sample and for the exhaustion dyed sample. Up to 2000 rubbing cycles were considered. Bursting strength of the untreated control fabric sample and the exhaustion dyed samples were tested under the standard of BS EN ISO 13938.

IV. RESULTS AND DISCUSSION

The application of the thermal conductive substances can be done on certain textile substrates according to their properties. Scoured and bleached cotton is usually taken for this type of applications to ensure that the cloth is dye stuff free and it would not react with the Graphene Oxide in an adverse manner. The reduction of Graphene Oxide through thermal method can be done only for the textiles with high degradation temperatures [8]. In order to perform thermal reduction method, heating temperatures should be maintained at high levels but this may affect the cellulosic structure. Cellulosic substrates have low stability at high temperatures and tend to degrade easily. By using chemical reduction method, Graphene Oxide reduction can be achieved at a lower temperature and with the addition of reducing agents. This helps to enhance the thermal conductivity and also have a minimal effect on the fabric structure.

When the Cotton fabric is dipped in the Graphene Oxide dispersion, the fabric gets coated because of Vander Waal forces between exfoliated Graphene Oxide which has functional groups such as Carboxyl, Hydroxyl and Cotton. These groups make Graphene Oxide hydrophilic. This hydrophilic nature supports strong adherence of Graphene Oxide onto the cotton fabric surface during the reaction time [8]. With the application of Graphene Oxide, there was a colour change of the fabric, as it changed from white to light brownish colour due to the brownish colour of Graphene Oxide dispersion.

TABLE I. THERMAL CONDUCTIVITY VALUES OF DIPPED AND DRY METHOD

Result	**12h Dipped Sample**		**24h Dipped Sample**	
	Before Reduction	***After Reduction***	***Before Reduction***	***After Reduction***
Thermal Conductivity	0.05072	0.0685	0.05169	0.07678
Improvement compared to untreated sample	1.02%	36.43%	2.95%	52.92%
Standard Deviation	0.000232	0.001339	0.000863	0.000671

A. *Comparison of Thermal conductivity values*

The thermal conductivity value of the untreated control fabric sample was measured to be $0.05021WK^{-1}m^{-1}$. According to the measured thermal conductive values of the treated samples, it can be concluded that there was an improvement of the thermal conductivity of the Cotton fabric after the application of Graphene Oxide dispersion. The test results showed that Dip and Dry method before reduction does not facilitate a major improvement in thermal conductivity. This is mainly because Graphene Oxide contains Oxygen functionality groups and they act as a barrier for phonon transportation through the textile material. Although the Graphene Oxide uptake increases with the dipping time duration, due to the above reason, there is a trivial difference between thermal conductivity value of 12h and 24h dipped samples.

When comparing Dip and Dry method with exhaustion dyeing process before reduction, results showed that exhaustion dyeing method is better than the Dip and dry before reduction method. When the bath is heated up to 80^{0}C as done in the exhaustion dyeing method, some of the Oxide functionality groups are stripped from the surface. This creates a thermodynamically stable carbon oxide species [14]. Although the stripping of Oxide groups occurs at high temperatures, very fine separations can occur at 80^{0}C which resulted in a slight improvement in thermal conductivity.

After adding reduction agents, NaHS, to the Graphene Oxide coated fabric obtained from both methods, a significant improvement of thermal conductivity could be observed. The most satisfactory thermal conductivity values were obtained by 24h dipped and reduced sample, which is 52.92% and by the reduced sample of exhaust dye method, which is 55% compared to the untreated sample. When considering the thermal conductivity of textile materials, the above results show a huge improvement. Generally, Graphene Oxide shows much better thermal conductivity when it is reduced than in the un reduced state.

The chemical reduction process in this research could be realized at 70^{0}C and this temperature is a suitable heating temperature range for Cotton fabric. The heating temperature

TABLE II. THERMAL CONDUCTIVITY VALUES OF EXHAUSTION DYEING METHOD

Result	Exhaustion Dyeing Method	
	Before Reduction	***After Reduction***
Thermal Conductivity (WK-1m-1)	0.06194	0.07806
Improvement compared to untreated sample	23%	55%
Standard Deviation	0.001114	0.000623

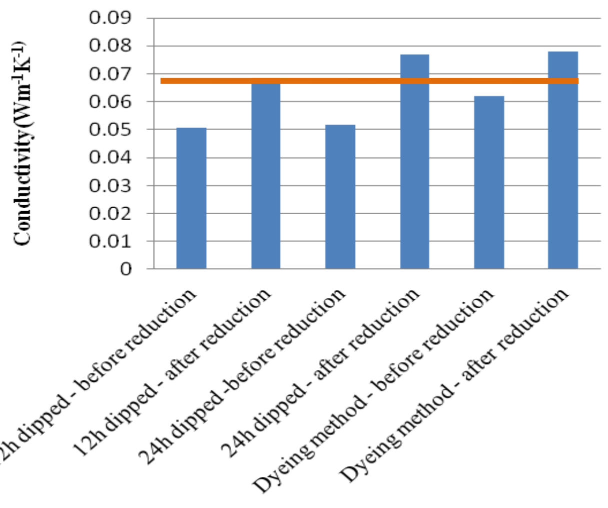

Fig. 3. Comparison of thermal conductivity values

should be selected between a range where it would not harm the cellulosic structure of the textile material. After the chemical reduction, coated fabric turned into a grpahite black colour which ensures the removal of oxide functionality groups and this explains the improvement of thermal conductivity as well.

