# Physical and Mechanical Properties of Palm Kernel Oil-Based Polyester Polyurethane/Multi-Walled Carbon Nanotube Composites

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## Abstract

In this study, polyurethane (PU) films from palm kernel oil-based polyester (PKO-p) incorporated multi-walled carbon nanotubes (MWNTs) are prepared *via* a evaporative casting method. Nanoparticle fluid dispersions containing 0.02%, 0.03%, and 0.05% wt. of MWNTs are added into PKO-p based resin and mixed by digital probe sonicator for 30 min followed by mixing with isocyanate to produce PU-MWNTs composite films. The mechanical properties, swelling, water vapour transmission rate (WVTR) and conductivity of the PU-MWNTs composite films are examined. Results show that the toughness (T) or flexibility, the tensile strength (TS), and Young's modulus (YM) values of PU-MWNTs composite films increase with the increasing concentrations of MWNT. In contrast, the water vapour transmission rate (WVTR) and swelling test of PU-MWNTs composite films decrease with the increase of MWNT concentrations. For conductivity testing, the film with 0.05 wt.% MWNT (PU-5) has the highest conductivity value at $2.19 \times 10^{-9}$ S cm$^{-1}$. In summary, incorporation of MWNTs has improved the mechanical properties of the polyurethane composites films.

## Abstract

**Sifat Mekanik dan Fisik Serat Komposit Poliuretana Poliester Berbasis Minyak Biji Sawit/Tabung Karbon Nano Berdinding Multi**. Dalam kajian ini, serat poliuretana (PU) dari poliester minyak biji sawit yang mengandung nanotube berdinding multi (MWNTs) dibuat dengan metode pengecoran evaporatif. Serat komposit PU-MWNTs telah dihasilkan dengan menambahkan 0.02%, 0.03%, dan 0.05% wt.% MWNTs ke dalam resin berbasis minyak kelapa sawit (PKO) dan kemudian dicampurkan menggunakan sonikator digital selama 30 menit sebelum dicampurkan dengan isosianat untuk membentuk serat komposit PU-MWNTs. Sifat mekanik, ketahanan terhadap air, laju transmisi uap air (WVTR), dan konduktivitas serat komposit PU-MWNTs telah diuji. Hasil kajian menunjukkan bahwa nilai ketahanan (T) atau fleksibilitas, serta kekuatan tarik, modulus Young serat komposit PU-MWNTs meningkat sejalan dengan meningkatnya kepekatan MWNT. Sebaliknya, laju transmisi uap air (WVTR) dan uji ketahanan terhadap air serat komposit PU-MWNTs menurun sejalan dengan meningkatnya kepekatan MWNT. Untuk uji konduktivitas, serat dengan kepekatan 0.05 wt.% MWNT (PU-5) mempunyai nilai konduktivitas tertinggi, yaitu $2.19 \times 10^{-9}$ S cm$^{-1}$. Secara keseluruhan, sifat mekanik serat komposit poliuretana mengalami peningkatan dengan penambahan MWNTs.

*Keywords: polyurethane, palm kernel oil, mechanical properties, multi-walled carbon nanotubes*

## 1. Introduction

Polyurethane (PU) is a synthetic copolymer and it has urethane moiety in the repeat unit structure [1]. The condensation reaction of polyisocyanates and polyols leads to the formation of intermolecular urethane linkage in polyurethane [2]. Polyurethane usually has three monomers, which are a diisocyanate, a macro-glycol (diol), and a chain extender [2]. Polyurethane is unique because even though it has the elasticity of a rubber, it

also has the toughness of a metal [3]. Polyurethane is also a versatile polymer because of the abundance in applications, such as an elastomer, adhesive, and also promising biomaterials [4].

Carbon nanotubes were discovered by Iijima in 1991 [5], and due to their extraordinary mechanical and physical properties, they have gained many attentions [6]. Even though they are relatively small in size with diameters in nanometre range, they are extremely strong, specifically

20 times stronger than high-strength steel alloys [7]. Carbon nanotubes have outstanding axial tensile strength, as well as superior thermal and electrical properties [3]. Carbon nanotubes can be classified according to the diameters, which are single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) [8].

Polyurethane/CNTs composites have unique mechanical properties, multi-functional properties, and big interfacial areas, which are some of the characteristics that attract great interest towards them [3]. There are several ways to make polyurethane/multi-walled carbon nanotube composites, such as via solution casting, melt-processing and in-situ polymerisation [4]. CNTs can be dispersed into polymer matrix by using acid for aggressive chemical modification on their surfaces or surfactant before dispersions, and sonicated at high frequency in order to disperse CNTs in solutions uniformly [6].

