

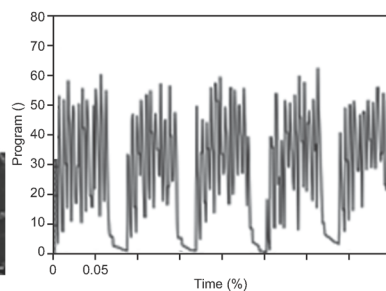
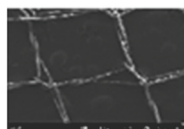
Applications of Nanocomposites

Ahalapitiya H. Jayatissa (ed.)

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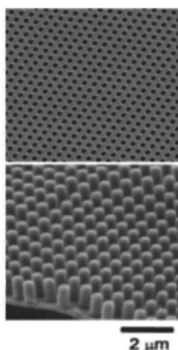
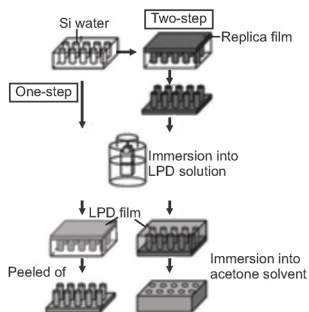


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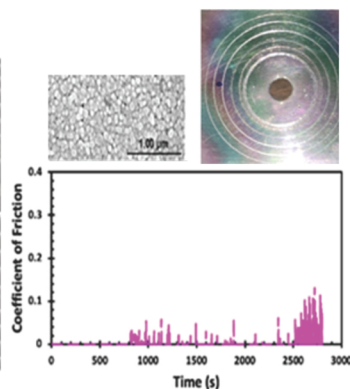


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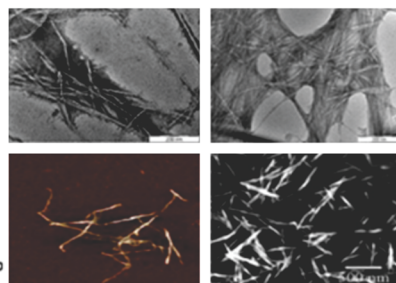
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Solid Lubricants



Nano-Cellulose Composites



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Applications of Nanocomposites

Editor

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Preface

The synthesis of nanomaterials has attracted a great deal of attention in the past two decades. The applications of nanomaterials have been investigated as a part of the characterization processes. These topics have been evolved in many different directions because functionalities of nanomaterials can be tuned to obtain numerous advantages over existing bulk materials. Currently, these materials have been used in some manufacturing technologies. There are many technologies at the transition stage between synthesis and applications. In this book, the authors present the possible application of nanomaterials and related scientific and economic impacts.

Chapter-1 brings the science behind the incorporation of nanomaterials in composite matrixes by surface treatments and modifications. This chapter will provide a greater understanding of the modification of carbon-based nanomaterials for various applications. This chapter also provides key technologies necessary to understand the interface characteristics of nanomaterial and polymer matrixes.

Chapter-2 brings the application of nanomaterials in automobiles and related industries. The chapter provides a substantial review of nanotechnology applications related to their mechanical properties. This chapter reviews and summarizes many published research on the application of nanomaterials in automotive industries.

Chapter-3 provides catalytic application of nanomaterials related to enhancing the surface area of nanostructured materials. This chapter also provides substantial fundamental knowledge of optoelectronic properties and surface modifications of nanomaterials.

Chapter-4 is related to the possible application of nanomaterials in energy storage in lithium-ion batteries. This is a current topic that attracted global attention in next-generation rechargeable batteries.

Chapter-5 gives recent developments related to flexible electronic devices, which use two-dimensional carbon sheets with one atom thick planar packed in a honeycomb crystal lattice structure has recently attracted significant academic and industrial interest because of its exceptional electronic and optoelectronic properties and excellent performance in mechanical, electrical, and thermal applications. This chapter describes the fabrication and characterization of flexible sensors using pure graphene sheets and graphene-based composites.

Chapter-6 discusses the importance of nanocomposites in tribology applications. The desirable qualities that make it superior to conventional liquid lubrication; reasons for their widespread acceptance are covered. The challenges, drawbacks of these coatings are explained from a cost and reliability standpoint. A comprehensive review of the application of metal, ceramic and polymer-based nanocomposites is covered in the chapter.

Chapter-7 is about the technological development and practical application of carbon fiber reinforced plastics, natural fiber-reinforced plastics, and GFRP recycling in Japan are described. First, the Carbon Fiber Reinforced Polymer (CFRP) parts having high-strength and lightweight using carbon fiber and epoxy resin were developed, and its practical use has expanded. The CFRP has been used in airplanes and automobiles, improving safety and fuel efficiency by reducing weight. Second, to reduce the consumption of petroleum resources, Natural Fiber Reinforced Polymer (NFRP) using natural fiber of reinforcement and Polylactic Acid (PLA) of base polymer made from biomass are also discussed.

Synthesis of nanocomposites by Liquid Phase Deposition is discussed in Chapter-8. These materials in which nanoparticles are dispersed into the matrix material to obtain improved properties. In recent years, the demand for lightweight and strong materials in the automotive industry, which directly affects fuel efficiency, vehicle performance, and exhaust gases emissions, are increasing to manufacture various auto parts such as brakes, engine covers, glasses, and mirror coatings, seat and door trim, chassis, and tires. These materials offer excellent mechanical, electrical, and thermal properties, flame retardance, wear and corrosion resistance, and self-cleaning, which ensure safety, comfort, and durability of the vehicle.

Chapter-9 describes the use of layered silicates inorganic material as nanofillers in the thermoset material to improve the mechanical, physical, thermal, and barrier properties of the polymer. Montmorillonite (MMT) is one of the layered silicates that are commonly used as reinforcement nanofillers in polymeric matrices, including the epoxy owing to its excellent physicochemical characteristics. This chapter reviews and summarizes the findings collected from several published research on the epoxy composites and nanocomposites with single and hybrid fillers, emphasizing the use of layered silicate as co-filler in the hybrid nanocomposite system. Furthermore, the published works on the epoxy nanocomposite with hybrid MMT/geopolymer fillers for piping application are compiled and summarized at the end of this chapter. These findings indicate that the use of hybrid MMT/geopolymer fillers can significantly improve the mechanical properties of the epoxy, revealing the great potential of this hybrid filler system in reinforcing the epoxy for piping application.

In Chapter-10, the properties and characterizations of MCC and NCC will be clarified, and their toxicity effect will be discovered to make them compatible as a new alternative approach in the pharmaceutical industry, especially for safety consumption purposes. The increasing use of nanomaterials in biomedical applications such as drug delivery and targeted drug therapy has triggered the global research community to develop strategies to improve engineered materials performance by incorporating nanomaterials with biocompatible polymers. Microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) from agricultural waste possess bio-composite characterizations, which offer significant sustainability and eco-efficiency in the development of biomedical products. The high crystallinity index and yield percentage from both MCC and NCC were proven they had the potential in the pharmaceutical industry in drug delivery, tablet formulation, and wound healing. They were non-toxic and did not show inflammation effects on both cell lines and animal modes when presented in low concentration. Possible applications of MCC and NCC from agricultural wastes are potential candidates are also discussed in this chapter.

Chapter 11 is devoted to describing recycling, landfilling, and incineration of waste containing nanoparticles (NPs) is handled. But there are still no specific methods or systems in place to efficiently capture and recycle the NPs released into the waste streams. To avoid landfilling non-recyclable nanomaterials, especially of the manmade engineered nanomaterials (ENMs), and to counteract their harmful effects on the environment, innovative approaches such as green synthesis of nanocomposites, manufacturing biodegradable nanocomposites using renewable sources as raw materials and magnetic nanoparticles have piqued the interest of researchers to help synthesize and manufacture sustainable nanocomposites. Further, the need for and importance of conducting life cycle analysis of nanocomposites along with the health, safety, and environmental hazards' assessment by considering the impact of all the stages throughout their manufacturing, service,

consumption, and disposal are emphasized. Some of the challenges faced by the emerging sustainable technologies and potential future directions of research are also outlined.

As the editor of this book, I owe a debt of gratitude to all the authors who prepared these manuscripts. Their dedicated work, patience, understanding of the process, and timely submission of manuscripts and reviews are greatly appreciated. I want to thank my graduate students, Suren, Victor, and Bodhi, for their support in contact with authors and reviewers continuously.

