

High Solid Alkyd Resin Coatings based on Soya Beans Fatty Acid with Improved Coating Performance; The Beneficial Effects of Fatty Acid Functionalized Carbon Nanotubes on their Water-Proofing and Biodegradability

Fatameh Rafiemanzelat (✉ Frafiemanzelat@chem.ui.ac.ir)

University of Isfahan <https://orcid.org/0000-0003-3314-437X>

Ziba Shirini

University of Isfahan

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Abstract

The environmental influence of the coating industry has led to the progress of lots of environmentally friendly products based on high solid alkyds. The problem of increasing viscosity in high solid coatings has tried to resolve by decreasing their molecular weight. However, this results in resins with inadequate properties. In our paper, we have tried to avoid this issue without changes in the chemistry of resin by the assisting of modified nano-materials in coatings. Thus a new medium oil alkyd resin based on soya beans fatty acid was synthesized. Then two differently surface modified Carbon nanotubes (CNTs) functionalized with renewable soya-bean & stearic fatty acids were incorporated into the alkyd resin. Different properties of these nanocomposites including heat resistance, drying time, gel content, hardness, chemical resistance, contact angle, hydrophobicity and biodegradability were improved comparing with the pristine resin. Coatings prepared from the modified resins dried quickly, were waterproof and their characteristic were satisfactory for decorative applications. Their improved properties designate effective reinforcement of these high solid resins using bio-based modified CNTs. Interestingly in spite of their good hydrophobicity and improved waterproofness they showed increased hydrolyze-ability and biodegradability because of the presence of bio-based modified CNTs.

1. Introduction

Alkyd is a special term that refers to a particular type of polyester resins which are modified with fatty acids]1[. They have been used as binders for paints since the 1930s. Alkyds are widely used for producing expansive range of coatings due to their low cost, possibility of synthesizing them from different naturally occurring products, miscibility with variety of polymers, suitable surface properties, good gloss, suitable interaction with polar surfaces like steel or wood, and very diverse formulation options. These include do-it-yourself paints and lacquers for wooden and metallic surfaces, paints for marking roads, anticorrosion paints, architectural and industrial finishes, industrial maintenance, nitrocellulose varnishes, curing coatings-based acids and two-parts isocyanate curable coatings, stove glazes, etc. One of the outstanding characteristics of alkyds is the opportunity of developing a wide variety of products with the same chemistry [2, 3]. Based on oil length, alkyd resins are classified in to long oil, medium oil and short oil alkyds that affects their properties and final applications [4].

Now a days, the extensive use of Petro-based chemicals and disposal of non-biodegradable waste plastics by burning them have been led to the worldwide climate changes, water pollution and emission of harmful gases. Using natural polymers as a potential alternate for solving these issues cannot be a complete solution because of their limited variety, physico-chemical and mechanical properties. However; bio-based products prepared from natural sources raw materials have attracted great attention due to their renewability, eco-friendliness, availability, degradability, cost effectiveness, toughness and acceptable mechanical properties etc. Growing use of renewable materials can develop a sustainable solution to existing global problems with plentiful environmental benefits. Most of the raw materials which are using for the preparation of the alkyds originate from natural renewable sources excepting for petro-origin phthalic-anhydride. Thus, making bio-based degradable polymers turns alkyd resins into

interesting coatings and binders from an environmental viewpoint [2]. One of the desired demands of coating manufacturers is enhancement of the degradability of resins without too much changes in the formulation of their backbone's monomers and properties. This can be almost achievable using suitable modified nano materials. However, another environmental concern of the alkyds is solvents used for adjusting their viscosity. Typical conventional solvent-based alkyds are mixed with toluene, xylene, white spirit or a combination of them. The evaporation of these organic volatiles (VOC) throughout the usage and drying course of alkyds lead to numerous ecological issues [3]. Thus, alkyd resins manufacturers have had to develop more naturally being form of their productions to compete with the customary thermo-plastic lattices that introduced to the market in the 1950s. Recently quite wide activities have been done for designing alkyd emulsions, acrylated alkyd emulsions, water thinned-able alkyd resins, high solid content alkyds and other water-based binders which can be used as binders for eco-friendly purposes [2,3]. For water-based alkyds one procedure is synthesizing high acid number alkyds that after neutralizing by amines and mixing with water and water mixable solvents such as glycol ethers, can be changed to a colloid solution. But the presence of amine results in slow drying and low yellowing resistance. Owing to the colloid character of the water thinned-able alkyd paints, systems exhibit an abnormal viscosity when diluted by water which causes unpleasant problems throughout their usage. In additions, the high pH of the colloidal system (typically $\text{pH} \geq 8$) results in gradual hydrolyzing of the ester groups which negatively affects polymer molecular weight and their soiling durability. These reasons have been resulted in minor success to the commercialization of these systems. Another solution for formulating zero VOC paints can be alkyd emulsions. With the right choice of surfactants, the use of amines is avoidable in alkyd emulsions [2]. The modification of alkyd resins by acrylates combines the favorable application and film formation properties of the alkyds together-with the weathering resistance and overall characters of acrylic systems. However, acrylation of alkyds performs via post-acrylation or monoglyceride method. These reactions add extra synthesis steps to alkyd production and change the formulation of the virgin alkyd. Thus, the preparation of high solids alkyd paints maintains alkyd resin originality as well as solving the high VOC content problem but causes the problem of increasing viscosity by decreasing of diluent solvent contents. There may be many strategies to solve this matter. For example, producing high solid content alkyds by reducing their molar mass through enhancing the OH/COOH groups ratio or enhancement of fatty acids contents. However, alkyd resins prepared via these methods show unsatisfactory properties because of their low molecular weight. Their drying time is long and their coatings performance is weak. One of the suitable ways to solve this issue has been synthesizing highly branched alkyd resins which lead to fast drying coatings with satisfactory properties for decorative end use [5].

On the other hands, alkyd coatings bear some short comings, like low alkaline and salt solutions stability, extended drying periods (particularly for non-drying oils) and low hardness [6]. Under these situations, paints show extensive chalking, writing, color diminishing or gloss loss. A good strategy for increasing paints' durability has been improving their weathering resistance, solvent resistance, thermal resistance and etc. via modifications of alkyds with other resins [4]. One way for the improvement of the aforementioned properties is making hybrid alkyds by mixing and blending alkyd resins with other

suitable resins like acrylates, polyurethanes etc. because of their suitable miscibility with different kinds of resins [6, 7]. Another way with no change in the alkyd resin chemistry can be using the benefits of nano technology. SiO_2 , Al_2O_3 , TiO_2 , ZnO , CaCO_3 , Fe_2O_3 and organo clay are nanoparticles which have been widely used for the polymeric coatings [3, 8]. The resulting polymeric coating nano-composites have exhibited greater mechanical, electrical, thermal and chemical properties compare to pure one [3,9,10]. CNTs (Carbon nanotubes) have gained great consideration because of their exceptional mechanical, thermal and electrical properties which result in their widespread usages [8,11–13]. CNTs/polymer nanocomposites show improved thermal and electrical conductivity and strengthened adhesive and cohesive properties of coatings [10]. However, owing to their large surface area together with strong van-der-Waals interactions between CNTs, they can't disperse uniformly in the polymeric matrix and tend to aggregate together. Thus, in order to provide a well dispersed CNTs/polymeric nanocomposite their surface modification with suitable chemical groups for attending desired properties is helpful [11–15]. On the other hands these attached groups on the CNTs' surface can lead to new interactions between modified CNTs and polymer matrix resulting in generating new properties.

In this study we tend to synthesize a new medium oil alkyd resin (Alk) based on soya beans fatty acid using a one-step fatty acid method. Then two kinds of surface modified Carbon nanotubes (CNTs): "stearic acid modified" (CNTs-sa) and "soya beans fatty acid modified" (CNTs-fa) are prepared and incorporated into the alkyd resin. Then different properties of these nanocomposites such as thermal stability, drying time, gel content, hardness, chemical resistance and anticorrosive features, and hydrophobicity are studied and compared. In the present study, high solid alkyd resins containing CNTs modified with a saturated non-drying fatty acid (sa) and an unsaturated drying fatty acid (fa) with a good (not excellent) drying speed are prepared for the first time. Our objective is to prepare developed alkyd resins using the same chemistry and maintaining alkyd originality. It is expected that unlike acrylic, polyurethane, phenolic modified alkyds, amine containing alkyds or high acid value alkyds, without decreasing of alkyd's molecular weight, changing its structure or chemistry altered alkyds with improved chemical and solvent resistance, good durability, thermal stability, drying time, gel content, hardness, and hydrophobicity are obtained. Although we have used non-drying or medium speed drying oils, these fatty acids result in good- excellent gloss and non-yellowing on aging properties, instead. Thus, we try to improve thermal and coating properties of resins as well as their drying time and gel content using the benefits of CNTs nanotechnology without changing the alkyd resin originality and using low cost, available and biologically renewable raw materials. We tend to prepare ecofriendly low VOC high solid alkyds with relatively unchanged viscosity, improved water-proofness as well as biodegradability.

