

Preparation and Characterization of Nanocomposite Soy-Carbon Nanotubes (SPI/CNTs) Adhesive from Soy Protein Isolate

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Abstract— The multifunctional properties of carbon nanotubes (CNTs) as nanofiller in polymer matrix have necessitated the development of adhesives with improved bond strength, and water resistance. However, good dispersion and interfacial interaction between adhesive matrix and carbon nanofiller is essential to obtaining the aforementioned properties. An environmentally friendly adhesive to replace formaldehyde and petrochemical adhesive was prepared from soy protein isolate (SPI) by incorporating CNTs as reinforcement. Sonication with mechanical (shear) stirring was a simple and effective approach to obtain the adhesives with rather uniformly dispersed CNTs in the SPI matrix. Characterization technique employed was scanning electron microscopy which showed the homogeneous dispersion of CNTs in SPI using two mixing methods (shear mixing and sonication/mixing). In addition, Fourier transmission infrared (FTIR) spectroscopy was used to analyze the surface functionalities and the type of functional group on the surface of the adhesive nanocomposite. Thermogravimetry analysis (TGA), gave the percentage weight loss and thermal stability of the samples. The result showed that sonication with 30 minutes of mixing gave a homogenous dispersion more than in shear mixing only.

Keywords — adhesive, carbon nanotubes, dispersion, soy protein isolate, shear mixing, sonication.

I. INTRODUCTION

Recently, most wood industries are interested in petrochemical-based and formaldehyde-based adhesives such as, phenol formaldehyde resin and urea-formaldehyde resins in the production of wood composites [1]. Though, adhesives produced from them possess high glue strength and high water resistance, but formaldehyde released from wood composites was recently discovered to be poisonous and toxic to human. These endanger the lives of workers and users of the wood composite. In addition to these, petrochemical-based adhesives are non-renewable, limited and costly [2]. Therefore, the development of environmental-friendly adhesive from renewable agricultural resources has awakened noteworthy attention. Among many of the renewable resources, the vegetable protein has been found to be the best applicable raw material for wood adhesive [3]. A soy protein based adhesives, when modified chemically is said to have the same good adhesive

properties as petroleum-based and formaldehyde-based adhesives for interior wood products [2].

Filler is incorporated into a polymer to improve its properties, regulate the viscosity, modify the surface properties or simply reduce cost [4]. The commonly used fillers such as talc, calcium carbonate fibers, wood flour, which were introduced previously in the preparation of adhesive from soy protein often require large amounts of fillers in the polymer [4]. However, nanofillers improve the properties of a polymer at reduced concentration.

In recent years, nanosized fillers such as nanoparticles, nanotubes, nanoclay and nanofibers have been considered as filler materials for epoxy and protein adhesive to produce high performance composites with enhanced properties [5]. Carbon nanotubes (CNTs) have created a vast activity in most areas of science and engineering, since their discovery in 1991, due to their exceptional physical and chemical properties. No material prior to this time has exhibited the combination of matchless mechanical, thermal and electronic properties attributed to them. These properties make nanotubes ideal for a wide range of applications [6]. These materials are continuously attracting the interest of most researchers due to their unique structures, improved strength (approx. 100 times stronger than steel) and modulus (about 1 TPa), enhanced thermal conductivity (twice as high as diamond), excellent electrical properties (higher than copper 1000 times), and thermal stability (2800°C in vacuum) [7–9]. Owing to these unique multifunctional properties, CNTs are considered to be ideal candidates for applications as fillers in composite materials [10]. Gojny et al. [11] reported that incorporating CNTs into polymers resulted in an enhancement of electrical and thermal conductivities. Kwon et al., [12] compared thermal conductivity of multiwalled carbon nanotubes (MWCNTs)/epoxy composites (with diglycidyl ether of bisphenol F (DGEFBF)) and bisphenol A (DGEBA) (used as epoxy resins) and reported that thermal conductivity of MWCNTs/epoxy composite was higher than that of the pure epoxy resin. The enhanced thermal conductivity was attributed to the presence of CNTs in the epoxy resins. In addition, the thermal conductivity of the composite material could be enhanced if the CNTs are homogeneously dispersed within the epoxy. Many investigations have been carried out on the preparation of CNT/polymer composites for structural and functional applications [13–15]. Owing to the technical hitches associated with dispersion of entangled CNTs during processing and poor interfacial interaction between CNTs and polymer matrix, the complete potential of employing CNTs as filler has been strictly restricted.

