

Potential of oxidative polymerization coating of cellulose nano-fiber by dopamine

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Abstract. In order to develop functional natural fiber reinforcements derived from cellulose nanofibers (CNF), surface modification of CNF by oxidative polymerization of dopamine was carried out. Resulting polydopamine (PDA)-coated CNF was blended with polypropylene (PP) to prepare the surface-modified CNF/PP nanocomposites. Obtained PDA-coated CNF and its nanocomposites were analyzed as to their morphologies, structures, and various properties. From analyses by Fourier transform infrared spectroscopy, scanning electron microscopy equipped with energy dispersive spectroscopy, X-ray photoelectron spectroscopy, and thermogravimetry, it was clarified that the treated CNF surface was homogeneously coated by PDA without re-aggregation of CNF. Moreover, it was confirmed that the PDA-coated CNF/PP nanocomposites had excellent mechanical performances and good antistatic properties.

1. Introduction

Cellulose as a typical natural fiber is the most abundant renewable biomaterial. The effective utilization of natural fibers as indispensable component in composites with polymers for developing novel eco-friendly composites with acceptable properties is one of the most required research fields [1]. The blended cellulosic fibers in matrix polymers have valuable effects on various composite properties [2]. Many studies concerning the composites have been focusing on effects on mechanical strength of chemical treatments [3], fiber size [4] when the cellulosic fibers were used as fillers and reinforcements, and on the development of appropriate compatibilizers [5].

Many researchers have been extensively studying the preparation method of nanofibers from wood and other plant fibers. The development of cellulose nanofibers (CNF) has been attracting significant interest in the last few decades due to the unique characteristics of CNF that endows such as high surface area-to-volume ratio, high Young's modulus, high tensile strength and low coefficient of thermal expansion [6]. CNFs have shown great potentials in nanocomposites as well as other several applications including biomedical, gas barrier films and optically transparent functional materials.

Cellulose/polymer nanocomposites also have been attracting much interest of researchers for their mechanical performance. However, it is well known that the performance of biomass/polymer composites is strongly depending on the interface adhesion between cellulose surface and matrix polymers [7]. Therefore, the appropriate compatibilizer between biomass and polymer is the key point to demonstrate the ability of biomass.

Dopamine and its catecholic derivatives are able to undergo oxidative polymerization in the presence of oxygen as an oxidant. During the oxidative polymerization of dopamine, a tightly adherent



polydopamine (PDA) layer is created on the surface of a substrate [8] based on interactions between the PDA layer and the substrate surface including covalent and noncovalent bonds [9]. Actually, the PDA coating on polymer surfaces has good stability and durability in various environments [10,11].

Previously, there are some reports as to the PDA coating of cellulose fibers for developing flame retardant composites [12], Fe^{3+} -pollutant detector [13], etc. In this study, in order to develop functional CNF-reinforced nanocomposites, surface modifying of CNF by oxidative polymerization of dopamine was carried out. Obtained PDA-coated CNF was analyzed with Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS), X-ray photoelectron spectroscopy (XPS), and thermogravimeter (TG). These analyses clarified that CNF surfaces were homogeneously coated by polydopamine without re-aggregation. Moreover, the PDA-coated CNF was blended with commodity plastic polypropylene (PP) to prepare PDA-coated CNF/PP nanocomposites. The nanocomposites showed excellent mechanical strength and good antistatic properties.

2. Experimental

2.1 Materials

Cellulose nanofiber (CNF, 1 wt% aqueous solution) was kindly provided from Chuetsu Pulp & Paper Co., Ltd., Takaoka, Japan). The CNF was freeze-dried to obtain a solid-type CNF. Buffer: tris(hydroxymethyl)-aminomethane (Tris-HCl, pH8.5, 0.1M) was purchased from SIGMA-Aldrich (St. Louis, USA) and dopamine hydrochloride (LKT Laboratories Inc., St. Paul, USA) was purchased from Wako Pure Chemical Industries, Ltd. (Wako, Japan). Polypropylene (PP): extrusion grade NOVATEC-PP FY6, density 0.90 g/cm³, melt flow index 2.5 g/10 min (Japan Polypropylene Corporation, Tokyo, Japan) was used as a matrix polymer.