Fig. 3 shows the thermal conductivity values comparison obtained from each technique and the comparison with untreated sample. The coloured horizontal line shows the thermal conductivity of untreated control sample which is $0.05021 Wm^{-1}K^{-1}$. The significant improvements in thermal conductivity of dip and dried and exhaust dyed samples after reduction can be clearly seen on this. It also shows the negligible improvement of thermal conductivity of the samples obtained through dip an dry method before reduction.

When considering the thermal conductivity variation after the first wash, it has been increased in the Graphene Oxide applied samples before carrying out the reduction process. The Table III shows an improvement of the thermal conductivity after these samples are being treated with the washing cycle.

TABLE III. THERMAL CONDUCTIVITY OF FABRIC AFTER WASHING

Sample	**Conductivity after wash (Wm-1K-1)**	**Improvement compared to samples before washing**	**Standard Deviation**
12h dipped - before reduction	0.053357	5.20%	0.000476
24h dipped -before reduction	0.054998	6.40%	0.000751
Exhaustion method before reduction	0.064603	4.30%	0.001032
Exhaustion method after reduction	0.07359	-5.70%	0.009827

TABLE IV. TEST RESULTS OF COLOUR FASTNESS TO WASHING

Sample	**Grey Scale Rating**	
	1st Wash	***2nd Wash***
12h Dipped Sample	2 – 3	1-2
24h Dipped Sample	3	2
Exhaust Dyeing Method	4 – 5	3

The change in the conductivity can be due to the reducing agents contained in the detergent used for washing. It is known that the detergent ECE used contains sulphate compounds which can act as a weak reducing agent [15]. There is a possibility that a weak reduction process of Graphene Oxide has occurred in the washing bath. Even weak reducing agent can chemically reduce the Graphene Oxide which would lead to better thermal conductivity value of the substance. But it can be seen that there is a thermal conductivity reduction of 5.7% in the chemically reduced sample after washing. This figure confirms that the chemically reduced Graphene coated sample would not react with ECE Reference detergent as they are already being reduced. It is shown that even after the first wash, chemically reduced sample has a higher thermal conductivity value than the samples obtained through other methods even after the loss during washing process.

B. Test Results of Textile properties

Several textile testings were done to determine the effect on the textile properties of the Graphene Oxide coated fabric. After treating the samples with a washing cycle as per the standard procedure, the samples were tested for their colour fastness properties to determine the suitability of the Graphene Oxide applied fabric for day to day usage. The grey scale was used to determine the rating under D65 light source. According to the experiment, colour fastness level of the fabric samples have decreased with the increased number of washing cycles. Table IV shows these values. When comparing the application method, there is a higher colour fastness rating for the exhaust dyed before reduction sample than other method. The better colour fastness ratings of exhaustion dyed sample before reduction can also be explained due to the fact of stripping of Oxide components from the surface. Still, there is a tendency of the overall colour fastness getting decreased. It would be better to maintain the colour fastness of the fabric over subsequent washing cycles so that the value to the customer can be further increased.

The fuzzing and pilling resistance of fabric is a factor that affects the wear ability and the appearance of clothing [16]. With the application of Graphene Oxide, the pilling level of the fabric improved when compared with the untreated sample.

TABLE V. PILLING LEVELS OF THE TEST SAMPLES

Number of Rotations	Untreated Cotton Fabric	Exhaustion Dyed Fabric
125	4 – 5	4 – 5
500	3 – 4	4
1000	2 – 3	3
2000	2	2.-3

The pilling level values are shown in Table V. Pilling level has decreased because an application of a coating prevents the hairiness of the fabric surface. The coating would act as deterrent to surface pill formation.

Bursting strength of a fabric shows how much pressure is needed to burst a fabric when uniform force is applied in a direction perpendicular to the fabric surface. This test method is specifically used in testing the strength of knitted fabrics. The results showed that bursting strength of untreated sample is $5 kgcm^{-2}$ and of exhaustion dyed sample before reduction is $4.83 kgcm^{-2}$. As per results, it is shown that the bursting strength of exhaustion dyed sample is reduced by 3.4% compared to the untreated sample. But this is a negligible amount.

V. CONCLUSION

A 100% cotton knitted textile material was successfully fabricated by coating Graphene Oxide and improvement in textile thermal conductivity was observed when compared with the untreated control sample. The thermal conductivity was seen to improve further when the coating was chemically reduced. The test results on the textile properties showed that there is no significant effect on the strength properties, colour fastness and pilling levels of the coated fabric but some level of change of colour of the material was observed. With the further development to the material, much better results could be obtained. The coating technique employed in this research offers advantages over the other currently used methods due to its flexibility of application to semi-finished and finished products.

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