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Synthesis Conditions for Natural Rubber and Natural Rubber reinforced with Graphene Fibre Production by Electrospinning

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In this study, the parameters in the electrospinning process including needle-target distances (9-12 cm), stirring time before electrospinning (1-3 d), and concentration of polymer solution (1-2 wt% of natural rubber) were optimized. Graphene nanoplatelets (GNPs) was chosen as conductive filler in order to enhance properties of polymer solution. The characterization of electrospun fibre was reported using scanning electron microscopy and Fourier transform infrared spectroscopy. Morphologies of fibre should be uniform, homogeneous, and defect-free. The best results of natural rubber fibre were produced by using 3 d of stirring time, concentration of 2 wt% of natural rubber, feed rate of 2.5 mL/h, and needle-target distances of 15 cm. The best results of natural rubber and graphene nanoplatelets fibres were at 3 d of stirring time, concentration of 3 wt% of natural rubber, feed rate of 2.5 mL/h, and needle-target distance of 15 cm. From the results, when the needle-target distance was increased, the fibre diameter was decreased. When the concentration was increased, the fibre diameter was decreased. Model of natural rubber and graphene nanoplatelets fibre was also determined.

1. Introduction

The prices of natural rubber are decreased so the demand of natural rubber used can raise the price of the rubber. The outstanding properties of natural rubber are elasticity, high tensile strength, cohesion, and tear resistance (Costa et al., 2013). Natural rubber in form of natural rubber fibre is used in many manufacturing such as tires, gloves, surgical materials, adhesives, automobile, fabric, etc. (Cacciotti et al., 2015). The electrospinning process has been used for many years in manufacturing of different materials in both melt form and solvent solution such as polymers, ceramics, metals, composites, inorganic, and hybrid materials (Blanco et al., 2010). The electrospinning process consists of three main components. First, a syringe pump contains polymer solution, syringe, and needle. Secondly, an applied voltage causes electronic field between a needle and a collector. The last, collector covers with aluminium foil that collects the fibres which produce from the process (Hu et al., 2012). This process is easy to produce, make high surface area per volume ratio, low cost, and easy to control diameter. The diameter range of electrospun fibre is between nanometers to micrometers (Blanco et al., 2010). There are many parameters that affect diameter of electrospun polymer fibre such as type of polymer, concentration of polymer solution or melt polymer, distance between needle and collector, feed rate of syringe pump, voltage of high voltage supplier (Chen et al., 2015). The glass transition temperature (Tg) of natural rubber is around -60 °C. At room temperature, it is higher than glass transition temperature leading to the broken of fibres from electrospinning process. This is because chain segments of rubber macromolecules can move in electrospun fibres (Tian et al., 2011). This movement occurs when electrospun fibre lay on collector. Conductive filler, such as silver nanoplatelets and carbon black, had been selected to make better properties of mix materials (Cacciotti et al., 2015). Graphene nanoplatelets (GNPs) are good conductivity, excellent electrical, high Young's modulus, great strength, and light weight. The applications of graphene nanoplatelets as filler in natural rubber polymer solution are in packaging, pressure sensor, self-regulated heating, and electromagnetic interference shielding (Cacciotti et al., 2015). The

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optimization of condition from response surface of fibres produced by the electrospinning process was found (Saimon et al., 2019) and the variable was analysed as the main factor of the process (Han et al., 2018). In this study, morphology of natural rubber fibre and natural rubber/GNPs fibre were studied by scanning electron microscopy (SEM), Fourier transform infrared spectrometry (FTIR) and response surface. The response surface study parameter included day of stirred, feed rate, needle-target distances, and concentration of dry rubber while the previous study on similar topic as in Cacciotti et al. (2015) had less study parameters.

2. Materials and method

2.1 Preparation of dry rubber

Natural rubber latex (NRL) (from National Metal and Materials Technology Center) consisted of 60 wt% dry rubber (ammonia 0.7 % Lauric acid, Tetramethyl Thiuram Disulfide and Zinc Oxide). NRL was poured on petri dish mixed with acetone (C_3H_6O, 99.5%, ρ = 0.79 g/cm^3, ACI Labscan) for extraction of dry rubber from NRL.