To the best of authors' knowledge, the study related to palm kernel oil-based PU incorporated MWNTs composite films is yet to be addressed. Most of the studies produced PU–CNTs composites by using polyols-based polyether and petroleum-based polyester, and they show promising results in terms of mechanical characteristics and electrical conductivity [9-12]. Thus, this study is aimed to produce flexible polyurethane films from palm kernel oil-based polyester incorporated multi-walled carbon nanotubes (MWNTs) and to investigate their mechanical properties, swelling, water vapour transmission rate (WVTR) and electrical conductivity.

## 2. Methods

**Preparation of PU-MWNTs composite films.** Nano-particle-fluid dispersions containing PKO-p, polyethylene glycol (PEG 400) and acetone with 0.02 wt.%, 0.03 wt.%, and 0.05 wt.% of MWNTs were prepared by using a digital probe sonicator (Qsonica-Q500, USA) with a diameter of 6 mm, in a pulse mode (0.5 s on/off) with an amplitude set at 40%. Different intervals of sonication were carried out to determine the optimum sonication time (min). During sonication, the sample vials were placed inside a water bath to keep dispersion temperature constant. The dispersions were then mixed with 4.4'-diphenylmethane diisocyanates (MDI) containing 35% of acetone and stirred for 5 min. The mixtures were casted onto a Teflon plate and dried in the oven at 55 °C for 24 hours to remove solvents. The PU composite films contain 0.02 wt.%, 0.03 wt.%, and 0.05 wt.% of MWNTs (hereinafter referred to as PU-2, PU-3, and PU-5, respectively). The PU-MWNTs composite films were then pre-conditioned at the same temperature for the next 24 hours prior to any characterisations.

**UV-Visible Spectroscopy.** UV-visible absorption spectra of homogenous PU-MWNTs dispersion were obtained with a dual beam UV-vis spectrophotometer (Shimadzu UV-1800) using quartz cuvettes (path length = 10 mm). All samples were measured after a 10-fold dilution with Triton X-102. The absorption spectra of the samples were measured in the range of 200-700 nm light wavelengths.

**Mechanical behavior.** Stress-strain measurements were obtained using an Instron Universal Testing Machine (model 3366) with ± 10 kN grips and cross-speed set at 20 mm/min. Young's modulus (MPa) and tensile strength (TS) were calculated from the slope of the linear part of the stress-strain curve and maximum stress, respectively. Flexibility of the films is measured in terms of strain-at-break ($\gamma$).

**Swelling.** Swelling was measured by weighing the dried films ($W_{dry}$) prior to immersion into phosphate buffer solutions of pH 7 in water bath (37 ± 0.5 °C). The films were removed after 24 hours, wiped gently with a tissue paper to expel surface water, and then weighed ($W_{wet}$). Swelling was then determined from the equation:

$$[(W_{wet}-W_{dry})/W_{dry}] \text{ x } 100 \qquad (1)$$

**Water vapor transmission rate (WVTR).** The water vapor transmission rates (WVTR) of the samples were measured by following a modified ASTM E96 standard method [13]. Each film was fixed on the circular opening of a permeation bottle (diameter = 1.5 cm, height = 5.0 cm) with the effective transfer area ($A$) of 1.33 cm$^2$. The permeation bottle was placed in a temperature humidity chamber at 37 °C and 50 ± 5% relative humidity. The WVTR was then determined by the rate of change of mass (m) in these-water filled permeation bottles at 24 hours exposure time as follows:

$$WVTR = m/A\Delta t \qquad (2)$$

where m/$\Delta t$ is water gain per unit time of transfer and $A$ is the area exposed to water transfer (m$^2$).

**Electrical conductivity test.** The electrical conductivity properties of the PU-MWNTs films were measured *via* electrochemical impedance spectroscopy (EIS), model HIOKI 3532-50 LCR Hi-TESTER. The electrical conductivity ($\sigma$) of the composite films was obtained from the measured electrical bulk resistance ($R_b$) which was determined from the intercept of the real part of complex-plane impedance plot (Cole-Cole plot), thickness ($t$), and electrode-electrolyte contact area (A) of the composite films tested.

$$\sigma = t/(R_b A) \qquad (3)$$

## 3. Results and Discussion

**Dispersions of MWNTs.** To prepare the PU-MWNTs composite films, the optimum sonication time is required to successfully disperse the multi-walled carbon nanotubes (MWNTs) in the PKO-p solution. The optimum sonication time was defined as the minimum amount of time

required to effectively disperse the multi-walled carbon nanotubes (MWNTs) in the dispersions [14]. An excess sonication can shorten the required time or cause defects to the tubes and thereby diminish their properties [15-17]. The optimization process was determined by monitoring the level of the UV-Vis absorption intensity at different sonication times and disappearance of visible aggregates. UV-vis was used to investigate the MWNTs dispersion quality based on the assumption that the employed dispersants do not contribute to absorption and the given dispersed nanotubes were linked to any remaining absorption beyond 300 nm [18]. Figure 1 shows that the UV-Vis absorbance intensity (λ=660 nm) increases with longer sonication time, reflecting to an increasing amount of MWNTs [0.01, 0.04 and 0.08% (w/w)] which becomes dispersed over time. The absorbance of the dispersions at 660 nm was plotted as a function of sonication time and shows that sonication becomes irrelevant after 30 minutes for all dispersions. This particular wavelength was selected as it correlated with the maxima of an absorption band arising from the Van Hove singularities for single-walled carbon nanotubes (SWNTs) [19-21].

