Nonflammable pre-carbonized polyacrylonitrile nanofiber webs

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Abstract

For non-flammability usages, composite structures with nano-additives or carbonized form of polyacrylonitrile (PAN) are generally preferred. In this study, a pre-carbonized form of nanofiber webs (OxPAN) is firstly proposed as a non-flammable material to eliminate the need for carbonization. The thermal oxidative stabilization process is applied to the PAN nanofibers to achieve high structural stability. This prevents melting and fusing during the thermal treatments and thereby improves the thermal stability of the web. PAN nanofiber webs were successfully obtained via the electrospinning technique and the thermal oxidation process was then applied. The structural properties of the oxidized PAN nanofiber webs were investigated by Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy, Raman Spectroscopy and X-Ray Photoelectron Spectroscopy and Electrochemical Impedance Spectroscopy. The surface morphology of the OxPAN was examined by scanning electron microscopy and the average fiber diameter was measured as 265 ± 64 nm. The thermal properties were analyzed with a differential scanning calorimeter and a thermal gravimetric analyzer. The flammability performance was tested via the Limiting Oxygen Index (LOI), and it was found that in addition to being lightweight, OxPAN nanofiber webs exhibit splendid performance with a LOI value of 48–49%.

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Graphic abstract

Keywords PAN nanofiber · Thermal oxidation · Nonflammable · Electrospinning · Carbon nanofiber

1 Introduction

The most common parameter of defining the flammability of materials is LOI which provides quantitative information about the burning of material [1] where higher LOI means improved flame retardant behavior [2]. Limiting oxygen index (LOI) defines the combustion behavior of the material and air contains 21% oxygen. The material is classified as “combustible” and “self-extinguishing” if LOI is below and above 21, respectively. Their combustion cannot be performed at ambient temperature without an external energy contribution. Thus, higher LOI means improved flame retardant behavior [2]. In the literature, the most common parameter of defining the flammability of material is LOI and it makes a chance to sort the flammability of the materials quantitatively according to their LOI values [1]. Example LOI values of some well-known fibers such as polyethylene, cotton, polyacrylonitrile, wool are measured as 18, 18–20, 19.9, 25, respectively [3–5]. According to environment-friendly solutions, the fire-retardant fibers should provide low smoke, low toxicity and should be halogen-free, in terms of environmental protection and human safety [6]. Figure 1 indicates some well-known LOI

% values of common polymeric fibrous materials together with the comparison between the findings of the study.

Commercial oxidized PAN fiber brands are; Pyromex® (Toho Tenax), Lastan® (Asahi), PANOX® (SGL Carbon Group), Zoltek® (Toray Group), and their LOI values for micro-level products varies between 40 and 60%. Oxidation process brings nonflammable as well as non-melting characteristics to PAN fiber which results from that; oxidized PAN fibers do not melt or adhere to the direct exposure to flame [1, 7]. Due to its excellent good thermal stability and chemical resistance, oxidized and thermally stabilized PAN nanofiber can be used in a wide variety of applications namely heat-protective clothing, spark protection in welding blankets, flame-retardant mattresses, in automotive and aviation industries, and in industrial seals and packaging thanks to its exceptional thermal stability and favorable chemical resistance. OxPAN nanofibers meet the expectations of these applications considering that they are heavily dependent on requiring a high surface to volume ratio. Therefore, while providing a lightweight feature, nanofibers in this way have a significant effect on such application properties.

Fig. 1 Selected LOI % values of common fibrous materials together with the finding of this study

In the literature, flammability performance of the polymeric materials is gained with either nanoparticle addition or usage of carbon fibers/nanofibers. In this study, different from the existing studies, a pre-carbonized form of nanofiber web (OxPAN) was developed to boost the non-flammability of the web in terms of nanofiber level. Due to its unique chemical structure (which does not burn, melt, drip or soften) oxidized and thermally stabilized polyacrylonitrile (OxPAN) nanofiber web was obtained as fire-retardant nanofibers which have a LOI value about 49%, is far superior in this respect to other organic fibers.

