Advances in Colloid and Interface Science 207 (2014) 3–13

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Magneto-responsive nanocomposites: Preparation and integration of magnetic nanoparticles into films, capsules, and gels

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ARTICLE INFO

Available online 3 October 2013

Keywords:
Magnetic nanoparticle
Nanocomposite
Film
Capsule
Gel

ABSTRACT

This review reports on the latest developments in the field of magnetic nanocomposites, with a special focus on the potentials introduced by the incorporation of magnetic nanoparticles into polymer and supramolecular matrices. The general notions and the state of the art of nanocomposite materials are summarized and the results reported in the literature over the last decade on magnetically responsive films, capsules and gels are reviewed. The most promising concepts that have inspired the design of magneto-responsive nanocomposites are illustrated through remarkable examples where the integration of magnetic nanoparticles into organic architectures has successfully taken to the development of responsive multifunctional materials.

Contents

1. Introduction

The aim of this review is to provide an overview of the latest research activity in the field of magnetic nanocomposites, especially highlighting those concepts that have inspired the design of magnetically responsive films, capsules and gels.

Many reviews have been published over the last few years about nanocomposite materials (i.e., multi-phasic materials composed by a matrix incorporating units with at least one dimension in the 100 nm size range or smaller). A comprehensive overview of the latest efforts towards functional hybrid materials can be found in a paper by Kao et al. [1]. The potential applications of polymer-based inorganic nanoparticle

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http://dx.doi.org/10.1016/j.cis.2013.09.006

composites have been recently summarized [2], showing that the stability and processability of polymers and the peculiar electronic and magnetic properties of inorganic nanoparticles could be synergistically combined to generate improved materials [3].

Including magnetic nanoparticles in composite materials introduces responsiveness to magnetic fields, opening up new perspectives in terms of functionalities and applications. For instance, several cases where magnetic nanocomposites are effective in environmental remediation have been lately highlighted in the literature [4]. Smart composite materials have also been obtained through the combination of magnetic nanoparticles and thermally responsive polymers, where an alternating magnetic field (AMF) is used to trigger localized heating, which in turn causes a change in the structure of the composite matrix [5]. The potentials introduced by peculiar properties of the matrix are well illustrated by recent papers reviewing the progress in the fields of stimuli-responsive membranes [6], mesoporous structures [7,8], and liposomes [9].

In such a crowded scenario, this review is not intended to provide the reader with an overview of the preparation methods and the potential applications of magnetic nanocomposites. To this purpose, the reader is referred to the reviews cited within the introduction of this paper and the references therein. The focus of this report is indeed on magnetically responsive films, capsules and gels. Most importantly, rather than on the available materials and methods to obtain them, our review is especially focused on those concepts that have recently inspired their design, their preparation and their application.

Following a brief introduction to the general notions and the state of the art of nanocomposite materials, the progress over the last decade in the field of magnetically responsive nanocomposites is shortly reviewed. The most promising concepts that have inspired the design of magneto-responsive films, capsules and gels are then critically discussed. To this aim, this review is mainly focused on the illustration of selected case studies where the integration of magnetic nanoparticles into organic architectures has successfully taken to the development of responsive multifunctional materials. In particular, examples are used to highlight the possible key aspects for the advances in the field, which are outlined in the last section of this paper.

1.1. Nanotechnologies and nanocomposites

Nanotechnology aims at designing, building, and manipulating materials characterized by at least one dimension below 100 nm. When the dimensions of a material are reduced in the size range of nanometers, the physico-chemical behavior significantly departs from that of the bulk state. Nanostructured materials display peculiar electrical, mechanical, chemical, magnetic, and optical properties that are of interest to a broad range of applications. Tailoring their nanostructure produces therefore materials that can be exploited to overcome the shortcomings of traditional approaches. Among many others, sectors like electronics, medicine, and optics greatly extended their potential over the last decade by taking advantage of these new tools.

Nowadays nanometric building blocks are available through innovative synthetic routes and technologies making possible to arrange them into functional structures and/or to include them into a supporting material. It is worthwhile to recall that nanocomposites combine the properties of both the supporting material (matrix) and the nanoparticles (often referred to as the filler or the guest) generating new functional materials able to match specific needs.

The materials constituting the matrix of a nanocomposite (also indicated as the host) can be extremely diverse: metals, ceramics, and polymers have all been employed in the past, even though the use of metals and ceramics as matrices is confined to a limited number of applications. The primary role of the matrix is to provide a support for the filler, imparting stability and processability to the final product. Polymers represent so far the most popular choice: in fact, inorganic nanostructures are often easily dispersed and stabilized (or even directly prepared) in polymer solutions. Furthermore, many technologies developed in the past for plastics were straightforwardly transferred to the production of polymer nanocomposites (PNCs).

1.2. Polymer nanocomposites: improving host performances

Very often the first step in the manufacture of PNCs is the choice of the proper fabrication method to ensure a good dispersion of the nanoparticulate material in the matrix [2,10,11]. Various techniques have been developed for preparation of PNCs, and are divided into two categories: *in situ* synthesis and direct compounding.

In the in situ methods the nanoparticle precursors and/or the monomers are first mixed and, successively, the formation of nanoparticles and/or the polymerization are activated by means of a physico-chemical trigger or a chemical initiator. This approach commonly ensures a high homogeneity of the final composite [12].

In the direct compounding methods, nanofillers and polymer are separately prepared, and then they are mixed together, commonly by means of mechanical forces or fusion. These preparations are cheap and suitable for the production of large amounts of material. Direct compounding methods are therefore the most used at the industrial level and they are often intended to improve and eventually extend the properties of the host.

Polymers offer a wide range of individual properties that can be exploited in a nanocomposite material: mechanical, thermal, optical properties, as well as biodegradability, toxicity, hydrophobic/hydrophilic balance can be introduced and adjusted into the final composite material by choosing the most suitable polymer. An application where polymers are particularly useful is the preparation of films. Polymer thin films are nowadays essential to many technologies and play a ubiquitous role in improving people's everyday life. Packaging, coatings, and microelectronics are just few examples of the areas where polymeric films have become more and more important. Thanks to the development of nanotechnologies, the last decade has seen a growing interest in providing added value to polymer thin films. This is particularly evident in the improvement of the mechanical properties of plastic films through the introduction of either organic or inorganic nanometric fillers. The incorporation of low amounts of nanometric clays in the pristine polymer increases the mechanical performances and enable producing films with lower content of plastics, which is a beneficial effect from an environmental point of view [10,13].

1.3. Green polymers: matching the performances of synthetic plastics

Besides the reinforcement of the synthetic plastics, several “green” polymers derived from natural sources have been identified as possible substitute of petroleum-derived plastics. The great benefit of these polymers produced from renewable material sources is related to their environmental friendly disposal, which occurs naturally and does not produce polluting gases [14]. Unfortunately, when compared to conventional polymers and plastics, the performances of green and bio-polymers are not always matching the needs of existing technologies, generating major drawbacks for their use. This issue has been tackled by including nanofillers in the polymeric matrix to obtain bionanocomposites. In particular, the introduction of fillers such as natural fibers, anisotropic in shape, allows for the preparation of green biocomposites [15,16] with enhanced performances [17–19], especially in terms of mechanical properties [20], while keeping the characteristic ductility properties of the polymer [21]. These bionanocomposites have been gaining a constantly increasing attention in recent years. Because of their intrinsic nature, these materials opened up new perspectives for many applications where biocompatibility, stability in aqueous media, and biodegradation should be addressed [21–23].