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High flame resistant and strong electrospun polyacrylonitrile–carbon nanotubes–ochre nanofibers

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ABSTRACT

Environmentally friendly, colorful, and flexible electrospun polyacrylonitrile (PAN)–carbon nanotubes (CNTs)–ochre (Oc) nanofibers (as-spun, stabilized) with very high flame resistance (heat release capacity of 24–143 J g^{-1} K^{-1}, total heat release of 2.1–8.7 kJ g^{-1}, char yield of 55–74%, limiting oxygen index of 22.5–34.5%) and mechanical properties (ultimate tensile strength of 80–177 MPa) were produced using a mineral, non-toxic, economic Oc and CNT in 1% CNTs and 10% Oc based on polymer concentration from a predominant synergistic effect between CNTs and Oc. This approach using a mineral material is an environmentally friendly method which may possibly solve a number of problems related to materials science and economics such as improving a flame resistance and lowering the cost for various applications in automobile, protective textile, and other areas.

1. Introduction

The damage to human life by fire and the toxic gas it generates has been increasing, but the dilemmas between flame retardation and toxicity still remain, although smoking and fire deaths are rapidly decreasing [1–3]. Proposed new flammability regulations could add tens of millions of additional pounds of potentially toxic flame-retardant chemicals such as bromine- and chlorine-containing flame retardants to bed clothing and foam used in upholstered furniture [1–3]. In California, Assemblyman Mark Leno introduced AB 706, a bill that authorizes the state to consider human health and environmentally impacts, as well as fire safety, when regulating flammability. This bill would prohibit the most toxic classes of chemicals in furniture, mattresses, and bed clothing and stop the cycle of replacing one toxic flame retardant with another. New European regulations for the Registration, Evaluation, and Authorization of Chemicals (REACH) require industry to provide data to establish the safety of new and existing chemicals [2]. Flame retardant chemicals in our homes should not pose a greater hazard to our health and environment than the risk of the fires they are supposed to prevent. Equivalent or greater fire safety can be achieved with new technologies and materials, furniture design, and green chemistry [2]. One strategy, to reduce a smoke density without toxic halogen gases is to induce char formation which can act as a barrier and prevent flame spread during a combustion process.

The influence of nanoscale materials such as clays, carbon nanotubes has shown to improve the flame resistance, thermal, mechanical, and electrical properties of polymers [4–10]. However, there are no reports in the literature investigating the flame resistance properties of ochre (Oc, a mineral) in electrospun polymer nanofibers system even though they have been widely used in flame resistant and biomedical applications, and other areas.

Electrospinning enables production of continuous polymer nanofibers that can be used in protective clothing, biomedicine, composites, and other areas, these nanofibers are expected to possess high axial strength combined with extreme flexibility and very high open porosity coupled with remarkable specific surface area [11].

Introduction of mineral fillers into a polymer makes it possible to solve a number of problems related to materials science (extending the raw materials base, improving the flame resistance property, etc.), technology (controlling the viscosity and thermal stability), and economics (lowering the production cost of polymeric composites materials) [12].

Oc, economic material, is a natural composite composed of kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$), montmorillonite ($Al_2O_3 \cdot 4SiO_2 \cdot 6H_2O$), pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$), illite ($KAl_2(OH)_2[AlSi_3(O,OH)_{10}]$), talc ($3MgO \cdot 4SiO_2 \cdot H_2O$), and iron oxides. Oc, which has a honeycombed/duplex structure and a high specific area, is among the earliest pigments used by mankind, derived from naturally tinted

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clay containing mineral oxides [12–14]. It can be efficiently used as a compatibilizer [14] and flame retardant with a smoke-suppressing effect from their instinct high absorption and viscous properties, and variable inorganic components.

Here, we report on an environmentally friendly method to improve the flame resistance using carbon nanotubes (CNTs) and Oc with various inorganic components and high specific surface area in an electrospun polymer nanofibers system. The polyacrylonitrile (PAN)–CNTs–Oc nanofibers without toxic flame retardant chemicals were prepared by convenient electrospinning technique considering various potential applications such as automobile, protective textile, and other areas. The morphology, flame resistance, and mechanical properties of as-spun and stabilized electrospun nanofibers are reported herein.

2. Experimental

2.1. Materials

PAN copolymer with a molecular weight of 112,000 g mol^{-1} was received from an industrial source. Dimethylformamide (DMF) was obtained from Sigma Aldrich Co. Single-walled carbon nanotube (SWCNT) with diameter of 1.2–1.5 nm was obtained from Sigma Aldrich Co., and multi-walled carbon nanotube (MWCNT) with diameter of 3–20 nm was purchased from Wako Pure Chemical Ind. Oc, dried and sterilized, was purchased from Chamtowon Co. (Republic of Korea) [14]. The energy dispersive X-ray spectroscopy (EDS) data of aggregated Oc with nano-to-micron size were shown in Fig. 1.

