



All-polymer nanocomposites with nanofibrillar inclusions generated *in situ* during compounding



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ABSTRACT

An idea to deform highly crystalline polymer particles with unentangled macromolecules into nanofibers by shearing via viscous media has been exploited in the paper. It has been shown that nanofibers can be generated during uniform shearing of solid polytetrafluoroethylene, PTFE, particles dispersed in a molten polymer. PTFE powder particles should be of high crystallinity with unentangled macromolecules and should consist crystals with melting temperature exceeding that of equilibrium melting temperature (332–336 °C). The larger the deformation ratios and shear rates, and the longer the shearing times the thinner and stronger PTFE nanofibers are obtained. Shearing during compounding results in generation of PTFE nanofibers and thus, forming all-polymer nanocomposite. Isotactic polypropylene, high density polyethylene, low density polyethylene and atactic polystyrene were used as polymer matrices for the generation of all-polymer nanocomposites during compounding with selected PTFE powders. The process is characterized by simplicity just by shearing the dispersed crystalline polymer inclusions in another molten polymer.

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1. Introduction

Polymer–polymer nanocomposites are rare and known only when ready-made nanofibers or nanodroplets are dispersed in the matrix. Presently, electrospinning technique is frequently used to produce polymer nanofibers on a lab scale [1]. Also Salim et al. [2] have shown that nanofibers of poly(3-hexylthiophene), P3HT, can be produced by gradual cooling of P3HT solution. Nanofiber polymer composites are also known from few papers concerning polylactide, PLA, reinforced by microfibrillated cellulose, i.e. pulp mechanically fibrillated into nano or submicron wide fibers that form a web-like network [3], cellulose nanofibers separated from kenaf pulp [4] and electronspun cellulose nanofibers [5]. Additionally, Fakirov et al. [6] applied three-step preparation method to fabricate a composite structure where the isotropic polypropylene, PP, is reinforced with poly(ethylene terephthalate), PET, nanofibrils, comprising (1) melt blending of PP with PET; (2) spinning of the PP/PET blend into fibers (filament of 30 μm diameter); and (3) remelting of PP matrix without melting of PET fibrous inclusions in order to obtain all-polymer composite with PET fibrous reinforcement.

Previous attempts of formation of polymer nanocomposites with fibrillar inclusions by compounding were unsuccessful, because it was impossible to deform solidified polymer inclusions during compounding. Contrary to that molten inclusions can be deformed but it is difficult to preserve the shape of extended threads due to capillary instabilities leading to their breakup into droplets. The idea of this paper is to find a way to deform strongly inclusions during compounding and preserve their shape after deformation, i.e. to act against capillary instabilities. A range of means can be proposed but there are limits of achievable deformation. It seems to be a promising alternative to generate polymer nanofibers through shearing of a polymer matrix in which easily deformable crystalline inclusions are dispersed. The higher the capillary number the more efficient is the stress transfer from sheared polymer matrix to inclusions. In order to deform polymer crystals embedded in a viscous medium a critical shear stress, resolved in a slip plane of the respective slip systems, must be reached and exceeded. There is only one estimation published assessing the possibility of deformation of an idealized sheet crystal embedded in a viscous matrix under shearing flow [7]. Shearing of the matrix was found to lead to a mechanical instability of a crystal first layer which results in a continuous decrease in the coherence length of crystalline order in the sliding layers as the shear rate increases. The shear modulus and shear yield stress of the sheet crystal were at the level of 2 MPa, which value is characteristic for

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crystals of many polymers at temperatures slightly below their melting temperatures. The above estimation makes the idea to transform polymer crystals into nanofibers by shear deformation quite realistic.

Deformation of polymer crystals to large strains is possible when the density of entanglements persisting in the amorphous phase is drastically reduced. Hence, selection of polymer powder grains for the studies undertaken in the paper was based on the criteria of low chain entanglements along with their high crystallinity. This state can be achieved by crystallization under pressure (e.g. for polyethylene, PE, and poly(vinylidene fluoride), PVDF), crystallization from dilute solutions (e.g. DSM technology for Dyneema ultra strong PE fibers) and crystallization during polymerization (e.g. for polytetrafluoroethylene, PTFE, and PE). As polymerized PTFE powder grains can possess either chain-folded or chain-extended crystals and can be drawn to ultra high strains if the polymer chains are unentangled. In the case of PTFE, much less entangled system with either fully or nearly chain-extended crystals can be obtained by the crystallization during polymerization. If the number of catalytically active sites is very low and/or the polymerization temperature is far below the melting temperature, the polymerization rate becomes lower than the crystallization rate and it is possible to reach the state when growing polymer chains can be considered as separated from each other. This results in an independent growth of monomolecular crystals – a single chain forming a single crystal [8]. Polymer crystals grown during polymerization are called nascent or as-polymerized crystals [9]. The relatively slow polymerization of tetrafluoroethylene, TFE, which results in much faster crystallization compared to polymerization, enables the formation of separate chain-extended crystals of PTFE and/or their small agglomerates. Because of reduced density of entanglements and chain-extended fashion, easy deformation of PTFE by moderate shearing is possible. However, materials with chain-folded crystals even with unentangled macromolecules after melting lose entirely the advantageous ultradrawing feature. This confusing phenomenon was considered by Barham and Sadler [10] in the studies of melting of chain-folded crystals. Using neutron scattering and deuterated PEs they measured the changes in radius of gyration. For chain-folded crystals the radius of gyration is rather low and upon melting it suddenly inflates to the equilibrium value of a random coil. The expansion of chains is very rapid, less than few seconds, and pays no attention to the neighboring chains, which is in contrast to the reptation theory based on the reptation tube formed by fragments of neighboring chains. The phenomena associated with the melting of chain-folded crystals are termed “coil explosion”. Once the constraints, i.e. lattice forces are removed by melting, folded molecules expand rapidly, driven by the fold surface energy and the need to increase their entropy. Chain segments are then ejected with a high kinetic energy into already molten surrounding and interlace with other chains rapidly leading to significant increase of the number of entanglements. The phenomenon of “coil explosion” during melting is responsible for much lower crystallinity of PTFE during subsequent crystallization. Crystallization is impeded by entanglements formed during melting that are rejected to the amorphous phase. It is also an indication that molten and recrystallized PTFE loses its ultradrawing feature.