**Physical properties**. PU-MWNTs composite films were successfully prepared using an evaporative casting method. The PU-MWNTs composite films had smooth surface, void free, and semi-translucent. However, the films become opaque when the amount of MWNTs increases.

**Stress-strain measurements**. The stress-strain properties of PU-MWNTs composite films are shown in Figure 3 and summarized in Table 1. The stress of PU-2, PU-3, and PU-5 composite films was higher than that of pure PU film (PU-0), indicating that the modulus (YM), tensile strength (TS), and elongation (γ) of the composites were improved by the addition of MWNTs. It can be seen that PU containing 0.05 wt.% of MWNTs recorded the highest tensile strength (7.82 ± 2.1 MPa) and modulus (21.97 ± 10.1 MPa), and was more flexible (66.5 ± 18%) compared to pure PU and other PU composite films. Our
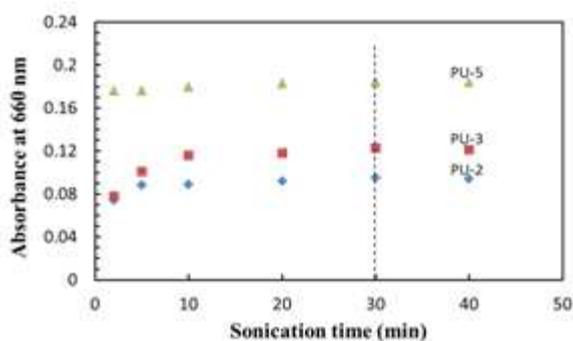


**Figure 1.  Effect of Increasing Sonication Time on the UV-Visible Spectra of PKO-P Dispersions Containing 0.02 wt.% (PU-2), 0.03 wt.% (PU-3), and 0.05 wt.% (PU-5) of MWNTs**
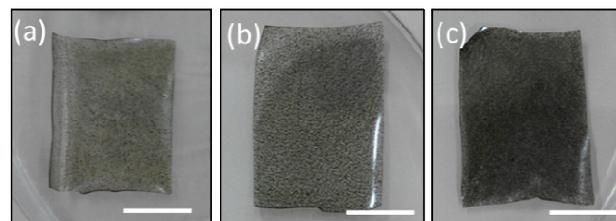


**Figure 2.  Physical Appearance of PU-MWNTs Composite Films (a) PU-2, (b) PU-3, and (c) PU-5. Scale Bars Represent 1 cm**
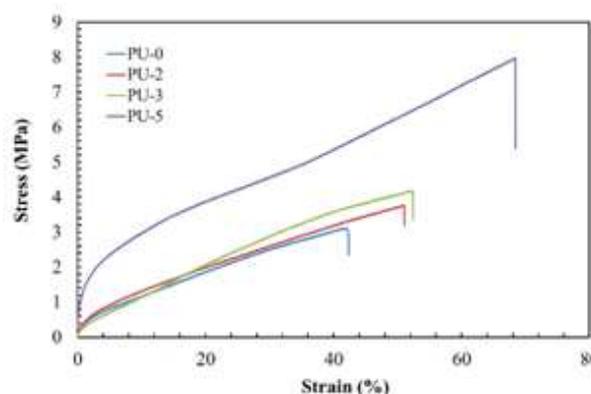


**Figure 3.  Stress-Strain Curves of PU-0 and PU-MWNTs Composite Films at Different Loadings**

**Table 1.  Summary of Tensile Strength (TS), Modulus (M) and Tensile Strain (γ) of Polyurethane Film (PU-0), PU Film Containing 0.02 wt.% MWNT (PU-2), PU Film Containing 0.03 wt.% MWNT (PU-3), and PU Film Containing 0.05 wt.% (PU-5)**

| Sample | TS (MPa) | M (MPa) | γ (%) |
|---|---|---|---|
| PU-0 | 3.51 ± 0.7 | 11.1 ± 3.4 | 49.9 ±16 |
| PU-2 | 4.42 ± 1.6 | 12.5 ± 2.6 | 52.9 ± 15 |
| PU-3 | 4.75 ± 1.7 | 13.1 ± 8.7 | 56.0 ± 15 |
| PU-5 | 7.82 ± 2.1 | 21.9 ± 10 | 66.5 ± 18 |