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Surface Functionalized Nanoparticles

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1 INTRODUCTION

Industrial nanoparticles are essential for modern times and have advanced technological applications such as in automotive tires, inks, lithium-ion batteries and consumer goods such as sun block lotions and cosmetics. The dispersion of nanoparticles in viscous polymers is dictated by kinetics, the interaction potential between particles and the interfacial compatibility between the matrix and dispersed phases. Industrial polymer nanocomposites can be produced by a variety of processes. A common method is to melt mix viscous polymers with nanofillers including shear mixing in a Banbury mixer, twin-screw or single-screw extrusion and calendaring in a two-roll mill. Dispersion and subsequent distribution and re-aggregation/network formation of nanoparticles do not occur under equilibrium. However, a pseudo-thermodynamic approach can be used that takes advantage of an analogy between the kinetically mixed polymer compounds and thermally dispersed colloids. A pseudo-second-order virial coefficient can adequately delineate the systemic interactions while having the ability to quantify dispersion as a function of the accumulated strain during the mixing process (Jin et al. 2017; McGlasson et al. 2019). It also has the advantage of being used as an input for coarse-grained simulations thereby combining experiments with modeling (Gogia et al. 2021). The degree of filler dispersion is dictated by binary filler-polymer interactions which

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depend on the surface characteristics. Weakly interacting systems such as carbon black, surface-modified silica in low dielectric constant polymers can be described by a mean field. However, this approach is expected to fail for nanoparticles with inherent surface charges such as precipitated and pyrogenic silicas, especially in high dielectric constant polymers since the fillers interact strongly. Conversely, a mean-field model may be suitable for surface-charged nanoparticles in low dielectric polymers with filler particle spacings larger than the Debye screening length (low concentrations), while specific interactions may dominate at higher concentrations and for higher dielectric constant polymers (McGlasson et al. 2020; Rishi et al. 2020; Okoli et al. 2021).

Commercial polymer nanocomposites involve a multi-hierarchical structure that includes a material spanning filler network leading to many of the signature properties such as tear resistance, conductivity, strength, optical scattering for paints and pigments and cosmetics. The network emerges from a complex interplay between miscibility, immiscibility, kinetic dispersion, particle breakup and aggregation. The multi-hierarchical nanofiller structure includes primary nanoparticles and fractal nano to colloidal scale aggregates and larger agglomerates and clusters that grow to an emergent network. Surface functional groups, surface polarity and charge, the Debye screening length dependent on the dielectric constant of the polymer, and the processing kinetics often described by the mean accumulated strain (Rishi et al. 2019a) have a tremendous impact on the properties of nanocomposites (Rishi et al. 2019a; 2020; McGlasson et al. 2019). For example, in commercial tires carbon, black nanofillers form hierarchical filler networks at different size scales that impact the dynamic response at highway speeds (Rishi et al. 2018) as well as the tear strength (Hamed 1991). On the contrary, fumed and precipitated silica nanofillers tend to correlate into somewhat ordered structures (McGlasson et al. 2020) that could potentially impact the rolling resistance of the tire. This chapter discusses how to leverage small-angle X-ray scattering to quantify binary interactions in these systems. It also describes how these interactions dictate both the local as well as the global structural emergence at multiple percolation concentrations pertaining to different sizes of the multi-hierarchical structure. The impact of these multi-hierarchical architectures on the dynamic and dielectric response in polymer nanocomposites is explored.

2 INDUSTRIAL NANOPARTICLES: IMAGING THE FRACTAL STRUCTURE AND HIERARCHICAL LEVELS THROUGH SMALL-ANGLE X-RAY SCATTERING (SAXS)

During the flame synthesis of industrial nanoparticles such as carbon black, silica and titania, etc., the first stable structures that form following nucleation are primary particles. The primary particles, which are on the order of 10 nm in size, serve as the building blocks for the hierarchical structure. These primary particles sinter downstream in the flame into ramified mass-fractal aggregates. The fractal aggregates that are on the order of 100 nm in size further cluster into agglomerates due to van der Waals forces. The clustered agglomerates which are on the order of microns in size are further compacted into powders that are visible to the naked eye. However, during shear mixing in a Banbury mixer or an extruder, these micron-scale agglomerates dissociate and disperse to aggregates. This inherent structural hierarchy impacts the percolation, network formation and dispersion while dictating the dynamic, dielectric and optical properties of the final nanocomposite (Donnet et al. 1993; Friedlander 2000; Brinker and Scherer 2013).

Structural characterization of these hierarchical structures is possible through advanced visualization techniques. As opposed to microscopy which is a direct imaging technique, the interpretation and analysis of Small-Angle X-ray Scattering (SAXS) occur in reciprocal space (q is the reciprocal space vector) which is a Fourier transform of real space. q is directly related to the sine of the scattering angle and inversely proportional to the incident X-ray wavelength,

thus bearing units of inverse length. Analysis of SAXS data involves performing model fits to the reduced scattering intensity, $I(q)/\phi$, which is based on some assumption of the filler structure. However, despite its limitations, SAXS has numerous advantages. Firstly, the spatial resolution in combined small-angle scattering techniques can extend from Angstroms to microns, about four decades in size yielding information about the different structural levels in the filler hierarchy. To image this size range, one would have to use optical, scanning electron and transmission electron microscopes. Secondly, the sample preparation for SAXS measurements needs minimal effort whereas for electron microscopy one needs to either sputter coat the surface to prevent electron buildup in SEM or prepare extremely thin microtomes at cryogenic temperatures often with staining for transmission mode. AFM and SEM are limited to surface analysis. Thirdly, the data interpretation in microscopy is confined to 2D projections of 3D structures which limits a detailed understanding of the filler morphology. More importantly, for direct imaging on the nanoscale through transmission electron microscopy, the cryo-sectioned samples need to be about 100 nm thick, and any information thus gleaned is only a local measure of the filler structure. On the contrary, SAXS measurements are made over macroscopic dimensions resulting in an exploration of the nano to the macroscopic structure at 20 μm to 5 mm sample sizes. Although electron tomography to reconstruct a 3D picture of the aggregate is gaining traction (Liu et al. 2017; Song et al. 2017), it is limited to micron size structures. Finally, scattering measurements are free from operator bias.

The scattered intensity, $I(q) = \phi V \Delta \rho^2 P(q) S(q)$, depends on the form factor, $P(q)$, the interparticle structure factor, $S(q)$, the particle volume, V , the overall filler volume fraction, ϕ and the scattering contrast between the filler and the matrix, $\langle \Delta \rho \rangle^2$. When the filler concentration in the

polymer is dilute (ϕ_0), $S(q) = 1$ and the above expression reduces to $\frac{I_0(q)}{\phi_0} = V \Delta \rho^2 P(q)$. The form factor for spherical particles, $P(q) = \frac{9\{\sin(qR) - (qR)\cos(qR)\}^2}{(qR)^6}$ is the square of the spherical

amplitude function where R is the radius of the particles. This definition of the form factor is valid for perfectly spherical colloidal silica particles (Akcora et al. 2009). However, this choice would be insufficient to describe scattering in complex multi-level hierarchical, nano- to macro-scale structures. Industrial nanofillers typically display three structural levels comprised of the primary particle (level 1), mass-fractal aggregates of primary particles (level 2), and agglomerates of aggregates (level 3) due to their synthesis as discussed earlier (Jin et al. 2017; Hashimoto et al. 2019). To account for these multi-scale structural hierarchies, the concentration normalized dilute scattering can be interpreted using the Unified Scattering Function (Beaucage 1995; 2004; Beaucage et al. 2004) such that,

$$\frac{I_0(q)}{\phi_0} = \sum_{i=1}^n \left[G_i \exp\left(\frac{-q^2 R_{g,i}^2}{3}\right) + B_i (q_i^*)^{-P_i} \exp\left(\frac{-q^2 R_{g,i=1}^2}{3}\right) \right] \quad (1)$$

where “ i ” is the structural level, G_i and B_i , normalized by the volume fraction, are the Guinier and Porod pre-factors that account for the particle volume, V and the scattering contrast, $\Delta \rho^2$; the radius of gyration, $R_{g,i}$, specifies the size of each structural level in the hierarchy; the power-law exponent, P_i , specifies the morphology of each structural level and is generally 4 for solid three-dimensional moieties with no surface roughness whereas it varies between 1 and <3 for mass-fractal objects. Additionally,

$q_i^* = q \left[\text{erf}\left(\frac{kqR_{g,i}}{\sqrt{6}}\right) \right]^{-3}$, wherein “erf” is the error function and k equals 1 for three-dimensional

structures and approximately 1.06 ± 0.005 for mass-fractal structures (Beaucage 1995). The

advantage of using the Unified Scattering function is that it uses no additional variables other than the ones stipulated by the Guinier (Guinier and Fournet 1955) and Porod (Porod 1982) laws and yet accounts for the size-related dependence of adjacent structural levels in the nanofiller hierarchy.