2. Experimental

2.1. Materials

Polybasic acids; phthalic anhydride and maleic anhydride as well as glycerol, soya beans fatty acid and xylene (all commercially grade) were used with no more purification. Industrial grade white spirit solvent

and driers including cobalt octoate, lead octoate and calcium carbonate were used for dilution and film production, respectively. Analytical grade acetone (98 wt. %, Petro Chem), potassium hydroxide (Riedel), phenolphthalein (99 wt. %, Merck), and hydrochloric acid (37 wt. %, Ghatran Chem Co) were used for titration tests. Multi walled carbon nanotubes CNTs (diameter 10–20 nm, length 30 μm , purity > 95 wt. %) was obtained from Neutrino Co. (Iran). Sulfuric acid (98 wt. %, Ghatran Chem Co), potassium permanganate (99 wt. %, Merck), stearic acid (98 wt. %, Merck), chloroform (99 wt. %, Petro Chem) and n-hexane (Industrial grade) were used without further purification.

2.2. Characterization

FTIR spectrum was studied using a Jasco FTIR 6300 spectrophotometer (Japan). KBr discs were used for recording spectra of solids. For uncured resin, a thin film of resin was casted on KBr disk. Vibrational transition frequencies were stated in wavenumber (cm^{-1}). Band height and descriptions were specified as weak (w), medium (m), shoulder (sh), strong (s) broad (br), stretching (st.) and bending (bend). The average size and size distribution of modified CNTs dispersion was determined by Dynamic Light Scattering [DLS, Malvern instrument LTD (Japan)] in the acetone (0.1 g mL^{-1}) at RT. Thermogravimetric analysis (TGA) of CNTs, alkyd and alkyd-CNTs nanocomposites (ALK and ALK-CNTs) films was performed using a thermogravimeter (Mettler TA 4000 Switzerland). A 2 mg of sample was put in an alumina crucible and heated between 25–800°C at the heat speed of 15°Cmin^{-1} in N_2 . The morphologies of CNTs, the functionalized CNTs and ALK-CNTs were studied by means of field emission scanning electron microscopy (FE-SEM). The images were obtained at 15 kV by a SIGMA VP-500, ZEISS instrument (Germany). The viscosity (cP) of the synthesized alkyd resin was evaluated with a Brookfield viscometer (Type DV III-USA, spindle-34). To evaluate hydrophilic-hydrophobic features of coatings the static water contact angles were evaluated for 5 times at different places and their mean-average was considered as the final value by means of a contact angle meter (CA-ES10, Ezdiad Bardash-e Fars Technology Co. Iran) and data were analyzed using image-J software. Droplets of deionized water, with a volume of 5 μL , were placed gently onto the surface at room temperature and the angle was measured from the captured image. Pictures were taken, and contact angles were measured after one sec. of placement of water globule on the surface. Dispersion stability of CNTs in solvent was evaluated to assess the hydrophilic-hydrophobic features of the modified CNTs. 1 mg mL^{-1} of CNTs was sonically dispersed in deionized water as well as in n-hexane for 1 h and the storage stability of dispersion was studied after 12 h [16–18]. The nano fillers were well dispersed in resin matrix by using an ultrasonic instrument (PARSONIC 11s, Pars Nahand Co. Iran, $2.8 \times 10^4 \text{ Hz}$, 150W). ASTM D-1640 was used for checking the surface drying period. Set-to-touch time was specified as the non-transferability of the coating based on lightly stroking the coating with finger. Film dryness was ascertained as the non-adhering the coating to the finger after firm pressing and not rubbing up after light rubbing. Through drying time was considered as the non-distortion of the coating when the thumb was pressed on it and swiveled through a 90° angle. The prepared films put in the dust free place at RT and were examined orderly to follow out its dryness or stickiness by finger tips and filter paper. The physico-chemical properties of the ALK and modified ALKs were determined by

ASTM test methods including pencil hardness (ASTM D 3363), gel content (ASTM D 2765), water absorption (ASTM 570) and chemical resistance (ASTM D 1308).

2.3. Synthesis of medium oil alkyd resin

Alkyd sample of 56% oil length was prepared with glycerol (GL), soya beans fatty acid (fa) (or sa), phthalic anhydride (PA), and maleic anhydride (MA) employing the one step fatty acid method. The recipe used is shown in Table I. Polyesterification reaction was continued to acid number ≤ 12 mgKOH/g. Vacuum, xylene as the azeotropic solvent and N₂ purge were used for the removal of water by-product depending on the case.

Table I Synthesis recipe of alkyd resin

Glycerol (mole)	Soya beans fatty acid (mole)	phthalic anhydride (mole)	maleic anhydride (mole)
2.34	1.85	1.96	0.09

To synthesize medium oil soya beans fatty acid-based alkyd resin, glycerol and soya beans fatty acid were charged in to a 3 necked 500 mL flask which assembled with mechanical stirrer, thermometer, Vigro column, a condenser with dean-stark-trap (to remove the generated water). Afterward, phthalic anhydride and maleic anhydride were added at 140°C. Then the temperature was increased slowly to 180°C and stirred for 2 h. Then the reaction mixture was warmed up to 245°C slowly and was followed under N₂ purge till acid value ≤ 12 mgKOH/g. Every 30 min the acid number was measured by sampling the reaction mixture according to ASTM D 1639-90. Once the acid value was about 12 mgKOH/g, the reaction was quenched by cooling down to 120°C and it was diluted with white spirit solvent to get alkyd resin with 70% solid content.

2.4. Modification of CNTs with soya beans (CNTs-fa) and stearic acid (CNTs-sa) fatty acids

2.4.1. Oxidation of CNTs (CNTs-OX)

Oxidized CNTs were obtained through acidic KMnO₄ solution method [15]. 2 g of CNT was dispersed in 120 mL solution of sulfuric acid (4.5M) containing 2g of dissolved potassium permanganate. The mixture was refluxed at 95°C and stirred for 100 min. The reaction mixture was filtered after cooling it up to room temperature (RT). Then the resulting product was rinsed and filtered sequentially with H₂O and concentrated hydrochloride acid. The resulting CNTs-OX were rewashed with H₂O until neutralization of the filtrate and dried at 120°C for 15 h.

2.4.2. Preparation of CNTs-fa or CNT-sa

For the preparation of CNTs-fa, 2 g as prepared CNTs-OX and 10 g of soya beans fatty acid (or 4 g stearic acid) were mixed ultrasonically in 30 ml deionized water at 70°C. After that, 50 mL of 2 M sulfuric acid solution was added to the reaction vessel and was refluxed under stirring at 100°C for 2 h. Subsequently, the resulting mixture was cooled to RT, filtered, washed with chloroform and n-hexane, rewashed with H₂O till neutralization and finally dried at 80°C for 4 h [14,19].

2.5. Preparation of alkyd film and its nanocomposites

In order to study film properties, dried films of ALK or ALK modified with CNTs-sa or CNTs-fa (ALK/CNTs-sa or ALK/CNTs-fa) were made as follow: The resins (14.29 g 70% solid content) were mixed with drying agents (0.6 g cobalt octoate, 0.3 g lead octoate and 0.5 g calcium carbonate) and allowed to stir for 30 min at 70°C. Then the resulting mixture was applied on the glass panels or wood by using a film applicator and cured at RT under relative moisture of 40% (760 × 25 × 0.17 mm).

In order to prepare nanocomposite films, at first 0.2 wt. % of CNTs-sa or CNTs-fa was added in to the alkyd resin and was dispersed in resin under sonication to form a homogeneous dispersion. Then the same procedure was followed for making nanocomposite films.

3. Results And Discussions

3.1. Surface modifying of CNTs

In this work, we made a comparative investigation of different oxidation techniques of CNTs through different chemical agents that have various level of oxidation ability. The extent of oxygen functionality on the CNT side-wall requires for making certain functional nano size materials and attachment of new other functionalities. For oxidation of the CNT, the original CNT was reacted with H₂SO₄/KMnO₄ mixture under heating [15], H₂SO₄/HNO₃ (8 molar) under sonication [20], or concentrated HCl then H₂O₂ under heating [13] (Scheme 1). The characteristic of treated CNTs (CNTs-OX) and pure CNTs were compared on the bases of the gained weight of the resulting product, reaction time and amount of oxygen functionality. The oxidized CNTs were characterized by FTIR, TGA and titration methods. It was shown that reaction method 1 lead to better results upon the gained oxygen functionality onto the CNTs surface. Boehm titration method was shown that the amount of mmol of total OH groups per g of CNTs was 0.48, 0.092 and 0.056 (mmol g⁻¹) correspond to 2.16%, 0.41% and 0.25% (g g⁻¹) for methods 1, 2 and 3 respectively [15,21].

The fatty acid surface modified of the CNTs-OX was prepared by heating them with stearic or soya beans fatty acid in the presence of H₂SO₄ (Scheme 2) and characterized by FTIR, TGA, DLS and FESEM methods.

3.2. Characterizing of surface modified CNTs

3.2.1. FT-IR characterization

FTIR spectra of oxidized and fatty acid modified CNTs are shown in the Figs. 1 and 2.

The FTIR spectrum of CNTs-OX showed the characteristic absorption bands of carbonyl and hydroxyl groups of carboxyl (COOH) and phenol (OH) groups. Stretching vibrations of OH, C = O, and C-O- were shown at 3426, 1707, 1032 and 1165 cm^{-1} respectively. Figure 1 compares FTIR spectra of CNTs-OX₁, CNTs-OX₂ and CNTs-OX₃ prepared by oxidation methods 1, 2 and 3 respectively. It can be seen that the peak intensity and peak area of carbonyl and C-O- groups around 1700 and 1100 cm^{-1} related to COOH and OH groups in the case of CNTs-OX₁ are more than that of CNTs-OX₂ and CNTs-OX₃. This confirms that reaction method 1 lead to higher oxygen functionality onto the CNTs surface (Fig. 1).