**Table 2.  Swelling and Water Vapor Transmission Rates (WVTR) Values of PU-0, PU-2, PU-3 and PU-5 Composite Films**

| Sample | Swelling (%) | WVTR (g m$^{-2}$ d$^{-1}$) |
|---|---|---|
| PU-0 | 50 ± 2 | 732 ± 9 |
| PU-2 | 44 ± 3 | 612 ± 18 |
| PU-3 | 33 ± 2 | 512 ± 27 |
| PU-5 | 25 ± 2 | 404 ± 5 |

results are also in agreement with the previous studies, whereby they reported that the incorporation of small quantities of MWNTs into starch/MWNTs nanocomposites resulted in highly improved tensile properties [22].

**Swelling test**. Swelling ratio values of the PU-MWNTs composite films are shown in Table 2. It can be seen that pure PU (PU-0) recorded the highest swelling ratio at $50 \pm 2\%$ and the values decreased upon addition of MWNTs. Incorporation of MWNTs reduced swelling of the PU films possibly due to the increasing in hydrophobicity of the polyurethane matrix. This phenomenon possibly was due to the hydrophobic property of the MWNTs [23-26].

**WVTR measurements**. Water vapor transmission rates (WVTR) are depicted in Table 2. It can be seen that the WVTR values of pure PU (PU-0) and PU-MWNTs composite films (PU-2, PU-3, and PU-5) were in the range of 404-732 g m$^{-2}$ d$^{-1}$ (Table 2). Addition of MWNTs slightly decreased the WVTR values which could be due to the homogenous dispersion of MWNT aggregates in the polyurethane matrix and that blocked the water vapor transmission [24]. A study reported by Haider and co-workers (2007) was in accordance with our results whereby homogenous dispersion of MWNT aggregates in polymer matrix reduced water vapor transmission [27]. However, these values still remain within the range of WVTR of commercial wound dressings values at 90-2893 g m$^{-2}$ d$^{-1}$ [13].

**Electrical conductivity study**. In this study, the electrical conductivity of PU film and PU-MWNTs composite films were determined by EIS (Electrochemical Impedance Spectroscopy). The results are shown in Table 3. It is clear that incorporation of MWNTs enhances the electrical conductivity. At 0.05 wt.% of MWNT (PU-5), the electrical conductivity was improved by almost 90% compared to pure polyurethane (PU-0). This could be due to the high conductivity of MWNTs [28]. Theoretically, charge transfer occurs between PU and MWNTs, which then causes the composite to have more active sites for faradic reaction, hence the increase of electrical conductivity and the decrease of resistivity of the films [30]. Our results are also consistent with the previous studies, whereby the addition of small amounts (1-5%) of MWNTs can improve the electrical conductivity and rubbery modulus by a factor of 2-5 [31]. We also examined the electrical conductivity of PU film containing 0.08 wt.% of MWNTs (results not shown in Table 3) and the result shows that the composite film exhibits conductivity values of $1.84 \times 10^{-8}$ S cm$^{-1}$. Hence, it proves that increasing concentration of MWNTs increases electrical conductivity of the films.

**Table 3. Thickness (t), Electrode-electrolyte Area (A), Bulk Resistance (Rb), and Ionic Conductivity ($\sigma$) of PU-MWNTs Composite Films**

| Sample | $t$ (cm) | A (cm$^2$) | $R_b$ ($\Omega$) | $\sigma$ (S cm$^{-1}$) |
|---|---|---|---|---|
| PU-0 | $2.1 \times 10^{-2}$ | 3.142 | $3.3 \times 10^7$ | $2.06 \times 10^{-10}$ |
| PU-2 | $2.2 \times 10^{-2}$ | 3.142 | $2.9 \times 10^7$ | $2.39 \times 10^{-10}$ |
| PU-3 | $2.3 \times 10^{-2}$ | 3.142 | $9.1 \times 10^6$ | $8.10 \times 10^{-10}$ |
| PU-5 | $2.3 \times 10^{-2}$ | 3.142 | $3.3 \times 10^6$ | $2.19 \times 10^{-9}$ |

## 4. Conclusion

The polyurethane composite films with 0.02 wt.% (PU-2), 0.03 wt.% (PU-3), and 0.05 wt.% (PU-5) of multi-walled carbon nanotubes (MWNTs) were successfully prepared by using palm kernel oil-based polyester. The effect of MWNTs application on the mechanical behavior and electrical conductivity were examined. It shows that incorporation of MWNTs improves the mechanical properties and results in the potential to conduct electricity.

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