Industrial nano-aggregates are convoluted mass-fractals (fractal dimension, for level 2 from the Unified fit (Beaucage 1995; 2004; Beaucage et al. 2004) in equation (1) with a tortuous topology as shown in Fig. 1.1. The topological parameters that can be derived from the Unified fit parameters in equation (1) include: the size of the primary particle or the equivalent Sauter mean diameter, $d_p = 6V/S$; the degree of aggregation or the average number of primary particles in an aggregate, $z = (G_2/G_1) + 1$; the aggregate end-to-end distance, $R_{\text{eted}} = d_p z^{1/d_f}$; the aggregate tortuosity, $d_{\text{min}} = B_2 R_{g,i}^{d_f} / (C_p \Gamma(d_f/2) G_2)$; where, C_p represents the aggregate polydispersity; the short circuit path, $p = (R_{\text{eted}}/d_p)^{d_{\text{min}}}$ the aggregate connectivity dimension, $c = d_f/d_{\text{min}}$; the connective path, $s = (R_{\text{eted}}/d_p)^c$; and the branch fraction, $\phi_{br} = (z - p)/z$ (Mulderig et al. 2017a; Rai et al. 2018; Beaucage 2004; Beaucage et al. 2004).

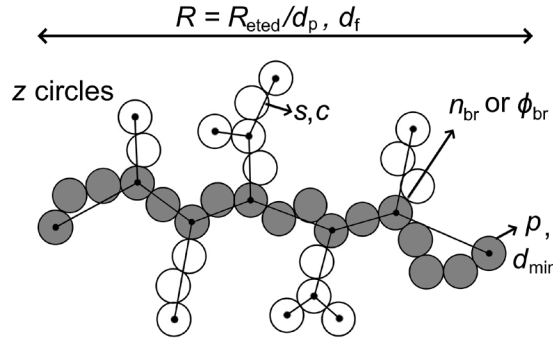


Figure 1.1 A fractal aggregate represented on a two-dimensional plane. The aggregate topology is described by the ratio (R) of the end-to-end distance (R_{eted}) to the primary particle size (d_p), its fractal dimension, (d_f), the number of primary particles (circles) that comprise the aggregate (z), the minimum path (p), the dimension of the short-circuit path (d_{min}), the connective path (s), the connectivity dimension (c), the number of branches (n_{br}) and branch fraction (ϕ_{br}). Reprinted from Journal of Aerosol Science, 109 (March), Mulderig et al. 2017a. Quantification of Branching in Fumed Silica, 28–37, Copyright 2017, with permission from Elsevier.

To image these filler nano-aggregates from scattering, a particle-cluster aggregation code was developed on a 3D grid (Mulderig et al. 2017a) that uses only the average number of primary particles in an aggregate as the input to the simulations. This measure of the degree of aggregation is used to truncate the growth of particles which is controlled only by a probability of sticking (ranging from 0 to 1). The simulation uses a path-finding procedure to determine the topological parameters of the aggregate wherein a neighbor list for each stuck particle in the aggregate is created and the distance between all combinations of end points is computed. The weight average distance between all possible end points equals R . R is a dimensionless number that equals the ratio of R_{eted} to d_p . To determine the minimum path, multiple percolation pathways along the aggregate are traced such that any given pathway commences and terminates at a random end point while being constrained to move backward. The weighted average of all such pathways equals the short circuit path, p . Since $R = z^{1/d_f} = p^{1/d_{\text{min}}}$, the other structural parameters d_{min} , d_f , c and ϕ_{br} from the simulation can be compared to the same parameters derived from scattering and the simulation iterated until a match between the simulated 3D structure and the measurement parameters is found.

Figure 1.2(a) compares the TEM images of single carbon black nanoaggregates in polybutadiene rubber at dilute loading to aggregates simulated from the fit to the reduced scattering intensity vs. q plot (inset). An exploded view of the two inset TEM micrographs show an R_{eted} of 120 nm that quantitatively agrees with the scattering result (Rishi et al. 2018). A qualitative comparison

of the two micrographs in Fig. 1.2(a) to the simulated aggregates based on scattering indicates a good agreement although a quantitative comparison was not attempted since the micrograph is a 2D projection of the actual aggregate. Figure 1.2(b) shows a similar qualitative comparison for a porous precipitated silica aggregate with the aggregate simulated from scattering (McGlasson et al. 2020). The simulation procedure is available in the Irena software package provided by Jan Ilavsky at Argonne National Laboratory (Ilavsky and Jemian 2009; Ilavsky 2012; Ilavsky et al. 2013; 2018).

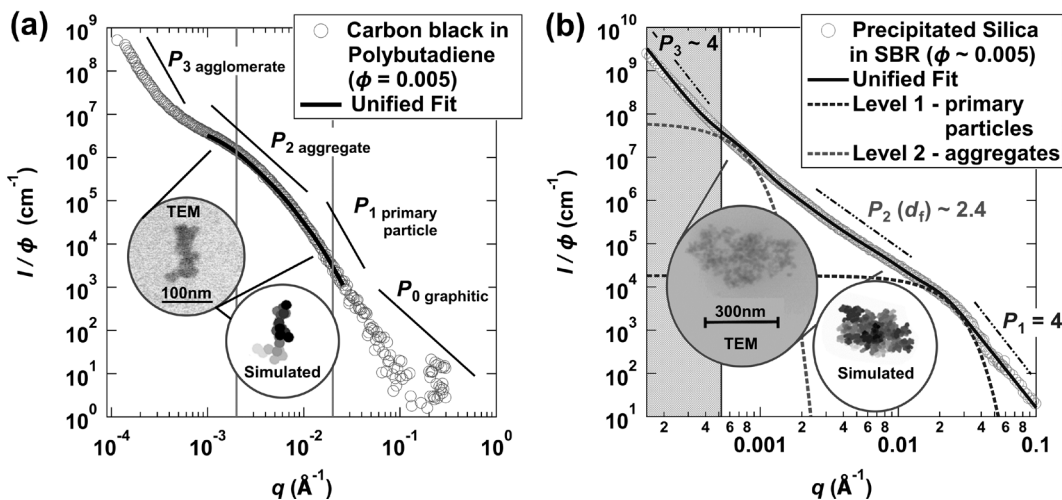


Figure 1.2 (a) Concentration (dilute) normalized scattering intensity, $I_0(q)/\phi_0$, as a function of reciprocal space vector, q fit using the Unified Scattering Function (Beaucage 1995; 2004; Beaucage et al. 2004) for carbon black filled polybutadiene. The inset images compare the micrographs of carbon black nanoaggregates to those simulated from the scattering result. Reprinted (adapted) with permission from Rishi et al. 2018. Impact of an Emergent Hierarchical Filler Network on Nanocomposite Dynamics. *Macromolecules* 2018, 51(20): 7893–7904. Copyright 2018 American Chemical Society (b) Concentration (dilute) normalized scattering intensity, $I_0(q)/\phi_0$, as a function of reciprocal space vector, q fit using the Unified Scattering Function (Beaucage 1995; 2004; Beaucage et al. 2004) for precipitated silica filled styrene-butadiene rubber. The inset image compares the micrograph of a silica nanoaggregate to the simulated aggregate based on scattering. Reprinted (adapted) with permission from McGlasson et al. 2020. Quantification of Dispersion for Weakly and Strongly Correlated Nanofillers in Polymer Nanocomposites. *Macromolecules* 2020, 53(6): 2235–2248. Copyright 2020, American Chemical Society.