2.2 PDA coating of CNF

Solid-type CNF 5 g was added into a Tris-HCl buffer solution 250 mL, and then dopamine hydrochloride (dopamine) 500 mg was added. The solution was stirred at 1200 rpm on a magnetic stirrer at room temperature at around 20 °C under atmospheric conditions to start the oxidative polymerization of dopamine. During the polymerization, the solution became gradually black. After 24 and 48 h, solid products were filtered to isolate polydopamine (PDA)-coated CNF.

As a reference, the dopamine-HCl was polymerized in the same manner in the Tris-HCl buffer solution without CNF. The solution also became gradually black, and after 24 h solid products were filtered to isolate PDA.

2.3 Preparation of PDA-coated BLCNF/PP composites

PDA-coated CNF was blended with PP in a twin-screw extruder IMC-160B (Imoto Machinery Co., Ltd., Japan, screw diameter 20 mm, L/D 25) equipped with an air vent was used for the blending under the cylinder temperature profiles of 160, 180, 180, and 180°C for four zones from hopper to die, respectively, with a screw rotational speed of 25 rpm. After retention time of 5-7 min in the cylinder, nanocomposite strands were extruded from die, followed by pelletization by cutting the strands with a pelletizer.

2.4 Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer GX2000R infrared spectrophotometer (Waltham, USA) in a range of 500–4000 cm⁻¹ at a resolution of 4 cm⁻¹. Reflection spectra were measured by the single-reflection ATR method on a Golden Gate Diamond attenuated total reflectance (ATR) (10500) module with a germanium crystal.

SEM-EDS images were observed using a scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS) (JCM 6000, JEOL Ltd. Tokyo, Japan). The samples were firstly coated with platinum using a vacuum sputter coater prior to observation by SEM-EDS.

X-ray photoelectron spectroscopy (XPS) measurements were made on an AXIS-HSi surface analysis instrument (Kratos Analytical Ltd., Manchester, UK) with a Mg-K α X-ray (photon energy 1253.6 eV).

Thermogravimetric (TG) and differential TG (DTG) measurements were conducted on a SEIKO Instruments Inc. EXSTAR 6200 TG system (Chiba, Japan) in aluminum pans (5 mm in diameter) at a prescribed heating rates, ϕ , of 9 °C min⁻¹ in a temperature range of 50 to 550 °C under a constant nitrogen flow (100 mL min⁻¹) using about 5 mg of sample. A blank aluminum pan was used as a reference. The pyrolysis data were collected at regular intervals (about 20 times °C⁻¹) by an EXSTAR 6000 data platform, and recorded into an analytical computer system.

Antistatic properties of CNF/PP nanocomposites were evaluated by measurement of surface electric resistivity of samples. The electric resistivity of CNF/PP nanocomposite sheets was measured on a Hiresta UP (Mitsubishi Chemical Analytech Co., Ltd., Chigasaki, Japan) equipped a probe UR-100 (measurement range: 10¹⁰–10¹⁸ Ω , main electrode: ϕ 50 mm, inner diameter of guard: ϕ 53.2 mm). After charging at an applied voltage 1000 V for 60 s, the surface electric resistivity of samples was measured at 23 °C.

2.5 Estimation of PDA deposition on CNF from FTIR spectrum

In order to estimate the deposition amount of PDA on CNF surface, a calibration curve was prepared using mixtures of intact CNF and PDA that was synthesized without CNF. FTIR spectra of mixtures in a range of CNF:PDA=100:0-60:40 (wt/wt) were measured and an isolate and PDA-specific absorption peak at 1542 cm⁻¹ was used to prepare the calibration curve. The peak in an absorbance plot was simulated using Gauss function in a PeakFit software version 4.12 to estimate the intensity of the peak area, resulting in the calibration curve shown in figure A1 in Appendices.