After modification of CNTs-OX₁ with soya beans fatty acid (fa), the presence of characteristic sorption bands at 1705 (ascribe to C = O st.), 2851, 2920 and 3004 cm^{-1} (ascribe to CH st.) also 1573 cm^{-1} (assigned as CH₂ bend.) demonstrates that the fatty acid chains are successfully bonded to the surface of CNTs-OX₁ through esterification reaction resulted in CNTs-fa (Fig. 2).

In the FTIR spectrum of CNTs-sa, the appearance of new bands at 2846 and 2915 cm^{-1} (due to CH₃ & CH₂ st.) and at 1457 and 720 cm^{-1} (due to bending vibration of CH₂ in the alkyl chains) which are characteristic absorption bands of stearic acid aliphatic chains confirms the successful modification of CNTs-OX₁ with sa chains through esterification reaction resulted in CNTs-sa (Fig. 2).

3.2.2. TGA Study

TGA was used to study thermal stability of CNTs and modified CNTs and to determine the functionality of oxidized and modified CNTs (the amount of organic components attached to the CNTs' surface).

TGA curves of CNTs and CNTs-OX₁₋₃ prepared via reaction methods 1, 2 and 3 are shown in Fig. 3. It can be seen that oxidation reaction has resulted in increasing initial thermal stability and char yield of CNTs-OX₁₋₃ compared with pristine CNTs ($T_{5\%} = 533^\circ\text{C}$, Char % = 82 at 800°C). This can be due to the elimination of amorphous carbon during acid treatment and oxidation reaction. CNTs-OX₁ showed lower initial thermal stability and char yield ($T_{5\%} = 413^\circ\text{C}$, Char % = 86.85 at 800°C) in comparison with CNTs-OX₂ ($T_{5\%} = 802^\circ\text{C}$, Char % = 95.98 at 800°C) and CNTs-OX₃ ($T_{5\%} = 804^\circ\text{C}$, Char % = 95.70 at 800°C). This can be explained by the higher amount of organic functionality linked to the CNT-OX₁'s surface. The resulting weight losses of CNT and CNTs-OX₁₋₃ below 150°C is related to the elimination of the absorbed H₂O on their surfaces. Thus, the amount of lost water was about 0.07%, 2.11%, 0.33% and 0.29% in the case of CNTs, CNTs-OX₁, CNTs-OX₂ and CNTs-OX₃ respectively. These results showed more hydrophilic nature of the CNTs-OX₁'s surface because of more COOH, OH functionalities attached on its surface compared with CNTs-OX₂ and CNTs-OX₃. The observed weight losses of CNTs-OX₁₋₃ between 150–450°C can be correlated to the thermal decarboxylation of CNTs-OX₁₋₃'s surfaces together with the decomposition of part of the phenol OHs.

TGA analysis of CNT, CNT-OX₁, CNT-fa and CNT-sa are presented in figure. 4 and their data are presented in Table II.

A minor weight loss (0.07%) below 150°C was recorded for unmodified CNTs owing to the vaporization of the adsorbed H₂O. A significant mass loss started above 450°C which was due to the decomposition of amorphous carbons and additional impurities.

A weight loss of about 2.11% was detected below 150°C for CNTs-OX₁ corresponded to the vaporization of the adsorbed H₂O. As mentioned before higher initial weight loss of CNTs-OX₁ in this region in comparison with CNTs can be related to the existence of CO₂H and O-H hydrophilic, water absorbing functional-groups on the CNTs-OX₁ surface. The mass loss values of CNT-fa & CNT-sa are less than that of CNTs-OX₁ in this region which confirms their hydrophobic character because of their surface modifications by hydrophobic fatty acids and thus lower absorbed H₂O.

A weight loss of about 1.93% between 150–450°C is ascribed to the CO₂H loss of CNTs-OX₁. The decomposition of remaining amorphous carbon was mainly started above 500°C. Thermal degradation between 370–640°C can be described by the removal of phenol OH functional groups, overlapping decomposition of disordered carbon. Finally, at the temperatures above 640°C, thermal decomposition of the remaining disordered Carbon was continued. Thus the estimated surface functionality of CNTs-OX₁ was about 2% according to Eq. 1.

Comparing with unmodified CNTs the reduced degradation of CNTs-OX₁ above 500°C treated by the H₂SO₄/KMnO₄ shows the elimination of amorphous Carbon in the sample.

$\{[(Total\ weight\ loss\ of\ CNTs-OX_1\ at\ 450^\circ C) - (its\ water\ mass\ loss\ at\ 150^\circ C)] - [(Total\ mass\ loss\ of\ CNTs\ at\ 450^\circ C) - (its\ water\ weight\ loss\ at\ 150^\circ C)]\} = COOH\ \&\ OH\ functionality$ **Eq. 1**

The TGA curves of modified CNTs-fa and CNTs-sa showed total weight loss of about 17.56% and 23.67%, respectively between 150–450°C. This can be related to the thermal degradation of fatty acid chains attached to the surface of CNTs-OX₁ as well as decarboxylation/dehydroxylation of unreacted OH and COOH on the CNTs-OX₁'s surface. Thus 14.21% for (CNTs-fa) and 20.31% for (CNTs-sa) can be considered as the degree of functionality of fatty acid components attached onto the CNTs'-OX₁ surface up on Eq. 2. Weight loss that occurred at the temperatures above 450°C is related to the breakdown of amorphous Carbon and functionalities which were formed on the surface of CNTs during oxidation reaction.

The char residue of CNTs-fa and CNTs-sa at 800°C was lower than that of CNT-OX₁. This confirms the attachment of organic components on the CNTs-OX₁'s surface and the modification of CNTs-OX₁ with aliphatic fatty acid chains.

Calculated LOI values of CNTs, CNTs-OX₁, CNTs-fa and CNTs-sa showed that these nano materials can be considered as self-extinguishing elements.

Table II TGA data of CNTs and modified CNTs

sample	T _{Onset} (°C) ^a	T _{5%} (°C) ^b	Char residue (%) ^c	LOI ^d	% F ^e
CNTs	25	533	82.56	50.52	-
CNTs-OX ₁	25	413	86.85	52.24	1.93
CNTs-fa	140	240	64.98	43.49	14.21
CNTs-sa	156	233	54.55	39.32	20.31

^a Temperature at which the initial mass loss was started by TGA at a heat rate of 15°C min⁻¹ in N₂. ^b Temperature at which 5% mass loss was verified by TGA at heat rate of 15°C min⁻¹ in N₂. ^c Percentage of weight residue at 800°C recorded by TGA at heat rate of 15°C min⁻¹ in N₂. ^d Limiting oxygen index (LOI); Char residue was considered as a criterion for estimating LOI of compounds according to Van-Krevelen-Hoftyzer equation $LOI = 175 \times 10^{-1} + 1^{-10} \times 4 CR$ that CR = char residue at 800°C. ^e Surface functionality of modified CNTs created by surface modification reaction of CNTs or CNTs-OX₁. It was estimated up on the absolute value of difference between the weight loss of modified CNTs and unmodified CNTs at 450°C, minus the amount of the lost water; e.g. **Eq. 2**: For CNT-fa or CNT-sa; $F = \{[(CNTs-sa \text{ or } fa \text{ weight loss at } 450^\circ C) - (its \text{ water lost at } 150^\circ C)] - [(CNTs-OX_1 \text{ weight loss at } 450^\circ C) - (its \text{ water lost at } 150^\circ C)]\}$; For CNT-OX; $F = \{[(CNTs-OX_1 \text{ weight loss at } 450^\circ C) - (its \text{ water lost at } 150^\circ C)] - [(CNTs \text{ weight loss at } 450^\circ C) - (its \text{ water lost at } 150^\circ C)]\}$.

3.2.3. DLS and FESEM study

The morphology of modified CNTs was studied using FESEM. The FESEM images of dried powders of Au coated CNTs-fa are presented in Fig. 5. It can be seen that modified carbon nanotubes have maintained their tubular morphology which comprise the non-aggregated bundles of CNTs. It is evident that the modification of CNTs with fatty acid chains has resulted in decreasing the highly agglomeration tendency of nanotubes. DLS and FESEM analyses showed average diameter size of about 40 nm, and average size of about 90 nm and 80 nm for CNTs-fa and CNTs-sa respectively. The changes in the size and diameter of CNTs confirms surface modification of CNTs with fatty acid chains.

3.2.4. Colloidal stability of CNTs suspensions

In order to evaluate the dispersion behavior and hydrophobic-hydrophilic feature of modified CNTs, the dispersion stability of their suspensions in water as a polar solvent and in n-hexane as a nonpolar solvent was assessed after 12 h. It can be seen that aqueous dispersions of CNTs-fa and CNTs-sa have low storage stability in water and precipitate because of their hydrophobic feature. The suspension of the above mentioned nanotubes in n-hexane was stable and didn't precipitate because of their hydrophobic

nature (Fig. 6). This fact indicates that the modification of CNTs with fatty acid chains has increased their dispersion stability in nonpolar solvents by improving the interfacial interaction between nanotubes and nonpolar solvents. Good dispersion stability of CNTs-fa and CNTs-sa in n-hexane demonstrates hydrophobic characteristic of grafted fatty acid chains on the surface of modified CNT and confirms their grafting on the CNT surface. The oxidized nanotubes, CNTs-OX₁, because of hydrophilic feature of polar hydroxyl and carboxyl groups showed hydrophilic character. They have an enhanced dispersibility in water solutions resulting in reduced aggregation of CNTs-OX. The dispersion test of the original CNT in both polar and non-polar solvents such as n-hexane and water showed aggregation and sedimentation. Thus, the surface chemistry of pure CNT, CNT-OX₁, CNTs-fa and CNTs-sa has elucidated the changes of dispersion states in polar and non-polar environments.

