Hyaluronic acid (HA)-based photocurable hydrogels

HA is a non-adhesive glycosaminoglycan, prevalent in connective, epithelial, and neural tissues. Since HA is involved in wound healing and angiogenesis and can interact with cell surface receptors like CD44, CD54 and CD168, it has been used for studies on tissue regeneration as well as drug delivery (Bae et al. 2014; Bae et al. 2011; Bian et al. 2013; Erickson et al. 2009; Khademhosseini et al. 2006).

HA consists of repeating disaccharide units, D-glucuronic acid and D-N-acetylglucosamine, possessing many functional groups such as glucuronic acid carboxylic acid, primary and secondary hydroxyl groups. The major modification method for its photopolymerization (e.g., HA-MA: hyaluronic acid methacrylate) is the methacryloylation of hydroxyl groups of HA by employing MAA, which can be prepared by the reaction of HA with MAA in water of pH 8 at 5ºC for 24 h as depicted in Fig. 7B (Chung and Burdick 2009; Levett et al. 2014; Smeds and Grinstaff 2001). Levett et al. reported that the addition of HA-MA to GelMA constructs enhanced chondrogenesis and produced a significant amount of cartilage-specific matrix proteins, which showed a great promise for effective cartilage tissue engineering (Levett et al. 2014). Another method is to use glycidyl methacrylate (GM); GMHA was synthesized by adding GM into HA aqueous solution with triethylamine and tetrabutylammonium bromide at room temperature for overnight (Baier Leach et al. 2003). Photocurable HA can be also obtained via EDC chemistry by the reaction of HA with N-(3-amonopropyl)-methacrylamide hydrochloride or 4-vinylaniline. In this method, first sodium HA was dissolved in PBS and stirred at 4ºC for half an hour in the presence of EDC. Aqueous solution of 4-vinylaniline was prepared separately and its pH was adjusted at 3. Finally, styrenated HA was obtained by mixing the two solutions at 4ºC for 24 h (Matsuda and Magoshi 2002). Vinylated HA and vinylated gelatin were used for the preparation of tubular photoconstructs. The addition of PEGDA to vinylated HA enhanced the burst strength of the hydrogels.

Chitosan-based photocurable hydrogels

Chitosan is one of the linear polysaccharides, derived from partial deacetylation of chitin (β-1,4-linked N-acetyl-D-glucosamine). It has been applied for tendon, bone and skin regeneration (Abarrategi et al. 2010; Baxter et al. 2013; Freitas et al. 2011; Gingras et al. 2003; Kim et al. 2014; Matsunaga et al. 2006; Olmez et al. 2007; Saraiva et al. 2015; Shim et al. 2008; Wang et al. 2015).

One of the pioneering modification methods for photocurable chitosan is to introduce azide and lactose moieties into chitosan using a two-step condensation method (Ono et al. 2000). Specifically, chitosan was dissolved in N,N,N',N'-tetramethylethylenediamine (TEMED) solution and subsequently EDC and 4-O-b-D-galactopyranosyl-(1,4)-D-gluconic acid (lactobionic acid) were added under stirring at room temperature for 24 h to obtain lactose-linked chitosan (CH-LA). Next, the product (CH-LA), EDC, and 4-azidobenzoic acid were added to the TEMED solution. The mixture was stirred at room temperature for 72 h to obtain the