2.6 Mechanical tests of composites

Samples for mechanical tests were fabricated using a hot press machine IMC-180C (Imoto Machinery Co., Ltd, Kyoto, Japan) in templates: 100 × 100 × 0.3 and 1 mm³ for tensile and bending tests, respectively. The hot press was conducted at 180 °C for 5 and 10 min for melting and pressing, respectively, at 50 MPa. Obtained film and sheet samples were cut to prepare the tensile (40 × 40 × 0.3 mm³) and bending (40 × 40 × 1 mm³) tests specimens, respectively.

Tensile and bending tests were conducted using an IMC-18E0 model machine (Imoto Machinery Co. Ltd, Kyoto, Japan) at a rate of 5 mm min⁻¹ at 23 °C. Five replicates were employed for both mechanical tests.

3. Results and Discussion

3.1 Preparation of PDA-coated CNF

Figure 1 shows the color change of CNF after the oxidative polymerization of dopamine. The surface of CNF became gradually black, which suggests the deposition or coating of PDA on CNF surface.



Figure 1. Color change of CNF before and after PDA-coating.

So far, a serious problem on the nanocomposite preparation was the re-aggregation of CNF to microscale fibers during the dispersion in polymer matrix. In order to confirm the re-aggregation of CNF during the oxidative polymerization, SEM observation of the treated CNF was conducted. Results are shown in figure 2. The diameter of original CNF (20-50 nm) was maintained in the same size of 20-50 nm after the PDA-coating, while reference sample, which was treated in the same manner without dopamine, was observed to increase in the diameter by around 100 nm. These results suggest that the treatment with dopamine suppressed the CNF re-aggregation during the oxidative polymerization.