Several dispersion techniques, such as, mechanical dispersion, optimum physical blending and chemical functionalization have been investigated to enhance the

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dispersion of CNTs in polymer matrices. Sandler et al. [16] dispersed CNTs in epoxy under high speed stirring (2000 rpm) for 1 hour, and reported that intense stirring was an effective process to achieve homogenous dispersion of the CNTs in the epoxy. Samal [17] synthesized epoxy- based MWCNTs reinforced composites by method of sonication. The author reported that a small change in chemical treatment of the nanotubes has a great effect in the mechanical and morphological properties of the nanocomposites due to effective load transfer mechanism and state of dispersion. Yu et al. [7] employed a mechanical stirring with ultrasonication as a simple and operational approach to obtain the adhesives with rather homogeneously dispersed CNTs in the epoxy matrix. The results revealed that the thermal stability and electrical conductivity improved with the addition of CNT and the adhesive thermal degradation temperature with 1 wt. % of CNT was about 14°C above that of control epoxy. Functionalization is another method of enhancing dispersion in polymer matrix [18]. Therefore, in this study, functionalized CNTs were incorporated into soy protein isolate adhesive by shear mixing and sonication methods of mixing to obtain homogeneous sample of CNTs/soy protein nanocomposite adhesive.

II. MATERIALS AND METHODS

Commercial soy-protein isolate (SPI) was purchased from Solae, LLC, and sodium hydroxide pellets were purchased from Sigma Aldrich. The original moisture and protein content of SPI were 5.5% and 90.0%, respectively. Carbon nanotubes (CNTs) and functionalized carbon nanotubes (FCNTs) were synthesized via carbon vapour deposition (CVD) technique using a horizontal CVD reactor as described elsewhere [19].

About 10.0 g of SPI was stirred in 90 mL distilled water at room temperature for 90 minutes. The pH of the mixture was adjusted to 10.0 by adding 1.0 M of NaOH solution. The SPI-NaOH mixture was stirred for 1 hour at 50°C. The pH of the mixture was taken and recorded. 25 g of the mixture was placed in a petri dish and oven dried.

Varied amounts of CNTs and functionalized CNTs ranged from 0.1 to 0.7% were dispersed in modified SPI adhesive by two different methods of dispersion. In the dispersion method 1, the alkali modified SPI/CNTs and SPI/FCNTs mixture was stirred on a magnetic stirrer at 1250 rpm for 2 hours at room temperature. The pH values were taken and recorded. 25 g of the mixture was oven-dried at 120°C for 3 hours. In the dispersion method 2, the alkali modified SPI/CNTs and SPI/FCNTs were sonicated in an ultrasound sonicator (UMC 20) for 90 minutes and stirred on magnetic stirrer for 30 minutes at 1250 rpm. The pH values of the SPI nanocomposite solution were taken and recorded. 25 g of the mixture was oven-dried at 120°C for 3 hours.

About 25 g of samples mixture of the SPI-NaOH and SPI nanocomposites was measured before and after oven-drying in a petri dish for 3 hours at 120°C. The weight of the samples after drying was calculated and the percentage solid and moisture content were determined. The percentage solid content and the moisture content of the materials were determined using Eq. (i) and Eq. (ii) respectively:

$$\% \text{ Solid content} = \frac{\text{Final wt}}{\text{Initial wt}} \times 100 \quad (i)$$

$$\% \text{ Moisture content} = \frac{\text{Initial wt} - \text{Final wt}}{\text{Initial wt}} \times 100 \quad (ii)$$

The morphology, surface chemistry and the thermal stability of the oven dried samples were checked with scanning electron microscopy (CARL ZEISS), Fourier transmission infrared (Bruker Tensor 27) and thermogravimetric analysis (TA SDT Q600 Thermogravimetric analyzer), respectively. For the FTIR, the oven-dried powdered samples (2 mg) were mixed with 200 mg of potassium bromide (KBr) and pressed for 2 minutes at 200 MPa prior to the commencement of the scanning.