2 Materials and methods

Both Acrylonitrile (AN) 99% and DMF reagent grade were purchased from Sigma Aldrich and were used as received. Polyacrylonitrile was synthesized as explained in our previous studies via free radical polymerization [8]. Electrospinning is a facile method to produce submicron fibers. Electrospinning can be supported with needle or needles, in the needle system, polymeric solution or melt is drawn through the needle [9–11]. Electrospinning solution was placed into a syringe needle (outer diameter of 0.7 mm) which was connected to a high-voltage direct current (DC) power supply (ES 30 Model Gamma High Voltage Inc., Florida, USA). PAN solution was horizontally electrospun onto rotating collector wrapped with aluminum foil at 15 kV driving voltage with a collection distance of 15 cm. The flow rate of the solution was 0.8 mL/h and controlled by

a syringe pump (NE-500 Model, New Era Pump Systems, Inc. New York, USA).

PAN solution can be easily fabricated to obtain nanofiber web via electrospinning technique. During the electrospinning process rotating collector was used to achieve nanofiber orientation instead of the fixed collector. Rotating collector not only improves the fiber alignment but also assists to improve mechanical properties of the web [7]. The electrospinning solution was prepared according to the weight ratio (8%wt) of PAN/DMF and fed into the syringe. Electrospinning parameters were set to; 0.8 ml/h feeding ratio, 15 kV, 15 cm (tip to collector distance) and 400 rpm was the rotational speed of the collector during 4 h. Fabricated webs have a weight apx. 0.001 g for 1 × 1 cm pieces. Thermal oxidative stabilization of PAN nanofiber web Binder 9010 furnace was used and it was performed under oxygen-rich, ambient atmosphere during 1 h, at 300 °C (heating rate is 2 °C/min.) to obtain OxPAN web. Moreover, in order to prevent the shrinkage during thermal stabilization, stretching was applied to the samples with the purpose of improving the crystallinity and orientation and the image of the placement can be seen in Fig. 4 as an inset.

The structure of the samples was characterized by FTIR-ATR spectroscopy (Perkin Elmer, Spectrum One), with a Universal ATR attachment with a diamond and Zinc Selenide (ZnSe) crystal and an effective angle of incidence 45°, allowing to be used for sensitive polymer films, and powders, number of scans is 16, scan resolution 4 cm⁻¹ and scan range is 4000–650 cm⁻¹. Surface morphology of OxPAN nanofibers was examined via scanning electron microscopy (Quanta FEG 250-SEM) and samples were coated with thin gold film using a sputter to prevent the accumulation of charge on the sample surface. The microstructure of the sample was investigated by Raman spectroscopy, DXR Raman spectrometer- Thermo Scientific, was equipped with laser wavelength at 532 nm, brightfield/darkfield illumination, 10× microscope objective. Thermal properties of the samples were investigated via DSC (Perkin Elmer, Q4000), temperature and heat flow was calibrated before the measurement and via TGA (Q50, TA instruments) and heat rate is 10 °C/min.

For LOI measurements, the oxygen index module from Concept Equipment was used and during the measurement flow set as 17 nl/min at room temperature and it indicates the oxygen index directly in % Oxygen. During the measurement, the nanofiber web was attached inside the chimney of the device and waited to reach the stabilized flow rate in the chimney. After that flame was approached to the sample and the burning behavior of the sample was examined. At least 5 measurements were done to determine the LOI value of the sample. Gradually oxygen content of the chimney was increased during the

Fig. 2 **a** SEM image of OxPAN nanofiber web, **b** nanofiber diameter distribution

burning and to see which level oxygen content is enough to blow out the fire. Electrochemical Impedance (EIS) measurements were conducted with potentiostat 2263 Electrochemical Analyser (Princeton Applied Research, USA) were investigated in 0.1 M NaClO₄/ACN electrolyte in a frequency range of 10 mHz to 100 kHz at open circuit potential with an AC perturbation of 10 mV.