3 SURFACE FUNCTIONALIZATION OF FRACTAL NANOPARTICLES

Filler-polymer incompatibility results from differences in the surface chemistry of nanofillers and the polymer. For example, the presence of surface hydroxyls on silica renders it polar due to which it is incompatible with non-polar polymers like styrene-butadiene rubber. Although, the surface of carbon black may contain many functional groups, the reactions involving oxygen complexes do not necessarily lead to improved rubber-carbon black interactions in SBR (Leblanc 2002). The density of functional groups on the surface plays a critical role in determining whether the nanoparticle surface is amenable to functionalization. The extent of polarity in nanofillers is characterized by differences in the polar and disperse components of surface energy (Wang et al. 1991a, b; Wolff and Wang 1992). Classical methods to improve filler-polymer interactions in incompatible systems were based on the addition of different coupling agents to the melt during processing. These coupling agents tether nanoparticles to the polymer matrix. Block co-polymers have also been used to nanoparticles compatible with

polymeric matrices. For example, Raut et al. (2018) used poly(butadiene-graft-pentafluorostyrene) block copolymer as a compatibilizer in Styrene-Butadiene Rubber (SBR) carbon black nanocomposites to improve dispersion. The electron-rich aromatic rings of carbon black attract the electron-deficient pentafluorostyrene, whereas the butadiene backbone shows affinity towards SBR.

For chemically bonded coupling agents, estimating whether the coupling reaction occurred on the particle surface, limited by reaction kinetics and processing conditions, can only be determined by secondary gauging of improvements in the mechanical properties, tear strength, etc., (Hamed 1991). To overcome this challenge, chemical treatments to introduce different functionalities, and grafting polymers or short-chain oligomers to the surface of bare nanoparticles before melt compounding is performed. For example, lignosulfonates were modified with cyclohexylamine to enhance compatibility which led to improvements in nanocomposite strength (Bahl and Jana 2014). Similarly, the addition of carboxylic acid functionalities to the surface of zirconia nanoparticles via a silane coupling agent resulted in an improvement in Young's modulus of the polystyrene matrix composite as compared to neat polystyrene (Kockmann et al. 2018). Additionally, altering the surface of zinc oxide nanofillers led to an enhancement in dispersion in high-density polyethylene (Benabid et al. 2019). To improve the mixing of colloidal silica nanoparticles prepared by the Stöber process in a bismaleimide/diamine matrix surface modification was achieved by chemically introducing amine and epoxide functionalities (Sipaut et al. 2015). The impact of varying the graft chain length and particle size in PDMS-grafted silica particles on the interparticle interaction potential quantified via rheology has also been studied (McEwan and Green 2009). The different strategies for surface functionalization have been comprehensively detailed by Kango et al. (2013). For other *in situ* surface functionalization techniques, advanced characterization of the functionalized surfaces, and modeling the dynamics of these novel functionalized nanoparticles the reader is referred to a succinct review by Hore et al. (2020).

Compared to model colloidal silica nanoparticles for academic studies, industrial-grade nanofillers such as silica rely on simpler surface modification techniques that involve reacting the inherent silanol moieties. The surface of fumed silica particles is characterized by the presence of isolated silanol and hydrogen-bonded silanol groups, which are statistically distributed over the surface as shown in Fig. 1.3. This nature of the fumed silica surface results in strong hydrophilic characteristics with high surface energy which reduces its compatibility with highly non-polar polymer matrices. These monoenergetic surface hydroxyls can react with hexamethyldisilazane (HMDS) to cover the silica surface with trimethylsilyl groups (Hair and Hertl 1971) rendering it compatible with non-polar polymers, as shown in Fig. 1.3. A less common surface modification technique relies on the introduction of a carbon precursor during flame-spray pyrolysis (Mädler et al. 2002; Mueller et al. 2004) of silica, also shown in Fig. 1.3. Carbon-coated silica was synthesized using a commercial hydrogen-air burner, by oxidation of hexamethyldisiloxane (HMDSO) (Kammler et al. 2001). It was found that by increasing the production rate and lowering the hydrogen concentration in flame at a constant airflow, nano-aggregates of silica-carbon composite particles with varying surface carbon contents could be produced (Kammler et al. 2001). More recently, Okoli et al. (2021) have attempted to characterize the surface carbon content in terms of carbon monolayers and gauged the impact of varying the number of monolayers on the dynamic properties of the nanocomposite.

4 STRUCTURAL EMERGENCE IN INCOMPATIBLE NANOFILLER-POLYMER SYSTEMS

The Unified Scattering Function (Beaucage 1995; 2004; Beaucage et al. 2004), equation (1), can be used to model the structure of nanoaggregates at dilute concentrations as discussed earlier. Modeling the structure through SAXS is limited to dilute nanofillers in polymer since above the

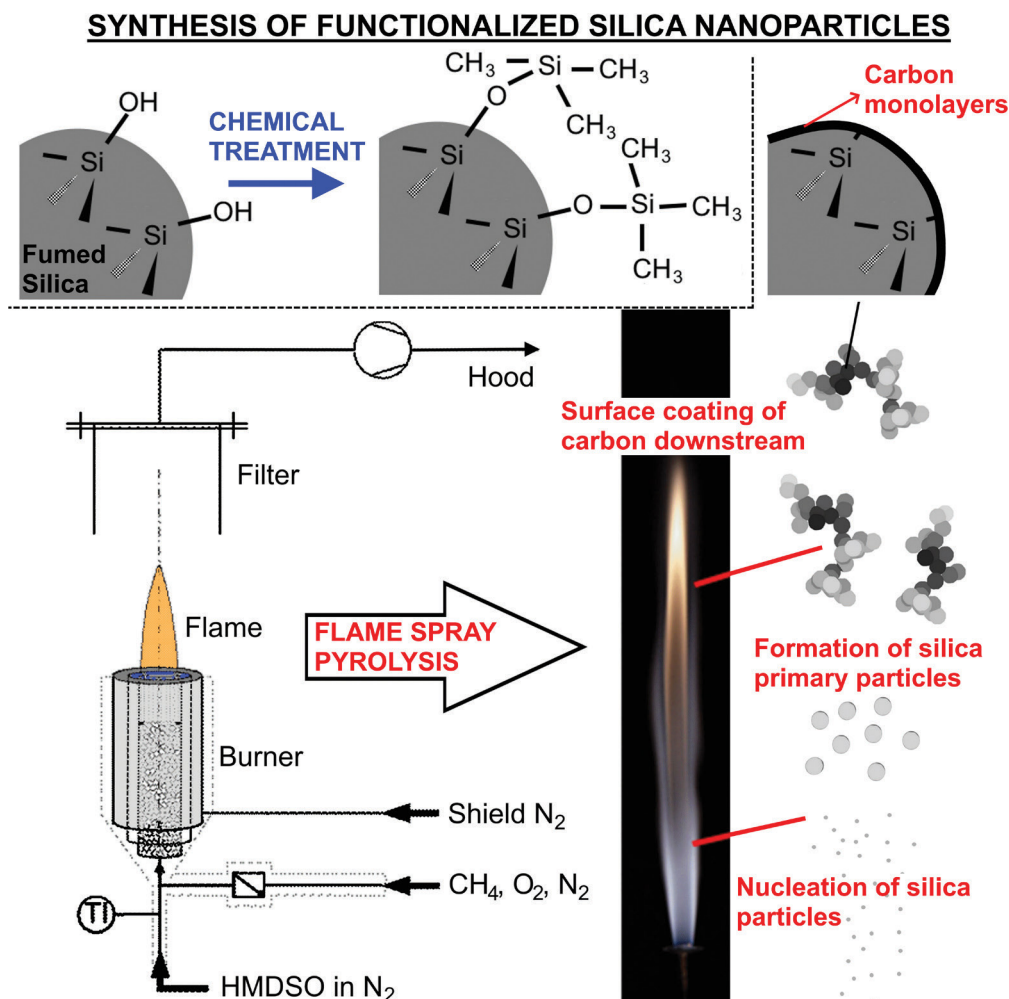


Figure 1.3 Routes of functionalizing the surface of industrial grade pyrogenic silica: chemical post-treatment with HMDS to generate trimethylsilyl functional groups, and introduction of carbon precursors during flame-spray pyrolysis. The carbon/soot is coated downstream in the flame. Reprinted (adapted) with permission from Okoli et al. 2021. Dispersion and Dynamic Response for In-Flame and Chemically Modified Fumed Silica Nanocomposites. *In: Bulletin of the American Physical Society*, 2021 (top figure). Reprinted with minor changes from Powder Technology, Vol 140/Issues 1-2, Mueller, R., Kammler, H.K., Pratsinis, S.E., Vital, A., Beaucage, G. and Burtscher, P. Non-agglomerated dry silica nanoparticles, Pages 40–48, Copyright 2004, with permission from Elsevier. (bottom schematic)