3.3. Characterization and properties of synthesized alkyd resin and its CNTs-nanocomposites

3.3.1 Alkyd synthesis and acid value

Esterification reaction occurred between phthalic anhydride, maleic anhydride, soya beans fatty acid and glycerol. The reaction progression was followed by changes in acid value (AV) from 241 to 12 (mg KOH g⁻¹) according to the titration method "ASTM D 1639-90" with an ethanolic solution of potassium hydroxide. Thus the degree of polymerization and reaction progress can be expressed by the acid value, which is an industrial measure for the conversion and can be determined by titration with an ethanolic solution of potassium hydroxide (KOH). The conversion percentage of the esterification reaction was determined using Eq. 3 which was about 90%.

H₂O byproduct was removed using N₂ purge or vacuum or xylene azeotrope distillation. We preferred vacuum removal method because of its better efficiency since the quantity of initial O-H functions measured in the reaction mixture was decreased faster than that of other methods. The absence of xylene as VOC in vacuum method was its other benefit.

$$\% \text{ Reaction conversion} = [1 - V_0 / V_j] \times 100 \text{ Eq. 3}$$

Where V₀ and V_j are the consumed volume of KOH solution (in milliliters) at the beginning and any time intervals of esterification reaction respectively.

Once the acid value was near 12 mgKOHg⁻¹, the reaction was quenched by cooling down to 120°C and it was diluted with white spirit solvent to get alkyd resin with 70% solid content. The Brookfield viscosity of resin was 50.40 cP. It is worthy to mention that by adding the modified CNTs in to the resin there was not observed much changes in the viscosity.

3.3.2. FTIR study of Alk

The structure of prepared alkyd resin was determined by FTIR as given in figure. 7. The band at 3006 cm^{-1} matches = C-H vibration of unsaturated fatty acid and maleic acid residue existing in the backbone of polymeric chains. Two peaks at 2854 & 2925 cm^{-1} are ascribed to the aliphatic C-H stretching bonds. Appearance of C = O & -C-O- stretching vibration bands at 1734 , 1280 and 1124 cm^{-1} ; consequently, suggest the formation of ester functionality. The bending vibration band for -C-H emerged at 1461 cm^{-1} . The broad absorption band at 3511 cm^{-1} indicates the stretch vibration of terminal O-H groups. The FTIR confirmed the formation of ester groups and the presence of double bonds in the alkyd resin.

3.3.3. The film properties of alkyd film and its nanocomposites

The pure resin or resins containing well dispersed CNTs-fa or CNTs-sa were mixed with drying agents (cobalt octoate, lead octoate and calcium carbonate) and allowed to stir at 70°C . Then the resulting mixture was applied on the glass panels or wood by using a film applicator and cured at RT under relative moisture of 40%. Then their different properties were compared. The dried coatings were left to complete drying for two weeks at RT prior to the measurements.

3.3.3.1. Drying time, gel content and film hardness

The dry-to-touch periods of Alk and its CNTs-nanocomposites were measured. The drying pathway of alkyd resin coatings is typically happened in 2 steps. In the first step the coatings become solid by the evaporation of the solvent due to physical drying. The second step includes the oxidation of the fatty acid and maleic acid residues, which finally makes a crosslinked polymer. Several parameters for example the amount of unsaturated bonds, the molar mass and molar mass distribution, the amount and type of the drying catalyst, the solid content, the viscosity, the solvent, the amount of conjugated unsaturated bonds, etc. affect the drying time. In our study, all of the aforementioned parameters kept the same except the degree of unsaturation associated to the presence of CNTs-fa or CNTs-sa in the resin matrix. It was shown that drying time of Alk/CNTs-fa (13h) and Alk/CNTs-sa (14h) were decreased comparing with Alk (15h). The improvement of drying rate of nanocomposites can be related to the presence of modified CNTs. It can be said that saturated (sa) and unsaturated (fa) fatty acid chains on the surface of CNTs-sa and CNTs-fa have brought together polymeric chains and facilitated the formation of crosslinks (Scheme 3). In addition, unsaturated fatty acid chains on CNTs-fa contributed to the formation of crosslinks and film drying because of the existence of extra double bonds of Soya beans fatty acid chains linked to CNTs-fa (Scheme 3). Thus Alk/CNTs-fa dried faster than Alk/CNTs-sa and ALK. The data obtained by gel content measurements have confirmed this allegation.

Gel content measurements of dried films according to ASTM D3363 were performed to compare the degree of crosslinking of the films. The results showed that the gel content of ALK/CNTs-fa (73.85%) and ALK/CNTs-sa (70.76%) films were more than that of ALK film (68.67%). Thus in the presence of modified CNTs the degree of crosslinking of the alkyd films has increased and a denser network has been formed. The gel content of ALK/CNTs-fa was more than that of ALK/CNTs-sa which confirms the role of the

unsaturated soya fatty acid chains attached on the surface of CNTs-fa in contributing crosslinking reactions. Generally, the presence of chemical bonds between nano-fillers and polymer matrix is a routine strategy to increase their compatibility and stress transference throughout loading.

The scrape hardness was evaluated by appraising pencil hardness of the coating. The hardness was defined upon the determination of the hardest pencil which not to scrape the film. The measured pencil hardness (ASTM D 3363) was consistent with the gel content data of the Alk and nanocomposite films. It was shown that the scratch resistance of ALK/CNTs-fa (B) and ALK/CNTs-sa (3B) films are better than that of Alk (5B) film. The order of film hardness ALK/CNTs-fa > ALK/CNTs-sa > Alk is in accordance with gel content data.

3.3.3.2. Thermal stability study

Heat resistance and decomposition manner of the prepared coatings were studied with TGA under N₂ atmosphere. Degradation profiles of the films and the resulting data are shown in Fig. 8 and Table III. A wide one step degradation can be considered for alkyd film between 230–560°C resulted in about 81% weight loss. The nanocomposites films showed multi steps degradation patterns and they began to decompose at higher temperatures. The multi steps degradation can be related to the fact that in the range of 230–620°C in addition to the alkyd resin chains, thermal decomposition of the remained disordered carbon of CNTs as well as thermal degradation of functional fatty acid chains attached on the surface of CNTs have occurred. Alk/CNTs-fa lost 90% of its weight between 230–590°C in the form of three step degradation peaks related to the degradation of alkyd chains, unsaturated and saturated parts of fatty acid chains of (fa) attached on the surface of CNTs-OX₁, residue of unreacted OH and COOH and disordered carbon of CNTs. Alk/CNTs-sa lost more than 90% of its weight between 230–620°C as two major degradation peaks related to the degradation of alkyd chains, saturated fatty acid chains of (sa) attached on the surface of CNTs-OX₁, residue of unreacted OH and COOH, and disordered carbon of CNTs. The complete thermal degradation of the extra organic compounds including fa and sa chains on the CNTs have resulted in the decreasing of the char residue of Alk nanocomposites in comparison with Alk.

As it can be seen in the presence of modified CNTs, degradation peaks and degradation steps have shifted to the higher temperatures. The improved heat resistance of nano-composites is attributable to the good dispersion of modified CNTs in the polymer matrix and the increased gel content and crosslinked network structure of the polymer.

Table III TGA data of Alkyd film and its nanocomposites films

sample	T _{5%} ^a	T _{peak1} ^b	Char Residue (%) ^c	LOI ^d
ALK	198	357	10	21.5
ALK/CNTs-sa	220	360	8	20.7
ALK/CNTs-fa	226	366	9	21.1

^a Temperature at which 5% mass loss was verified by TGA at heat rate of 15°Cmin⁻¹ under N₂. ^b The first decomposition temperature at peak point. ^c Percentage of residual mass at 800°C detected by TGA at heat rate of 15°Cmin⁻¹ under N₂. ^d Limiting oxygen index (LOI); LOI = 17.5 + 0.4 CR where CR = char yield at 800°C.

3.3.3.3. Hydrophobicity, chemical and water resistance

Based on the measurements of the contact angle the surface hydrophobicity of Alk film and its nanocomposites were compared. The contact angle considers as the angle at which a liquid interface (water) encounters a solid surface. The contact angles of Alk, Alk/CNTs-fa and Alk/CNTs-sa were 103.2°, 105.3° and 105.9° respectively which are in the range of highly hydrophobic materials ($\theta > 90$). There was a small increasement in the contact angle as the modified CNTs were added into the polymer matrix. This means that fatty acid modified CNTs have made the alkyd more hydrophobic as they showed more hydrophobic character when dispersed in n-hexane. Since nanocomposites have more hydrophobic surface than alkyd film, it is expected that they show less water absorption tendency. The results of water absorption study confirmed this assumption. The data of water absorption measurements of Alk and its nanocomposites films after 24, 48 and 72 h and after one week are presented in table IV. It was observed that the percentage of absorbed water of ALK/CNTs-fa and ALK/CNTs-sa was less than that of Alk film which was related to more hydrophobic character of them. The presence of two differently surface modified CNTs has decreased water absorption tendency of the Alk film about 70–80%.

