A Journey along the Extruder with Polystyrene:C₆₀ Nanocomposites: Convergence of Feeding Formulations into a Similar Nanomorphology

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S Supporting Information

ABSTRACT: We investigated the effect of the feeding formulation (premixed powders of pure components versus solvent-blended mixture) of polystyrene–C₆₀ composites on the dispersion and reagglomeration phenomena developing along the barrel of a twin-screw extruder. The dispersion of C₆₀ in the PS matrix is studied over different length scales using a combination of optical microscopy, spin-echo small-angle neutron scattering (SESANS), small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), and wide-angle X-ray scattering (WAXS). When a solvent-blended mixture is used as the feeding formulation, the inlet material contains essentially molecularly dispersed C₆₀ as revealed by the nanodomains with very small phase contrast. However, C₆₀ reagglomeration occurs along the extruder, creating a morphology still containing only nanodomains but with much higher phase contrast. In the case of mixed powders, the material evolves from the initial macroscopic mixture of pure polystyrene and C₆₀ into a composite simultaneously containing micro- and nanoaggregates of C₆₀ as well as C₆₀ molecularly dispersed in the matrix. Our results show that the two different initial feeding formulations with widely different initial morphologies converge along the extruder, through opposite morphological pathways, into a similar final nanomorphology which is dictated by the interplay between the thermodynamics of the system and the flow. Correlations between the morphological evolution along the extruder and the thermorheological properties of the composites are identified.

1. INTRODUCTION

Polymer nanocomposites containing carbon nanoparticles such as graphenes,^{1,2} carbon nanotubes,^{3–7} and fullerenes⁸ open a new horizon for polymeric-based materials. These materials benefit from a synergistic combination of useful polymer properties, such as low density, flexibility, ease of processing, and cost efficiency, with nanoparticles that not only significantly enhance the mechanical, electrical, and thermal properties of the resulting composite⁹ but also create novel functionalities. Although the homogeneous dispersion and distribution of carbon nanoparticles in a polymer matrix is generally desired to maximize performance, some level of particle aggregation can be advantageous in specific applications.^{10,11} Though property improvements have been achieved in a variety of nanocomposites, carbon nanoparticle dispersion remains difficult to

control, with both thermodynamic and kinetic processes playing significant roles.

The dispersion of carbon nanotubes and graphenes is complicated by their strong van der Waals interactions, chemical inertia that creates weak interfaces with most polymers, and difficulty to control initial size and shape of these nanoparticles. These parameters influence the cohesiveness of the agglomerates and have been related to dispersion routes such as rupture and erosion.^{12,13} Conversely, fullerene C₆₀ (also known as buckminsterfullerene) has a very well-defined size and shape: it is a bucky-ball with a diameter of 0.7 nm.^{14,15} When replacing graphenes or carbon nanotubes by

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fullerenes in a polymer composite, particle size and geometry change (these being associated with entropic changes) while the differences in enthalpic interactions between the particles and the matrix are kept at a minimum. For this reason, polymer composites with C_{60} can be used as model systems to help understand the dispersion of carbon nanoparticles.

In the past two decades, polystyrene (PS) composites containing fullerene nanoparticles have been the subject of a number of studies^{15–33} reporting improvements in properties such as electrical conductivity,^{22,23} thermal stability,^{24–27} and permeability.^{28,29} The impact of C_{60} loading and sample preparation conditions on the corresponding glass transition temperature (T_g) and melt viscosity has also received attention.^{16,19,34}

Campbell et al.²¹ used wide-angle X-ray scattering (WAXS) to determine the miscibility limit of C_{60} in PS as being ~ 1 wt %. In this context miscibility is understood as an absolute thermodynamic value associated with molecular homogeneity and which is reversible and independent of the pathway followed from aggregates to molecular dispersion; i.e., it is a maximum value that is independent of processing. An identical miscibility threshold was determined by Sanz et al.³⁴ using a combination of microscopy, SANS, and WAXS experiments. Additionally, these authors also determined a dispersibility threshold of ~ 4 wt % C_{60} , where this is the maximum C_{60} loading associated with the maximum observed increase in the T_g of the composites. Loadings beyond this concentration gradually reverted the composite T_g toward the neat PS value. Increases in T_g with C_{60} loadings in PS composites were also reported by Weng et al.³² and by Wong et al.,¹⁹ with the latter also concluding that beyond 1 wt % nanoparticle concentration the C_{60} is aggregated in polydispersed aggregates. Self-assembly of C_{60} into clusters within PS- C_{60} thin films was also reported, with the size of the clusters becoming macroscopic for C_{60} concentrations in the range 3–4 wt % C_{60} .³⁰

The impact of C_{60} on the melt viscosity of PS- C_{60} composites was studied by Tuteja et al.¹⁶ They showed that a viscosity reduction in the PS- C_{60} nanocomposites may occur if the polymer is entangled ($M_w > M_c$, where M_c is the critical molecular mass for entanglement coupling) and if the average interparticle half-gap (h) is less than the polymer size (i.e., $h < R_g$), where $h/a = [\Phi_m/\Phi]^{1/3} - 1$, Φ_m being the maximum random packing volume fraction (~ 0.638) and a being the particle radius (~ 0.4 nm). For nonentangled polymer melts ($M_w < M_c$), a viscosity increase is observed upon the addition of C_{60} . In practice, the authors observed a viscosity decrease in well-dispersed fullerene-polystyrene nanocomposites prepared via rapid precipitation from solution and using a PS with $M_w = 393$ kDa. On the other hand, a viscosity increase was observed when using a PS with $M_w = 19.3$ kDa.

In most of the preceding studies, PS- C_{60} blending was achieved through the use of solvents, using methods such as solvent casting or rapid precipitation from solution. Despite the fact that in the commodity plastics industry melt extrusion is a ubiquitous process for the manufacturing of polymer nanocomposites, with solvents rarely being used, in the scarce literature studies in which polymer- C_{60} blending was performed in an extruder no attempts were made to assess the dispersion achieved.²⁷ Therefore, there is an obvious fundamental and practical interest in studying how C_{60} nanoparticles can be mixed with polystyrene in a melt extruder.