overlap concentration, ϕ^* , the aggregate structure can no longer be observed, by it being screened from view by the other, overlapping aggregates. Concentrations above ϕ^* but below concentrated conditions are referred to as semi-dilute solutions since substantial regions devoid of aggregates still exist. In the semi-dilute regime for immiscible fillers, aggregates form clusters. Typically, ϕ^* is about 3 to 5 weight percent filler (Jin et al. 2017). Percolation at the 100 nm scale does not lead to global percolation and the formation of a conductive pathway for immiscible systems. At a concentration of about 16 to 20 weight percent filler a second, global percolation of nanoclusters occurs which can lead to a bulk conductive pathway, ϕ^{cc} . This involves size scales of about 1 μm . At concentrations above ϕ^{cc} independent clusters can no longer be resolved. Following this motif, complex multi-hierarchical structures emerge when the nanofiller content in polymers increases.

Referring to the nanoscale semi-dilute regime above ϕ^* binary aggregate-aggregate interactions dominate,

$$S(q) = \frac{I(q)/\phi}{I_o(q)/\phi_o} \neq 1 \quad (2)$$

over the entire q -range. Owing to the inherent structural hierarchy, $S(q)$ varies with the size scale of observation. Increasing concentration beyond a local percolation threshold, ϕ^* , is expected to have no impact on the structure of primary particles observed at high- q where $S(q) = 1$. However, $S(q)$ is expected to vary considerably from 1 in the intermediate- q and low- q regions reflecting the different configurations of nanoaggregates, agglomerates, clusters above ϕ^* ; and networks above ϕ^{cc} .

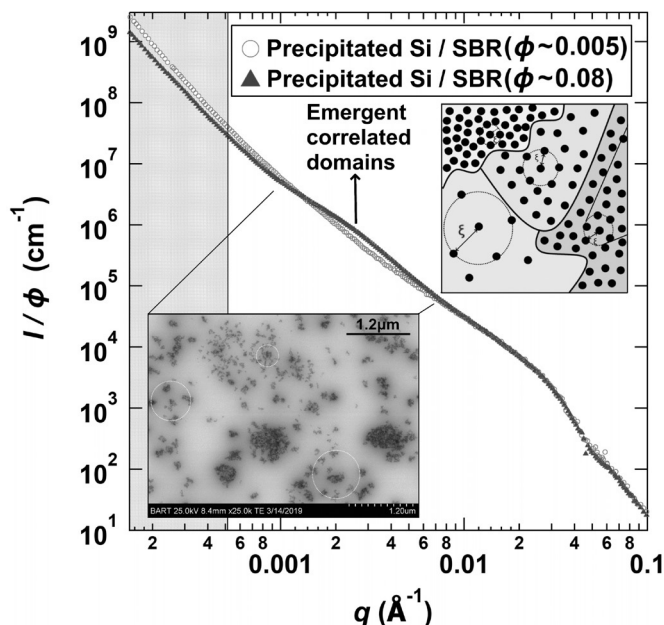


Figure 1.4 Reduced scattering intensities, $I_o(q)/\phi_o$ (dilute, light circles) and $I(q)/\phi$ (semi-dilute, dark triangles) as a function of reciprocal space vector, q for unmodified precipitated silica in SBR rubber. Notice the emergence of a broad peak in the dark curve at intermediate- q associated with aggregate correlations. The inset cartoon depicts these emergent structures in the same bulk with varying correlation distances as evidenced in the inset TEM micrograph (McGlasson et al. 2020). Reprinted (adapted) with permission from McGlasson et al. 2020. Quantification of Dispersion for Weakly and Strongly Correlated Nanofillers in Polymer Nanocomposites. *Macromolecules* 2020, 53(6): 2235–2248. Copyright 2020, American Chemical Society.

Although electrostatic effects leading to correlations in a low dielectric media such as in a polymer matrix are not obvious, several recent papers theoretically predict moderate electrostatic forces over about 4 microns between weakly charged spheres (Bichoutskaia et al. 2010; Stace and Bichoutskaia 2012). For industrial nanoparticles such as precipitated/fumed/colloidal silica, the electrostatic charge varies due to the density of silanol functional groups on the surface (Croissant and Brinker 2018). A larger surface charge leading to increased repulsive interactions between the nanoaggregates presents a weak correlation peak in the small-angle X-ray scattering pattern (Baeza et al. 2013; Bouty et al. 2014; 2016; Beaucage et al. 1995; Anderson and Zukoski 2007; 2010; Jethmalani et al. 1997; Jin et al. 2017). Figure 1.4 shows the emergence of this correlation peak in scattering for precipitated silica ($\phi \sim 0.08$) SBR nanocomposite. The surface hydroxyls on precipitated silica are polar which detracts from their compatibility with non-polar SBR. Whereas the concentration normalized scattered intensity for both dilute and semi-dilute concentrations

match at high- q indicating no change in the primary particles, at intermediate- q the aggregates correlate. A peak in scattering indicates periodicity with a repeat on the order of $2\pi/q^*$ following Bragg's law. It is to be noted that this USAXS peak, unlike the sharp peak in diffraction/wide-angle scattering, is weak and broad as shown in Fig. 1.4.

Binary interactions for non-functionalized nanoparticles with charged surfaces like colloidal silica due to silanol moieties are described by the Ornstein and Zernike (O-Z) function, equation (3). The O-Z function describes the interactions of particles in the liquid state such that the total correlation function, (Egelstaff 1967)

$$h(r) = c(r) + \rho \int c(|\vec{r} - \vec{r}'|) h(r') d^3 \vec{r}' \quad (3)$$

is the sum of the direct binary correlations, $c(r)$, and the higher-order interactions expressed by a convolution $h(r)$ of $c(r)$ over all distances r . Here, ρ indicates the number density of particles. While the O-Z expression describes the total interactions within a system, owing to the recursive nature of the function, obtaining a solution to the expression in equation (3) is difficult. To solve the expression various closure relationships are used. The Percus-Yevick (P-Y) approximation (Percus and Yevick 1958) is a commonly used closure relationship for the O-Z expression and has been used to describe the dispersion of hard spheres within a matrix such as monodisperse spherical colloidal silica. An analytic solution to the direct binary correlations, $c(r)$ in the O-Z expression in equation (3) was given by Wertheim (1963) as,

$$c(r) = -\alpha - \beta \left(\frac{r}{\xi} \right) - \delta \left(\frac{r}{\xi} \right)^3 \quad (4)$$

where ξ is the mean distance between the centers of spherical particles and the coefficients,

$\alpha = \frac{(1+2\phi)^2}{(1-\phi)^4}$, $\beta = \frac{-6\phi(1+0.5\phi)^2}{(1-\phi)^4}$, and $\delta = \alpha\phi/2$ are related to the filler volume fraction. The Fourier

transform of the binary correlation function in equation (4) is, (Wertheim 1963)

$$\begin{aligned} \rho C(q) = & -24\phi \left\{ \left(\frac{\alpha}{(q\xi)^3} \right) [\sin(q\xi) - (q\xi)\cos(qD)] - \right. \\ & - \left(\frac{\beta}{(q\xi)^4} \right) [(q\xi)^2 \cos(q\xi) - 2(q\xi)\sin(q\xi) - 2\cos(q\xi) + 2] - \\ & - \left(\frac{\delta}{(q\xi)^6} \right) [(q\xi)^4 \cos(q\xi) - 4(q\xi)^3 \sin(q\xi) - 12(q\xi)^2 \cos(q\xi) \\ & \left. + 24(q\xi)\sin(q\xi) + 24\cos(q\xi) - 24] \right\} \quad (5) \end{aligned}$$

From the convolution theorem, (Roe 2000) the Fourier transform of equation (3) given by $H(q) = C(q) + \rho H(q)C(q)$, is used to determine the inter-particle structure factor, $S(q)$ as

$$S(q) = \frac{H(q)}{C(q)} = \frac{1}{1 - \rho C(q)} \quad (6)$$

McEwan et al. (2011) quantified the impact on particle interactions of polydimethylsiloxane (PDMS) brushes grafted on to model monodisperse colloidal silica nanospheres in PDMS matrices of varying molecular weights. Small-angle X-ray scattering was used to determine $S(q)$ and the radial distribution function, $g(r)$ through the P-Y approach described above. $S(q)$, determined by normalizing the measured scattered intensity by a simulated form factor (dilute scattering intensity

vs. q), was fit with an arbitrary power-law function by Baeza et al. (2013) Instead of simulating the correlated aggregate structure and interactions within, Bouty et al. (2014) fit the structure factor to the analytical solution of the P-Y integral equation developed by Wertheim (1963) described in equations (5) and (6) for colloidal silica in SBR. In a later study, Bouty et. al. (2016) used a similar model system to understand the effects of chain conformation on the dispersion of colloidal silica nanoparticles without attempting a P-Y fit.

