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Custom-built electrostatics and supplementary bonding in the design of reinforced Collagen-g-P(methyl methacrylate-*co*-ethyl acrylate)/ nylon 66 core-shell fibers

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ABSTRACT

In this study, Acid Soluble Collagen-g-P(methyl methacrylate-*co*-ethyl acrylate) (CME) was synthesized to take advantage of the flexibility of the resulted branched polymer chains and the high density of their chain entanglement. The coaxial electrospinning technique was applied to study the effect of electrically and structurally varied materials on fiber formation and fiber morphology when CME and Nylon 66 were electrospun as core and shell respectively. By tailoring the electrostatic field, different fiber content was achieved. The effect of chain orientation and intermolecular forces between the polymeric chains was investigated in the formed fibers by measuring thermal and mechanical properties, hydration degree and degradability. This approach to in situ fiber formation is not restricted to biomedical but has potential end-uses in a variety of multi-functional applications.

1. Introduction

Development of engineered materials with tailored properties e.g. thermal or mechanical for specific applications is a promising field in material science (Correia et al., 2016; Pezzoli et al., 2017). In biomaterials and particularly in natural-based polymers such as collagen, it is essential to modify their properties to desired conditions (Averous and Pollet, 2011; Bledzki and Gassan, 1999; Li et al., 2002). There are several methods for modifying natural-based polymers such as grafting, blending and curing and associated derivations (Bhattacharya and Misra, 2004; Kaith et al., 2009).

Collagen is a natural polymer with excellent biocompatibility that cannot be applied freely due to its inherent drawbacks such as poor mechanical properties and fast degradability when their protein chains are switched to random coil conformation (Li et al., 2005, 2013; Poormasjedi-Meibod et al., 2016; Yang et al., 2008; Zeugolis et al., 2008). Most researches on collagen, are focused on reducing its hydrophilic behavior whilst benefiting from its controllable biodegradation (Abbah et al., 2015). Therefore, the main uses of collagen-based materials have been found in drug delivery, filtration, tissue scaffolds and wound dressing by mostly applying crosslinking methods (Li et al., 2005; Mariod and Adam, 2013; Matthews et al., 2002). These methods are basically performed as post-treatment on produced collagen-based materials, e.g., films and fibrous assemblies. However, it is believed that prior to reaching the post-treatment step, collagen chains lose their properties, e.g., thermal and mechanical, to conform to severe process conditions (Yang et al., 2008; Zeugolis et al., 2008).

The lost properties are mostly due to the fast denaturation of hydrolyzing chain of the collagen in acidic solvents. Even though high concentration solutions (Cross et al., 2010) and applying salt crystals (Zeugolis et al., 2009) can slightly reduce the effect of the acid denaturation on electrostatic repulsion resulting from the positive charge build-up, the complete elimination of ions before crosslinking can be problematic for desired morphologies. However, collagen can be modified by graft polymerization to reduce its superhydrophilicity and to control biodegradation (Bhuiyan et al., 2015; Fujisawa and Kadoma, 2010; Solouk et al., 2015). This methodology can be applied to collagen and its derivations before processing. In this approach, different vinyl group monomers with varied physiochemical properties can be branched over the protein chain.

Hence, to control the degradation rate and hydrophilicity of the collagen chains, the achieved branched copolymer can have new behaviors different from the origin (e.g., rheological, thermal, electrical) (Bazrafshan and Stylios, 2017). This presents new challenges and opportunities. More specifically, in fiber formation, collagen-based copolymers with branched structure require to be spun under specific conditions to prevent Rayleigh instability of high entanglements. This issue can be easily addressed by the electrospinning method (McKee et al.,

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2004; Song et al., 2017; Wood-Adams et al., 2000) when the branched copolymers are spun in low concentrations.

When it comes to mechanical reinforcement of collagen-based materials, blending with (semi-)synthetics is mainly recommended in traditional fiber formation methodologies (Mercader et al., 2010; Satyanarayana et al., 2009). Even though, this method is not as simple as it seems; phase segregations and viscosity changes are the simple examples of incompatible (co)polymeric fluids. This issue is due to different properties such as electrical and structural that can significantly limit the application (Krissinel and Henrick, 2007) of collagen-based materials in fibrous assemblies. Interestingly, with coaxial electrospinning, working fluids with a wide variety of properties can be tuned for creating core-shell nanostructures (Bhardwaj and Kundu, 2010) simply with pure solvents (Wang et al., 2017; Yu et al., 2017). However, the performance of this technique in large scale fiber formation and fiber collection is still in its infancy.

In this work, we investigate a new approach to form hierarchical, robust fibrous electrospun collagen-based materials which have a promising potential to conjugate with a variety of nanostructured materials from minerals to medicines. This is a novel attempt for spinning hydrophilic collagen-based polymers whilst improving their mechanical properties. This is achieved by benefitting from the different performance of the participated materials by supplementary bonding. P (Methyl Methacrylate-*co*-Ethyl Acrylate) was grafted onto the acid soluble collagen (ASC). The ASC-g-P(MMA-*co*-EA) was co-electrospun wherein Nylon 66 was used as a core fluid. End-uses can consequently take the advantage of in situ fiber formation of the natural segment of collagen in the shell and mechanical strength of the core as a composite in the shape of a fiber to fabric, as shown in Fig. 1. We show that different polymeric content in core and shell can demonstrate improved properties by means of a tunable electrical field. The mechanical, chemical, thermal and swelling behaviors of the core-shell composite fiber structure were established. This work can be considered as a promising alternative to existing fibrous assemblies intending to exploit the advantages of chain flexibility in hydrophilic reinforced copolymers.