2.2 Preparation of natural rubber and natural rubber with GNPs solutions

Dry rubber was weight and dilute it with 30 mL chloroform (CHCl3, 99.8%, Cambridge Isotope Laboratories) in ratio of 1 and 2 wt% (0.45 g and 0.90 g of dry rubber). The all component was stirred using blending time of 1-3 d. For natural rubber with GNPs, 1 wt% GNPs was blended with dry rubber (0.0045 g, 0.009 g and 0.0135 g for 1 %, 2 % and 3 wt% concentration) and 30 mL of chloroform. Then, the solution was sonicated for 20 min followed by magnetic stirred for 20 min. This was repeated for 3 times. Then, dry rubber was weighted and diluted to 1-3 wt% dry rubber and stirred using blending time of 1-3 d.

2.3 Electrospinning process

The high voltage supplied at 20 kV was set with the needle target distance (NT) of 9, 12, and 15 cm using a fix collector and 20 G stainless needle with its diameters of 0.9 mm. Collector was covered with aluminum foil. Volume of syringe of 15.9 cm (10 mL syringe), feed rate of 1.5, 2.5, and 5 mL/h were set. The positive charge of the high voltage was supplied to the needle was set whereas the negative charge of the high voltage was supplied to aluminum foil on the collector.

2.4 Characterization methods

A hundred of fibres were measure each sample. The average diameter of the fibres was determined from SEM (Quanta 450, FEI) micrographs using Image J software. The study focused on the uniform arrangement and the smoothness of the fibre surface. Fourier transform infrared spectroscopy (FTIR; Bruker TENSOR2, attenuated total reflectance (ATR) mode) was used in the range of 650-4,000 cm^{-1} to observe the structure and functional group of the dry rubber, natural rubber fibre, and natural rubber fibre with GNP.

3. Results and discussion

The average fibre diameter of natural rubber fibres was determined from SEM micrographs using Image J software as shown in Table 1 (1 wt% and 2 wt% natural rubber at different days of stirring, NT, feed rate, and concentration of dry natural rubber.

Table 1: Average diameter of 1 wt% and 2 wt% of natural rubber fibres

Sample no.	Concentration of dry rubber (%)	Feed rate (mL/h)	NT (cm)	Day of stir (d)	Diameter (um)	SD
1	1	2.5	9	1	24.0	5.6
2	1	5	9	1	29.1	10.7
3	1	2.5	9	1	18.1	6.9
4	1	2.5	15	1	17.5	4.9
5	1	2.5	9	2	8.6	4.4
6	1	2.5	9	3	6.3	1.9
7	2	2.5	9	2	7.3	2.4
8	2	2.5	9	3	7.5	1.9
9	2	2.5	12	2	6.2	2.1
10	2	2.5	12	3	16.2	4.6
11	2	2.5	15	2	9.9	3.3
12	2	2.5	15	3	10.8	4.5

3.1 Days of stirring

From Table 1, for sample no. 1, 5, and 6 (days of stirring of 1, 2, and 3 d, diameter of 24.0, 8.6, and 6.3 um, and SD of 5.6, 4.4, and 1.9), it was found that more days of stirring time caused smaller diameter of fibre. The morphology of fibres that was specified by SEM is shown in Figure 1 to 2. From Figure 1 a, e, and f (sample no. 1, 5, and 6), it showed that more days of stirring time caused more uniform and smoother fibre. More days of stirring made more homogeneous dry rubber in chloroform that caused homogeneous polymer solution. More homogeneous polymer solution gave more uniform fibre. The days of stirring in these experiments were 1, 2, and 3 d. The best condition of days of stirring was 3 d because the fibre obtained was smooth, uniform, and the diameter of the fibre was the smallest.