3 Results and discussions

The surface morphology of the OxPAN nanofibers was examined via SEM which is presented in Fig. 2a and magnification is 50000× and scale is 1 μm. Nanofiber alignment was achieved with a rotating collector and rotational speed was set to 400 rpm. Average nanofiber diameter measured as 265 ± 64 nm and nanofiber diameter distribution is shown as a histogram in Fig. 2b. Compared to bulk and nanofibers, it is assumed that OxPAN nanofibers present enhanced non-flammability behavior due to the increment on the surface area.

Nanofiber diameter was measured with ImageJ software and the average value is 265 ± 64 nm. Our previous studies showed that the oxidation process does not have a remarkable effect on the nanofiber diameter change and morphological properties [7, 8]. During the thermal oxidation process as a result of occurred chemical reactions color of the web changes and it can be explained by the rate of discoloration and of the rate of oxygen uptake [7, 12]. A significant reduction in the diameter is changed with the applied high temperatures during the carbonization process [13, 14].

Limiting Oxygen Index (LOI) test was carried out for oxidized web according to BS 4589-2 standard. LOI value of oxidized web was recorded as 48–49%. OxPAN nanofiber webs degraded without burning. It could be compared

with LOI values of some well-known fibers i.e., polyethylene, cotton, polyacrylonitrile, wool (Fig. 1) moreover, OxPAN nanofiber webs not only exhibits a high thermal stability but also represents the excellent heat and fire protection.

Due to the nanofiber web structure of samples Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (FTIR-ATR) is used for the characterization of samples since FTIR-ATR extensively in many applications that require surface-sensitive and/or non-destructive characterizations. When an infrared (IR) beam is totally reflected on the inner surface of an ATR crystal, an evanescent wave is generated and penetrates the sample in contact with the crystal. The sample molecules absorb the IR radiation with wavelengths corresponding to their characteristic

Fig. 3 FTIR-ATR results for synthesized PAN powder and OxPAN NF web and as an inset schematic description of the oxidation mechanism of PAN nanofibers

Fig. 4 Scheme of tentative stabilization mechanism and structure of pre-carbonized PAN nanofiber and color change of the nanofiber web before the treatment, during the treatment inside the furnace and end of the treatment

vibration modes. FTIR-ATR and Raman spectroscopy were used to record the characteristic peaks of the OxPAN and synthesized PAN powder. FTIR-ATR results were coherent with the literature and an absorption band of around 2243 cm^{-1} was assigned as $C\equiv N$ triple bond [15–17]. 1590 cm^{-1} was mainly assigned to $C=N$ double bond [15, 16, 18–22] also, together with the combination of $C=N$, $C=C$, $N-H$ [16, 18, 21, 22] and are presented in Fig. 3.

The thermal oxidation process has two main stages; one is named cyclization and consists of the conversion of $C\equiv N$ bonds to $C=N$ and the other stage is dehydrogenation which leads the aromatic and supramolecular structures [23] and seen from Fig. 4. These combined reactions promote the creation of a ladder structure from the linear molecule of PAN [22, 24, 25]. The oxidation process gives a chance to create a ladder-like structure from a linear polymer chain where ladder structure polymers are thermally more stable than the linear ones [24, 26, p. 734]. Conjugated $C=C$ structures generated from dehydrogenation or from imine-enamine tautomerization and subsequent isomerization [18]. During the oxidation step, triple $C\equiv N$ bonds start to become a double ($C=N$) bond and $C-N$, and the oxidation process is not enough to eliminate all $C\equiv N$ triple bonds [18–20, 22]. In cyclized structure nitrile group was converted to $C=N$ and $C-N$ groups and naphthyridine type rings were recorded and through the cyclization mechanism it was also recorded that absorbance of the $-C=N-$ content starts to increase

