Tailoring of Graphene Morphology in Polymer Nanocomposites: Self-Assembling of Reduced Graphene Oxide Layers on Zein Microspheres

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The objective of this study is the design and engineering of zein microspheres covered by reduced graphene oxide (rGO) sheets to be used for the production of ordered 3D segregated network structure [1,2]. The formation of segregated architectures can improve the electrical conductivity, reducing the electrical percolation threshold, the efficient EMI shielding or electromagnetic absorption materials and the gas and water vapor barrier properties. Zein is a protein extract from corn which show high film-forming ability, biodegradability and biocompatibility. Therefore, zein finds many potential applications in food and pharmaceutical industries including but not limited to coating and free-standing films for packaging materials. Moreover zein is also particularly suitable for the formation of sub-microparticles by using ternary systems and specific conditions of pH, salt, and temperature. The use of composite microparticles consisting of reduced graphene oxide self-assembled on zein particles may be a valuable approach to prepare multifunctional composite materials with a 3D segregated graphene morphology. The formation of the three-dimensional network is obtained due to the forced segregation of graphene layers in the excluded volume arisen from the compacting of spherical microparticles to form a continuous film/coating system.

We report a simple water/alcohol-based method to form reduced graphene oxide (RGO)/zein composite microspheres by self-assembly of conductive rGO sheets and zein microspheres. Zein microspheres were fabricated using a ternary phase diagram of zein in ethanol and water (Figure 1) [3]. Zein (3 mg/mL) was dissolved in ethanol-water binary solvent (70:30 v/v). Afterwards, the solution was sonicated for 2 minutes using an ultrasonic processor, the (3-glycidyloxypropyl) trimethoxysilane (GOTMS, 25% w/w) was added as crosslinking and the mixture was heated at 60 °C and stirred overnight [4]. Decreasing the ethanol concentration of zein solutions by the addition of water results in the formation of a zein-rich microspheres phase (coacervation). Zein microparticles had a spherical shape, smooth surface (Figure 2 (a)), size ranges from 0.4 to 1µm and a ζ-potential value of about +20mV measured at pH 4.3. Afterwards, 30ml of graphene oxide (GO, 0.1 mg / ml) aqueous dispersion prepared by sonication of 3 mg of GO powder dispersed in 30 mL of DI water and sonicated for 1h in an ultrasound bath were added to the zein microsphere phase. The ζ-potential value of GO dispersion was equal to -30mV measured at pH = 4.4. The different surface charge among the GO sheets (negative charge) and zein microparticles (positive charge) allows GO to self-assemble on the surface of the microspheres through electrostatic interactions during mixing. GO self-assembled on zein microspheres was chemically reduced with L-Ascorbic Acid (GO:L-AA 1:10) to form RGO/zein composite microspheres. The dispersions of zein microspheres covered by RGO sheets were freeze-dried. SEM images confirm the presence of a rough surface ascribed to the deposition of graphene oxide layers on the surface (Figure 2b).

The obtained results have to be considered as preliminary results of an ongoing research addressed to prepare biodegradable and multifunctional materials with controlled 3D

morphology of graphene for packaging applications. The next step will be the development and characterization of new materials obtained by hot-pressing the resultant powder with the presence of chemical crosslinkers to form a continuous films with an ordered 3D segregated network structure. This work has been carried out in the framework of the international Multifunctional Polymers and Biomaterials, MPB Research Center established between the Department of Chemical Science and Materials Technology of the National Research Council (Italy) and the Sichuan University (China) [5].

References

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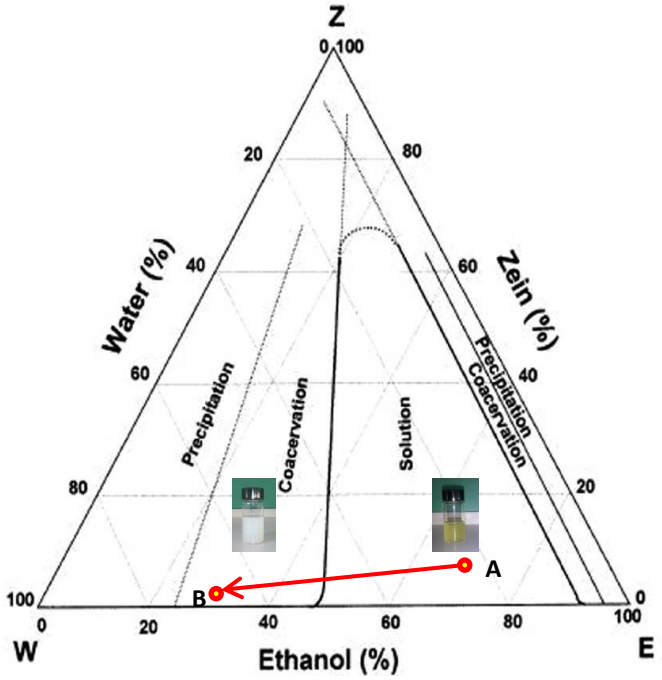

Figure 1: Ternary phase diagram of zein in ethanol and water. A) Starting point: solution of GOTMS functionalized zein and B) End point: coacervation dispersion.

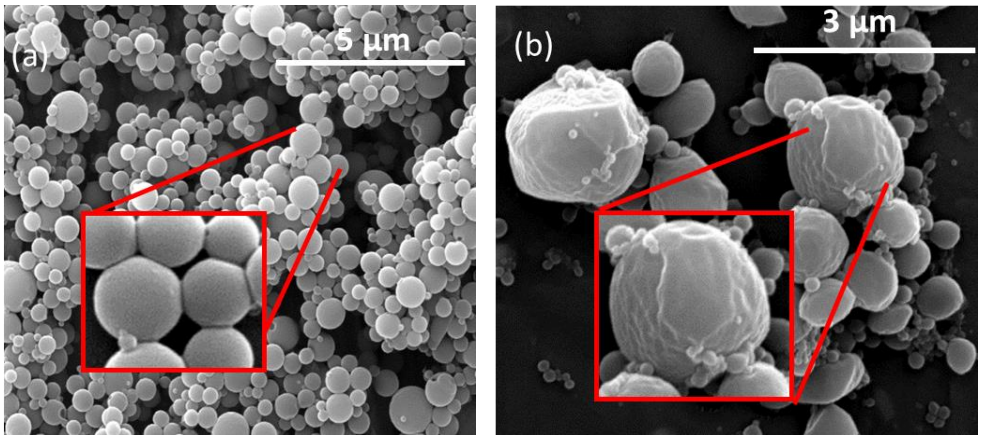

Figure 2: Zein microspheres (a) and GO/zein composite microspheres (b).