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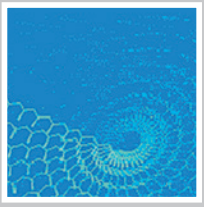

Polymer and Colloid Highlights

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Polymer–Nanoparticle Hydrogels

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A current goal of materials design is to engineer responsive soft matter that can be processed and recycled, can be molded and reshaped, and that can engage with living systems. Recently, a class of moldable materials were introduced, which are assembled from polymers and colloidal nanoparticles (NPs) in aqueous solution.[1] Polymer–nanoparticle (PNP) hydrogels form spontaneously upon mixing a liquid suspension of NPs (below the colloidal glass transition) and a liquid solution of polymer. Physical interactions between the NPs and the polymers percolate a network (Fig. 1). In this manner, a viscoelastic gel is assembled *via* transient and reversible interactions. As the physical cross-links can exchange under ambient conditions, PNP gels can flow upon application of shear stress (shear-thin) and reform rapidly upon relaxation of the applied force (self-heal), making them attractive as injectable materials and complex rheology modifiers.

Initially, PNP hydrogels were assembled from polystyrene NPs and cellulose-derivatives.[1] Rheological characterization demonstrated that the NP size and the number density of interactions between polymer and NPs controlled the mechanical properties of the final gel. In addition, the gels exhibited a high-degree of shear-thinning and rapid self-healing. Biomedical PNP gels were then assembled from poly(ethylene glycol)-*block*-polylactide (PEG-*b*-PLA) NPs and hydrophobically-modified hydroxypropylmethylcellulose, both GRAS-listed materials.[1] The general PNP design paradigm has been further demonstrated for a range of additional NPs and polymers.[2] In each case, the simple combination of a suspension of colloidal NPs with a polymer solution formed a moldable gel.

The unique rheological properties as well as the simplicity of fabrication and design of PNP gels makes these materials attractive for a range of applications. Biomedical formulations of PNP gels were developed as syringe injectable depots for local delivery of both hydrophilic and hydrophobic therapeutics or as immune-modulatory materials for the recruitment of dendritic cells to the site of injection.[1,3] Stapleton *et al.* demonstrated that spraying PNP gels on the epicardium could mitigate the formation of post-surgical adhesions.[4] Recently, Guzzi *et al.* leveraged the shear-thinning and self-healing rheology of PNP gels to engineer a universal nano-carrier ink for extrusion-based additive manufacturing and 3D bioprinting.[5] Uniquely, the versatile platform enabled the inclusion of a range of secondary polymers for post-print stabilization and tailored biofunctionality for both tissue engineering and drug delivery applications. Other PNP gel variants have exploited the tunable rheology of the platform for pipe maintenance in the food industry and as prophylactic coatings for wildfire prevention.[2,6]

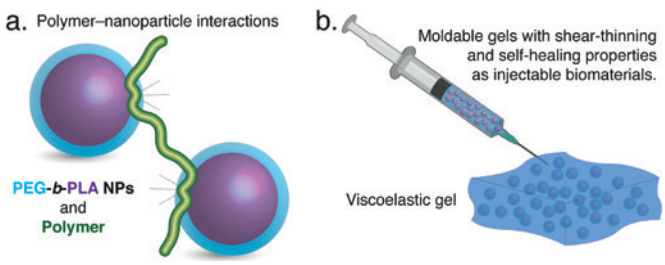

Fig. 1. **a.** Polymer–nanoparticle (PNP) hydrogels form by mixing core-shell NPs and polymers, whereby physical interactions between polymer and NPs form a network *via* transient cross-links. **b.** The resultant viscoelastic gels are useful for biomedical and industrial applications.

As PNP gels form spontaneously upon mixing of the NP and polymer solutions, they can be produced on scale given sufficient quantities of the precursors. With the growing interest in biomedical use of PNP gels, there is a need to produce PEG-*b*-PLA NPs, and other biomedical NPs, on scale, which are often produced in small batches. Therefore, Bovone *et al.* engineered a coaxial jet mixer for the controlled, scalable, and automated production of polymeric NPs.[7,8] The flow-based synthesis of the colloidal building blocks offered additional control over NP size and chemical functionality as well as scalable fabrication of biomedical PNP gels.

In total, the rational design of polymer–nanoparticle interactions provides an attractive strategy to engineer next-generation moldable (bio)materials. Yet, open research and engineering challenges remain. A more precise understanding of the molecular mechanisms that drive network formation is needed to improve the macromolecular design of PNP gels. Further, current PNP gel formulations are quite soft (low modulus) and additional methods to promote reversible yet strong cross-linking between gel components would enable more robust variants and broaden the utility of this class of materials.

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