The semi-empirical Born-Green (B-G) approximation (Guinier 1955) of the O-Z equation was also proposed to describe the distribution of hard spheres. Beaucage et al. (1995) prepared aggregated silica nanoparticles in PDMS *in situ* via a sol-gel process in which silica was generated from the excess cross-linking agent, tetraethyl orthosilicate (TEOS). In these systems correlations are developed in a low viscosity oligomer during crosslinking so there is no residual stress or variable accumulated strain in the sample, resulting in close to monodisperse correlation distances between aggregates. Further, under these synthetic conditions, the interpenetration of aggregates is not possible since there is no mixing, aggregates form near crosslink sites or in regions where there is excess TEOS. To describe structural correlations of the B-G function,

$$S(q) = \frac{1}{1 + p\theta(q)} \quad (7)$$

was used. In equation (7), the dimensionless packing factor, p , is 8 times the ratio of the average “hard-core” occupied volume of the filler to the total volume. The packing factor determines the strength of the correlation peak in equation (7). $\theta(q)$ is the sphere amplitude function, $3 \frac{(\sin q\xi - q\xi \cos q\xi)}{(q\xi)^3}$, reflecting spherical correlations about a central aggregate and ξ is the average correlation distance between particles as shown in the inset cartoon in Fig. 1.4. The packing factor reflects the degree of adherence to the organization in a spherical shell through the ratio of occupied to available volume. For spherical particles, p varies from 0, indicating no correlations, to $8(0.74) = 5.92$, for closest packed structures where the packing factor for closely packed spheres is 0.74. Note that $\theta(q)$ parallels the first term in equation (5) of the P-Y approximation. At $q = 0$, $\theta = 1$ and the structure factor in equation (7) is $S(0) = 1/(1 + p)$ indicating that the strength of the correlation peak determines the $q \rightarrow 0$ intercept for the structure factor. The $q \rightarrow 0$ intercept is related to the second virial coefficient as is discussed below.

Although the P-Y and B-G closure relationships are able to sufficiently describe correlations for spherical colloidal silica particles (McEwan et al. 2011), and even aggregated silica structures with low dispersity in correlation distance and the absence of aggregate interpenetration using the Unified Function (Beaucage et al. 1995), manipulation of the two approximations are needed for melt blends of mass-fractal nanoaggregates. If the less cumbersome, B-G approximation is used for mass-fractal aggregates, one would expect the packing factor, p , to have higher values due to nanoaggregate asymmetry and the likelihood of aggregate overlap above ϕ^* in melt blends. For example, p , eight times the occupied to available volume, could be a larger number for highly asymmetric objects such as lamellae, up to a value of $p = 8$ for space-filling stacked lamellae. Asymmetric fractal nanoaggregates can align but can also interpenetrate resulting in a higher packing density than regular objects like lamellae. An estimate of the fraction interpenetration, I , is,

$$I = \frac{p}{8} - 1 \quad (8)$$

where the maximum value of p with interpenetration is 16, reflecting complete interpenetration of the aggregates. p can also be interpreted as a thermodynamic parameter since $S(0) = 1/(1 + p) = \frac{1}{d\Pi/d\phi} = \frac{1}{kT(1 + 2\phi B_2)}$. From the thermodynamic perspective, there is no upper limit to p .

When fractal nanoaggregates are kinetically mixed with highly viscous polymers, the correlations result from a balance between the accumulated strain and the repulsive charge. Note that colloidal silica (McEwan et al. 2011) and silica prepared *in-situ* (Beaucage et al. 1995) in low-viscosity PDMS represent systems with no accumulated strain and the mobile polymer phase would result in close to a regular separation of aggregates such that an average value for the correlation distance, ξ , in the P-Y and B-G equations can be used. On the contrary, milling of highly viscous nanocomposites results in non-uniform application of accumulated strain, as indicated by Baeza et al. (2013), such that the correlation distance could vary through the polymer bulk. This variation could be envisioned through the formation of domains with varying accumulated strains in the highly viscous nanocomposites. McGlasson et al. (2020) modified the B-G approximation to account for this variation in correlation distance over different domains in the polymer bulk due to the processing history of the nanocomposite by introducing a lognormal distribution for correlation distances, (Beaucage et al. 2004; Crow and Shimizu 1987) $P(\xi) = (1/\sqrt{2\pi}\xi\sigma)\exp(-\{\ln(\xi/m)\}^2/2\sigma^2)$ such that,

$$S(q, \xi) = \int_0^\infty P(\xi) \left[\frac{1}{1 + p\theta(q, \xi)} \right] d\xi \quad (9)$$

Here, $m = \xi \exp(-\sigma^2/2)$ is the geometric mean of correlation lengths whereas, σ is the geometric standard deviation. The mean correlation length, ξ then represents an average distance between structural features across different domains of correlation. This modified B-G approximation by McGlasson et al. (2020) is compared to the P-Y and B-G fits for a precipitated silica SBR system in Fig. 1.5(a). Quite clearly, the modified B-G function fits the data at intermediate- q and high- q . The function is not expected to fit the low- q range due to agglomeration of aggregates above ϕ^{cc} as noted by the shaded region in the graph.

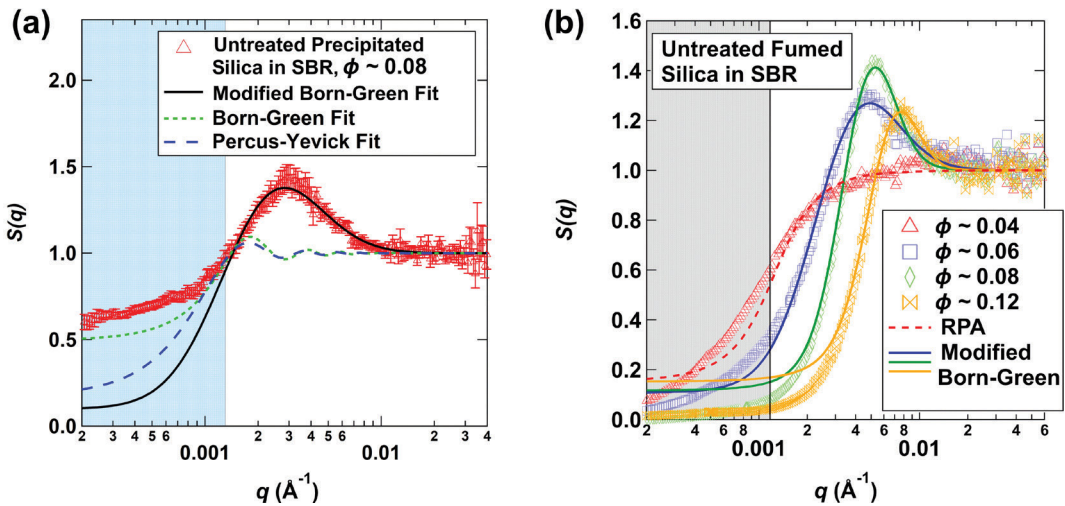


Figure 1.5 (a) $S(q)$ for precipitated silica in SBR at semi-dilute filler concentration fit using the P-Y function, B-G function, and the modified B-G function. Reprinted (adapted) with permission from McGlasson et al. 2020. Quantification of Dispersion for Weakly and Strongly Correlated Nanofillers in Polymer Nanocomposites. *Macromolecules* 2020, 53(6): 2235–2248. Copyright 2020 American Chemical Society. (b) $S(q)$ for unmodified fumed silica in SBR at different semi-dilute filler loadings. At low concentrations, a correlation peak is absent, whereas correlated peaks appear above the critical ordering concentration that is dictated by the dielectric constant of the matrix. The low concentration curve (red triangles) was fit using an equation based on the Random Phase Approximation (RPA) model, described later. Reprinted from Rishi et al. 2020. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. *J. Appl. Phys.* 2020, 127(17): 174702, with the permission of AIP Publishing.