III. RESULTS

Table I: SPIH₂O-SPI mixed with water in ratio 1:9, SPINaOH- SPI adjusted to pH 10 with NaOH solution stirring by high speed magnetic stirrer, SPISNaOH – stirring by sonication method/mixing, SPI0.1-0.7-SPI/CNTs with varying concentration from 0.1-0.7wt% by high speed magnetic stirring, SPIFCNTs0.1-0.7- SPI with varying concentration(0.1-0.7wt%) of FCNTs by high speed magnetic stirring, SPISCNTs0.1- CNTs (0.1%) dispersed in SPI by sonication method/mixing and SPISFCNTs0.1-FCNTs (0.1%) dispersed in SPI by sonication method/mixing.

TABLE I.
PERCENTAGE MOISURE AND SOLID CONTENT OF
ADHESIVE NANOCOMPOSITE AT VARYING
CONCENTRATIONS OF CNTs AND FCNTs

Adhesive nanocomposite samples	Initial wt of samples (g)	Final wt of samples (g)	Weight loss Initial wt-Final wt	% Solid content	%Moisture content
SPI/NaOH	25	1.99	23.01	7.96	92.04
SPISNaOH	25	2.10	22.90	8.40	91.60
SPIH ₂ O	25	1.80	23.20	7.20	92.80
SPI0.1	25	2.37	22.63	9.48	90.52
SPI/FCNTs0.1	25	2.36	22.64	9.44	90.56
SPI/CNTs0.3	25	2.47	22.53	9.88	90.12
SPI/FCNTs0.3	25	2.46	22.54	9.84	90.16
SPI/CNTs0.5	25	2.55	22.45	10.20	89.80
SPI/FCNTs0.5	25	2.54	22.46	10.16	89.84
SPI/CNTs0.7	25	2.67	22.33	10.68	89.32
SPI/FCNTs0.7	25	2.66	22.34	10.64	89.36
SPISCNTs0.1	25	2.40	22.60	9.60	90.40
SPI/SFCNTs0.1	25	2.39	22.61	9.56	90.44
SPISCNTs0.7	25	2.69	22.31	10.76	89.24