Table IV The data of water absorption measurements of Alk and its nanocomposites films

Sample	24 h (%)	48 h (%)	72 h (%)	One week (%)
Alk	0.14	0.18	0.18	0.23
Alk/CNTs-fa	0.05	0.07	0.07	0.20
Alk/CNTs-sa	0.03	0.03	0.05	0.21

The chemical resistance of the films was evaluated by applying the coatings on the glass plates. Then plates were cured and dunk in different solutions and solvents for 48 h. The edges of the plates were covered using beeswax to prevent solvent penetration between plate and coating. The plates were assessed and viewed for any indication of changes in the coated resins. The nanocomposites films

showed superior resistivity and expressed better resistance in salt and acid solutions compared with Alk film.

The coated glass plates which dunked in distilled water showed no change. This can be attributed to their increased hydrophobicity.

The coatings immersed in CH_2Cl_2 for evaluating their lipophilic solvent resistance. They displayed gloss loss and whitening for the all-coating compositions. Most of the coatings exhibited variations during 5 h of immersion and totally detached within 48 h. This can be due to the lipophilic nature of the films.

A solution of 5 wt. % aq. solution of HCl was used to study the acid stability of coatings. The films showed good acid resistance. Later gloss-loss and color-changes were observed in all the films soaked in HCl solution. Then films of Alk showed blistering and films of Alk/CNTs-fa or Alk/CNTs-sa showed only shrinkage.

The alkali resistance of coatings was examined using 5 wt. % of NaOH solution. The changes in coated plates were clear within 48 h of soaking. The Alk coatings exhibited whitening, crumpling and removal, but the Alk/CNTs-fa coatings showed whitening, wrinkling and blistering while Alk/CNTs-sa coatings showed only swelling and gloss-loss may be due to its higher hydrophobicity. The films of Alk were completely removed within two days whereas Alk/CNTs-fa(sa) showed no change. The films of Alk/CNTs-fa(sa) were more stable than ALK film and could remain on the glass plate for about 48 h. The poor resistance of alkyd films and its nanocomposites in the alkali medium was probably because of the existence of hydrolysable ester bonds in the alkyd resin chains.

Alkyd resins are extensively utilized as binder for paints production which are commonly confronted to high moisture or salt solution. Under these conditions, the paints show extensive scribbling, color diminishing and gloss-loss. Thus, in this study the aqueous salt solution resistance of covered glass plates was studied using 5 wt. % NaCl solution. The coatings of Alk showed whitening and swelling after 24 h. The resistance of the Alk/CNTs-fa or Alk/CNTs-sa films was found to be good against the aqueous salt solution. They showed no change against NaCl solution after 48 h due to their increased hydrophobicity because of the presence of fatty acid modified CNTs. Thus, it can be a suitable strategy to enhance the durability of alkyd coatings and improving their weathering enduring without changing the chemistry of alkyds and changing their original formulation.

The biodegradability test was performed for 50 days in a self-made environment rich in microorganisms (water + compost fertilizer) and the weight loss of coatings was followed at different times (Table V). The results showed Alk-nano composites in spite of being more water-proof than Alk were more biodegradable than Alk in water due to higher content of bio-based fatty acids in their matrix. The biodegradability order of the coatings was as follows: Alk/CNTs-sa > Alk/CNTs-fa > Alk. It was observed that the Alk/CNTs-sa coating was completely degraded in the environment containing microorganisms. This can be due to its lower crosslink density (gel content) which allowed better water diffusion into its

network matrix. The amount of weight loss of coatings over time indicated that the modification of alkyd resins with fatty acid-modified CNTs resulted in coatings with a higher biodegradability nature (Fig. 9).

Table V. Weight loss of different alkyd coatings immersed in water + compost fertilizer mixture

Sample	Weight loss (%)	Weight loss (%)	Weight loss (%)	Weight loss (%)
	After 10 days	After 20 days	After 30 days	After 50 days
Alk	0.18	2.43	7.76	10.56
Alk/CNTs-fa	1.47	10.53	21.30	35.60
Alk/CNTs-sa	3.43	14.98	28.93	-

3.3.3.4. SEM analysis

Surface morphologies of Alk/modified-CNTs nanocomposite films were investigated with the FESEM. FESEM micrographs of films showed that the modified CNTs have well dispersed into alkyd resin matrix (Fig. 10).

4. Conclusion

In this study a new medium oil bio-based high solid alkyd resin (Alk) based on soya beans fatty was synthesized. Then its properties such as thermal stability, drying period, gel content, hardness, chemical resistance and hydrophobicity were successfully improved with two kinds of fatty acid surface modified CNTs. CNTs-fa and CNTs-sa showed good dispersion stability in nonpolar solvents which confirmed the attachment of hydrophobic fatty acid chains on the surface of CNTs.

Thermal studies showed that the oxidized CNTs had higher heat resistance and char residue than those of unmodified CNTs due to the elimination of disordered carbon. Calculated LOI values of CNTs and modified CNTs showed that such nano-materials can be considered as self-quenching elements. Alkyd film nanocomposites showed increased thermal stability ($T_{5\%}$, T_{peak}) owing to the good dispersion of modified thermally resistance CNTs in the polymer matrix. Their initial thermal degradation temperature was improved up to more than 14%.

The presence of fatty acid modified CNTs in the polymer matrix led to the reduced drying time and increased gel content of the alkyd resin up to 14% and 8% respectively.

It was shown that the measured pencil hardness of nanocomposites films and their solvent resistance increased and their water absorption tendency highly decreased in the presence of modified CNTs. Thus in the presence of fatty acid modified CNTs the degree of crosslinking of the alkyd films has increased and a denser and more hydrophobic network has been formed.

These surface modified CNTs showed negligible water absorption and caused the water absorption tendency of Alk film to reduce about 70–80%. This resulted in increased acid and salt solution resistance and enhanced durability of Alk nanocomposites films. However, the results showed Alk-nano composites in spite of their more water-proof character than Alk were more biodegradable than Alk in water due to higher content of bio-based fatty acids in their matrix.

Thus, the results showed that developed alkyd resins using the same formulation and maintaining originality of the alkyd chemistry were successfully prepared. Using the benefits of nanotechnology of fatty acid modified CNTs and using low cost, available and biologically renewable raw materials, low VOC high solid alkyds with relatively unchanged viscosity and molecular weight with reduced drying time, increased gel content and hydrophobicity were obtained. We have shown that using non-drying or medium speed drying oils, which are known to result in coatings with good-excellent gloss and non-yellowing on aging properties, alkyd resins with improved properties successfully were prepared.

Declarations

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Competing Interests

“Financial interests: Author Fatemeh Rafiemanzelat and Ziba Shirini¹ declare they have no financial interests. “The authors have no relevant financial or non-financial interests to disclose.”

Author Contributions

All authors contributed to the study conception and design.

Material preparation, and the first draft of the manuscript was written by Fatemeh Rafiemanzelat. All authors read and approved the final manuscript.

Data collection, experiments and analysis were performed by Ziba Shirini.

Author	Contribution
Fatemeh Rafiemanzelat	Corresponding author, Conceptualization, Investigation, Writing, Formal analysis, Data Curation, Validation, Visualization, Software, Supervision, Project administration, Funding acquisition, Resources, Review and Editing,
Ziba Shirini	Methodology, Investigation, Writing, Formal analysis, Data curation, Validation, Visualization, Soft ware

Data Availability

"The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request."

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Scheme

Scheme 1-3 are available in Supplementary Files section.

