Their structure has a repetition of tripeptide, (Gly-X-Y)n, where X and Y are often proline and 4-hydroxyproline, respectively. The major chemical modification method for collagen/gelatin utilizes mainly free amino groups from lysine and hydroxylysine, which can react with methacrylic anhydride (MAA) as shown in Fig. 7A. The pioneered method was to dissolve gelatin in phosphate buffered saline (PBS) at 50ºC, followed by drop-wise addition of MAA to yield gelatin methacryloyl (GelMA) (Bulcke et al. 2000). This method was applied to collagen methacryloylation with the use of 10 mM HCl at 4ºC as a buffer solution (Brinkman et al. 2003). Recent studies on GelMA showed that the use of carbonate-bicarbonate buffer and pH maintenance at pH 9 produced GelMA with a higher degree of methacryloylation at relatively a low feed ratio of MAA to gelatin since this method minimized protonation of amino groups and allowed gelatin to effectively react with MAA, as seen in Fig. 8 (Lee et al. 2016a; Shirahama et al. 2016). Collagen and gelatin methacryloyl hydrogels have been studied extensively and applied to many bioapplications including 3D printing technologies (Billiet et al. 2014; Chen et al. 2012; Egger et al. 2016; Klotz et al. 2016; Loessner et al. 2016; Nguyen et al. 2016; Prakash Parthiban et al. 2017; Wu et al. 2016; Yue et al. 2015).

There are other chemical functionalization methods for the preparation of photocurable collagen; Dong et al. utilized 6-aminohexyl cinnamate (AHC) to react with glutamic acid and aspartic acid of collagen via EDC (1-ethyl-3-(3-dimethylamino)

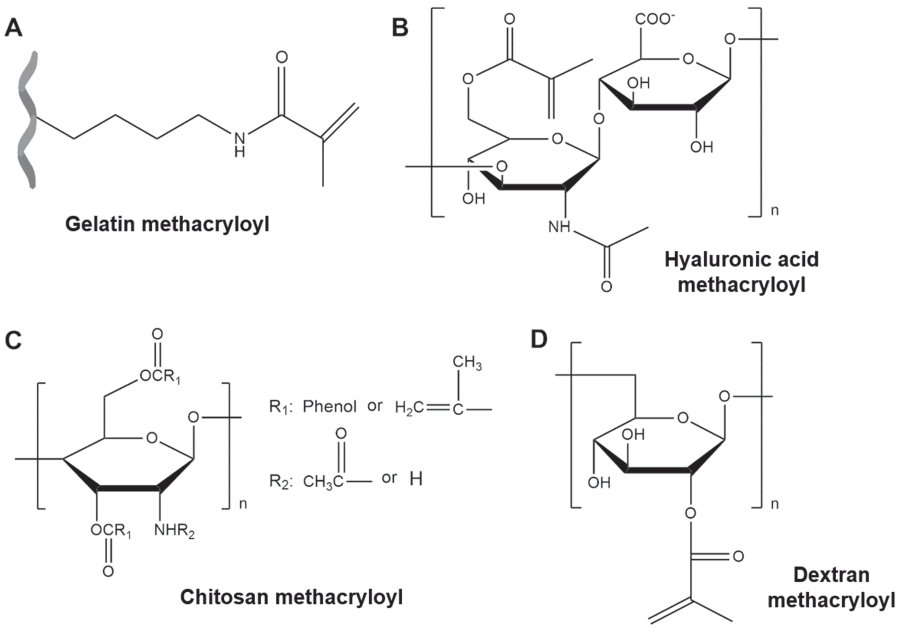


**Fig. 7.** Examples of chemically modified photocurable natural polymers. (A) Gelatin methacryloyl (GelMA) via reaction of gelatin with methacrylic anhydride (MAA). (B) hyaluronic acid methacryloyl (HAMA) via reaction of HA with MAA. (C) Chitosan benzyol (or methacryloyl) via reaction of Chitosan with benzoyl chloride and methacryloyl chloride. (D) Dextran methacryloyl (DexMA) via reaction of Dextran with MAA.