



Processing of nanostructured polymers and advanced polymeric based nanocomposites



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ABSTRACT

The control of the nanostructure and the addition of nanoparticles to polymers have led to structural and functional property enhancements in a number of polymeric systems as a material answer to continuous requirements from advanced industrial sectors. The availability of new nanoparticles with extraordinary properties (i.e. carbon nanotubes, graphenes, but also nanoclays, nanocellulose, metals and ceramics) have determined new and exciting possibilities for a continuous enlargement of polymer markets. However, the potentialities of these new materials are still strongly dependent on the development and scaling-up of reliable processing routes. Therefore, the purpose of this report is to review the main processing approaches for nanostructured polymers and nanocomposites starting with a brief review of available nanoparticles and on their functionalization to promote a better polymer–particle interaction. Regarding processing, the review firstly addresses the bottom-up approaches typically adopted for nanostructured polymers, blends and copolymers. Then, the different technologies required by the top-down processing of thermoplastic and thermosetting polymer matrix systems are reviewed. Finally, the report addresses the recent applications of nanostructured polymers and nanocomposites as matrices of advanced composite materials. In all cases, the main processing approaches and the main structural and functional properties characterizing these materials and their potential and current industrial applications are specifically addressed.

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Abbreviations and symbols: AFM, atomic force microscopy; APTS, aminopropyltriethoxysilane; ATRP, atom transfer radical polymerization; BC, block copolymer; BCC, body-centered cubic structure; BGY, Born–Green–Yvon theory; CEC, cation exchange capacity; CNC, cellulose nanocrystal; CNS, cellulose nanofibril; CNT, carbon nanotube; CNW, cellulose nanowhisker; CCVD, catalytic chemical vapor deposition; CVD, chemical vapor deposition; DDM, diaminodiphenyl methane; DDS, 4,4'-diaminodiphenylsulfone; DETA, diethylenetriamine; DGEBA, diglycidyl ether of bisphenol A; DMF, dimethylformamide; DPD, dissipative particle dynamics; DT, dodecanethiol; DTA, dodecyltrimethylammonium; E, Young's modulus; EFM, electrostatic force microscopy; FITC, fluorescein-5-isothiocyanate; FRP, fiber reinforced polymer; FTIR, Fourier transform infrared spectroscopy; GFET, graphene field-effect transistor; GFRP, glass fiber reinforced polymer; GNP, graphite nanoplatelet; GO, graphene oxide; GONP, oxidized graphite nanoplatelet; GRAPOSS, graphene-POSS hybrid; HDT, heat distortion temperature; HEX, hexagonal microphase (cylinders); HRR, heat release rate; ISO, International Organization for Standardization; ITO, indium tin oxide; kB, Boltzmann constant; LAM, lamellar morphology; MCDEA, 4,4'-methylene bis (3-chloro-2,6-diethylaniline); MFC, microfibrillated cellulose; MMT, montmorillonite; MWCNT, multiwall carbon nanotube; N, degree of polymerization; NMP, N-methyl pyrrolidone; NP, nanoparticle; PB, polybutadiene; PBT, poly(butylene terephthalate); PCL, poly(ϵ -caprolactone); PDMS, polydimethylsiloxane; PE, polyethylene; PEDOT, poly(3,4-ethyldioxythiophene); PEE, poly(phenylene ether); PEI, poly(ethylene imine); PEO, poly(ethylene oxide); PEP, poly(ethylene-alt-propylene); PLA, polylactide; PLLA, poly(L-lactide); PMMA, poly(methyl methacrylate); POSS, polyhedral oligomeric silsesquioxane; PPE, poly(phenylene ether); PPO, poly(propylene oxide); PPy, polypyrrole; PS, polystyrene; PSS, poly(styrene sulfonic acid); PTMO, poly(tetramethylene oxide); PU, polyurethane; PVA, poly(vinyl acetate); PVCH, poly(vinyl cyclohexane); P3HT, poly(3-hexylthiophene); rGO, reduced graphene oxide; RIFT, resin infusion under flexible tool; ROP, ring-opening polymerization; Rs, surface resistivity; RTM, resin transfer molding; SAXS, small angle X-ray scattering; SBM, poly(styrene-*b*-butadiene-*b*-methyl methacrylate); SBS, poly(styrene-*b*-butadiene-*b*-styrene); SCRIMP, Seemann[®] composites resin infusion molding process; SEBS, poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene); SEM, scanning electron microscopy; SIBS, poly(styrene-*b*-isobutylene-*b*-styrene); SIS, poly(styrene-*b*-isoprene-*b*-styrene); SMMA, styrene-*b*-(methyl methacrylate); SWCNT, single walled carbon nanotube; T, temperature; TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl; T_g, glass transition temperature; TGA, thermo gravimetric analysis; TGDDM, tetraglycidyl-4,4'-diaminodiphenylmethane; TEM, transmission electron microscopy; TPE, thermoplastic elastomer; TPU, thermoplastic polyurethane; TRG, thermal reduced graphene; UV, ultraviolet; UV-vis, ultraviolet-visible; VARIM, vacuum assisted resin infusion method; VARTM, vacuum assisted resin transfer molding; wAB, interaction energy between monomers A and B; XRD, X-ray diffraction; Z, number of the nearest neighbors of the copolymer configurational cell; ϕ_A , volume fraction of component A; χ , Flory–Huggins interaction parameter; σ , tensile strength; OD, zero-dimensional; 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional.

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1. Introduction

1.1. Top-down and bottom-up processing of polymer nanocomposites

Nanostructured polymers and hybrid inorganic–organic nanocomposites have gained popularity in the last two decades due to their exciting bulk and surface properties. The control of the nanostructure of polymers and the addition of nanoparticles has led to structural and functional property enhancements in a number of polymer systems as a material answer to continuous requirements from advanced industrial sectors. The availability of new nanoparticles with extraordinary properties (i.e. carbon nanotubes, graphenes, but also nanoclays, nanocellulose, metals and ceramics) have determined new and exciting possibilities for a continuous enlargement of polymer markets. However, the potentialities of these new materials are still strongly dependent on the development and scaling-up of reliable processing routes. In fact, it has been already assessed that the bottleneck for the exploitation of the theoretical excellent properties of polymer nanocomposites is the complete dispersion of the nanoparticles in the matrix and the consequent development of a huge interfacial area. This complete dispersion will allow maximizing the available matrix–particle interphase optimizing then the organic–inorganic interaction, responsible of the enhanced properties of the final

material. So, most of the research efforts in this area have been focused on developing rational processing strategies for nanostructured polymers and nanocomposites and in promoting better matrix–particle interactions.

Since the extraordinary development of polymer nanocomposites, more than two decades ago, many reviews have been published in the scientific literature on this topic. Several of these reviews have been focused on the different processing aspects and on the processing–structure–properties relationships of these specific materials [1–13]. However, most of them are concentrated on a particular type of matrix or nanofillers and none of them report a comprehensive analysis of the physicochemical fundamentals affecting the processing behavior of polymer nanocomposites.

Bottom-up and top-down approaches have been typically reported for material nanotechnologies. In particular, it must be evidenced that polymer nanotechnologies are characterized by a predominant top-down approach. In fact, the application of typical processing technologies like extrusion (and other similar melt mixing processes) are clear top-down processes where ingredients (polymer and nanoparticles) are introduced and macroscopically melt mixed in the equipment. The quality of the dispersion is given by macroscopic processing factors like equipment design, mixing velocity, residence time, etc. with very limited possibilities for

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