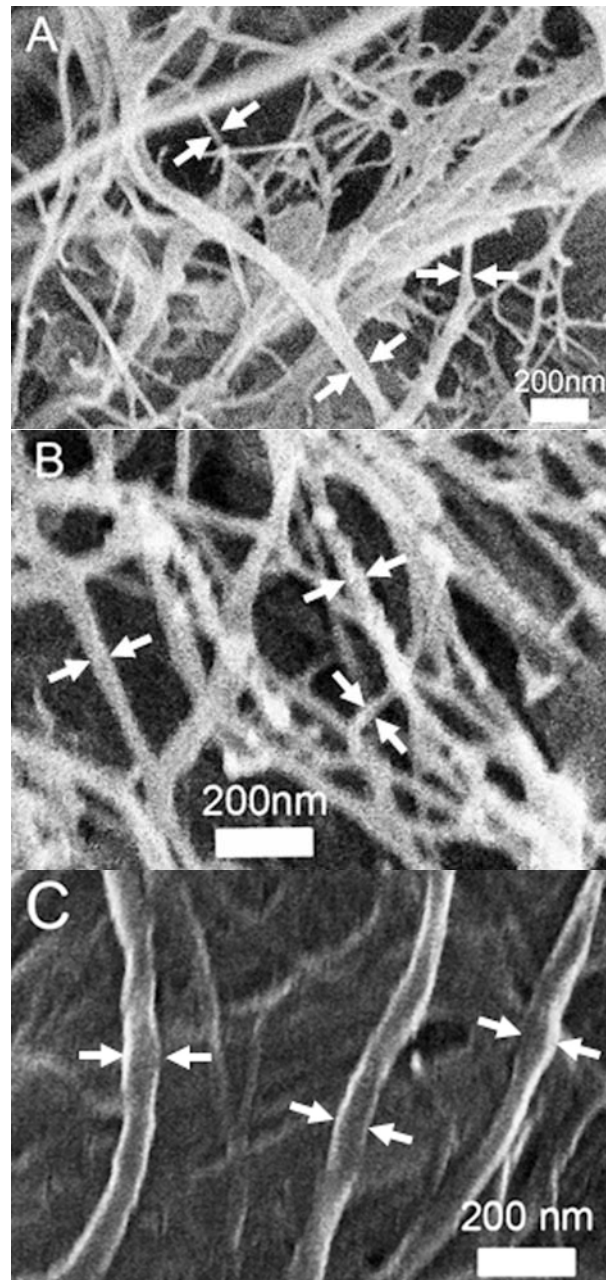


Figure 2. SEM images of CNF before (A) and after PDA-coating (B), and reference CNF sample (C). Arrows show typical diameters of fibers.

3.2 Confirmation of PDA-coating on CNF surface

To confirm the progress of oxidative polymerization on the CNF surface, the treated CNF surfaces were analyzed with FTIR, TG/DTG, SEM-EDS, and XPS.

Changes in FTIR spectrum of CNF before and after the oxidative polymerization of dopamine are shown in figure 3. The dopamine-treated CNF showed new absorption peaks at 1610 and 1540-1550 cm^{-1} assigned to $\nu_{\text{C=O, quinone}}$ [14] and $\nu_{\text{C=C, aromatic ring}}$ [15], which are specific absorption bands derived from catechol group. These absorption peaks were detected from the black product prepared from dopamine only as the reference without CNF, which are PDA [16]. The referential PDA showed an additional weak peak around 1500 cm^{-1} assignable to $\delta_{\text{N-H}}$ of secondary amine [8]. These results reveal that the black coating material appeared on CNF surface is PDA as the oxidative polymerization of dopamine.

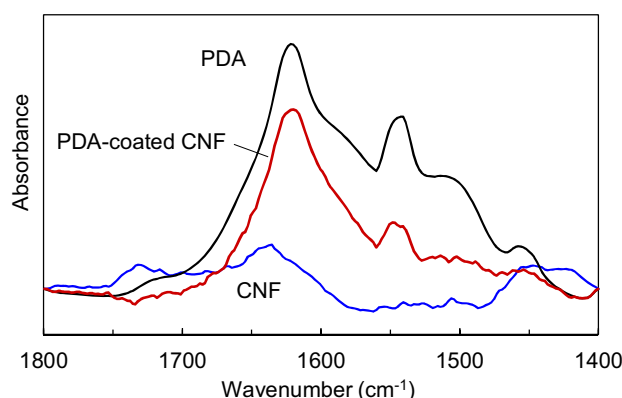


Figure 3. FTIR spectra of CNF surfaces before and after PDA-coating.

In order to determine the CNF-surface coating by PDA, SEM-EDS analysis was employed. Figure 4 show the SEM-EDS images of CNF before and after the dopamine treatment. Morphologies of both SEM images are nearly the same, however, the N-K α X-ray mapping images were obviously different between the treated CNF and intact CNF. The treated CNF surfaces were covered by N-element, meaning the PDA coating of CNF surface.

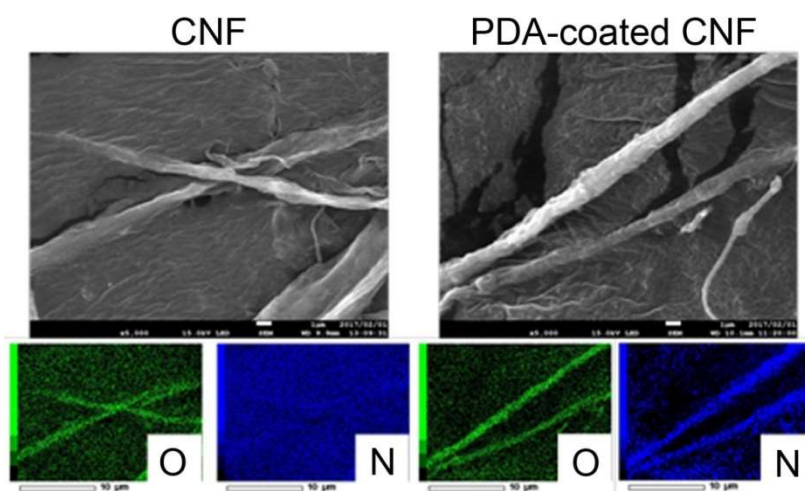


Figure 4. SEM-EDS images of CNF before and after PDA-coating.