In this work, we conduct a detailed investigation of the dispersion of fullerene C_{60} in polystyrene composites along an

intermeshing corotating twin-screw extruder. We study and compare two different types of melt-processed PS- C_{60} composites that were prepared using identical C_{60} loadings (1 wt %) and processing conditions (flow rate = 130 g h^{-1} , screw speed = 80 rpm; extruder and die set temperature = 200°C), but which differ widely on the quality of dispersion of the initial material: (i) mixed powders of pure polystyrene and pure C_{60} and (ii) a solvent preprocessed PS- C_{60} blend. The morphological characterization of the composites was performed using both direct and indirect characterization techniques. Five direct morphological characterization techniques were used to probe four different length-scale regimes, namely, optical microscopy for the $\sim 1 \text{ mm}$ – $1 \mu\text{m}$ range; spin-echo small-angle neutron scattering (SESANS)³⁵ for the $\sim 20 \mu\text{m}$ – 200 nm range; small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) for the $\sim 200 \text{ nm}$ – 1 nm range; and wide-angle X-ray scattering (WAXS) for the subnanometer range. Additionally, the composites were characterized by differential scanning calorimetry (DSC) and rheological measurements, as indirect morphological characterization techniques, to provide an overall understanding of the processing–structure–property relationships in these model polymer–fullerene systems.

This paper is organized as follows. We first describe the sample preparation methods. Then we characterize the dispersion of C_{60} in the composite samples using optical microscopy, SESANS, SANS, SAXS, and WAXS. Next, we study the variation of the glass transition temperature with sample preparation conditions, and we characterize the samples rheologically. Finally, we discuss and rationalize all the results obtained.

2. EXPERIMENTAL SECTION

2.1. Materials. The C_{60} fullerene used in this work was supplied by Solenne BV ($>99.5\%$ purity, $M_w = 720.64 \text{ g mol}^{-1}$ and density = 1.65 g cm^{-3}). The polystyrene was purchased from Sigma-Aldrich (catalog # 430102) with average $M_w \sim 192\,000$, MFI = 6.0 – 9.0 g/10 min (200°C/5 kg), and density of 1.05 g cm^{-3} at 25°C . The polymer R_g is approximately 12 times larger (estimated from $R_g \cong 0.27M_w^{1/2}$ ³⁶) than the diameter of C_{60} ($\sim 1 \text{ nm}$).

2.2. Nanocomposite Preparation. Two different types of PS- C_{60} formulations were prepared as feeding material for the twin-screw extruder: (a) 1.0 wt % C_{60} was simply mechanically mixed with PS (hereafter simply referred to as “mixed powders”), and (b) mixtures with 1.0 wt % C_{60} were prepared by solution blending followed by coprecipitation in a nonsolvent (hereafter referred to as “pre-solvent blended”).

In the preparation of the mixed powders formulation, the granulated polystyrene was milled into a fine powder and then thoroughly mixed with the, as purchased, fine C_{60} powder in a rotating mixer.

In the preparation of the pre-solvent blended formulation, appropriate amounts of PS and C_{60} were dissolved in toluene, while stirring at 80°C for 4 h. Then, the solution was added dropwise into a 5-fold volume excess of precooled methanol ($T < 0^\circ\text{C}$) under continuous stirring, to enable the coprecipitation of the PS- C_{60} composite. The solids were vacuum filtered from methanol using a nylon membrane filter with a pore size of $0.45 \mu\text{m}$ (Whatman, cat no. 7404-004) and washed with cold methanol. This was followed by drying at $\sim 100^\circ\text{C}$ and 10^{-2} mbar for several hours, until no mass changes were detected using a balance with a precision of $\pm 0.01 \text{ g}$. Upon drying, light purple fiber composites were obtained. The yield of composite preparation was $\sim 100\%$, showing that no C_{60} and polystyrene losses had occurred. The total amount of pre-solvent blended formulation prepared was $\sim 35 \text{ g}$ (after drying). Finally, the fibrous composite was milled into a fine light purple powder.

The two types of feeding formulations were then melt processed in a prototype corotating intermeshing twin-screw extruder of modular

construction (Figure S.I.1.(a) in Supporting Information), designed to process small amounts of material (in the range of 30–300 g/h) while retaining the same characteristics of larger equipment. The screws have a diameter of 13 mm and an L/D ratio of 27 (Figure S.I.1.(b)). The screw profile is built by sliding along a shaft conveying (with distinct pitches and lengths) and kneading elements (that can be stacked with variable staggering angles to induce different hydrodynamic stress levels and therefore variable balances of distributive/dispersive mixing). The barrel contains nine material sampling ports, evenly distributed along its length. These are manually operated rotary valves which allow one to quickly remove small volumes of material from within the extruder during steady state operation.^{37,38} A miniaturized prototype volumetric feeder is positioned upstream. The screw profile used in this work contained two kneading zones consisting of four 3 mm thick kneading disks staggered at -30° (for intensive mixing) separated by a conveying zone. The flow channels had a maximum depth of 1.5 mm so that shear rates were relatively high, even at low screw speeds.

Each PS- C_{60} mixture was compounded at a flow rate of 130 g/h, with the screws rotating at 80 rpm. The temperature profile along the barrel and the slit die (5 mm $\times$ 1 mm) was kept at a constant 200 °C for all the processing experiments. In order to track the quality of the mixing along the extruder, spherically shaped composite samples in their molten state were collected at sampling ports P2 and P9 during steady state extruder operation. These molten samples were then sandwiched between two Teflon sheets placed between two metal plates and slightly compressed, while cooling down to room temperature, into approximately circular disks with thickness $\sim$ 1.5 mm and diameter $\sim$ 20 mm (see Figure S.I.2). These samples, hereafter simply referred to as samples P2 and P9 depending on the sampling port from which they were collected, as well as the extruded ribbons collected after air cooling and winding were then stored for subsequent characterization. To keep the extrusion line running continuously, the lowest possible draw-down (i.e., the ratio between the linear velocity of the winder and the extrudate velocity) was applied.

Additionally, reference samples with C_{60} :PS weight ratios 1:99 were prepared by compression molding: (i) a mixture of the pure powders at 170 °C and 10 MPa during 5 min (one sample produced); (ii) powders of the solvent blended composite at 90 and 170 °C and 10 MPa during 5 min (two samples produced). These three reference samples were also stored for subsequent characterization.

All the samples are shown in Figure S.I.2. The initial sample compression molded from mixed powders is mostly colorless and transparent, albeit containing a few macroscopic black spots in it. The initial pre-solvent blended sample is purple and transparent. The samples from mixed powders collected at P2, P9, and ribbon are all dark brown and optically opaque. The samples from pre-solvent blend collected at P2, P9, and ribbon are light brownish and still optically transparent to some degree.