Figures

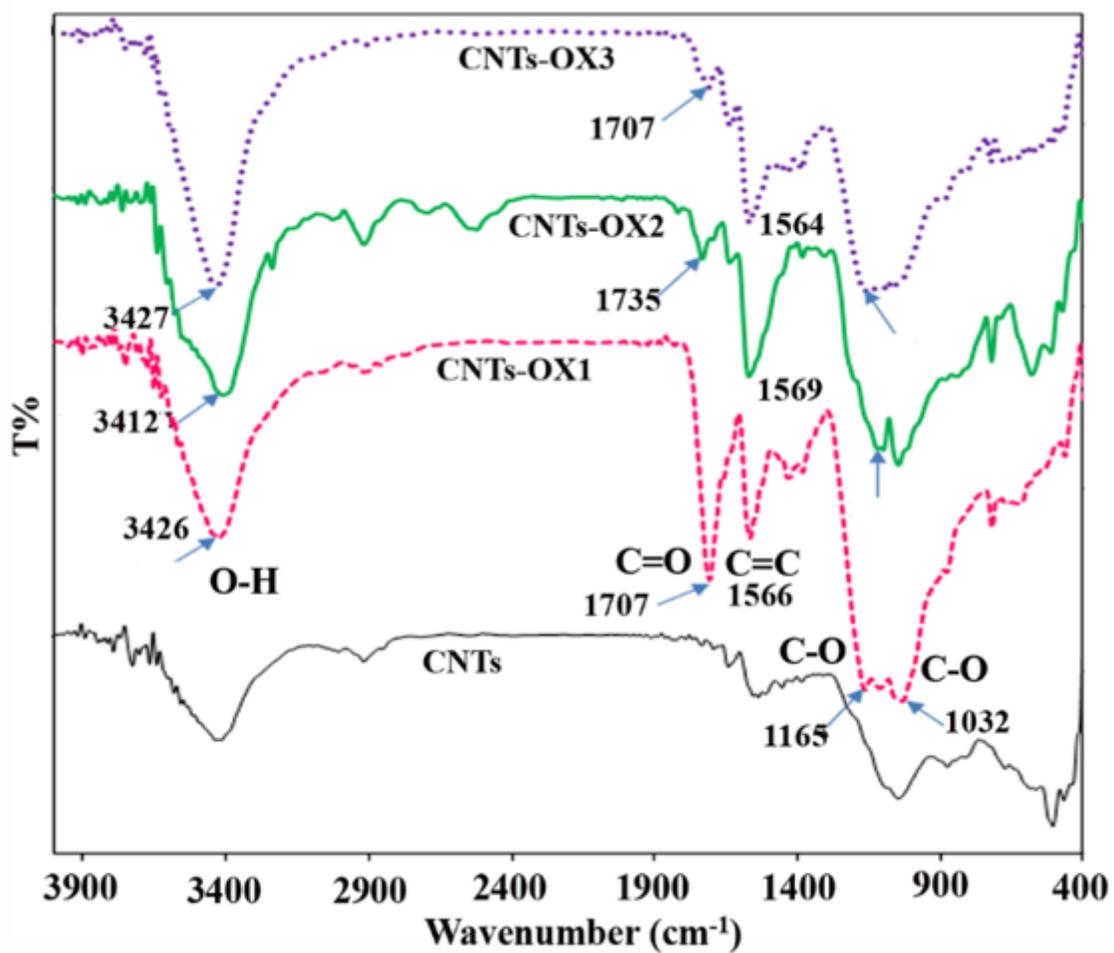


Figure 1

FTIR spectra of CNTs-OX₁₋₃ prepared with different oxidation methods (KBr)

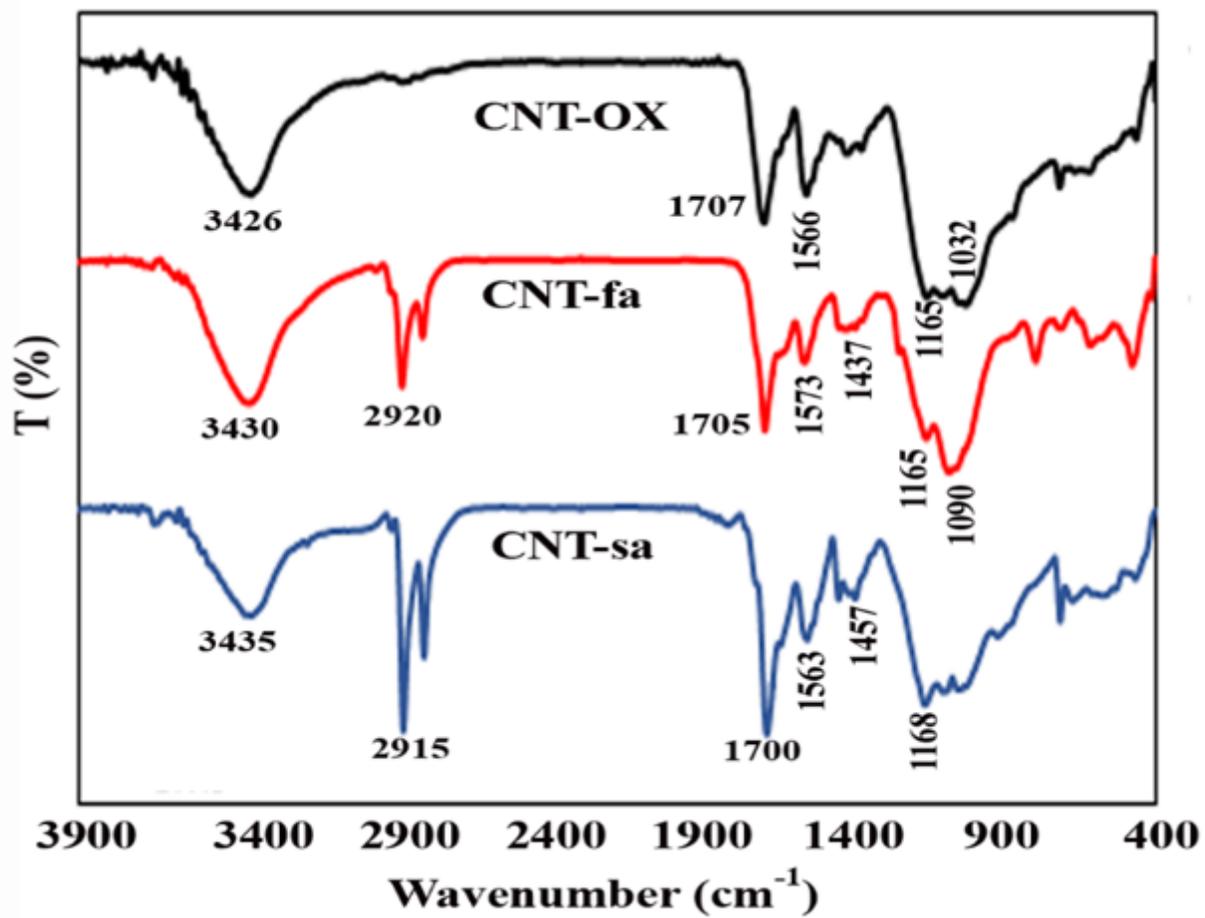


Figure 2

FT-IR spectra of CNT-OX₁, CNT-fa and CNT-sa (KBr)

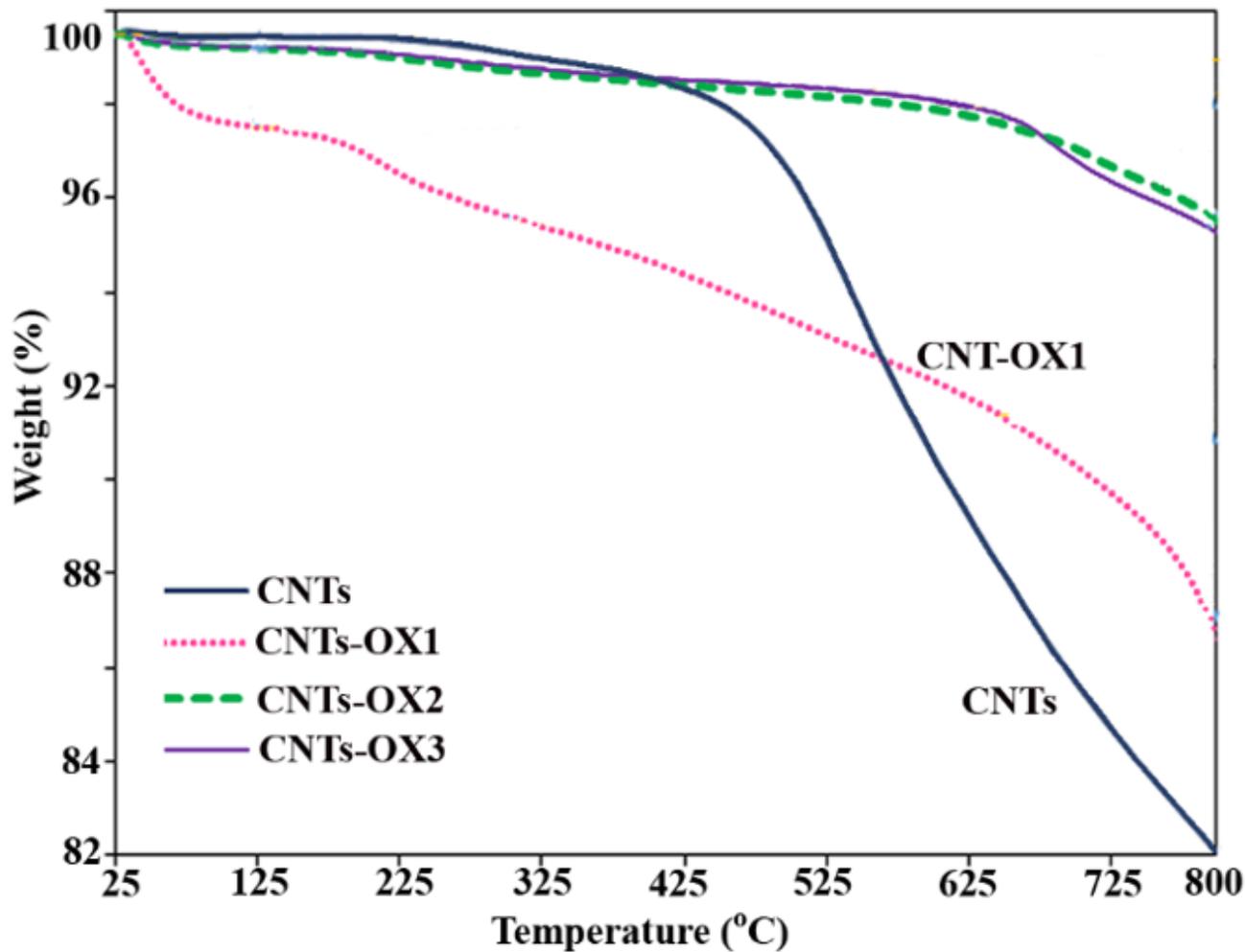


Figure 3

TGA traces of CNT & CNT-OX₁₋₃ prepared via reaction methods 1, 2 and 3.