Figure 5 depicts the N1s XPS core-level spectra of CNF surfaces before and after PDA-coating. Both the PDA-coated CNF and the referential PDA indicated broad peaks in a wide binding energy range of 395–402 eV. Interestingly, the PDA-coated CNF indicated a main peak around 398 eV and a minor peak around 400 eV, while the referential PDA appeared the main and minor peaks oppositely. In previous reports, these peaks around 398 and 400 eV have been assigned to tertiary/aromatic amine (C=N–R) and secondary amine (R–NH–R) functionalities [15,17]. These XPS results clearly showed the oxidation reaction of amino group to form N–C bonds (scheme 1). Above FTIR results also indicated the difference in the additional absorption peak around 1500 cm^{−1} assignable to secondary amine (R–NH–R) functionality of the referential PDA.

These XPS, SEM-EDS, and FTIR results indicate that the oxidative polymerization of dopamine progresses according to an expected reaction mechanism shown in scheme 1. Here, it is considered that from the XPS and FTIR results CNF affects the mechanism to promote the formation of tertiary/aromatic amine (C=N–R), suggesting the relative increase in reactivity of C₆–H bond compared to hydroxyl groups at C₁ and C₂ in catechol group due to the interaction between cellulose units and thereby steric hindrance.

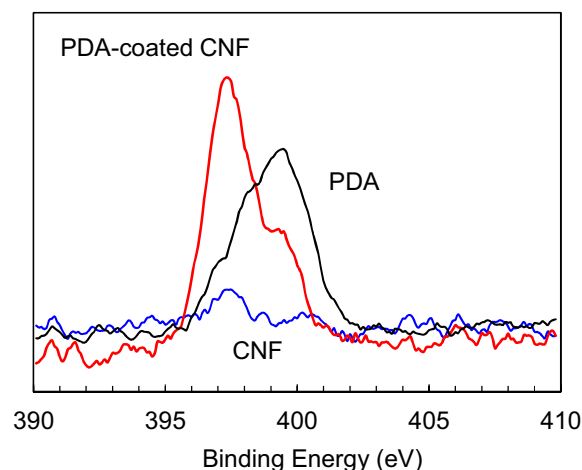
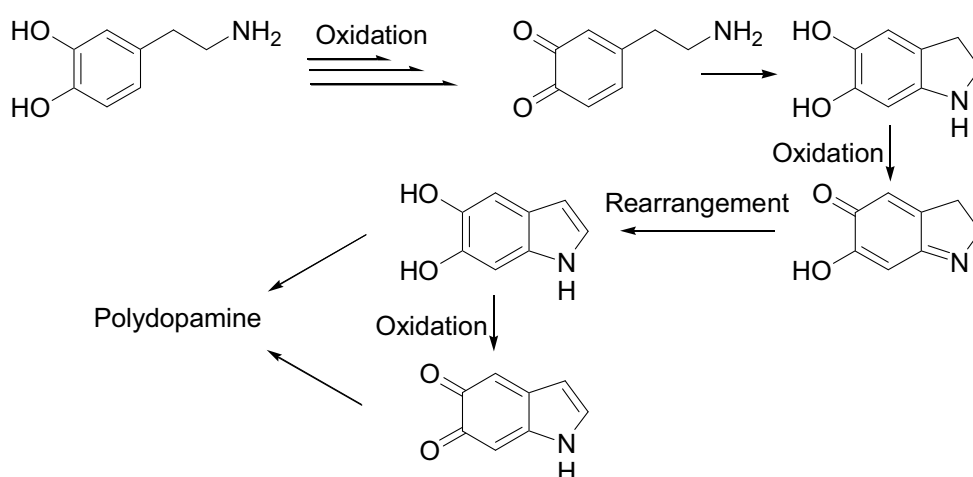


Figure 5. N1s XPS core-level spectra of CNF before and after PDA-coating.