2.2. Electrospinning set-up

The compositions of the PAN–CNTs–Oc solutions are presented in Table 1. All solutions of PAN–CNTs–Oc in DMF were prepared at room temperature under constant mixing. The electrospinning apparatus consists of a high voltage power supply, a syringe infusion pump, and a grounded stationary (a rectangular, 20 cm × 15 cm, aluminum foil) and rotating (10.2 cm diameter × 2.4 cm width) target. Polymer solution is loaded into a 10 mL syringe capped with a 18-gauge blunt needle and an electrode is clipped onto the needle. The needle, electrode, and grounded target are all enclosed in order to reduce the effect of air currents on the trajectory of the electrospun jet. The flow rate of the solution to the needle tip is maintained

Table 1
Composition of the PAN–CNTs–Oc solutions and average diameter of the electrospun nanofibers made at applied voltage of 16 kV, flow rate of 0.004 mL m^{-1}, take-up velocity of 9.8 m s^{-1}, and distance to target of 14 cm.

Samples	Composition (%)				Average diameter (nm)
	PAN	CNT	Oc	DMF	
10P[a]	10.0	–	–	90.0	155 ± 25
10P–0.1SWCNT[b]	10.0	0.1	–	89.9	160 ± 34
10P–0.2SWCNT	10.0	0.2	–	89.8	166 ± 40
10P–0.2MWCNT[c]	10.0	0.2	–	89.8	175 ± 45
10P–1.0Oc[d]	10.0	–	1.0	89.0	163 ± 35
10P–2.0Oc	10.0	–	2.0	88.0	174 ± 28
10P–0.1SWCNT–0.5Oc	10.0	0.1	0.5	89.4	161 ± 37
10P–0.1SWCNT–1.0Oc	10.0	0.1	1.0	88.9	162 ± 27
10P–0.1SWCNT–2.0Oc	10.0	0.1	2.0	87.9	170 ± 30
10P–0.2SWCNT–2.0Oc	10.0	0.2	2.0	87.8	176 ± 42
St220[e]–10P-brown	10.0	–	–	90.0	144 ± 22
St220–10P–0.1 SWCNT–1.0Oc-brown	10.0	0.1	1.0	88.9	153 ± 25
St240[f]–10P–0.1 SWCNT–1.0Oc-dark brown	10.0	0.1	1.0	88.9	150 ± 20
Commercial-St–PAN microfiber-black	–	–	–	–	1051 ± 89

[a] P: polyacrylonitrile (PAN) copolymer.
[b] SWCNT: single-walled carbon nanotube.
[c] MWCNT: multi-walled carbon nanotube.
[d] Oc: ochre.
[e] St220: stabilized at 200 °C/30 min → 220 °C/30 min.
[f] St240: stabilized at 200 °C/60 min → 230 °C/60 min → 240 °C/60 min.

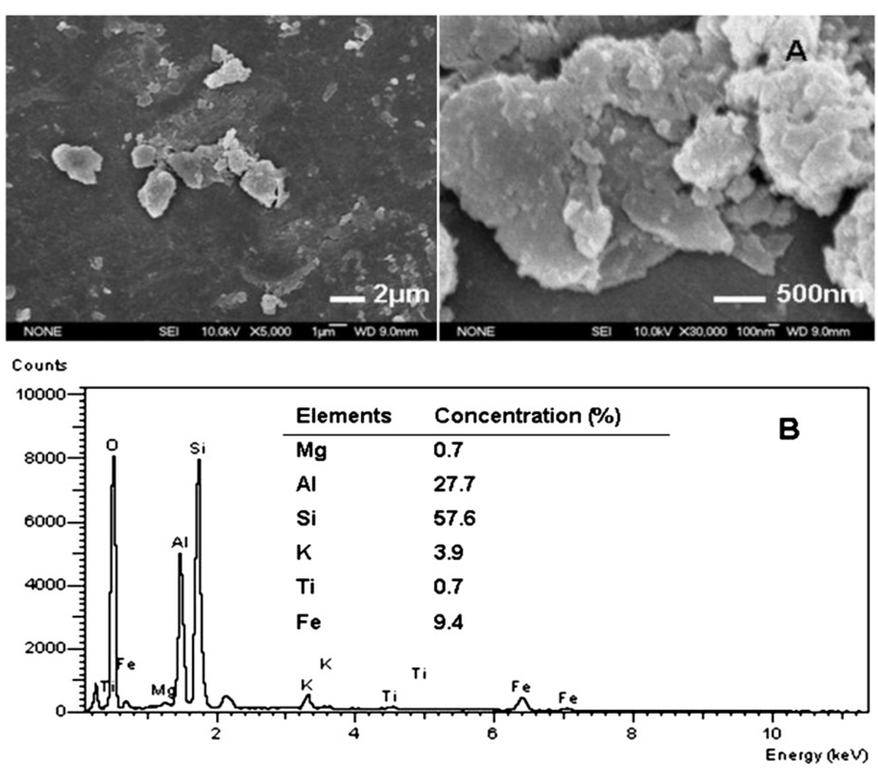

Fig. 1. A) SEM images and B) EDS data of the aggregated Oc with nano-to-micron size.