2.3. Nanocomposites Characterization. **2.3.1. Optical Microscopy.** The agglomerate size distribution in the initial, i.e., before melt compounding, pre-solvent blended and mixed powder formulations was determined by light transmission optical microscopy (OM) using a BH2 Olympus microscope coupled to a Leica DFC 280 camera, with a 1.6 $\times$ ocular and 20 $\times$ objective magnification. For microscopy observations, the feeding formulations (in powder form) were softened at 160 °C and spread onto a glass slide.

The evolution of dispersion along the extruder was estimated by OM. For this, 10 μ m thin sections were cut from samples at room temperature with a Leitz 1401 microtome using glass knives with an angle of 45°. The extruded tapes were molded in an epoxy resin and cut perpendicular to the flow direction. Micrographs were acquired using the same microscopy equipment and under similar magnifications. To obtain sufficient statistics, at least six micrographs were analyzed using ImageJ Software, leading to an investigated total area of 2.1 mm².

The level of dispersion was quantified in terms of area ratio (Ar), which balances the total area of agglomerates and the total area analyzed, and cumulative relative distribution of the agglomerates

(C_{C60}). This is determined by summing the areas of the individual agglomerates in ascending area order and dividing by the total area of agglomerates. In particular, the size of the larger agglomerate contained in 75% ($A_{75\%}$) and 90% ($A_{90\%}$) of the total area of agglomerates were followed.

2.3.2. Spin-Echo Small-Angle Neutron Scattering (SESANS). Spin-echo small-angle neutron scattering (SESANS) is a relatively new technique to measure structures of materials. Structures can be determined over 3 orders of magnitude in length scale, from 10 nm to 20 μ m. This is 2 orders of magnitude larger than conventional SANS and comparable to what may be studied with light scattering or OM, though with the complementary benefits afforded by the use of neutrons such as contrast and probing the bulk. However, like OM, and unlike SANS (or SAXS), SESANS measures in real space.

Briefly, SESANS uses a series of magnetized permalloy films and magnetic fields to encode the scattering angle information in the spin precession of a beam of polarized neutrons. Neutrons scattered through different angles traverse magnetic fields of different lengths and thus precess differently to the unscattered neutrons. The structural length scale probed depends upon the applied magnetic field strength, hence varying the magnetic field strength provides tunability over a range of length scales, termed the spin-echo length.

The SESANS measurements reported here were performed at the Reactor Institute Delft (TU Delft, Netherlands), using a beam monochromatized (using a pyrolytic graphite crystal) to a wavelength $\lambda = 2.06$ Å.³⁵ The pre-solvent blend sample was measured for 4 h while the sample from mixed powders was measured for $\sim$ 12 h over the same spin-echo length range.

2.3.3. Small-Angle Neutron Scattering (SANS). Small-angle neutron scattering (SANS) measurements were performed at the LOQ diffractometer at the ISIS Pulsed Neutron Source (Rutherford Appleton Laboratory, Oxfordshire, UK) with a polychromatic incident beam of $\lambda = 2$ –10 Å and fixed sample-to-detector distance of 4 m, to provide a scattering vector range of $0.009 < q < 0.25$ Å⁻¹, where $q = (4\pi/\lambda) \sin(\theta/2)$ and θ is the scattering angle. Because of the high carbon to hydrogen content in C_{60} , there is a naturally high neutron scattering length density contrast with the hydrogenous polystyrene polymer removing the need for isotopic substitution (deuteration). However, there is a greater degree of incoherent background scattering from the matrix that degrades the signal-to-noise, particularly at larger q values.

The samples P2 and P9 were $\sim$ 1.5 mm thick, and the extruded ribbons were $\sim$ 0.7 mm thick although their exact thicknesses were measured by a micrometer and those values used in the data reduction procedure to ensure proper intensity scaling. Samples were mounted on a computer-controlled sample changer and SANS patterns were recorded at room temperature for approximately 90 min/sample. Each raw scattering data set was then radially averaged, corrected for the detector efficiency, sample transmission, and background scattering, and then converted to scattering cross-section data and plotted on an absolute scale ($\partial\Sigma/\partial\Omega$ vs q) using Mantid software.³⁹ For convenience, we shall follow the normal convention of referring to $\partial\Sigma/\partial\Omega$ as intensity (I). The corrected data were then fitted to appropriate models using SasView software (Version 3.1.1).⁴⁰ The neutron scattering length densities of hydrogenous PS and of C_{60} are respectively $\rho_N(\text{H-PS}) = 1.41 \times 10^{-6}$ Å⁻² and $\rho_N(C_{60}) = 5.50 \times 10^{-6}$ Å⁻² and therefore $\Delta\rho_N = 4.09 \times 10^{-6}$ Å⁻².

2.3.4. Small-Angle X-ray Scattering (SAXS). SAXS measurements were performed in-house on a Bruker instrument (NanoStar, Department of Chemistry, University of Sheffield, UK) equipped with a microfocus Cu $K\alpha$ source (8 keV, $\lambda = 1.54$ Å; Xenocs, France), collimating system with motorized scatterless slits (Xenocs, France) and a HiStar 2D multiwire gas detector (Siemens/Bruker). Scattering patterns were corrected for the detector's dark current, spatial distortion, flat field, and normalized using sample thickness, exposure time, sample transmission, and the detector normalization coefficient. The electron densities of hydrogenous PS and of C_{60} are respectively $\rho_X(\text{H-PS}) = 9.56 \times 10^{-6}$ Å⁻² and $\rho_X(C_{60}) = 1.40 \times 10^{-5}$ Å⁻² and therefore $\Delta\rho_X = 4.44 \times 10^{-6}$ Å⁻².

2.3.5. Wide-Angle X-ray Scattering. WAXS measurements, of samples P9 from both mixed powders and solvent processed blend, were performed on a Xeuss 2.0 SAXS/WAXS laboratory beamline using a liquid Gallium MetalJet (Excillum) X-ray source (9.2 keV, $\lambda = 1.34$ Å). The scattered X-rays were detected using a Pilatus3R 1M detector. Scattering from the samples was collected at room temperature for 3 min.