at the beginning of the oxidation process and after has a decreasing trend [15, 27, 28]. OxPAN has a relatively nonuniform structure with side chain groups [29]. During the dehydrogenation new peak appears at around 810 cm^{-1} due to $=C-H$ bonds [24, 30, 31] and was seen from Fig. 3. Moreover, a newly occurred peak around 1250 cm^{-1} , was assigned to the aliphatic CH group vibrations of different modes which come from CH and CH_2 [32, 33] and was pointed in Fig. 3. Byproducts of the oxidative degradation process are hydrogen cyanide (HCN), ammonia (NH_3), carbon oxides (CO_2) and water (H_2O) [1, 31, 34]. Oxidation supports to increment on carbonyl groups [35] and FTIR-ATR results indicated that; absorption of carbonyl groups was increased for the OxPAN. During the thermal oxidation process, $=C-H$ groups have created as the result of the aromatization of PAN and intensity of $=C-H$ groups and reduction of CH_2 groups was assigned to removed H atom from the CH_2 structure with the form of H_2O and this stage was named as dehydrogenation [24]. Oxidation is a chemically complex process and during the oxidation; linear polymer (PAN) transforms into a ladder structure which renders the polymer thermally stable and prevents melting through the carbonization [7, 36, 37]. The partially carbonized structure has achieved at the end of the thermal oxidation process.

Zhoe et al., studied that; fabricated clay/carbon nanofiber sheets combined with the polymeric matrix as a composite structure and it helps to reduce the heat

Fig. 5 **a** Raman spectroscopy of OxPAN nanofiber web, **b** XPS results of OxPAN nanofiber web, atomic % of elements and C 1s of OxPAN

release rates [38]. Another study showed that a hybrid nanopaper consisting carbon fiber lamination system helps to reduce heat release rate [39]. Commonly used nanoparticles (nanoclays, carbon nanofibers, and carbon nanotubes) for the fabrication of polymer nanocomposites not only reduce the flammability of the material but also improves the mechanical properties [39–41]. In this study, as an alternative to the addition of the nanoparticles in the polymeric matrix, directly polymeric nanofiber web is thermally treated and enhanced non-flammability property is achieved.

Peaks around 1340 cm⁻¹ and 1580–1600 cm⁻¹ have been defined as a D and G band respectively [42–45]. The intensity ratio of D band to the G band (I_D/I_G) which was previously defined as R value in the literature indicates the amount of structurally ordered graphite crystallites in the carbonaceous materials [45–47]. Figure 5a presents the characteristic peaks and peak centered near 1588 cm⁻¹ assigns the ordered graphitic crystallites of the carbons [48]. It was known that a perfect single crystal of graphite has a sharp single band at around 1588 cm⁻¹ [44]. The wavenumber of around 1340 cm⁻¹ is related to disordered turbostratic structures, and named as D band, whereas G band is related to ordered graphitic structures [42]. sp² hybridization of carbon atoms has an important role in the formation of the honeycomb structure. In this study OxPAN is not totally converted to carbon thus, the intensity of the G band is lower and R value was 3.6 for OxPAN. But the lower I_D/I_G value indicates higher crystallinity and an increased carbon amount in terms of graphitization [45].

During the oxidation process removal of -HCN resultant with the removal of N₂ and oxygen uptake through the thermal oxidation process assists to increment on the O₂ amount [44]. Oxidation reaction promotes the formation

of carbonyl groups [49]. While carbon and nitrogen content were decreased through the thermal oxidation process, the oxygen content was increased inside the partially aromatic structure. Figure 5b indicates the XPS measurement and C1s at 285 eV was recorded which has the coherency with the literature and indicates the comprise of carbonyl, carboxyl and neutral carbons [44]. Carbon, oxygen, and nitrogen content were changed through the oxidation process and oxygen amount was increased for OxPAN due to oxygen uptake which can be seen in Fig. 5b. Also, nitrogen amount did not change dramatically during the oxidation process, more energy is needed for breaking the nitrogen bonds thus further process with carbonization or graphitization promotes the removal of nitrogen atoms.

Combustion is a complex process, however, it proceeds with the volatiles occurred during the polymer degradation which reacts with oxygen in the air associating with the generation of a variety of radicals and heat releases during burning [50].