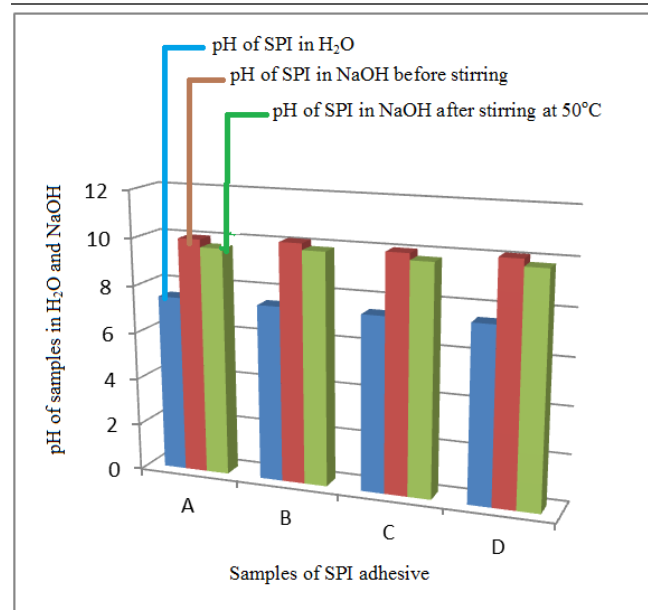


Fig. 1: Effect of temperature on the pH of SPI

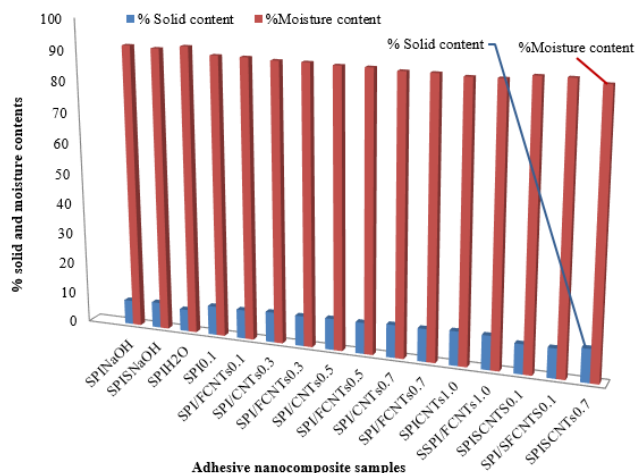


Fig. 2: Percentage solid and moisture content of adhesive nanocomposite at varying concentrations.

TABLE II
 EFFECT OF TEMPERATURE ON pH OF SPI ADHESIVE

Sample	pH of SPI in H ₂ O	pH of SPI NaOH before stirring	pH of SPINaOH after stirring at 50°C
A	7.48	10.00	9.68
B	7.46	10.12	9.85
C	7.44	10.02	9.74
D	7.48	10.10	9.80

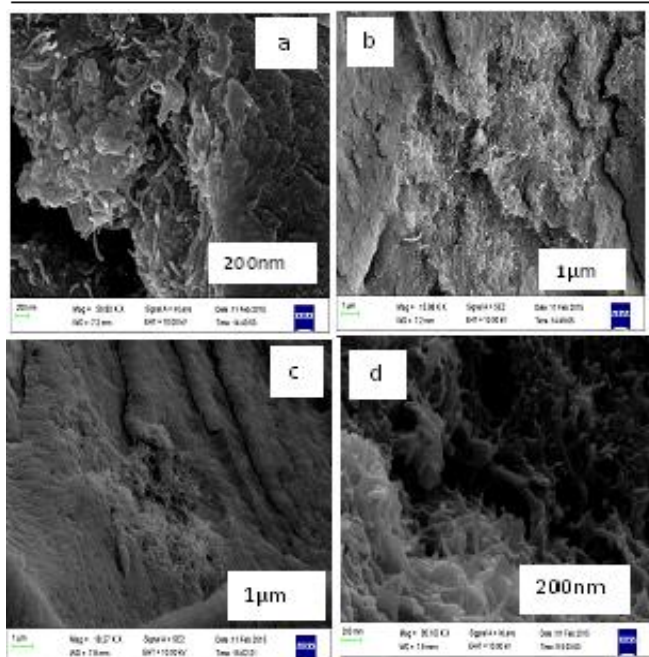


Fig. 3: SEM images 0.1wt% CNTs dispersed (a & b) in SPI adhesive nanocomposites by mechanical mixing method (c & d) by sonication and 30-minute mechanical mixing in SPI nanocomposite adhesive.

