Fundamental study of colloidal stability and dispersion of novel nanosized conductive polyaniline (PANI)/prevulcanised latex (PVL) film for antimicrobial applications

M F Banjar\textsuperscript{1}, H D Suphi\textsuperscript{1}, M I Sarizan\textsuperscript{1}, A N A Yahaya\textsuperscript{1}, N A Khalil\textsuperscript{1}, M Singh\textsuperscript{3} and M Zulkifli\textsuperscript{2}

\textsuperscript{1} Universiti Kuala Lumpur, Branch Campus Malaysian Institute of Chemical and BioEngineering Technology, 78000 Alor Gajah, Melaka, Malaysia
\textsuperscript{2} Green Chemistry and Sustainability Cluster, University Kuala Lumpur, Branch Campus Malaysian Institute of Chemical and Bioengineering Technology, Taboh Naning, 78000 Alor Gajah, Melaka, Malaysia
\textsuperscript{3} Malaysian Rubber Board, RRIM Research Station, 47000 Sungai Buloh, Selangor, Malaysia

Email: faizar.banjar16@s.unikl.edu.my; muzafar@unikl.edu.my

Abstract. A smart material possessed enhanced conductivity integrated in prevulcanized latex (PVL) film produced throughout this work. Also recognizing the synthesis route of PANI was vast and vary, choosing suitable method was great importance corresponding to the aim of study. PANI was prepared through chemical oxidative polymerization of aniline carried out in aqueous solution which aniline dissolved in strong acidic solution (1 M HCl) with the presence of Ammonium Persulphate (APS) as the oxidizing agent and Sodium Dodecyl Sulphate (SDS) as surfactant. However, PANI was readily in acidic condition while PVL in basic and consequently causes a state of immiscibility upon mixing. Hence, PANI formed then mixed with 0.1 – 0.5 % KOH via homogenizer to increase the pH and maintain the homogeneity as well as dispersion to be combined with PVL. Various studies on PANI synthesis and incorporation with latex had been reported but very limited in focusing the colloidal and dispersion stability of the mixture. Zeta potential measurements revealed an effective dispersion and the colloidal stability as the pH of PANI increases. Analysis of mechanical performance using Universal testing Machine revealed that addition of PANI improves greatly in novel film tensile strength and Young’s Modulus by 109 % and 230 %, respectively.

1. Introduction
Polyaniline (PANI) had gained a lot of attention among researchers due to the reversible doping/dedoping character, pH switching properties, good environmental stability and modifiable electrical conductivity [1]. This conducting polymer has been studied for potential applications including anticorrosion coatings, lightweight battery electrodes and sensors. However, PANI on its own do have few drawbacks such as poor mechanical properties, low infusibility and low solubility in organic solvents limiting its usage. Introduction of secondary component into PANI further optimizes its functionality and enhanced performance. Usage of conductive polymers such as PANI and polypyrrole (PPy) combined with natural rubber latex had been reported broadly [2, 3]. This combination create a
beneficial values especially in developing surgical gloves with enhanced conductivity that acts as antimicrobial defense agent and low percolation threshold. Current surgical procedures do involve hard practices and creates surgical site infections (SSI) which arise due to the failure of these gloves to protect the transmission of skin flora from surgeon’s hand to the surgical site. SSI is the most costly healthcare-associated infection type and associated with huge amount of additional inpatient-days annually [4].

Increasing the thickness of gloves appear to be inefficient since more cost will be required for the manufacturing processes or raw material. In this work, a smart material presented as solution and putting together the best method to develop a nanosized conductive polyaniline (PANI) with ammonium persulfate (APS) as initiator as well as surfactant, sodium dodecyl sulfate (SDS). PANI synthesized through one-step redox reactions where chemical oxidative polymerization and formation of nanoparticle take places. Production of nanostructures creates advantages where new physio-chemical properties and new functional materials could be yield [5]. PANI nanofibers could be obtained by suppressing secondary growth of irregular shaped polyaniline. Simple approaches taken by rapidly mixing the initiator solution into monomer solution.