The correlated aggregate structural emergence, described above, occurs above a local percolation threshold, ϕ^* . This threshold was defined at a filler volume fraction, ϕ , where $S(q) \neq 1$ in scattering for the aggregate and agglomerate regions in q . The question that arises then is whether these correlated structures emerge at all concentrations above the local percolation threshold, ϕ^* ? The emergence of correlations in Fig. 1.4 was observed at $\phi \sim 0.08$ for precipitated silica in SBR. Rishi et al. (2020) compared the $S(q)$ for untreated fumed silica with a high surface hydroxyl content mixed with SBR at different loadings above ϕ^* , as shown in Fig. 1.5(b). Note that $S(q) \neq 1$ in the intermediate- and low- q regions for all the concentrations. A complete absence of a correlation peak in $S(q)$ at filler volume fractions up to $\phi \sim 0.04$ was observed. Since for low dielectric materials, the Debye screening length is small, $\lambda_D \sim \kappa^{-1/2}$, it was hypothesized that the repulsive forces due to the charged aggregates were only felt at short distances (or at moderate concentrations). When the average aggregate separation distance approaches the Debye screening length of the polymer, λ_D , a critical ordering concentration is reached. The emergence of a correlation peak with increasing concentration for surface charged nanofillers such as precipitated and fumed silica is indicative of a free energy change on ordering, ΔG , analogous to the free energy change on micellization.

At low concentrations, the nanoaggregates are separated by distances larger than the Debye screening length, λ_D , and the effect of the charged surface hydroxyls on fumed silica is not felt by adjacent aggregates within a domain resulting in random distribution or lack of correlations. With increased concentration, the correlation length within the domains is reduced below λ_D such that the repulsive charges result in aggregate ordering within the domains. Although non-functionalized silica nanofillers mixed with SBR displayed a correlation peak with increasing concentration, this effect was not observed when fumed silica was mixed with polystyrene and PDMS at similar loading levels. It was argued that the low dielectric constant for polystyrene (Debye and Bueche 1951) ($\kappa_{PS} \sim 2.5$) and PDMS (Mark 1999) ($\kappa_{PDMS} \sim 2.56$) as opposed to SBR (Karásek et al. 1996; Gunasekaran et al. 2008) ($\kappa_{SBR} \sim 6.25$) meant that the Debye screening length is about 1.58 times larger for SBR (Rishi et al. 2020). Consequently, the critical ordering concentration for charged nanofillers, above which charges lead to repulsion and order would be about four times lower for SBR.

5 STRUCTURAL EMERGENCE IN COMPATIBLE SURFACE-FUNCTIONALIZED NANOFILLER-POLYMER SYSTEMS

For compatible nanofillers in non-polar polymers such as carbon black in SBR, $S(q) \neq 1$ above local percolation at ϕ^* (McGlasson et al. 2020). The same holds true for surface-functionalized nanoparticles mixed with compatible polymers (McGlasson et al. 2019; Rishi et al. 2020; Okoli et al. 2021). Nanoaggregates with chemically modified surfaces tend to not correlate, although the amount of surface treatment or carbon coating could impact the structural emergence (Okoli et al. 2021). The scattered intensity at intermediate- q shows a pronounced decrement instead of a correlation peak. Since no specific filler interactions dominate the scattering signal, the interactions of these randomly dispersed nanoaggregates can be approximated through a mean field. It should be noted that this random distribution of nanoaggregates could also show up with polar aggregates wherein the emergence is governed by the dielectric constant of the polymer as mentioned earlier. One way to describe mean-field interactions when the filler concentration is semi-dilute is through the Random Phase Approximation (RPA) as described by de Gennes (Anderson 1958; de Gennes 1979). This model was used to describe structural screening in polymer blends by Pedersen et al. (Zimm 1948; Benoit and Benmouna 1984; Pedersen and Schurtenberger 1999; Graessley 2002; Pedersen and Sommer 2005) and has been adapted for worm-like micelles by Vogtt et al. (2017) and highly-viscous polymer nanocomposites by Jin et al. (2017). Scattering from a homogeneous

phase arises from concentration fluctuations that are dampened by the osmotic compressibility, $d\Pi/d\phi$. The $q \Rightarrow 0$ scattered intensity from a uniform phase is proportional to $k_B T / (d\Pi/d\phi)$. At large size-scales or low- q , screening is likely since a uniform phase is observed. However, at smaller scales, higher- q , the structure can be resolved, and the phases are no long uniform. This is like a cloth that is made of fibers. At high magnification, the individual fibers can be seen, but at large scales a uniform fabric is observed. The random phase approximation quantifies a single mean-field parameter, v , that approximates the systemic interactions. This RPA is modeled as,

$$\left(\frac{I(q)}{\phi} \right)^{-1} = \left(\frac{I_0(q)}{\phi_0} \right)^{-1} + \phi v \quad (10)$$

At intermediate- q , the first term in equation (10), $\frac{I_0(q)}{\phi_0}$ reflects scattering from dilute nanoaggregates in the absence of structural screening. The second term, ϕv is a measure of the structural screening at large sizes. The second term's contribution to the reduced inverse intensity, $\left(\frac{I(q)}{\phi} \right)^{-1}$, increases linearly with concentration, dampening the low- q reduced intensity as shown in Fig. 1.6(a) and 1.6(b). The mean-field parameter, v , that bears the units of inverse intensity is used such that $1/\phi v$ approximates the plateau intensity at low- q for scattering from nanofillers in

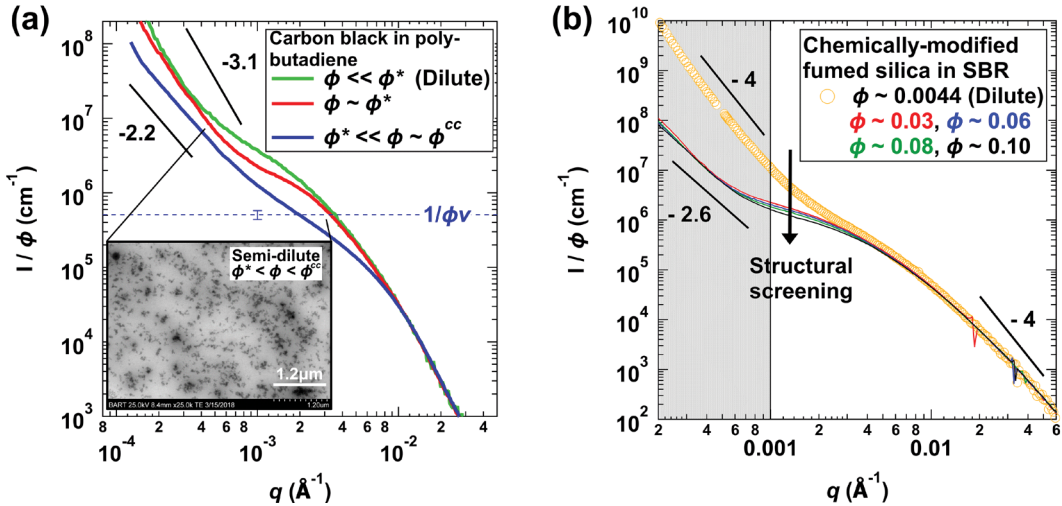


Figure 1.6 (a) Reduced scattering intensities, $I_0(q)/\phi_0$ (dilute, solid green curve), $I(q)/\phi$ (semi-dilute, solid red curve) and $I(q)/\phi$ (concentrated, solid blue curve) as a function of reciprocal space vector, q for carbon black in polybutadiene (PBD) rubber. At semi-dilute concentrations, the red curve shows screening at intermediate- q with surface fractal scaling at low- q . When the filler is concentrated, the screening at intermediate- q increases, and a mass-fractal scaling at low- q appears indicating the formation of a bulk network. Reprinted (adapted) with permission from Rishi et al. 2018. Impact of an Emergent Hierarchical Filler Network on Nanocomposite Dynamics. *Macromolecules* 2018, 51(20): 7893–7904. Copyright 2018, American Chemical Society. (b) Reduced scattering intensities, $I_0(q)/\phi_0$ (dilute, orange circles) and $I(q)/\phi$ (semi-dilute, all solid as a function of reciprocal space vector, q for chemically modified fumed silica in SBR. With increasing concentration, the screening increases at intermediate- q , although the large-scale network develops at a much lower concentration and does not change with increase concentration. Below the vertical line in q level 3 dominates the scattering so equation (10) is not appropriate. From Rishi et al. 2020. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. *J. Appl. Phys.* 2020, 127(17): 174702, with the permission of AIP Publishing.