Thermal analysis methods provide to detect the cyclization reaction of PAN due to the released intensive heat [51]. Figure 6a is pointed out that; TGA results under nitrogen and oxygen environments before the oxidation process PAN NF web dramatically lost its weight under O₂ however under N₂ reduction of weight is not major. It can be seen from Fig. 6a oxidation has a positive effect on the thermal stability of the nanofiber web. 300 °C has a critical role in the oxidation process, weight loss becomes significant after 300 °C if, the web is not thermally stable. OxPAN is sufficiently stable due to that; high-temperature treatment under the nitrogen environment does not assist significantly for further degradation on the sample [46]. OxPAN nanofibers do not exhibit a reduction of weight which is the proof of reduced degradation and thermally stabilized OxPAN web.

Fig. 6 **a** TGA curves of OxPAN nanofiber web and not oxidized nanofiber webs under N₂ and O₂, **b** DSC curves of OxPAN nanofiber web, PAN as powder form and PAN as nanofiber form

Fig. 7 (A) Nyquist diagrams of OxPAN and, (B) bode plots of OxPAN nanofiber webs

During the oxidation process, oxygen content gradually increases as a function of the temperature. Also, the oxidation temperature has an effect on the mechanical performance of the samples, improved oxygen content above the 300 °C results the decrease in the strength of the sample [52, 53].

Figure 6b, shows the DSC curves of powder and nanofiber form of PAN and peak values are quite similar however, the OxPAN nanofiber web exhibits a totally different curve due to its changed chemical structure. Both PAN powder and nanofiber tend to degrade around 300 °C due to its exothermic reactions; cyclization and cross-linking from -CN groups which are mentioned as exothermic reactions and followed by the oxidative reaction under the air [49]. Exothermic reaction promotes to accelerate

the degradation of the cyclic structure [54]. Onset point of the exothermic reaction represents the initiation of acrylonitrile cyclization hence greater the cyclization for PAN is, represents the less exothermic peak for oxidized PAN [55, 56] and heat release peak disappeared when oxidation temperature exceeds 250 °C [56]. Thus, after the oxidation process, a sharp peak around 300 °C which refers to the degradation did not record for the OxPAN, furthermore, it is the proof of oxidation that provides a more stable chemical structure. Thanks to the pre-carbonized structural form of OxPAN, the degradation process enhanced in terms of thermal stability towards flame without melting or dripping.

The EIS measurements of nanofiber webs were used as a self-standing working electrode. When EIS results (Fig. 7) were evaluated together with our previous studies [34, 57], the linear chain form of the PAN changed as a partially cyclized structure with side groups, around 100 times lower charge transfer resistances were obtained compared to Graphene oxide containing oxidized PAN nanofibers indicating the formation of cyclized structure which will be disturbed by the presence of graphene oxide in the structure. The oxidized linear structure of PAN becomes more resistive with the increased oxidation temperature due to its newly occurred partially cyclized form, which surrounds with side groups. For the oxidized PAN nanofibers, disappearance of the nitrile band indicates the cyclization of the linear polymeric structure. PAN nanofiber web shrinks in the electrolyte without thermal treatment and it is not suitable to get reliable results and use it as a self-standing electrode, but after the stabilizing of web of OxPAN nanofiber it can be properly used in this form as a self-standing working electrode. From Nyquist plots, the semi-circle represents the charge transfer resistance (R_{ct})

of the sample and the starting point of the Nyquist plot represents the solution resistance combination of the connection and attachment resistance.

4 Conclusions

In this study, OxPAN webs with a diameter of 265 ± 64 nm were fabricated to produce a fire-retardant unique chemical structure which does not burn, melt, drip or soften, leading to a LOI of about 49% which makes it far superior to other organic fibers in this respect and allows it to be classified as a non-flammable material. Through the oxidation process, dehydrogenation and cyclization were induced to create stable honeycomb-shaped polymeric structures. The most notable result is that OxPAN is a nano-sized material that exhibits a flame-retardant property. The fact that, a higher LOI value is obtained from partially carbonized nanofiber webs is considered as a success in terms of energy usage and cost efficiency. OxPAN nanofiber webs have not only an excellent flame-retardant property but also better performance concerning resistance to chemical reagents than synthetic nanofibers. Thus, in the search to improve the fire retardancy of materials, fabricating polymeric OxPAN nanofiber webs can be a good alternative to nanoparticle addition or the carbonization process, when the level of flammability and the light weight of the materials are critical factors.

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Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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