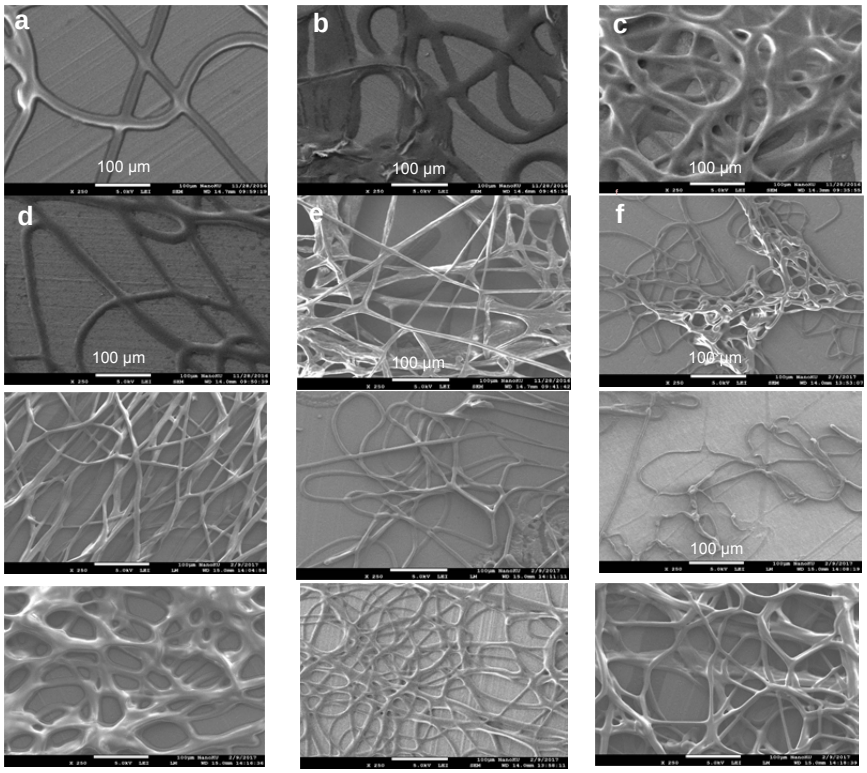

Figure 1: SEM micrographs of 1 wt% of natural rubber fibres (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4, (e) sample 5, (f) sample 6 and those of 2 wt% of natural rubber fibres (g) sample 7, (h) sample 8, (i) sample 9, (j), sample 10, (k) sample 11, and (l) sample 12

The average fibre diameter of 1 wt% natural rubber/GNPs fibre, 2 wt% natural rubber/GNPs fibre, and 3 wt% natural rubber/GNPs fibre at different concentration of natural rubber, NTs, and constant days of stirring of 3 d is shown in Table 2. The morphology of the fibres specified by SEM is shown in Figure 2 to 4.

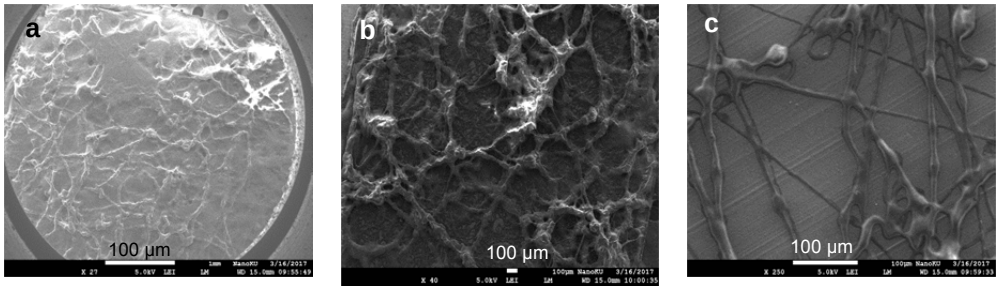

Figure 2: SEM micrographs of 1 wt% natural rubber and 1 wt% GNPs (a) sample 13, (b) sample 14, and (c) sample 15

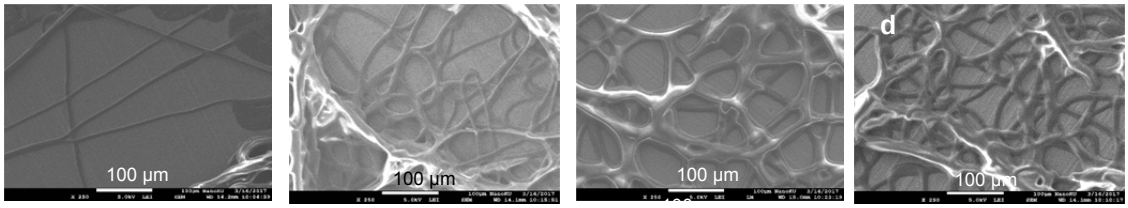

Figure 3: SEM micrographs of 2 wt% natural rubber and wt% GNPs fibres (a) sample 16, (b) sample 17, (c) sample 18, and (d) sample 19

