Understanding Physical and Chemical Interactions Deriving Polymer-Metal-Organic Framework Gel Formation for Drug Delivery

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Biomaterials that extend and control the release of drug molecules are useful for therapeutic applications such as wound healing. Polymeric hydrogels are a class of biomaterials that can serve as drug delivery depots for biologics like peptides and proteins. However, hydrogels suffer from poor loading capacity (10-200 mg/g) and fast release times (a few hours to a day). Conversely, metal-organic frameworks (MOFs), porous crystalline materials composed of inorganic metal clusters and organic linkers, have demonstrated exceptionally high drug loading capacity (0.15-1.0 g/g) and extended-release (a few days to a week) due to their large specific surface area (1000-6000 m2/g) and tunable pore sizes (5 Å – 40 Å). Nonetheless, the poor solubility of MOFs in an aqueous medium limits their biomedical applications. Therefore, combining MOFs and polymers to create polymer-MOF gels may overcome the limitations of both polymers and MOFs. To date, there is no systematic study showing the effects of interactions between polymer and MOF on polymer- MOF gel properties (i.e., gelation and crystallinity). Herein, we study interactions between polymer and MOF by varying polymer functional group chemistry (carboxyl vs hydroxyl) and density. We hypothesize that chemical interactions between polymer and MOF can cross-link polymer chains through MOF particles to make gels but can also disrupt MOF crystallinity. We prepare gels by forming MOFs in the presence of polymers at room temperature. We find both carboxyl and hydroxyl-containing polymers induce gel formation. However, carboxyl-containing polymers inhibit/disrupt MOF formation while hydroxyl- containing polymers preserve MOF crystallinity. On the other hand, the addition of MOF enhances the storage modulus of the gel relative to polymer gel alone. Surprisingly, the addition of a polymer having minimal chemical interactions with MOFs also induces gel formation indicating the possibility of polymer entrapment inside MOF pores. To demonstrate the utility of gels for drug delivery, we show the release of small drug molecules for up to 2 weeks from polymer-MOF gels. The understanding of polymer-MOF interactions developed here can be extended to a variety of polymers and MOFs to create a library of polymer-MOF gels for studying the release of peptides and proteins.