2.3.6. Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) experiments were performed on a PerkinElmer Pyris-1 calorimeter under nitrogen where temperature and heat capacity were calibrated using a sapphire standard. Thermal history was eliminated by ramping from 25 to 150 °C at 10 °C min⁻¹, isothermal annealing at 150 °C for 2 min, and then cooling to 30 °C at 10 °C min⁻¹. Two heating-cooling cycles were run. The glass transition temperature T_g was computed from the second heating run following the half- C_p extrapolation method. Error bars in T_g are estimated by the maximum deviation of three independent measurements.

2.3.7. Rheometry. Disks were loaded between the parallel plates (diameter 25 mm) of a stress-controlled rotational rheometer (ARG2, TA Instruments) at a temperature of 200 °C under air. Time was left for the samples to thermally stabilize and adjust to the defined gap between the parallel plates, as inferred from the online reading of the normal force relaxation. A time sweep was first performed at 1 Hz with a deformation of 0.1% (corresponding to the linear regime of viscoelasticity as inferred from separate strain sweep experiments performed at 1 Hz) to confirm the thermal stability of all samples within 20 min. Then a new sample was loaded and equilibrated as mentioned above, for the recording of a mechanical spectrum using a frequency sweep performed with a deformation of 0.1%.

3. RESULTS AND DISCUSSION

As an aid to the analysis and discussion of our experimental results, we start by showing in Figure 1 an idealized schematic of the different possible stages of C_{60} dispersion in a polymer matrix.

Figure 1. Idealized schematic of C_{60} dispersion in the polymer matrix along the extruder, starting from macroscopic agglomerates of C_{60} in a matrix of pure polymer and ending with an idealized mixture of individual C_{60} molecules homogeneously dispersed in the polymer matrix.

There are two extreme situations, namely situation A in which macroscopic and microscopic agglomerates of C_{60} coexist in a matrix of pure polymer and situation D consisting of an idealized mixture of individual C_{60} molecules homogeneously dispersed in the polymer matrix. Two intermediate cases (B and C) correspond to a mixture of microscopic and nanoscopic agglomerates of C_{60} in a polymer matrix containing some molecularly dispersed C_{60} and to a mixture of nanoscopic agglomerates in a polymer matrix containing a considerable amount of molecularly dispersed C_{60} , respectively.

The level of dispersion of C_{60} in the initial feeding formulations and in the samples collected along the extruder was first investigated by optical microscopy (OM), as shown in Figure 2 and Figure S.I.3.

Figure S.I.3 shows optical microscopy images of the initial feeding formulations. The image of the “mixed powders” feeding formulation shows large black aggregates in a matrix of essentially pure polystyrene. Overall, this formulation shows both a poor dispersion and poor distribution of the aggregates. By contrast, on the image of the “solvent-blended” feeding formulation, although some randomly distributed darker spots are visible, these are not large black aggregates. These darker spots most likely result from some possible heterogeneities (regions with different PS: C_{60} ratio) inherent to the precipitation process used in the preparation of this composite. Also visible in the “solvent-blended” figure is a larger, approximately circular, feature with ~ 50 μm diameter which corresponds to material that did not melt during the preparation of the optical microscopy samples.

The morphology development of PS nanocomposites containing 1 wt % of C_{60} along the extruder is presented in Figure 2a. As clearly shown, the extruded samples prepared from mixed powders contain a large number of microscopic aggregates. By contrast, in the extruded samples prepared from pre-solvent blend the number and size of microscopic features is much smaller. Figure 2b displays the corresponding evolution of the area ratio, and the dispersion characterization results are summarized in Table 1. As shown in Figure 2 and Table 1, in extruded samples from both mixed powders and pre-solvent blend, the area ratio remains approximately constant along the extruder.

It is well accepted that dispersion of solid agglomerates in a molten matrix occurs when the hydrodynamic stresses developed during flow are larger than the cohesive strength of the agglomerates. This balance is usually quantified by the fragmentation number, F_a . It has been suggested that when F_a is large, dispersion is dominated by the rupture of the agglomerates into successively smaller aggregates. When F_a is small, erosion should prevail. This is a much slower dispersion route, whereby small aggregates or individual particles detach from the agglomerates. Both phenomena were reported in studies of the dispersion of carbon nanotubes and graphite nanoplates.^{41,42} In the present work, as the area ratio remained constant along the extruder, this means that no substantial rupture took place, but some dispersion may have developed via erosion, as in this case the large agglomerates are still visible by optical microscopy.

The SESANS data from two nanocomposites extracted from port P9 are shown in Figure 3. The data from the mixed powder sample have been fitted to a model of monodispersed particles using the Gaussian approximation formalism detailed by Andersson et al.,⁴³ and the resulting fit is also shown in Figure 3.

This modeling approach is used as the system is low concentration, and no consideration of a structure factor is necessary. The best fit to the data, in which the radius was the only free parameter, was found for particles of radius 2.83 ± 0.10 μm . The scattering length densities were fixed at the values quoted in Table 2, as derived from the SANS data analysis detailed below. We note in passing that the extended tail of the data at longer spin-echo lengths suggests that there is in fact a dispersion in the particle sizes of the agglomerates.

Figure 2. (a) Morphology development of PS nanocomposites containing 1 wt % of C_{60} along the twin-screw extruder. (b) Area ratio evolution along the twin-screw extruder of PS nanocomposites containing 1 wt % of C_{60} .

Table 1. Optical Microscopy Dispersion Characterization Results for PS Nanocomposites Containing 1.0 wt % of C_{60}

position	pre-solvent blended			from mixed powders		
	$A_{\chi 75\%}$ (μm^2)	$A_{\chi 90\%}$ (μm^2)	N (per mm^2)	$A_{\chi 75\%}$ (μm^2)	$A_{\chi 90\%}$ (μm^2)	N (per mm^2)
P2	16.91	24.07	88 ± 10	59.31	161.88	988 ± 137
P9	17.48	28.95	88 ± 16	71.34	178.22	980 ± 76
ribbon	18.86	33.84	92 ± 16	87.43	374.48	1020 ± 235

No structure was observed in the pre-solvent blended sample on SESANS length scales; however, some depolarization is observed ($\langle P \rangle = 0.9953$ which can be attributed to very small structures (well below the micrometer level observed in the mixed powder sample). In the micrographs obtained by optical microscopy there is some evidence for larger structures in the pre-solvent blended sample. However, Figure 2b shows that the area ratio is 1 order of magnitude smaller than that of the mixed powders. The change in SESANS polarization ratio as a function of spin-echo length is given by $P = P_0 \exp(\sum_t [G(z) - 1])$, where $G(z)$ is the projection of the density distribution along the measurement axis and the term $\sum_t$ (the fraction of neutrons that are scattered only once) in a binary mixture scales with the volume fraction Φ as $\Phi(1 - \Phi)$. Hence, if one assumes that the area ratio of agglomerates measured at the

surface is consistent with their volume fraction in the bulk, then the change in polarization ratio would be of the order 1%, which is at the limits of detection for the instrument used.