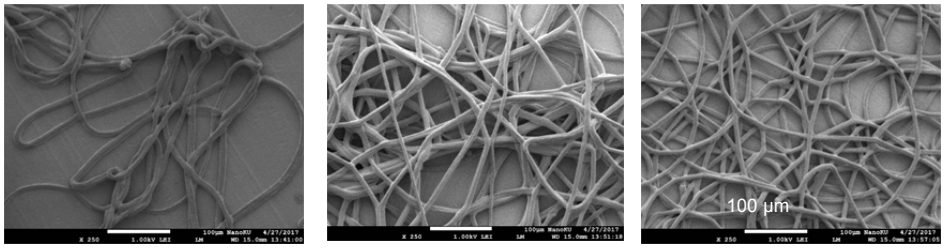

Figure 4: SEM micrographs of 3 wt% natural rubber and 1 wt% GNPs fibres (a) sample 20, (b) sample 21, and (c) sample 22

Table 2: Average diameter of 1-3 wt% of natural rubber/1 wt% GNPs fibres

Sample no.	Concentration (%)		Feed rate (mL/h)	NT (cm)	Diameter (um)	SD
	Dry rubber	GNPs				
13	1	1	2.5	9	35.9	11.2
14	1	1	2.5	12	18.8	15.3
15	1	1	2.5	15	14.2	5.9
16	2	1	2.5	9	22.1	5.4
17	2	1	1.5	12	11.3	2.6
18	2	1	2.5	12	8.2	2.0
19	2	1	2.5	15	8.0	36
20	3	1	2.5	9	7.6	1.9
21	3	1	2.5	12	7.2	1.3
22	3	1	2.5	15	7.0	1.6

3.2 Feed rate

From Table 1 and Table 2, comparing between sample 1 and sample 2 (feed rate of 2.5 and 5 mL/h) and sample 17 and sample 18 (feed rate of 1.5 and 2.5 mL/h), it was found that when feed rate was below 2.5 mL/h, the fibre size decreased but when feed rate was above 2.5 mL/h, the fibre size increased. These trends were the same as those in Chen et al., (2015). The higher feed rate caused higher surface tension. The higher surface tension defeated electrostatic force which resulted in higher diameter of fibre (Chen et al., 2015).

3.3 Needle-target distances

When NT increased, the diameter of fibre decreased and fibre appeared to be rounder because the solvent evaporated from the fibre more than that of small NT (Cacciotti et al., 2015). From Figure 5 a, b, and c (sample 20, 21, and 22 with the distances of 9, 12, and 15 cm and diameters of 7.6, 7.3, and 7.0 um), it was found that sample 22 (15 cm) had the smallest diameters and the quality of the fibre was better than sample 20 and 21. There was no bead found and uniform fibre was obtained.

3.4 Concentration of dry rubber

Comparison between sample 5 and 7 in Figure 1e and Figure 1g (concentration of 1 % and 2 %), the diameter of 8.6 and 7.3 um and SD of 4.4 and 2.4 was found. Comparison between sample 13, 16, and 20 in Figure 2a, Figure 3a, and Figure 4a (the concentration of 1 %, 2 % and 3 %), the diameter of 35.9, 22.1, and 7.6 um and SD of 11.2, 5.4, and 1.9 was found. It was found that high concentration of polymer solution led to smaller diameter of fibres (Cacciotti et al., 2015). At high concentration, the viscosity was higher than that at low concentration. At high viscosity, the diameter of fibre increased because the surface tension of polymer solution was increased

resulting in smooth fibre surface (Chen et al., 2015). In this research, the diameter decreased when concentration increased. At low concentration, it was found that beads were found due to low surface tension so polymer solution cannot overcome the electrostatic force. The average diameter was high because of the bead occurred and the standard deviation was also high. The diameter of fibres at low concentration was lower than that with high concentration was found only for the sample with no bead fibres. This was in good agreement with other research that the fibres with both smooth and rough surfaces were obtained when natural rubber concentration increased. The results showed that the smaller fibre diameters were obtained at the higher concentration of natural rubber (Costa et al., 2013).

3.5 Response surface

After measuring the diameter of natural rubber fibre with GNPs, response surface of natural rubber fibre with GNPs between NT (9-15 cm) and concentration of dry rubber (1-3 wt%) was developed. This model depicted the diameter of natural rubber with GNPs in a function of NT and concentration. The result was given in Eq(1) in general form: $Y = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2$ (model of the equation had two freedoms interaction, 2FI).

$$\text{Diameter} = 96.5 - (28.9 \text{ x } \%\text{concentration}) - (5.5 \text{ x needle target distance}) + (1.8 \text{ x } \%\text{concentration x needle} - \text{target distance}) \quad (1)$$

Response surface is shown in Figure 5a. R-squared of Eq(1) was more than 8 5% which was considered acceptable. P-value of equation was less than 0.05 which meant that independent variable (NT and concentration) affected the dependent variable (diameter).