Scheme 1. Expected mechanism of oxidative polymerization of dopamine.

Deposition amount of PDA on CNF surfaces was calculated from a calibration curve (figure A1 in Appendices). As results, the amounts of deposited PDA was 2 and 10 wt% for products after 24 and

48 h of the oxidative polymerization, respectively, resulting in a significant increase in deposition after 48 h compared to 24 h.

In figure 6, TG and DTG profiles of samples before and after PDA-coating are shown. TG/DTG profiles of CNF showed a one-step degradation process in a temperature range of 280–380 °C, while PDA degraded in a three-step process in a wide temperature range of 130–470 °C. The PDA-coated CNF showed an intermediate broad one-step-like degradation process, and, interestingly, the large amount of char was produced in comparison with CNF and PDA. This indicates that the PDA-coating layer makes interact with CNF surface, resulting in changes in the thermal degradation behaviors. Previously, it has been reported that the interactions between the PDA layer and the various polymer substrates include covalent and noncovalent interactions such as the hydrogen bonding interaction, π - π interaction, and electrostatic interaction [9].

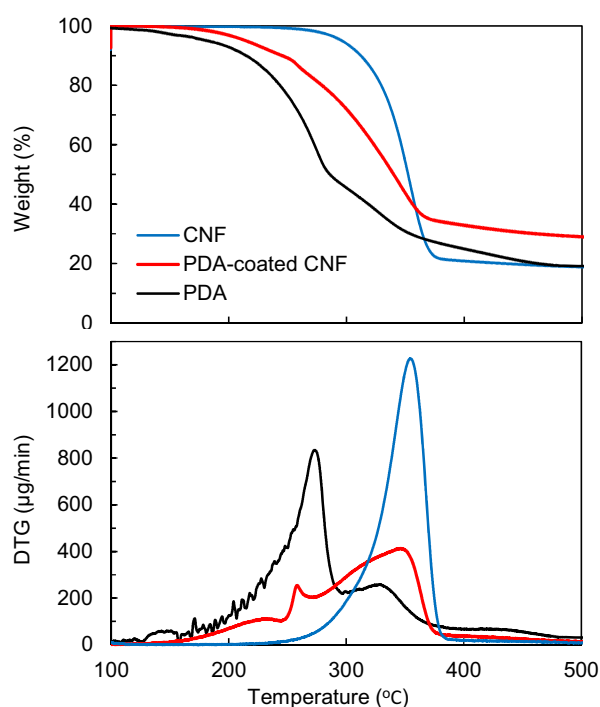


Figure 6. TG and DTG profiles of CNF before and after PDA-coating.

3.3 Mechanical properties of PDA-coated CNF/PP composites

In general, typical effect of CNF is reinforcement of composites. Thus, to evaluate the reinforcing effect the PDA-coated CNF was blended with PP in a composition ratio of PDA-coated CNF: PP = 5:95 (wt/wt), in which the amounts of PDA-coating were 2 and 10 wt% vs. CNF. Tensile tests of obtained PDA-coated CNF/PP and intact CNF:PP (5:95 wt/wt) composite films were carried out. Resulting strain-stress (S-S) curves are shown in figure 7.