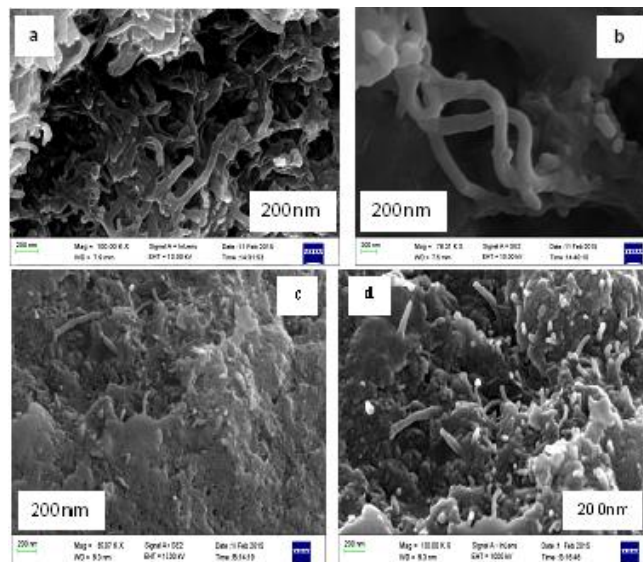


Fig. 4: SEM images of dispersion of 0.1wt% (a & b) FCNTs in SPI nanocomposite adhesive by mechanical mixing (c & d) FCNTs in SPI nanocomposite by sonication and 30 min mechanical mixing.

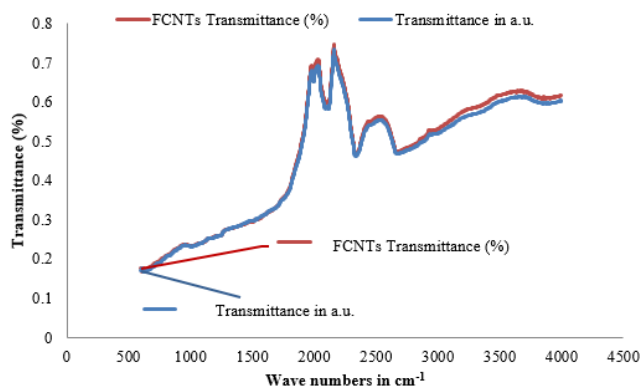


Fig. 5: FTIR spectra of CNTs and FCNTs

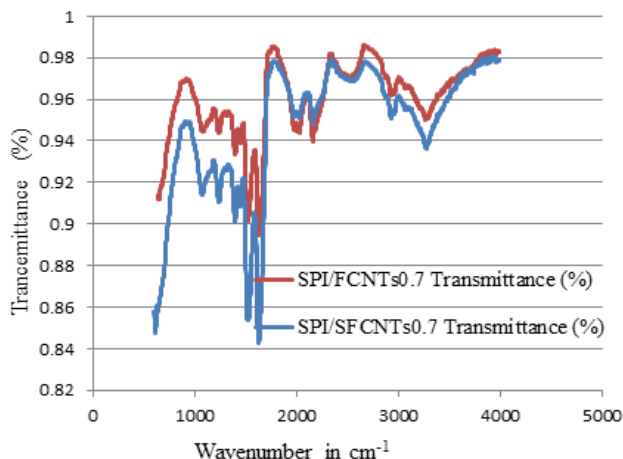


Fig. 6: FTIR spectra of SPI/FCNTs and SPI/SFCNTs

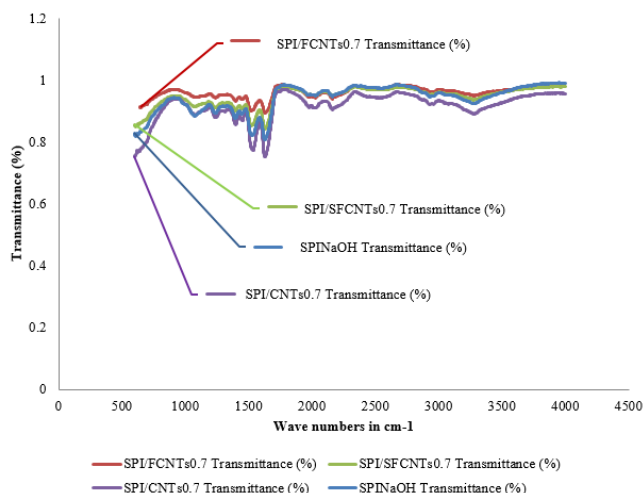


Fig. 7: FTIR spectra of dispersion of 0.7wt% of CNTs and FCNTs by mechanical mixing and sonication with 30 minutes shear mixing

