Polyelectrolyte complexes embedding reduced graphite oxide

Abstract

The aqueous dispersion of polyelectrolyte (PE)-based graphene-related materials (GRMs) represents an interesting intermediate in the development of advanced materials through sustainable processes. There is a lack of prominent work systematically studying the effects of typical parameters of PEs structure, molecular weight and charge density on the dispersion and stabilization of polyelectrolyte grafted reduced graphite oxide (rGO) in water. One of the main goals of this project is to reveal the interaction between PEs and rGO, and explore the balance of adsorption of polymers and the anti-aggregation ability of PE-rGO assembles. Four PEs were evaluated, including polyacrylic acid (PAA), branched poly(ethylenimine) (BPEI), sodium carboxymethyl cellulose (CMC), and poly(sodium 4- styrenesulfonic acid) (PSS). The charge density plays a critical role to weak PEs (PAA and BPEI) in dispersing rGO. Both of them revealed optimum performance at mild charge density where good adsorption and repulsive charges of polymers onto rGO were reserved. BPEI has been found to induce good dispersibility of rGO in water, also depending on polymer chain length. The negatively charged strong PEs (PSS and CMC) were inferior due to the high surface tensions and limited adsorption onto rGO. Therefore, the suitable PEs and dissociation conditions used for rGO dispersion were obtained.

On the other hand, the good dispersion of rGO in aqueous PE solutions offers the opportunity to further preparation of uniformly distributed rGO in polymeric composites via liquid-phase mixing. The graphene and GRMs reinforced polymer composites have been investigated in the last decade by researchers and used in batteries, sensors, biomedical and other fields. Using autonomous complexation of oppositely charged PEs eliminates the use of organic solvents and endows composites manufacture from thin layers to bulk materials. In this work, PAA and poly(diallyldimethylammonium chloride) (PDAC) were used to fabricate a polyelectrolyte complex (PEC). Based on the fundamental properties of polymeric matrix and incorporation of rGO in PECs, I focused on the mechanical properties of rGO-incorporated polyelectrolyte complexes (rGO-PECs) under different salt content and humidity conditions. The addition of a small amount of rGO could greatly improve the mechanical properties of composites under ambient condition,

and for the salt-plasticized samples, the addition of graphene is also beneficial to inhibit the polymer chains' mobility, thus improving the strength and reducing the deformation. At a high moisture environment, the polymer matrix tended to be ductile with extremely high deformation and low tensile strength owing to its humidity sensitivity, and the strong mismatch of soft matrix and hard rGO led to limited reinforcement. In this case, the salt affects the mechanical properties even with a tiny amount in PECs.

To further promote the applications of rGO-PEC composites in electronic components, the rGO content and dispersion in PECs are particularly important. The PAA has been proven to have good compatibility with rGO and was used in rGO dispersion, while there is no study focused on hybrid dispersing system consisting of oppositely charged PEs and high concentration of salt. The hybrid system contained all components in the final-prepared composite, which increased rGO content in rGO-PEC composites. Therefore, this work compared different dispersion methods on rGO content, rGO dispersion in PECs and the composites' mechanical, thermal and electrical properties. The PAA single-phase approach had advantage in terms of the rGO dispersion, requiring a short sonication time to achieve separation and dispersion of rGO, instead, the hybrid-phase approach showed much higher rGO content in the composite and fast transformation from dispersion condition into complexation condition. The mechanical property, thermal and electrical conductivities, as well as stability in water were compared in rGO-PECs prepared in two methods. To optimize desired properties, the effects of PAA:rGO and sonication time on the physical properties of rGO-PECs were further studied. In the single phase dispersion method, the low PAA:rGO ratio was critical to achieving the improvement of electrical conductivity but also brought a much higher salt fraction in PECs, which is unfavourable in terms of its mechanical strength and stability in water. On the other hand, the mechanical property, thermal and electrical conductivities of rGO-PECs fabricated by multiphase approach were dependent on the combined effects of rGO aggregates and the dispersed rGO size/defectiveness, which was dominated by sonication time. Indeed, longer sonication time led to a better dispersion of rGO in PECs, improved mechanical properties, and good stability in water, while also causing a slight decrease in thermal and electrical conductivity.