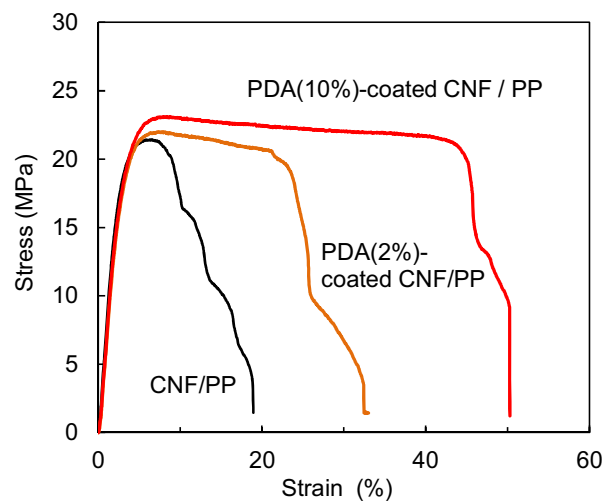


Figure 7. Examples of S-S curve in tensile tests of PDA-coated CNF/PP (5/95 wt/wt) and intact CNF/PP (5/95 wt/wt) nanocomposites.

Tensile strength, Young's modulus, elongation, and toughness values of the composites were calculated from the S-S curves and depicted in figure 8. Although the Young's modulus values were nearly equal, other values, especially, the toughness value was times more than these of intact CNF/PP composite. These results clearly demonstrated that PDA-coated CNF/PP composites had higher mechanical properties than intact CNF/PP composite, and the more the PDA-coating amount, the higher the mechanical properties increased. Thus, the PDA-coating layer effectively functioned as a compatibilizer between CNF surface and PP matrix to enhance the mechanical performance.

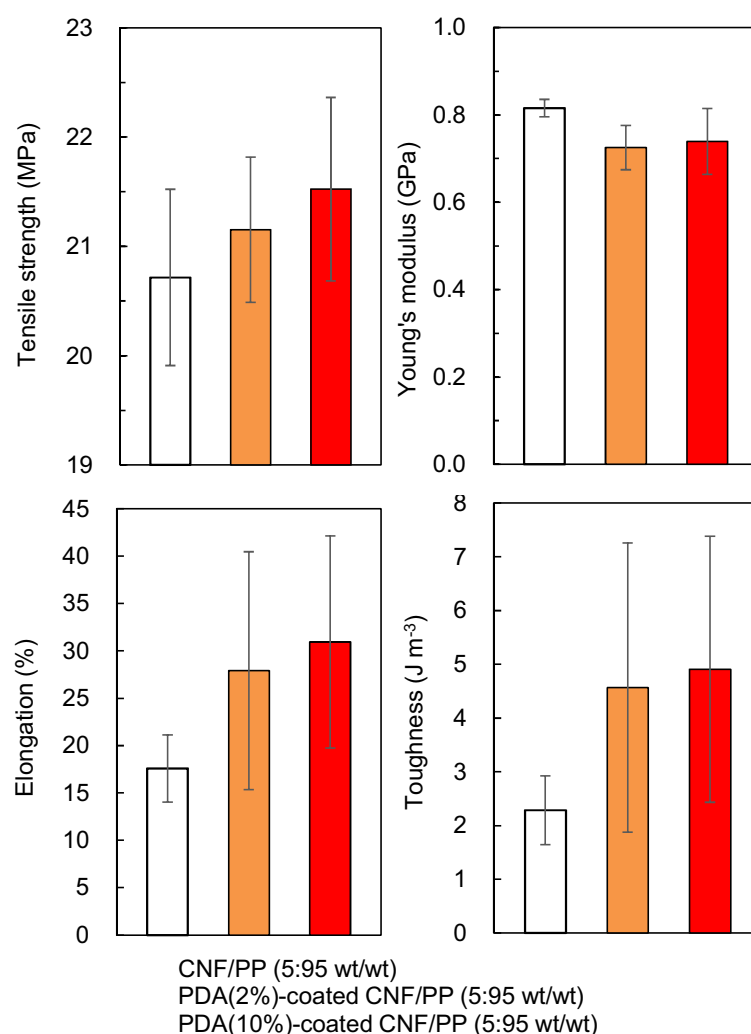


Figure 8. Mechanical properties of PDA-coated CNF/PP (5/95 wt/wt) and intact CNF/PP (5/95 wt/wt) nanocomposites.

