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Segmental dynamics in hybrid polymer/POSS nanomaterials

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Of the many nanomaterials available today, polyhedral oligomeric silsesquioxanes (POSS) are in a class of their own as they hold the capability to combine unique reactive inorganic–organic hybrid chemical compositions with nano-sized dimensionally stable cage structures. Depending on the structure and reactivity of their vertex groups, POSS may be blended in a polymer matrix, grafted as side chains, lie on the main macromolecular contour or even act as large, multifunctional chemical crosslinks. POSS is known to influence polymer segmental dynamics with several accelerating or decelerating mechanisms, that often lead to a significant decrease or increase of the glass transition temperature (T_g), respectively. This review explores these mechanisms with respect to the chemical nature of the organic substituents and the resulting particle–polymer interactions; the synthesis route, the chain topology, and the degree of dispersion. T_g vs content data are compiled from the primary literature in a series of comparative graphs. It will be shown that the dependence of T_g on the composition of the POSS nanomaterials can be often discussed and considered in terms similar to those used for polymer blends and copolymers.

Abbreviations: 6FDA, 2,2′-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride; AFM, atomic force microscopy; BD, butanediol; BEMA, bisphenol A ethoxylate dimethacrylate; BPTA, benzophenonetetracarboxylic dianhydride; BSA, 4,4′-(1,3-phenylenediisopropylidene) bisaniline; BSPA, 3-benzylsulfanylthiocarbonylsufanylpropionic acid; BTDA, 4,4′-carbonyl-diphthalic anhydride; CE, chain extender; DCP, dicumyl peroxide; DDS, diamino diphenyl sulphone; DEP, diethylophosphite; DGEBA, diglycidyl ether of bisphenol A; DICY, dicyan diamide; DMA, dynamic mechanical analysis; DMS, degree of microphase separation; DRS, dielectric relaxation spectroscopy; DSC, differential scanning calorimetry; FTIR, Fourier transform infra-red spectroscopy; HAB, 3,3′-dihydroxy-4,4′-di-aminobiphenyl; HHPA, hexahydrophthalic anhydride; IA, itaconic anhydride; IBoMA, isobornyl methacrylate; MA, methacrylic acid; MDA, 4,4′-diamine diphenyl methane,4,4′-methylene dianiline; MDI, methylene diphenyl diisocyanate; MHHPA, 4-methylhexahydrophthalic anhydride; MMA, methyl methacrylate; MOCA, 4,4′-methylenebis-(2-chloroaniline); Mw, molecular weight; NMR, nuclear magnetic resonance; ODA, 4,4′ oxydianiline; PA, polyamide; PACM, 4,4′-methylenebis(cyclohexylamine); PAS, poly(acetoxystyrene); PC, polycarbonate; PCL, poly(ε-caprolactone); PEEK, poly(ether ether ketone); PEMA, poly(ethyl methacrylate); PEO, poly(ethylene oxide); PET, poly(ethylene terephthalate); PI, polyimide; PLA, poly(lactic acid); PMDA, pyromellitic anhydride; PMMA, poly(methyl methacrylate); PNIPAM, poly(N-isopropylacrylamide); POM, poly(methylene oxide), poly(oxymethylene); POPD, poly(oxypropylene) diamine; POSS, polyhedral oligomeric silsesquioxane; PPG, polypropylene glycol; PPO, poly(propylene oxide); PS, polystyrene; PSOH, hydroxyl terminated polystyrene; PTMEG, poly(tetramethylene ether) glycol; PTMO, poly(tetramethylene oxide); PU, polyurethane; PVC, poly(vinyl chloride); RAF, rigid amorphous fraction; RAFT, reversible addition-fragmentation transfer; SEC, size exclusion chromatography; SEM, scanning electron spectroscopy; TBMA, tert-butyl methacrylate; TDI, toluene diisocyanate; TEM, transmission electron spectroscopy; TETA, triethylene tetramine; TFMA, 2-(trifluoromethyl) acrylic acid; T_g, glass transition temperature; TGDDM, N,N,N′,N′-tetraglycidyl-4,4′-diaminodiphenyl methane; THF, tetrahydrofuran; UDMA, urethane dimethacrylate; WAXD, wide angle X-ray diffraction; XRD, X-ray diffraction.

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Contents

1. Introduction

The effective modification of polymer matrices with nanoparticles depends, to a large extent, on the successful dispersion of the nanoparticles within the matrix. However, efficient and homogenous dispersion of a nanoparticulate phase remains a challenging task, and several approaches have been employed for its realization. Moreover, certain applications benefit from targeted arrangement of nanoparticles in the surface or the bulk of polymers or copolymers. Binding nanoparticles on the macromolecular structure as *nanobuilding blocks* facilitates both objectives. Polyhedral oligomeric silsesquioxanes (POSS) are ideal candidates for this approach.

Several industrial and technological applications have been proposed for the resulting organic–inorganic hybrid