However, limited papers were focusing on the colloidal and dispersion stability which are very vital characteristic in determining the stability of latex mixture [6]. Therefore, this work also concern on this aspect and carried out zeta potential analysis that reflect the stability of colloidal dispersions. Challenge was there as PANI was readily in acidic condition, attributed by the synthesizing method which mainly involve hydrochloric acid while PVL was base in nature. Different pH of substances to be mixed tend to create problem in dispersion, consequently prevent a homogenized mixture [7]. Realizing this particular issues, addition with KOH increased the pH and improve the homogeneity. The mechanical performances also evaluated in order to ensure further effectiveness of PANI upon addition. Manipulation of PANI loading in PVL was studied throughout this work.

2. Experimental section

2.1. Materials
Aniline monomers with density of 1.02 g/ml and molecular weight of 93.13 g/mol and ammonium persulfate (APS) were purchased from Bendosen. Sodium dodecyl sulfate (SDS) obtained from R&M Chemicals Sdn Bhd. Hydrochloric acid (HCl) purchased from Sigma Aldrich while PV (pre-vulcanized) latex obtained from Gethahindus (M) Sdn Bhd., and used as received without further purification.

2.2. Synthesis of PANI
PANI was prepared via chemical oxidative polymerization. The molar ratio of aniline monomers to oxidizing agents or initiator (SDS) is 1:1. The work began with mixing 36.6 mL of aniline into 2 L of 1.0 M HCl solution inside 5 L beaker and stirred for 15 minutes with 600 rpm speed. Then, 60 g of SDS added into the solution and further stirred for 45 minutes. On the other hand, preparation of APS solution carried out by mixing 91.2 g APS into 2 L of 1.0 M HCl solution. Next, the monomer and initiator solutions (in 1.0 M HCl) were rapidly mixed together all at once under ice bath condition. Using mechanical stirrer with fixed stirring speed (600 rpm), the solution stirred for 5 hours to disperse the monomer and initiator molecules evenly before polymerization. Polymerization of aniline occurred as the colour changes from colourless to dark green. Lastly, the sample sealed with aluminum foil and stored in refrigerator for 24 hours.

2.3. Synthesis of PANI/PVL film
After being stored in refrigerator for 24 hours, purification of PANI done by filtration in Buchner setup. The sample then heated using hot plate at temperature 80 °C to remove HCl and soluble oligomers via evaporation process, and becomes precipitated solution. With consistent stirring, 30 mL of 1.0 M potassium hydroxide (KOH) solution was added drop by drop till the pH reached 7. While reaching neutral condition, the sample was taken to be analyzed further in term of zeta potentials and pH correlations. Different PANI loading were incorporated into PVL, 3 phr, 5 phr, 10 phr, 20 phr and 40 phr.
phr. After weighted specifically, the samples were added into PVL and mixed using glass rod and casted into 50 mm × 50 mm × 10 mm casting plate. The film kept dry at ambient temperature for 24 hours.

2.4. Mechanical performance

Mechanical performance of each sample were performed using Universal Testing Machine characterizing in term of tensile strength (TS), Young’s modulus (YM) and elongation at break (EB). The prepared samples evaluated for tensile test according to ASTM D3039 with strain rate of 500 mm/min. The films cut into standardized size with constant rectangular section, 2.6 mm wide, 100 mm long and 10 mm gauge length.

2.5. Colloidal and dispersion stability

The colloidal and dispersion stability examined using zeta potential analyser as a function of pH. The instrument works by using electrophoretic light scattering (ELS) and laser Doppler velocimetry (LDV) to determine the electrophoretic mobility, μ.