In order to probe the bulk nanomorphology of the composite samples at length scales from ~ 1 to 200 nm, we used SANS, and the results are shown in Figure 4. In SANS, the intensity is proportional to the number, size, and contrast of the scattering entities in a sample, while the q -dependence of the intensity is related to their shape and local arrangement. So in our composites it is the scattering from the C_{60} that dominates the SANS, not the hydrogenous PS (which would be expected to contribute a mostly flat background).

We have started our analysis of the SANS data by determining if processing induces any nanoscale orientation in our samples. In the Supporting Information, Figure S.I.4.(a)

Figure 3. Spin-echo SANS signals, expressed as the depolarisation ratio P/P_0 , of extruded PS- C_{60} nanocomposites extracted from sampling port 9. The black line is a fit to a monodisperse sphere model while the blue line is a constant illustrating a small depolarisation over those length scales probed in the pre-solvent blended sample.

shows the 2D SANS patterns from extruded ribbons processed from both a pre-solvent blend and from mixed powders, and in Figure S.I.4.(b) we show the corresponding intensity ratios $I(Q_V)/I(Q_H)$ as a function of q for the vertical and horizontal quadrants of the 2D patterns. As clearly shown, the nanoscale distribution of C_{60} aggregates in the extruded ribbons is isotropic. Accordingly, the SANS data were circularly averaged to produce 1D graphs of intensity vs q .

As shown in Figure 4a for the pre-solvent blended composite, five different samples were analyzed using SANS, namely, (a) a compression-molded sample annealed at 90 °C for 5 min, (b) a similarly compression-molded sample annealed at 170 °C for 5 min, (c) an extruded sample collected at P2, (d) an extruded sample collected at P9, and (e) an extruded ribbon.

As can be seen in Figure 4a, the neutron scattering intensity $I(q)$ of the compression-molded sample annealed at 90 °C for 5 min is very weak and only increases slightly when the annealing temperature increases to 170 °C. Our goal on testing these samples at these two temperatures (90 and 170 °C), intermediate between room temperature and the extrusion temperature (200 °C), was to study the effect of temperature alone on the nanomorphology of the composite samples as they are heated at the very beginning of the extruder.

When the composites are fed into the extruder, an abrupt increase of nearly 1 order of magnitude in scattering intensity occurs in the early stages of the extrusion process, as revealed

Figure 4. SANS data from extruded PS- C_{60} nanocomposites (identical scales have been used for ease of comparison): (a) pre-solvent blended; (b) prepared from mixed powders of PS and C_{60} .

by a comparison between the two previous samples and the sample P2. Indeed, it can be seen that the scattering intensity continues to increase further along the extruder, reaching a maximum value in the extruded ribbon.

Figure 4b presents the SANS data for the corresponding composites prepared from mixed powders of the pure components PS and C_{60} . Also shown for comparison are the background (incoherent) SANS scattering of a ribbon of pure PS extruded under the same conditions as well as the SANS of a sample prepared by compression molding at 170 °C

Table 2. SANS Fitting Parameters (DAB Model) for the q Range 0.009–0.2545 $\text{\AA}^{-1}$ ^a

		C_{DB} ($\text{\AA}^{-4}$)	$\Delta\rho$ ($\text{\AA}^{-2}$)	length L (nm)	m
pre-solvent blended	90 °C	$2.5 \times 10^{-6} \pm 2.9 \times 10^{-7}$	3.91×10^{-7}	14.7 ± 4.1	1.2 ± 0.3
	170 °C	$3.9 \times 10^{-6} \pm 1.2 \times 10^{-6}$	4.88×10^{-7}	25.0 ± 12.3	1.8 ± 0.3
	P2	$3.8 \times 10^{-5} \pm 8.4 \times 10^{-7}$	1.52×10^{-6}	20.7 ± 0.8	2.7 ± 0.03
	P9	$7.3 \times 10^{-5} \pm 1.1 \times 10^{-6}$	2.11×10^{-6}	20.5 ± 0.5	3.1 ± 0.02
	ribbon	$9.7 \times 10^{-5} \pm 2.2 \times 10^{-6}$	2.44×10^{-6}	25.5 ± 0.9	3.3 ± 0.02
from mixed powders	P2	$3.2 \times 10^{-5} \pm 3.8 \times 10^{-7}$	1.40×10^{-6}	14.9 ± 0.4	2.6 ± 0.03
	P9	$3.0 \times 10^{-5} \pm 3.9 \times 10^{-7}$	1.35×10^{-6}	15.6 ± 0.5	2.5 ± 0.03
	ribbon	$2.4 \times 10^{-5} \pm 7.6 \times 10^{-7}$	1.21×10^{-6}	14.9 ± 1.2	2.4 ± 0.07

^a C_{DB} is the scaling factor, $\Delta\rho$ is the contrast between the two phases, L is the average distance between the two phases, and m is the slope of the SANS data in their linear region extracted using the power law model ($I(q) \propto q^{-m}$).

consisting of C₆₀ and PS powders in the weight ratio 1:99. This sample corresponds to the unmixed reference, i.e., a sample in which C₆₀ and PS are not intermixed (situation A in Figure 1). As seen in Figure 4b, there is again an almost 1 order of magnitude increase in scattering intensity in the early part of the extruder, i.e., from the powder mixture at the inlet (here represented by our “unmixed reference”) to sampling location P2. But, contrary to what is observed with the pre-solvent blended composites, the scattering intensity changes very little with processing from sampling location P2 to the die outlet.

We continued our SANS analysis by determining the slopes of the SANS data in their linear regions (between 0.009 and 0.015 Å⁻¹ for the pre-solvent processed composite samples compression molded at 90 and 170 °C and between 0.009 and 0.025 Å⁻¹ for the pre-solvent processed composite samples collected from the extruder and for the composite samples prepared from mixed powders) with a simple power law model fit of the form $I(q) \propto q^{-m}$, where m is related to the fractal dimension of the underlying structure.