2. Materials and methods

2.1. Materials

Collagen from cow skin was provided by Devro Company Inc., UK. Methyl methacrylate (MMA, 99%, Alfa Aesar), Ethyl Acrylate (EA, 99%, Alfa Aesar) were used as process monomers and were passed through a column of 5% sodium hydroxide acquis solution to remove any inhibitor existed in them. Benzoyl peroxide (BPO,97%, Alfa Aesar) was used as initiator and recrystallized in Acetone before applying. Distilled water was used as a medium in the polymerization process. Acetic acid (AA, 99.7%, Alfa Aesar), Formic Acid (FA, 97%, Alfa Aesar), Nylon 66 (N66, 262.35 g mol^{-1}, Sigma Aldrich) and Methanol (MeOH, 99.9%, Alfa Aesar) were applied as received. D&C Red 28 (Rdye, Acid Red 92, Clariant, Switzerland) and Sanolin Tartrazine X90 (Ydye, Acid Yellow 23) were utilized as tinted indicators to distinguish the core and shell components, respectively.

2.2. Synthesis of ASC-g-P(MMA-co-EA)

The procedure of the copolymer synthesis has been reported in detail in our previous work (Bazrafshan and Stylios, 2017). A typical graft polymerization procedure (See supplementary data, Fig. 1) was applied for the synthesis of branched ASC-g-P(MMA-*co*-EA (CME). Briefly, ASC (11 g) was prepared using collagen in 0.1 M of AA and

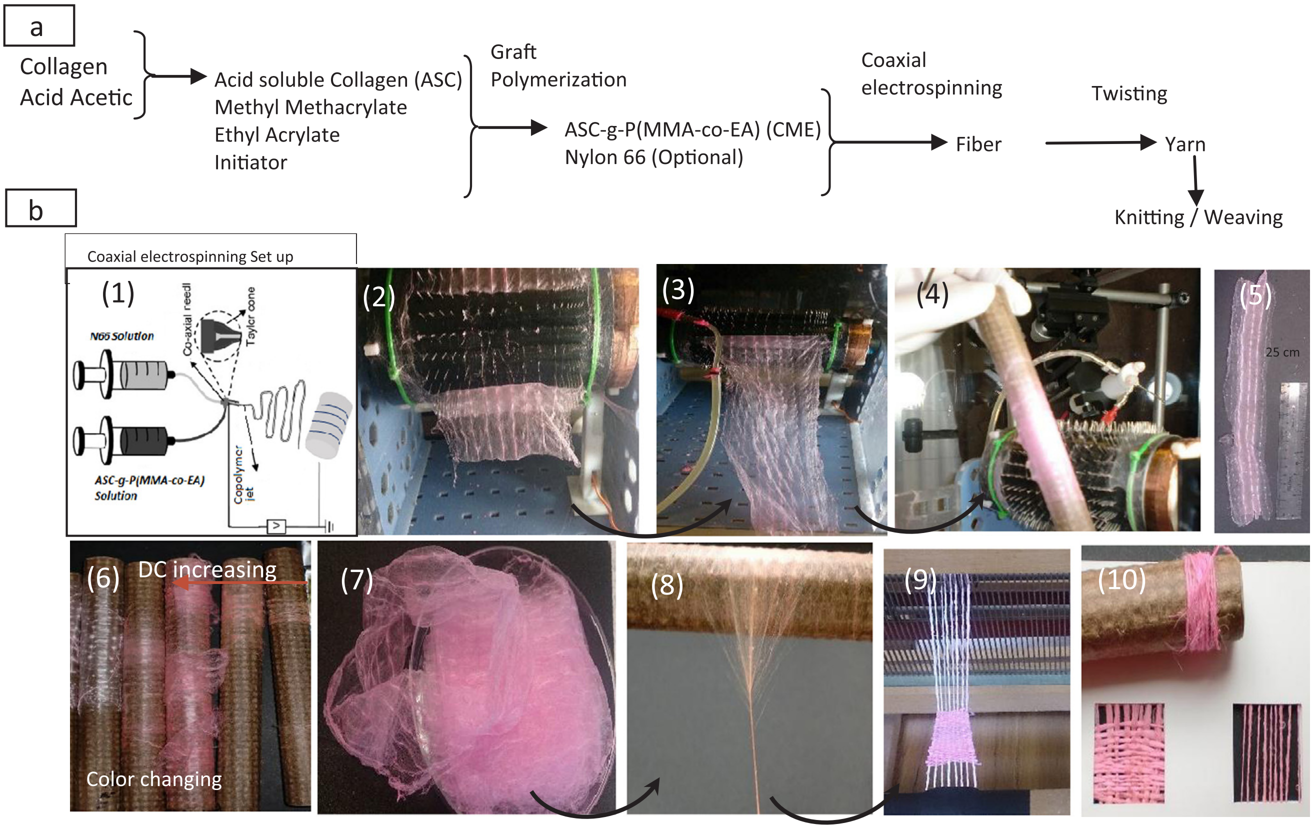

Fig. 1. (a) Process chart of CME/N66 yarn and potentially fabric production. (b) Coaxial electrospinning process and yarn twisting. (1) Coaxial electrospinning using rotating drum as a collector. (2 – 5) Manually CME/N66 filaments were taken up around the nail drum (6) the color changing from pinkish yellow to yellowish pink by increasing the applied voltage that indicates the varied fiber in components. (7 – 10) The fibers were twisted into a yarn with clockwise twisting(S-twists) that is mechanically strong to be knitted /woven.