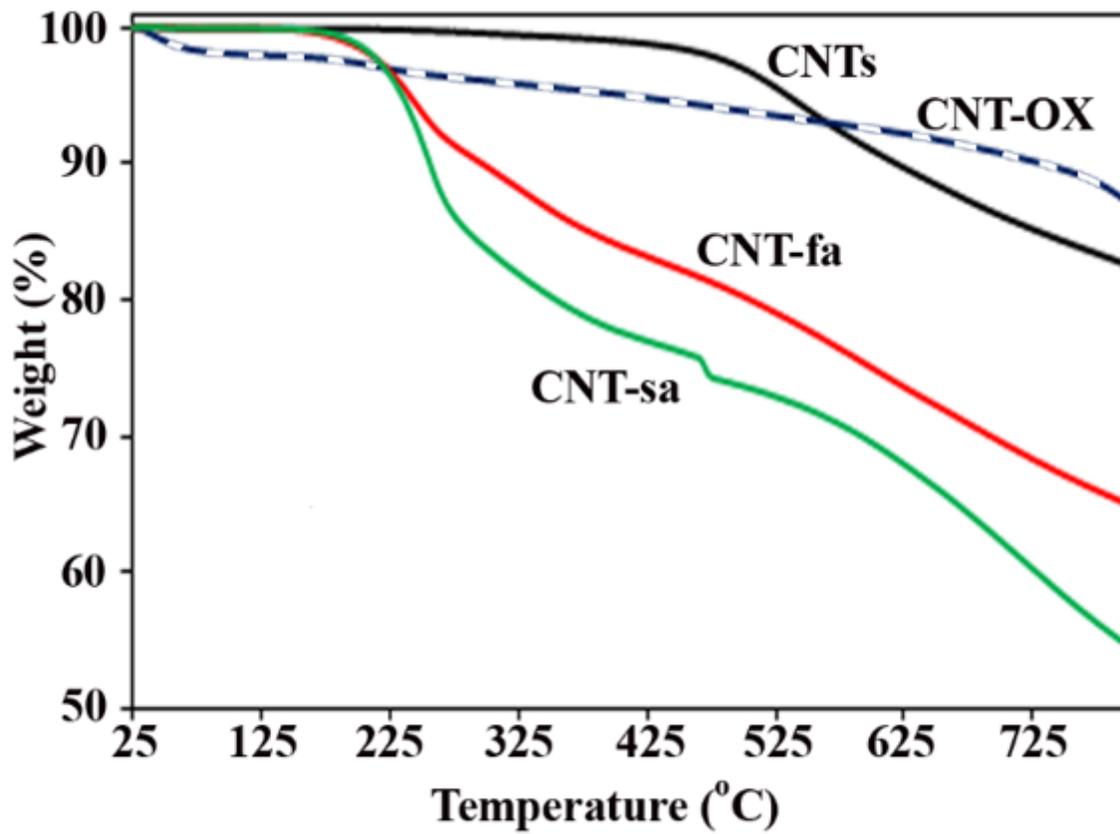


Figure 4

TGA curves of CNTs, CNTs-OX₁, CNTs-fa and CNTs-sa

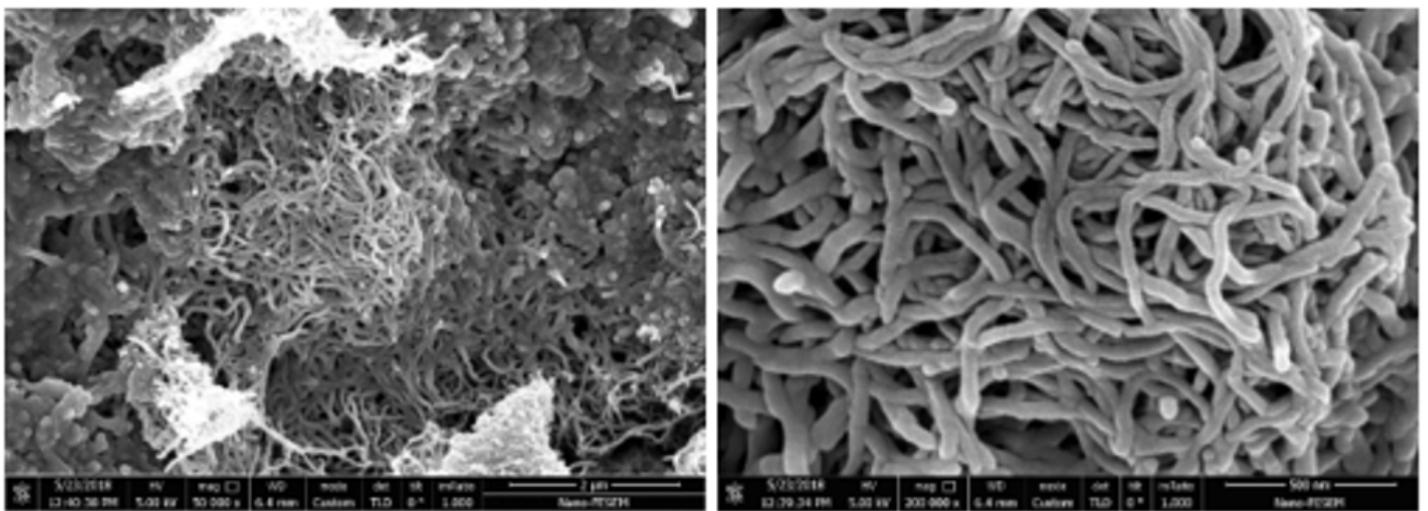


Figure 5

FESEM image of fatty acid modified CNTs

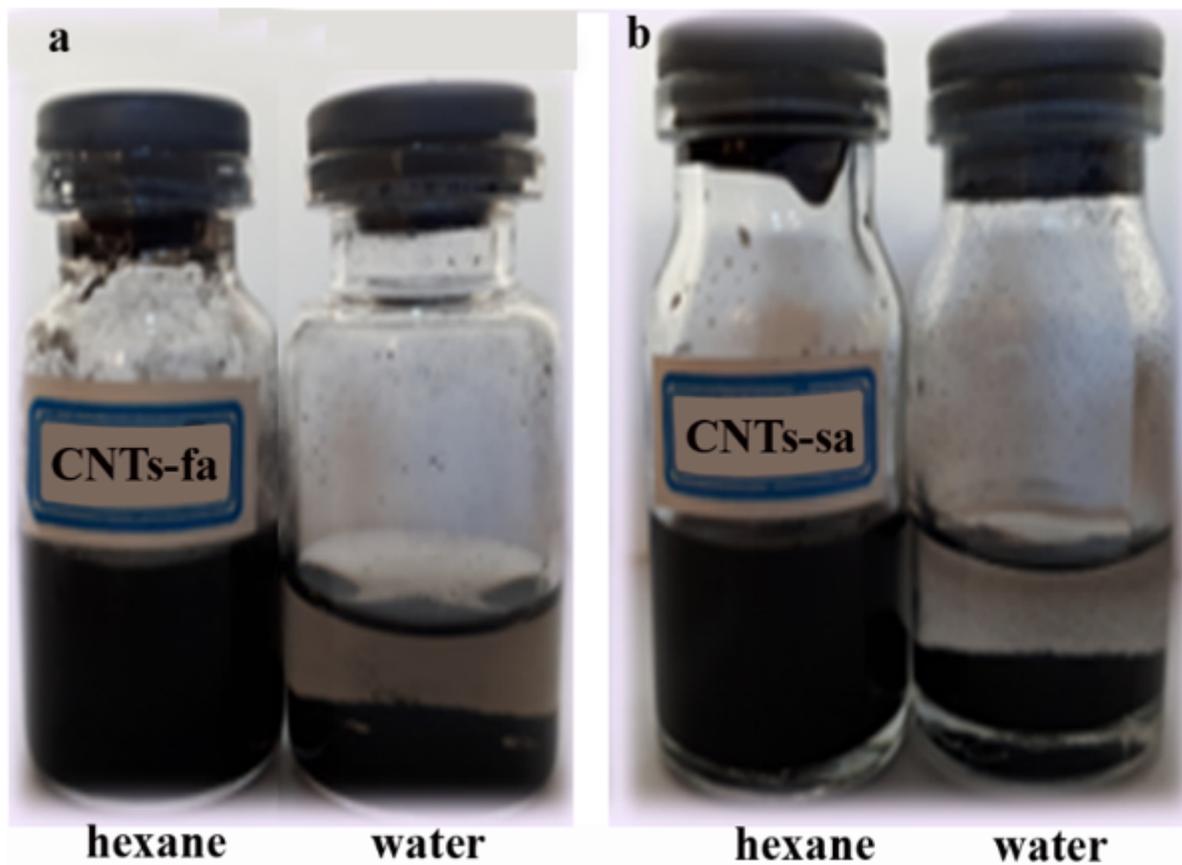


Figure 6

Pictures of the dispersion of (a) CNTs-fa and (b) CNTs-sa in the water and n-hexane. Samples were held for 12 h. CNTs were sonicated for 1 h to disperse in each solvent.