Considering first the samples prepared from pre-solvent processed composites, we find the value of m increases from 1.2 at 90 °C, to 1.8 at 170 °C, and to 2.7, 3.1, and 3.3 at sampling locations P2, P9, and the extruded ribbon, respectively (see details in Table 2). This indicates that with increasing temperature and residence time inside the extruder, the mass distribution of C₆₀ changes from something sparsely distributed to something more clustered, with the PS–C₆₀ interfaces becoming better defined. These factors point to nano-agglomeration of the C₆₀.

Turning now to the composite samples prepared from mixed powders of PS and C₆₀, we find that the value of m exhibits a small decrease from 2.6 in P2, 2.5 in P9, and 2.4 in the extruded ribbon (Table 2). This indicates that processing induces a slight shift in the C₆₀ mass distribution toward something less clustered and with more diffuse PS–C₆₀ interfaces, suggesting some improvement of dispersion in these composites.

A more quantitative approach to interpreting the SANS data is to model-fit it over its full range ($q = 0.009\text{--}0.2545\text{ Å}^{-1}$). The model we have chosen to use for this is the Debye–Bueche (DB), also called the Debye–Anderson–Brumberger (DAB), model^{44,45} (eq 1). This model calculates the scattering from a randomly distributed, two-phase system that is characterized by a single length scale—the correlation length, L —which is a measure of the average spacing between regions of the two different phases (1 and 2). Crucially, this model makes no assumptions about the underlying morphology of the sample. The DAB function has the form

$$I(q) = C_{\text{DB}} \frac{L^3}{(1 + (qL)^2)^2} + \text{background} \quad (1)$$

where the prefactor $C_{\text{DB}} = 8\pi K(\Delta\rho)^2\phi_1\phi_2$, where $\Delta\rho$ is the neutron scattering length density difference between the phases having volume fractions of ϕ_1 and ϕ_2 and K is a scalar to convert the units of L^{-1} to those of $I(q)$ (i.e., cm⁻¹).

As shown in Figure 4, the DAB model (solid lines) gives a good description of the data. We have not fitted the data for the sample of mixed powders compression molded at 170 °C (sample “mixed powders-initial” in Figure S.I.2) and for the extruded ribbon of pure PS because neither of these samples conforms to the physics of the DAB model. The small amount of residual low- q scattering that is evident in these two samples

results most likely from some large-scale heterogeneities (e.g., voids).

The values obtained from the fitting for C_{DB} and L using eq 1 are shown in Table 2. The values of $\Delta\rho$ calculated from the respective C_{DB} values are also included. All these values are depicted graphically in Figure 5.

Figure 5. Evolution of the correlation length (L), phase contrast ($\Delta\rho$), and slope (m) with processing for the samples prepared: (a) from pre-solvent blended composites; (b) from mixed powders of pure PS and pure C₆₀.

According to the values in Figure 5a and in Table 2, in the case of the samples prepared from solvent-processed blends, there is some increase in correlation length of the phase domains along the barrel of the extruder which indicates the occurrence of some phase domain coarsening. However, the most striking feature of these samples is the ~1 order of magnitude increase in the scattering length density difference between the two phases ($\Delta\rho$), from $3.91 \times 10^{-7}\text{ Å}^{-2}$ in the initial sample to $2.44 \times 10^{-6}\text{ Å}^{-2}$ in the extruded ribbon, which clearly indicates that during processing the phases become purer due to C₆₀ reagglomeration. In the extreme situation of having pure phases of PS and pure phases of C₆₀ the corresponding $\Delta\rho$ would be $4.19 \times 10^{-6}\text{ Å}^{-2}$.

According to Figure 5b and Table 2, in the case of composite samples prepared from powder mixtures of pure C₆₀ and PS, the correlation length between the two phases remains approximately constant (~15 nm) from sample P2 to the extruded ribbon, and the phase contrast decreases slightly, suggesting only a slight improvement in the quality of the nanodispersion.

In summary, therefore our SANS results show that the major changes in the nanomorphology of the PS–C₆₀ composites occur in the early stages of the extrusion process, between the

hopper and sampling port 2. This is in accordance with observations reported for other polymer-based systems, such as polymer blends and composites containing layered silicates, carbon nanotubes, or graphene derivatives. As the material reaches the first kneading zone of the screw, it melts as a result of a combination of conducted and dissipated heat. Since melt temperatures are still low, hydrodynamic stresses are high, favoring dispersion. Moreover, flow through kneading disks is complex, promoting distribution. Furthermore, according to our SANS results, in the case of composites prepared from the pre-solvent blend the main morphological evolution that occurs along the extruder is a continuous reagglomeration of the initially molecularly dispersed C_{60} into purer phase domains. In the case of composites prepared from mixed powders the main morphological evolution is an initial abrupt increase in the degree of dispersion up to sampling location P2, followed by a much less visible morphological evolution from P2 to the die exit.

Figure 6 illustrates the SAXS data for the same samples as in Figure 4, namely in Figure 6a for the pre-solvent blended

Figure 6. Small-angle X-ray scattering of extruded PS and PS- C_{60} nanocomposites: (a) pre-solvent blended; (b) prepared from mixed powders of PS and C_{60} .

composites heated to 90 and 170 °C, and also collected from P2, P9, and extruded ribbon, and in Figure 6b for the composites compounded from mixed powders and collected at P2, P9, and extruded ribbon. Again, data in the q range 0.009–0.025 $\text{\AA}^{-1}$ were fitted with a linear power law and obtained values of m . These are plotted in Figure S.I.5.

As seen, in both Figures 6a and 6b as well as in Figure S.I.5, the SAXS data show trends very similar to those observed in the corresponding SANS data, namely, (a) in the case of pre-solvent blended composites m increases progressively from $m = 2.5$ in the sample heated to 90 °C to $m = 3.4$ in the extruded ribbon; (b) in the case of composites from mixed powders m changes only very little between sampling location P2 and the extruded ribbon, specifically a small decrease is observed from $m = 3.0$ in location P2 to $m = 2.9$ in the extruded ribbon. These observations corroborate the previous SANS results showing that: (a) in the case of samples prepared from pre-solvent processed blends, PS- C_{60} interfaces become progressively sharper as the material progresses along the screw which points strongly to the occurrence of C_{60} reagglomeration; (b) in the case of samples prepared from mixed powders, there is a slight improvement in mixing from sampling location P2 to the extruded ribbon with the PS- C_{60} interfaces becoming slightly less sharp.