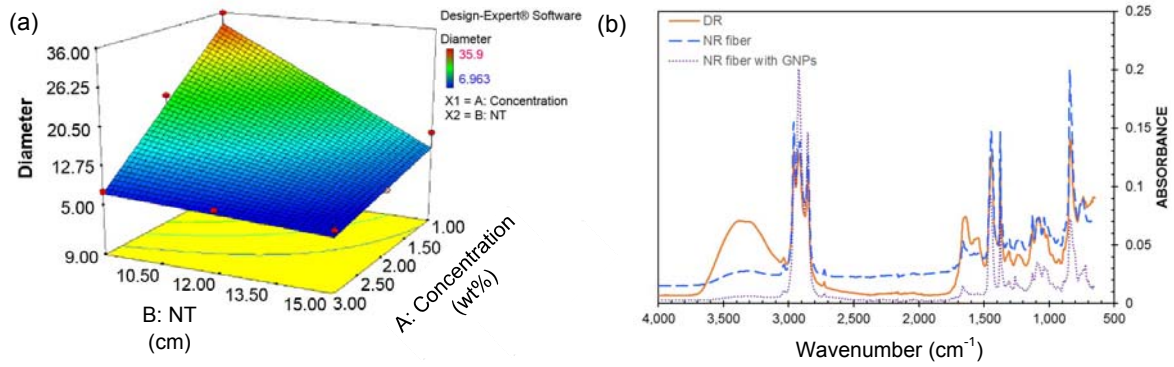

Figure 5: (a) Response surface of natural rubber fibre with GNPs (b) FTIR curve of DR, natural rubber and natural rubber with GNPs

R-squared of the model is 0.91 or 91% which was higher than 0.85 or 85%. Therefore, this model was acceptable. It was found that the diameter from the experiments were close to the diameter obtained from the model. P-value of the model was 0.0053 (lower than 0.05). Therefore, this model was significant to the fibre diameter. P-value of concentration was 0.0039 (lower than 0.05). Therefore, the concentration was significant to the diameter. P-value of NT (needle target distance) was 0.0113 (lower than 0.05). Therefore, needle-target distances was significant to diameter. P-value of concentration and NT (AB) was 0.0392 (lower than 0.05). Therefore, concentration – NT was significant to diameter). These results showed that both concentration and needle-target were significant to diameter (Wu et al., 2015).

3.6 Results from FTIR

FTIR curve of dry rubber (DR), natural rubber fibre (NR fibre), and natural rubber fibre with GNPs showed similar range of peaks (Figure 5b). Peaks around 838 cm^{-1} represented cis-double bond which were the same in all sample (DR, NR fibre, and NR fibre with GNPs). Peaks around 1,667 cm^{-1} represented C=C stretching vibration of cis 1,4-unit. Peaks around 2,900 cm^{-1} represented C-H stretching vibration of CH_2 and CH_3 in cis 1,4-unit. FTIR curve of DR had a peak at 3,363 cm^{-1} that represented O-H stretching of hydroxyl group. Both NR fibre with or without GNPs did not show the peak at 3,363 cm^{-1} (Anancharungsuk et al., 2010). The hydroxyl group was represented natural rubber latex. Therefore, DR consisted mainly of natural rubber. After electrospinning hydroxyl group was disappeared by evaporation (Cacciotti et al., 2015). The FTIR curve of DR, NR fibre, and NR fibre with GNPs did not have a peak at 1,720 cm^{-1} that representing C=O stretching of carbonyl group. Carbonyl group was one of peaks representing natural rubber latex (Thomas et al., 2015).

4. Conclusions

This research demonstrates the operating condition of electrospinning process to produce electrospun fibres and characteristic of NR fibre and NR fibre with GNPs at various conditions. Model of natural rubber with GNPs fibre diameter was obtained with its response surface related to NT and concentration of natural rubber. It was concluded that more days of stirring enhanced fibre quality. The diameter of the fibre decreased when the distance between needle target and collector was decreased. The higher feed flow rate resulted in greater fibre diameter. The fibre diameter decreased when the natural rubber concentration was increased and there was no bead found in the fibres. FTIR results of the dry rubber, natural rubber fibre, and natural rubber with GNPs fibre showed similar curves. From response surface of the fibre diameter, it was found that concentration and needle-target were significant to diameter of the fibres.

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