3.4 Antistatic properties of PDA-coated CNF

The PDA-coated CNF not only acts as a reinforcement of composites, but also is expected to function as an effective antistatic agent of hydrophobic plastics, because of the conjugated structure of PDA. In order to evaluate the function as an antistatic agent, PDA-coated CNF: PP = 5:95 (wt/wt) composite films were evaluated in comparison with PP and intact CNF/PP = 5:95 (wt/wt) composite films. Obtained surface resistivity values are illustrated in figure 9, showing the lowest resistivity values compared to PP and intact CNF/PP composite films. Thus, it was revealed that the PDA-coated CNF is able to act as the excellent antistatic agent.

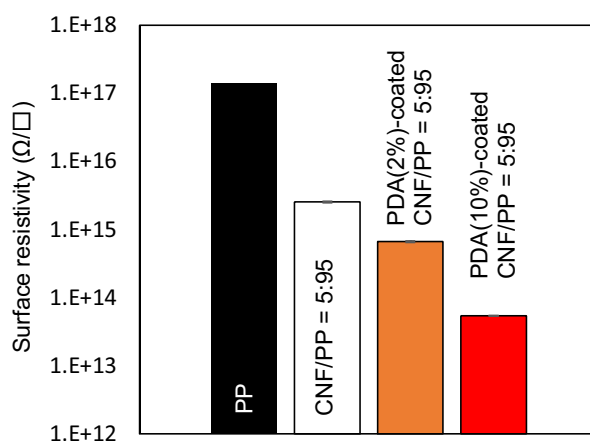


Figure 9. Antistatic properties of PDA-coated CNF/PP (5/95 wt/wt) nanocomposite films in comparison with intact CNF/PP (5/95 wt/wt) nanocomposite and PP films.

4. Conclusion

In this study, the surface coating of CNF by oxidative polymerization of dopamine was carried out to develop a functional CNF reinforcement for natural fiber/PP nanocomposite. From FTIR, SEM-EDS, XPS, and TG/DTG analyses, it was confirmed that the modified CNF surface was successfully coated by PDA. The morphology of PDA-coated CNF was maintained its original diameter in nano-size without re-aggregation during the oxidative polymerization. The obtained PDA-coated CNF were blended with PP to prepare PDA-coated CNF/PP nanocomposites. Resulting nanocomposites showed excellent mechanical properties: tensile strength, elongation, and toughness, as well as good antistatic properties.

5. Appendices

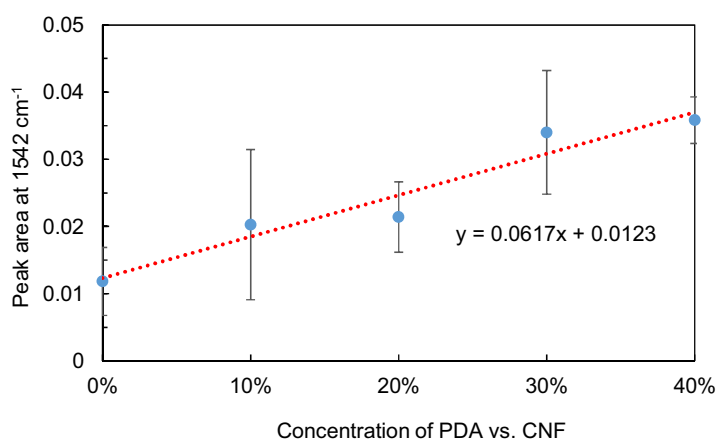


Figure A1. Calibration curve of PDA-coating on CNF surface based on PDA-specific absorption peak at 1542 cm⁻¹.

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