PTFE was used in the past to improve tribological properties of various polymers [11], although without motivation to deform PTFE grains into fibers. However, formation of fibers from grains of PTFE emulsions during shearing was noticed in the past in other studies [12–15]. Those studies aimed at the nucleation of crystallization of isotactic polypropylene, iPP, poly(methylene oxide), POM, and high density polyethylene, HDPE, by PTFE. Such deformation was also observed in our laboratory few years ago when nucleation of iPP

crystallization by up to 0.5 wt.% of PTFE inclusions was investigated [13]. Some PTFE grains were deformed into submicrofibers with lateral dimensions of 0.20–0.35 μm . But until now, no studies of critical conditions for nanofibrillation of PTFE and the mechanism responsible for deformation of PTFE crystals into nanofibers were conducted.

In this paper, we present a new way of preparation of *all-polymer* nanocomposites by generation of nanofibers *in situ* during compounding of molten polymer matrix with solid crystalline particles of another polymer. In particular we focused on controlled deformation of polymer grains into nanofibers by varying uniform shearing: shear rate and shear deformation, temperature in a rheometer as well as viscosity of a polymer matrix. To this end we selected *as-polymerized* PTFE crystalline powder, although, we think that the phenomenon is not limited only to this polymer, but many other highly crystalline polymer powders with low density of chain entanglements can be used for the purpose. The nanofibrillation of three brands of commercially available PTFE powders was examined and compared. The formation of nanocomposites with nanofibrillar inclusions was also studied during compounding using a twin-screw extruder and a batch mixer. Selected properties of the obtained *all-polymer* nanocomposites were also characterized.

2. Experimental section

2.1. Materials

Three grades of iPP differing in melt flow index, low density polyethylene, LDPE, HDPE, and atactic polystyrene, PS, were used as polymeric matrices. Three grades of commercially available PTFE powders were utilized as potential deformable fillers. Characteristics of thermoplastic polymers and PTFE fillers according to their manufacturers and codes used in the studies are presented below:

- iPP (1) (PP) having molecular weight, $M_w = 220$ kg/mol, melt flow index, MFI = 13.8 g/10 min (for 230 °C, 2.16 kg) and density, $d = 0.89$ g/cm³, by Polysciences, Inc.;
- iPP (2), Malen-P B200 (PPB) having MFI = 0.6 g/10 min (for 230 °C, 2.16 kg), $d = 0.91$ g/cm³, by Basell Orlen Polyolefins;
- iPP (3), Hostalen H 2150 (PPH) having MFI = 0.3 g/10 min (for 230 °C, 2.16 kg) and $d = 0.90$ g/cm³, by LyondellBasell;
- LDPE, Lupolen 1810D having MFI = 0.1–0.3 g/10 min (for 190 °C, 2.16 kg) and $d = 0.92$ g/cm³, by LyondellBasell;
- HDPE, S-2203 Hostalen ACP multimodal brand having MFI = 0.03 g/10 min (for 190 °C, 5 kg) and $d = 0.97$ g/cm³, by Basell Orlen Polyolefins;
- PS, having $M_w = 120$ –250 kg/mol and $d = 1.05$ g/cm³, by Polysciences, Inc.;
- PTFE (1), Teflon 7C (7C) having average particle size of 28 μm and melting peak temperature, $T_m = 346$ °C, by DuPont;
- PTFE (2), Microdispers-200 (M-200) having average particle size of 0.2–0.3 μm and $T_m = 325$ °C, by Polysciences, Inc.;
- PTFE (3), Fluoroplast-4 Reactor Bead (F4-RB) having $T_m = 345$ °C, by Kirowo-Chepieck Works, Russia.

2.2. Simple shear experiments

Simple shear experiments of selected materials for studying deformation of dispersed PTFE grains were performed using a strain-controlled rheometer (ARES LS2, TA Instruments). Parallel plates with diameter of 25 mm and the gap distance kept in the range of 0.8–0.9 mm were applied. Disk-shaped samples were cut out from 1 mm thick films prepared by compression molding at 200 °C of premixed components. Samples were subjected to

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