The 1D WAXS patterns for the two samples prepared from the two different feeding formulations and collected from sampling port P9 are shown in Figure S.I.6. In both samples the two broad amorphous halos with maxima at $q = 0.75 \text{ \AA}^{-1}$ and $q = 1.35 \text{ \AA}^{-1}$ are due to the amorphous polystyrene. For mixed powders, at location P9 a crystalline C_{60} peak is clearly visible at $q = 0.77 \text{ \AA}^{-1}$ as well as two small peaks at $q = 1.26$ and $1.48 \text{ \AA}^{-1}$.³⁴ These peaks, which are not visible in the pre-solvent processed sample, are due to the presence of crystalline C_{60} aggregates.^{21,34} These results reinforce those obtained by OM and SESANS showing that extruded samples processed from mixed powders retain crystalline C_{60} aggregates while the samples processed from pre-solvent blend either do not have any crystalline C_{60} aggregates or have them in such a low quantity that they are below the detection limit of the WAXS technique.

To investigate this morphological evolution further, we have performed some transmission electron microscopy (TEM) analysis of the samples collected from P2 and P9 for both the composites prepared from mixed powders and from pre-solvent blend. Figures S.I.7 and S.I.8 show some representative TEM images. The TEM images show that in the case of composites processed from mixed powders the size and number of aggregates decrease along the extruder, and in the case of composites processed from the solvent blend the size and number of the aggregates increase along the extruder, a finding in good qualitative agreement with our SANS data.

Before proceeding further, we believe it is important to make a few comments about the complementarity of some of the different direct measurement techniques for assessing nanocomposite morphology. While TEM is arguably more accessible than neutron scattering, it nonetheless has some drawbacks, particularly for studying polymer composites. First, there is the issue of the representative nature of the sampling process: TEM is subjective in the sense that the operator must search the sample for regions of interest, and those regions of interest must be at or near to the surface of the sample. In contrast, SANS is a bulk sampling technique: the beam is essentially the same size as the sample and the weak neutron–nucleus interaction conveys depth penetration. In the present work we have used a 10 mm diameter neutron beam, meaning the illuminated area $\sim 78 \text{ mm}^2$ ($= 78\,000\,000 \text{ }\mu\text{m}^2$). However, in the TEM pictures shown in the Supporting Information the maximum area probed in a single picture (Figure S.I.7.(a)) is only $\sim 60 \text{ }\mu\text{m}^2$. SAXS suffers from a similar limitation to TEM

in this respect. Second, to achieve any penetration into a sample with electron or X-ray beams, it is necessary to use beams of high energy (many keV), energies that are way beyond covalent bond energies meaning that there is a significant possibility of radiation-induced damage in the sample. The “cold” neutrons used in SANS, on the other hand, have energies of just a few meV, meaning SANS is a genuinely nondestructive technique. Lastly, there is the issue of phase contrast. Electrons and X-rays interact with atomic electrons meaning that the greatest contrast is obtained between elements of significantly different atomic number. In our samples we have carbon dispersed in a matrix of carbon and hydrogen. This means that for example, in the TEM pictures we have provided in the [Supporting Information](#), there is no reliable way of knowing if what we see are aggregates of C_{60} in a matrix of pure PS or regions rich in C_{60} in a soup of PS with some very well molecularly dispersed C_{60} . In SANS, however, the phase contrast also stems from the neutron–nucleus interaction and can be very different between nuclei of similar atomic number, as it indeed is between carbon and hydrogen. Thus, while our neutron measurements do not provide the same visually intuitive picture of a sample that TEM does, they are sensitive to structural information that TEM simply is not.

In [Figure 7](#), we show the DSC data, where we plot the variation of the glass transition temperature T_g with processing.

Figure 7. Variation of the glass transition temperature (T_g) along processing. T_g was determined using the extrapolated half- C_p method. Associated error bars are typically ± 1 °C.

The T_g of the pure polystyrene is ~ 102.4 °C. In the case of composites processed from mixed powders of C_{60} and PS, we observe that the corresponding T_g increases to ~ 103.2 °C at location P2 and then remains approximately unaltered at P9 and in the extruded ribbon. Based on previous work,^{19,32,34} this ~ 0.8 °C increase in T_g may be explained by the occurrence of some molecular dispersion of C_{60} in the PS matrix and corroborates our SANS results. It also shows that this molecular dispersion principally occurs in the first part of the extruder, i.e., between the hopper and sampling location P2. In the case of the samples extruded using pre-solvent blended composites we note that the T_g of the initial solvent blended powder was ~ 100 °C, i.e., lower than the T_g of the pure polymer. This most likely results from the fact that the solvent-blended composite still contained some traces of solvent trapped inside the material in spite of the drying under vacuum at 100 °C for several hours. In order to probe for the presence of trapped-solvent, we have performed some thermogravimetric analysis (TGA) of the

solvent-blended composites ([Figure S.I.9](#)) which showed no clear evidence of its presence, within the resolution of the technique. However, we did observe contamination on surface of solvent processed samples caused by the electron beam ([Figure S.I.10](#)). This well-known surface contamination is electron beam induced deposition of excess volatile carbonaceous species. These observations strongly suggest that trapped-solvent is present in very small amounts, although enough to decrease the T_g of the system by several °C.

The most interesting feature of the T_g of the solvent-blended composites is that it drops from ~ 99.7 to ~ 96.6 °C respectively at P2 and P9, and then it remains approximately constant between P9 and the extruded ribbon. Based also on previous work,^{19,32,34} this decrease in T_g along the extruder is most likely due to the fact that C_{60} is leaving the PS matrix and reagglomerating, as also supported by our SANS results.

[Figure 8](#) shows the mechanical spectra of the PS matrix and the composites obtained when processing the pre-solvent blended composites (a) or the mixed powders (b).

Figure 8. Frequency dependence of the dynamic viscosity $|\eta^*|$ of the solvent prepared composites (a) and the mixed powders composites (b) sampled at different locations along the extruder. Lines correspond to the dynamic viscosity of the PS matrix fed into the extruder whereas dashed lines represent the dynamic viscosity of an extruded PS ribbon.