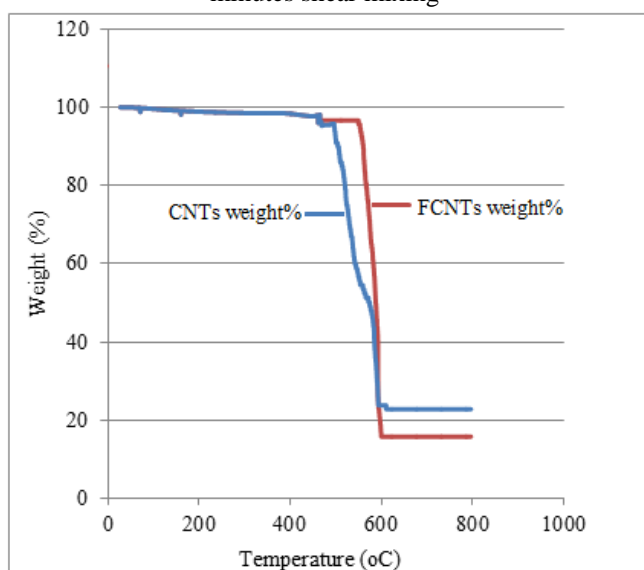


Fig. 8: TGA profile of as-synthesized CNTs and FCNTs

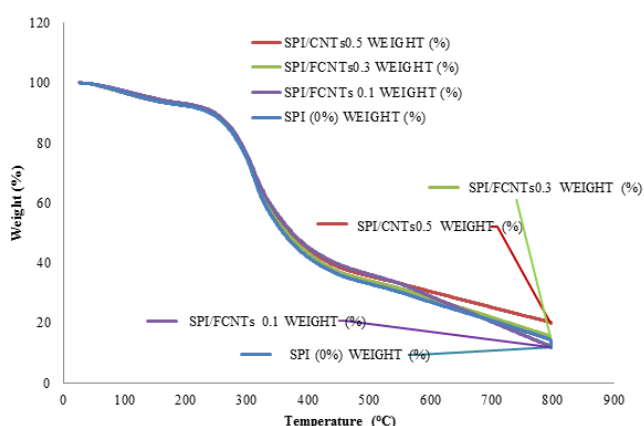


Fig. 9: TGA profile of the adhesive nanocomposites as a function of FCNTs percentage loading.

IV. DISCUSSION

Table I and Fig. 1 show that the percentage solid content of the SPI adhesive increased by 10.6% when the pH was adjusted from 7.37 to 10.00 (Fig.1). This observation indicates that increase in pH of SPI adhesive increases the percentage solid content and reduces the moisture content.

As the concentration of the CNTs and FCNTs increased, the percentage solid content also increased. Fig. 1 shows that as the solid content of the SPI reduces and the moisture content increases accordingly. The pH values of the samples also dropped by 3.2%. The decrease in solid content could be attributed to the drop in pH values. When the pH of SPI adhesive was adjusted to 10 and then stirred at 50°C for 1 hour, the pH and the viscosity of the SPI solution decreased. This result indicates that temperature decreases the pH of the adhesive.

The CNTs dispersed quite homogeneously in the SPI nanocomposite adhesive, only a few small aggregated bundles could be observed. Additionally, the CNTs were scattered randomly in the SPI matrix in all directions, providing the enhanced properties in all directions. There were no much apparent aggregations and damage of the nanotubes in the nanocomposite adhesives, suggesting the effectiveness of procedures and parameters used to disperse the CNTs into the SPI [20]. In high speed mixing, it was noticed that bubbles were generated which was difficult to remove. Nevertheless, the two methods have proven to be suitable for dispersion of CNTs in SPI adhesive. SEM images in Fig. 3 show that, the FCNTs seemed to be homogeneously dispersed in the modified SPI adhesive, although individual CNTs nanotubes could be observed as agglomerates that cluster together (Fig 3 (a and c)) [21].

