



Fabrication of polymer nanocomposites via ball milling: Present status and future perspectives



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ABSTRACT

This review aims to provide a description of the recent advances in the preparation of polymer nanocomposites via mechanical milling. An assessment of possible future scenarios that could be created by the utilization of improved experimental methodologies and a deeper understanding of structure-property relationship is also provided. It is then reported, in a logical sequence, crucial information on five subjects: (i) the motivation of fundamental and applied research in the field of thermoplastic and thermosetting polymer nanocomposites, (ii) the mechanochemical response of polymeric substances to mechanical activation, (iii) the broad spectrum of experimental behaviours exhibited by the most studied classes of polymers, (iv) the methodology for the mindful utilization of mechanical processing to mix polymers and disperse heterophases, and (v) the physico-chemical approach to describing the kinetics of mechanically activated transformations. In addition, critical questions regarding the advantages and disadvantages of mechanical processing compared to more conventional dispersion methods are highlighted. Finally, the general trends in the current research are discussed, and possible future perspectives in this field are briefly described.

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1. Introduction

Governing and directing the assembly of matter on the nanometre scale has the potential to provide new classes of novel materials and enable the unprecedented capability of tuning material properties by altering their microstructure [1–4]. As the characteristic length approaches the nanometre scale, it allows materials with an increased number of surface atoms with defective or unsaturated coordination numbers to be obtained [5–7]. By involving the surrounding surface and interface, the perturbed electronic states can modify the physical and chemical properties, which can differ markedly from those exhibited by the bulk material [6,8,9]. Regarding this behaviour, composite materials deserve a special mention.

These ubiquitous materials consist of a heterogeneous combination of two or more constituents with significantly different physical and chemical properties. Typically, one of the constituents forms the matrix within which the other constituents are dispersed as fillers. By combining the materials to various extents and at different length scales, the individual constituents maintain their distinct physical and chemical natures. However, the resulting composite material exhibits enhanced properties and performance compared to those of the constituent materials [10,11]. Not only do composite materials show promise for advanced technological applications in several fields, but they also raise fundamental issues that challenge the current understanding of structure-property relationships [10,12].

The increasing availability of nanometre-scale fillers has progressively shifted attention towards nanocomposites, which include metal-, ceramic-, and polymer-based systems [10,13]. All of these systems can be regarded as a disordered dispersion of nanometre-scale fillers inside a percolating host matrix [14,15]. Typically, the overall structure exhibits a high degree of randomness, mono- or multi-continuous inter-percolating topology depending on the number of materials constituting the matrix, reduced dimensionality, and high interface area-to-volume ratio [14,16].

While these structural features have been shown to affect electronic, optical, and chemical properties because of the smooth size effects [5,7], the degree of dispersion and matrix-filler interactions are expected to influence the behaviour of nanocomposites on larger scales [4,15]. This makes the relationships between structure and properties hard to unfold, especially for composites composed of a matrix and filler(s) with complex structures and different mechanical properties. Typically, this is the case for polymer nanocomposites [17,18], which is the subject of the present review.

Polymer nanocomposites consist of a continuous matrix, which is composed of one or more polymeric constituents, that hosts a random dispersion of nanometre-sized fillers, which are usually inorganic in nature [19]. The fillers can exhibit a wide range of dimensionalities, from nanoparticles to fibres and platelets [20]. Transmission electron microscopy micrographs of different representative microstructures of a polymer-clay nanocomposite system are shown in Fig. 1. When the polymer chains are able to intercalate (or penetrate) between the filler sheets a well-ordered multilayer morphology results with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained [21]. The remarkable degree of interest in polymer nanocomposites is motivated by the significantly enhanced properties and performances obtained with very small volume fractions of fillers [21,22]. Several studies on polymer nanocomposites have reported impressive increases in the modulus and strength, outstanding barrier properties, improved resistance to solvents and heat, and decreased flammability [23,24]. To a first approximation, these improvements can be ascribed to the decreased dimensionality of the fillers, which increases the degree of intimate contact between the filler and matrix [15,25]. On a deeper level, complex interactions between the electronic states at the polymer-filler interfaces, confinement effects, and purely mechanical restrictions on the movements of polymer chains can be invoked to explain the aforementioned improvements [26].

However, the fabrication method is crucial in determining the physical and chemical properties of polymer nanocomposites [22,27,28]. It must effectively disperse the fillers throughout the matrix [15,21,29,30]. For this reason, polymer nanocomposites were initially fabricated *ex situ* in the presence of a liquid phase [6,31,32]. For example, filler nanoparticles can be

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