Rheological data of PS samples collected along the extruder first reveal that the PS matrix is sensitive to processing. The PS ribbon spectrum is shifted to larger viscosity values for all frequencies with respect to the PS powder sample. Thermo-oxidative cross-linking reported recently for a PS nanocomposite⁴⁶ could explain the increase in the zero shear viscosity of PS ribbon samples. This degradation process is further supported by the rheological data presented in [Figure S.I.11](#), where a gradual increase in the zero shear viscosity of PS samples collected along the extrusion line relates with the increasing residence time of each sample in the extruder.

Although entanglements in the PS matrix are evident in the master curve (see [Figure S.I.12](#) which shows a rubbery plateau prior to the glass transition regime), no reduction in the zero shear viscosity of the PS nanocomposite produced with the solvent method is seen in [Figure 8a](#). Thus, the non-Einstein behavior reported elsewhere for a similar system^{16,47} and for other well-dispersed polymer nanocomposites^{46,48} is not reproduced here. The C_{60} dispersion quality required to produce a viscosity reduction is not met in the powder sample

produced with the solvent method. Indeed, SANS indicated that the minimum distance between aggregates is of the order of 15 nm in this sample, which is much larger than the size of the PS chain. This poor molecular dispersion of C_{60} therefore explains the reinforcement of the PS matrix mirrored in the enhanced viscoelasticity for all frequencies.

The melt processing of the solvent-based PS composite is accompanied by an increase in the dynamic viscosity. Indeed, the progressive increase from P2 to P9 does partially correlate with the viscosity increase of the thermally degraded matrix, as demonstrated by the constant viscosity ratio between composite and matrix which nearly matches an Einstein-like value between P2 and P9 (see Figure S.I.13).

However, the breakdown of Einstein-like behavior for the powder sample is concomitant with the presence of structural heterogeneities below 20 nm in the solvent-based PS composite which impedes the interpretation of the rheological data using classical continuum theories.¹¹ Overall, rheological changes along the processing of the solvent-based feeding formulation are in harmony with the reagglomeration process (SANS and TEM data both showing a coarsening of the structure along the extruder) which progressively leads to an Einstein-like reinforcement of the PS matrix.

The situation is changed for the mixed powders as the Newtonian viscosity in Figure 8b shows a monotonic decrease along the extruder. In contrast to this, the high-frequency regime of the dynamic viscosity is not sensitive to the residence time in the extruder or to the progressive structural rearrangement. Thus, the process-induced reduction in C_{60} aggregates size does not impact on the entanglement plateau, whereas it accelerates the terminal relaxation time of the PS matrix. Similar effects were reported in well-dispersed PS nanocomposites containing dendritic polyethylene particles⁴⁶ or PS nanoparticles.⁴⁹ Confinement of PS chain together with additional free volume brought by the nanoparticles were called for explaining the nonclassical viscosity reduction in the latter system, whereas such effects were ruled out for the former polymer nanocomposite. Although local chain confinement cannot be excluded (the SANS analysis suggests an aggregate–aggregate distance of the order of 15 nm), the existence of large aggregates in microscopic imaging supports the larger viscosity and slower dynamics of the mixed powders when compared to the neat PS.

Rationalizing the zero shear viscosities of the composites and the PS matrix shows that after P9, no evolution is observed in the rheology of the processed mixed powders. This is in contrast to the viscosity increase from P9 to the extrudate observed with the solvent route, which eventually results in a close matching between the rheological properties of the two extrudates (see Figure S.I.14).

Thus, this rheological similarity suggests a dynamically equivalent macroscopic morphology for the two types of composite extrudates. However, the routes for achieving similar viscosity levels are different, as the reagglomeration of the solvent-based feeding formulation opposes to the breakup/erosion of aggregates and molecular dispersion of C_{60} in the composites from mixed powders.

The relative sizes of PS chains and aggregates, the dynamics of the polymer close to the aggregates, the interfacial tensions, the aggregate–aggregate interactions, and C_{60} –PS interactions all contribute in a complex fashion to the rheology of these composites. Because the interplay between rheology and all these ingredients is far from being understood even in model

systems,⁵⁰ the rheological data collected in Figure 8 essentially indicate that for the present PS– C_{60} composite the reagglomeration process gives way to an increase in the dynamic viscosity, whereas the structural sizing down corresponds to reduced viscosity.

4. CONCLUSIONS

In this work we studied the effect of the initial feeding formulation on the morphology evolution of PS– C_{60} nanocomposites along the axis of a twin-screw extruder. Two markedly different initial feed formulations comprising 1 wt % C_{60} were used, namely, (a) a simple mechanical mixture of PS and C_{60} powders and (b) a PS– C_{60} composite prepared by solvent blending. The study was carried out by performing sequential sampling along the extruder and by characterizing the corresponding degrees of dispersion. A number of experimental techniques were used to probe the dispersion levels at different length scales, namely, optical microscopy, spin-echo small-angle neutron scattering (SESANS), small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), and wide-angle X-ray scattering (WAXS). These are complemented by differential scanning calorimetry (DSC) and rheological measurements.

According to our results, the vastly different morphologies of the initial feeding formulations (situation A for mixed powders and situation D for the solvent blend, in Figure 1) converge along the extruder into a similar final nanomorphology (situation C in Figure 1) which strongly suggests that the final morphology is mainly dictated by the coupling between thermodynamics and flow leading to a preferred steady state of the system which is independent of the initial conditions.

Furthermore, this work strongly suggests that starting from a perfectly solvent-blended mixed system and promoting its reagglomeration along the extruder might be a good strategy to prepare nanocomposites when some level of particle aggregation is advantageous to specific applications.^{10,11}

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b02283.

Figures S.I.1 to S.I.14 (PDF)

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G.B., J.A.C., and L.H. originated the initial experimental and overall motivation for the work. L.F. prepared the solvent-blended composite. H.G. and P.T. performed the extrusion experiments. R.S. undertook the optical microscopy characterization. W.G.B. and S.R.P. conducted the spin-echo SANS characterization. G.B., S.M.K., A.J.P., and N.C. performed the SANS measurements and analysis. M.W. and N.C. carried out

the SAXS measurements and analysis. A.J.P. undertook the WAXS analysis. G.B. and H.G. performed the DSC characterization. L.H., P.T., and H.G. performed the rheological characterization. C.J.H. undertook the TEM analysis. K.J.A. carried out the STEM characterization. G.B. performed the TGA study. G.B. wrote the initial draft of the manuscript with inputs from all the authors, and subsequently the draft was revised by all the authors.

Notes

The authors declare no competing financial interest.

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