The FTIR spectrum of as-synthesized CNTs is presented in Fig. 5, as observed, the CNTs show a peak at 1527 cm^{-1} which is assigned to the C-C bond. The weak peak at approximately 1720 cm^{-1} is attributed to the C=O bonds [22]. According to the FTIR spectra of bands of the SPI/CNTs nanocomposite samples, amide band I is the most susceptible to changes in the secondary structure of protein. This was found to be around spectra band of 1637 cm^{-1} -1664 cm^{-1} in all the SPI/CNTs nanocomposite adhesive samples, which is related to C=O stretching. This can be attributed to the pH adjustment of adhesive samples to 10 [23-24]. Amide band II which is related to N-H bending is located around 1535 cm^{-1} -1558 cm^{-1} in all the samples. Amide band III which is C-N and N-H stretching is located around 1245 cm^{-1} . The spectra band at 1404 and 1105 cm^{-1} (Fig. 6) is corresponding to the COO- and C-NH₂ bending in SPI/SFCNTs0.7. The band in all the SPI/CNTs nanocomposite adhesive samples around 3249 cm^{-1} - 3328 cm^{-1} (Fig. 7) is related to O-H functional group which is attributed to the availability of amide band due to unfolding of protein by adjustment of adhesive pH [23]. This result shows that carboxyl (COO⁻) functional group was successfully attached to the surface of the nanocomposite adhesive samples by the help of functionalized CNTs.

The TGA profiles of CNTs and FCNTs are depicted in Fig. 8. The TGA determines the derivative weight change and percentage weight as a function of temperature. This analysis was carried out to determine the thermal stability of the adhesive samples. The TGA profile for the as-synthesized carbon nanotubes shows a weight loss of about 2 % at a temperature from 25°C to 450°C. In addition, the functionalized CNTs shows a weight loss of about 2% at temperature from the room temperature to about 580°C, indicating the purity of the CNT and FCNTs. The weight loss observed at this stage could be attributed to the decomposition of the CaO, the catalyst support remaining after purification, and the moisture content.

At a temperature from 450°C for CNTs and 550°C for FCNTs, decomposition of CNTs commenced. At the temperature range of about 450°C to 550°C, weight loss for CNTs and FCNTs were about 78% and 80%, respectively. The residue of about 23% for CNTs and FCNTs could be attributed metallic particles of the catalyst that were not completely removed during the purification with HNO₃.

The result depicted in Fig. 9 indicates that all adhesive nanocomposite with different percentage of FCNTs underwent two stages of weight loss from 23°C to 800°C. The first weight loss occurred between 23°C and 200°C, which may be attributed to the lower molecular weight of material. The weight loss for the second stage occurred between temperature of 319°C and 387°C, which is attributed to the thermal degradation of soy protein isolate at higher molecular weight formed after oven-curing of the adhesive [20]. The TGA profile also shows that SPI/FCNTs0.5 had weight loss of 80% at 800°C while others with lower loading of FCNTs had over 80% weight losses. This may be as a result of metallic particles remaining in the CNTs. At temperature around 800°C, 11.77% was remaining for nanocomposite adhesive with 0 and 0.1%FCNTs, 15.20% for SPI/FCNTs with 0.3% and 19.96% for SPI/FCNTs with 0.5%.

V. CONCLUSIONS

A well CNT-dispersed adhesive was prepared successfully by use of two different dispersion methods; shear mixing and ultrasonication with 30min of shear mixing. The carbon nanotubes was distributed uniformly in the soy protein adhesive with no noticeable clusters at relatively reduced fractions of CNTs as shown in the SEM images. Thermogravimetric analysis of the sample also showed that the CNTs incorporated increases the thermal stability of the adhesive nanocomposite at higher loading fraction. The FTIR spectra showed the surface functionalities of the SPI adhesive nanocomposite and the attachment of COO⁻ functional group on the surface of the adhesive which contributed to effective dispersion of the CNTs in the nanocomposite adhesive prepared. The preparation of a new adhesive will replace the formaldehyde and petrochemical adhesive in the market and be of useful application in the industry.

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