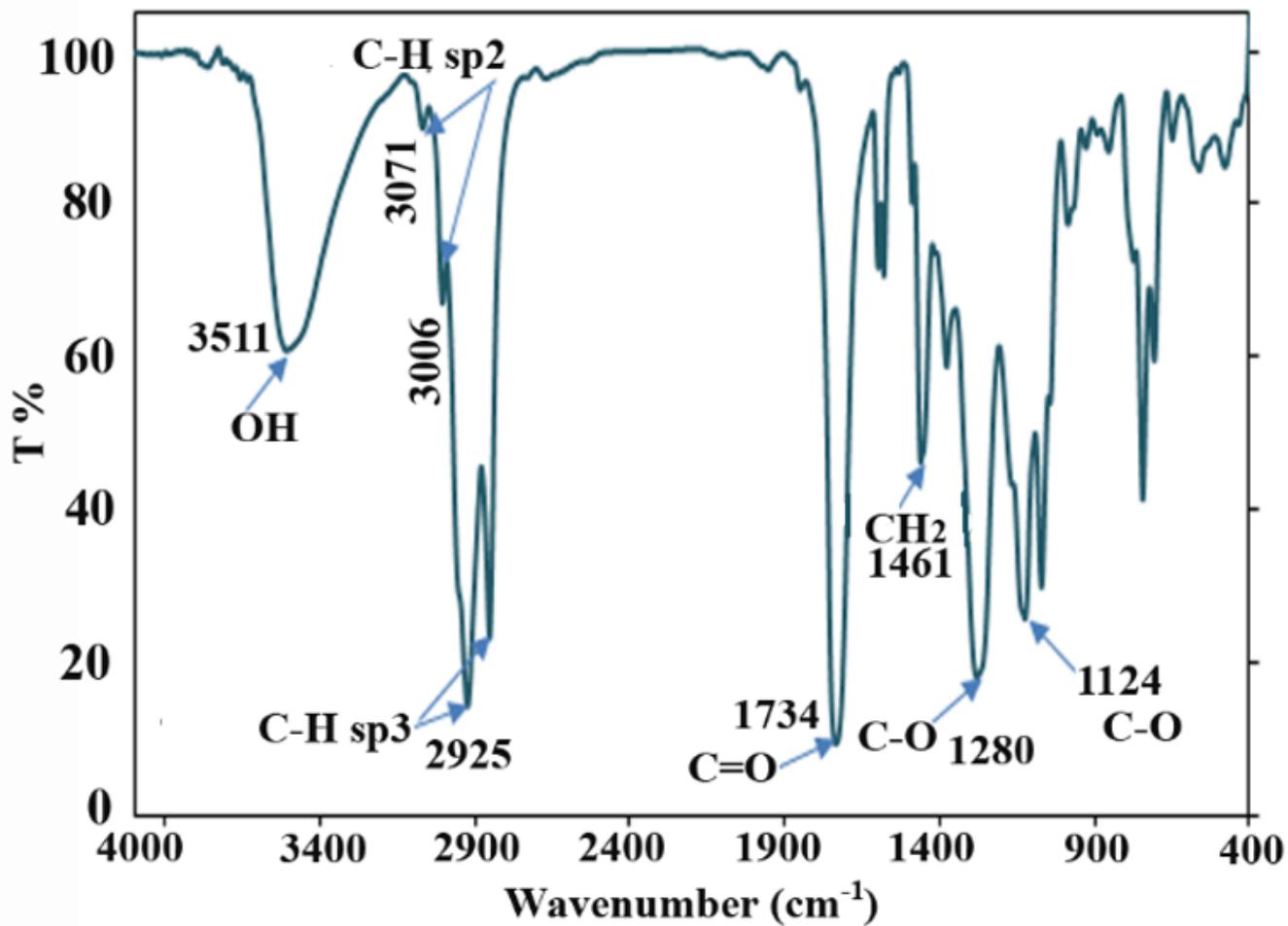


Figure 7

FTIR spectra of Alkyd resin before curing

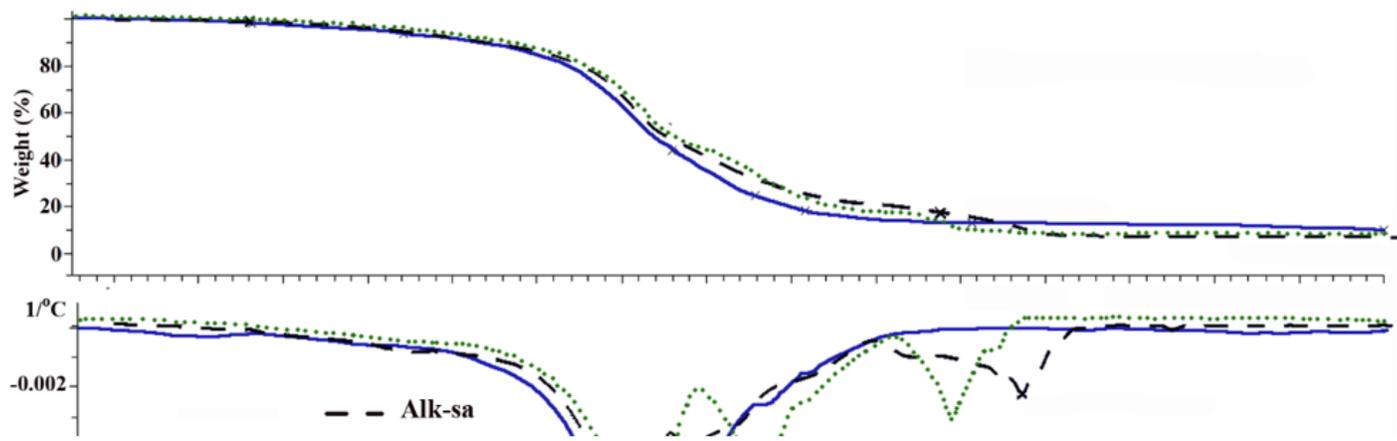


Figure 8

TGA curves of Alkyd film, ALK/CNTs-fa and ALK/CNTs-sa nanocomposites



Figure 9

Alkyd coatings after 50 days immersion in water + compost fertilizer mixture

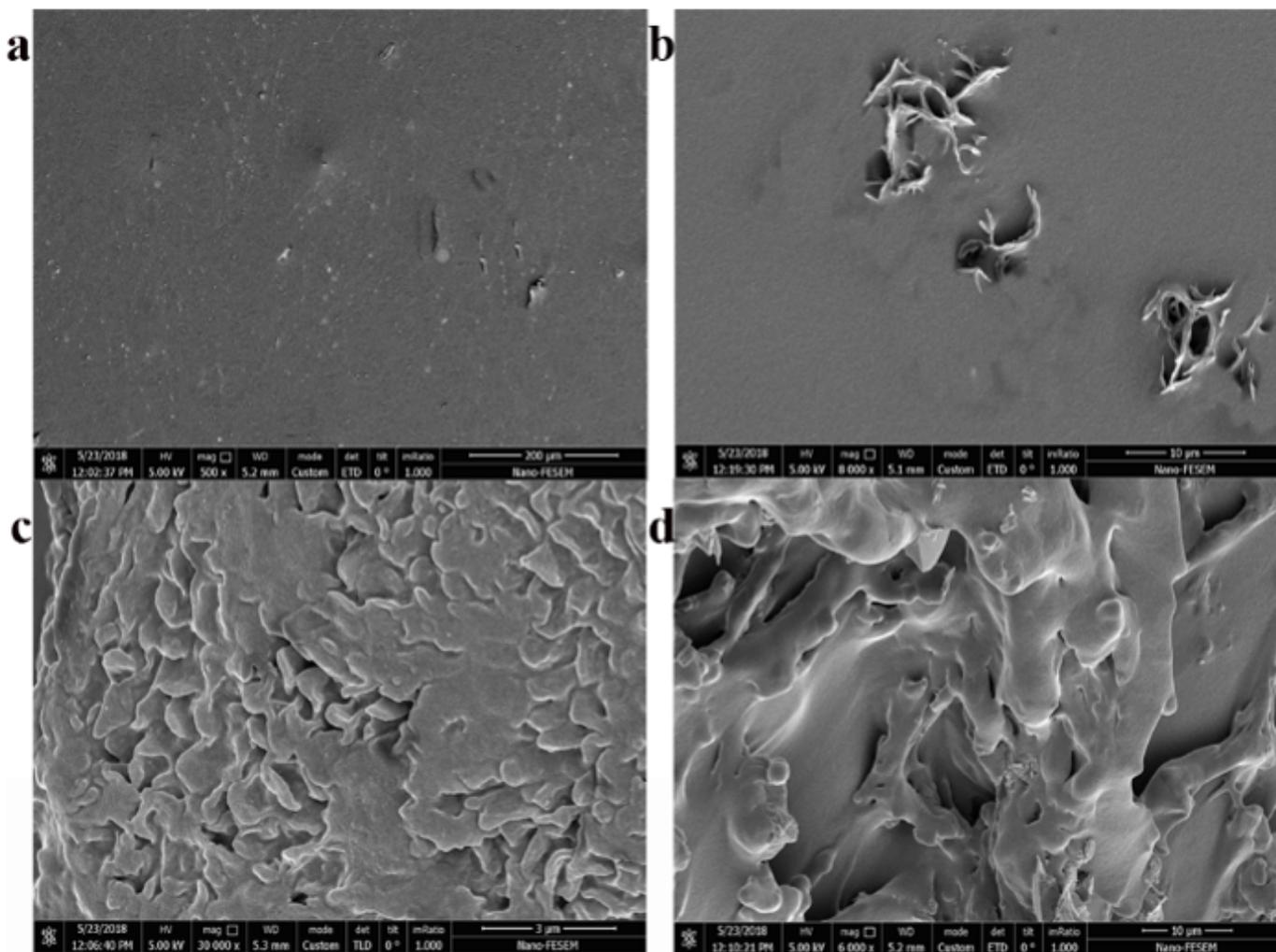


Figure 10

FESEM micrographs of Alk/modified-CNTs nanocomposite film with different magnification (a) 200 μm , (b) 10 μm , (c) 3 μm , (d) 10 μm .

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.png](#)
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