3. Results and discussion

3.1. Mechanical performance

3.1.1. Tensile strength. The tensile strength of PANI/PVL sample with different PANI content was observed and displayed in figure 1. With control sample, pure PVL with tensile strength of 17.39 MPa, comparable results obtained. The tensile strength of PANI/PVL composites depends on the effectiveness of stress transfer between matrix and fillers. The applied stress from tensile test able to be transferred effectively to the well-bonded PANI particles and improves the film strength significantly. However, further addition of particles could lead to strength reduction [8]. From the graph it was obvious that addition of PANI into PVL increase the tensile strength than pure PVL films except for 20 phr loading with 19.89 % decrement. The decrease in tensile strength at higher PANI loading is due to particle-particle aggregation and consequently poor interaction with rubber matrix [8]. Optimum reinforcement effect offered by 5 phr PANI/PVL film with 109.14 % increment, which attributed to the rigidity of PANI [9].

3.1.2. Young’s modulus. Young’s Modulus (YM) expressed as the ratio of stress to strain in elastic linear region or measurement of stiffness (MPa). The blank sample, PVL hold YM of 1.34 MPa at figure 2, incorporation of PANI into PVL shows significant increase in Young’s modulus as might be expected.
3.1.2. Young’s Modulus of PANI/PVL with different PANI loading. 

Elongation at break (%)

Figure 2. Young’s modulus of PANI/PVL with different PANI loading.

for an elastomer matrix filled with particulate filler. Adding up the loading to 5 phr, increasing trend of modulus obtained and further decrease as more loading applied. Such optimum improvement up to 230.56 % is due to the fact that PANI act like crosslinking points and restricting the movement of PVL chains [10].

3.1.3. Elongation at break. Elongation at break (EB) indicates the highest extension of sample could achieved under tension. Elongation at break for PANI/PVL film with different loading shown in figure 3. The EB depends on polymer-filler interaction. EB greatly reduced as PANI incorporated into PVL at 3 to 10 phr loading, and increase later at higher amount of loading. The reduction in elongation at break at lower PANI loading is apparently due to the increase in Young’s modulus as stiffer materials are expected to not elongate as much as soft materials [11].

3.2. Colloidal and dispersions stability

In this characterization, zeta (ζ) potential as a function of pH was carried out for samples of PANI during pH adjustment. The zeta potential is an important indicator of the stability of colloidal dispersions. The magnitude itself reflects on the degree of electrostatic repulsion between similar charged particles in a dispersion. Referring to figure 4, note that the ζ is mostly negative for the whole pH, and it increase in
Zeta potential

Figure 4. Zeta potential of PANI as function of pH.

absolute value till up to a pH close to electroneutrality. The chemical species involved is responsible for the generation of negative surface charge corresponding to dissociated sodium dodecyl Sulphate (SDS) end molecules. This is practicable, since it can likely described that part of the SDS used in synthesis adsorbed on surface of PANI even after cleaning process. Moreover, these results could qualitatively explain the stability. At acidic condition (pH below 7), the zeta potential value is low (10 to -10 mV), consequently formation of aggregates can occur at faster rate. Hence, the average particle-particle distance will be rather large. In contrast, at pH 7 and above, the Electrokinetic potential of particles is high (-18 to -38 mV) and this will encourage strong electrostatic repulsion between PANI particles. The film can be considered colloidal stable and the average particle-particle distance will be small, and particles will stay at primary minimum of their interaction potential [12].

4. Conclusions

Pre vulcanized latex (PVL) films can be modified with conducting polymer, polyaniline. The colloidal stability is maintained only if the pH of aniline adjusted to neutral state to prevent coagulation during film synthesis. The mechanical properties of PANI/PVL films are sufficient for gloves or antimicrobial applications as PANI loading increased up to 5 phr with optimum TS of 36.37 MPa and YM of 4.43 MPa. However, PANI incorporation have poor capability at low loading when prioritizing EB performance but slightly improved as more PANI used up (20 to 40 phr).

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