the semi-dilute regime as shown in Fig. 1.6(a). Note that for surface compatibilized, disorganized particles, local aggregate overlap develops, and the aggregates are no longer isolated entities. Thus, under semi-dilute conditions above ϕ^* , the mean-field approach predicts no change in the concentration normalized scattering intensity, $I(q)/\phi$ from primary particles (level 1), but a reduction in $I(q)/\phi$ at larger size scales (level 2). The agglomerate and network levels (level 3) are not considered so the region of scattering at lowest- q is excluded from fits. The corresponding structure factor using the RPA approach is obtained by rearranging equation (10),

$$S(q) = 1 / \left(1 + \phi v \frac{I_0(q)}{\phi_0} \right) \quad (11)$$

v is only valid for screening of nano-aggregates on the 100 nm size scale. For micron-scale agglomerates and networks of clusters above ϕ^{cc} the structural emergence can be visualized directly through scattering by monitoring the change in the power-law slope at low- q . In this region, an observed power-law slope lying between -3 and -4 is associated with surface scattering from these coarse agglomerates of nano-aggregates. Once the nano-aggregates screen at semi-dilute concentrations above ϕ^* , the agglomerates may or may not remain as well-separated entities as shown in Fig. 1.6(a), red curve. On further increase in a concentration above ϕ^{cc} , a mass-fractal slope appears (blue curve in Fig. 1.6(a) and all solid curves in Fig. 1.6(b)) indicating the formation of an agglomerate cluster network.

From the above observations, it is inferred that compatible nano-filled polymer systems present two hierarchically related filler networks, a micron-scale network of filler agglomerates composed of a nanoscale network of filler nanoaggregates. The nanoscale network forms once the filler aggregates locally percolate on the nanoscale with an increase in concentration from dilute ($\phi < \phi^*$) to semi-dilute ($\phi^* < \phi < \phi^{cc}$). Percolation of the local network at ϕ^* occurs well below global percolation and has been observed at about 3 volume percent for colloidal silica (Banc et al. 2014). The percolated aggregates on a nanoscale, agglomerate into clusters that further percolate on a micron-scale at a much larger volume fraction ($\phi > \phi^{cc}$) on the order of 20 volume percent. Although this could occur at much lower concentrations for surface-functionalized nanoparticles as shown in Fig. 1.6(b). These hierarchical levels of percolation are sensitive to the filler type, the specific surface area and the processing conditions. Rishi et al. (Rishi et al. 2018) likened this emergent dual-level network hierarchy to the arrangement of tables covered with tablecloths in a restaurant. If the restaurant ceiling were to be chosen as the point of perspective, the arrangement of tables would constitute a large-scale network. The arrangement of tables can be dilute when the tables do not touch (low concentration, bottom two images in Fig. 1.7, left) and semi-dilute otherwise (high concentration, bottom two images in Fig. 1.7, right). Converse to this large-scale network, if the perspective is from an individual table an observer on such a table would only be able to see the tablecloth with fixed fiber density on the weave which corresponds to the nanoscale aggregate network (top two images in Fig. 1.7, left). In fact, there is a fixed maximum semi-dilute concentration for the aggregate networks since they are bonded and cannot pack more densely than their internal, aggregate overlap concentration (top two images in Fig. 1.7, right). At higher concentrations than that the micron-scale network must cluster to compensate for the addition of more material.

Under semi-dilute conditions, above percolation, ϕ^* , individual aggregates cannot be observed due to overlap. A size scale emerges, the local mesh size, ξ , the length below the structure appears identical to the dilute condition and above which a uniform fabric network is observed. For systems that present a correlation peak, the aggregate correlation distance can be obtained by fitting $S(q)$ using equation (9). The mesh size of the emergent network for surface-modified compatibilized nanofillers is the average distance between the centers of mass of the aggregates. This mesh size is on the order of the nanoaggregate size at ϕ^* and reduces in size with increasing concentration following a fractal scaling law (Mulderig et al. 2017b). Attempts have been made to ascertain the

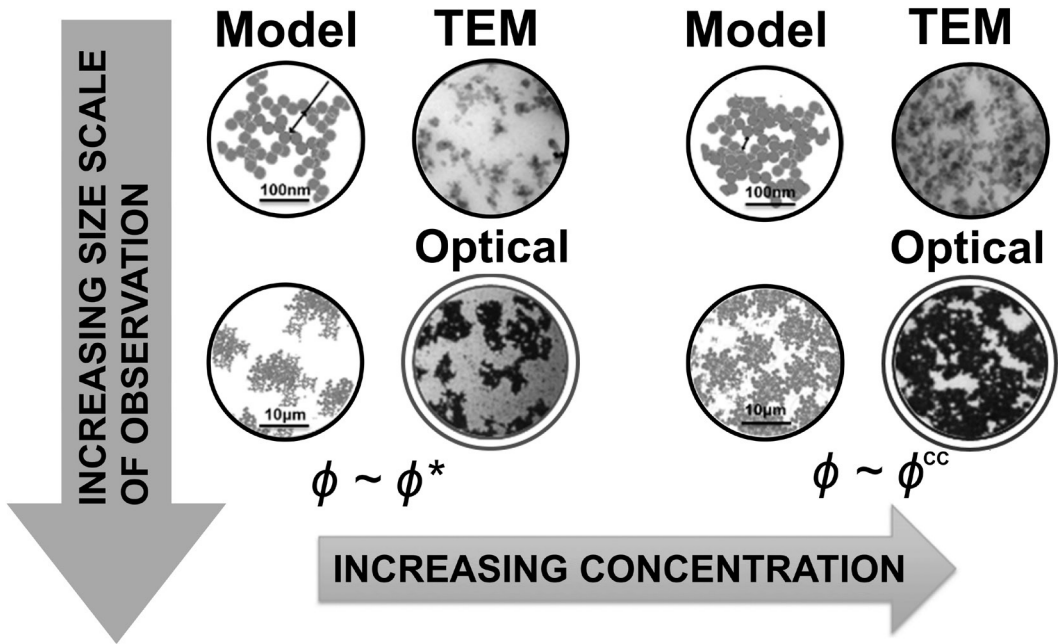


Figure 1.7 Sketch of structural hierarchies under semi-dilute ($\phi^* < \phi < \phi^{cc}$) and concentrated ($\phi > \phi^{cc}$) conditions. The local percolation is associated with a nano-scale network. All models and TEM micrographs in single circle: Reprinted (adapted) with permission from Rishi et al. 2018. Impact of an Emergent Hierarchical Filler Network on Nanocomposite Dynamics. *Macromolecules* 2018, 51(20): 7893–7904. Copyright 2018 American Chemical Society. Whereas, the global percolation is associated with a micron-scale network. Optical micrographs in double concentric circles: Reprinted (figure) with permission from Trappe and Weitz 2000. *Physical Review Letters*, 85(2), 449–452, 2000. Copyright 2000 by the American Physical Society. <https://doi.org/10.1103/PhysRevLett.85.449>.

interaggregate distance or mesh size by likening the aggregates to spherical particles packed in a cubic lattice (Polley and Boonstra 1957; McDonald and Hess 1977). Based on this model Polley and Boonstra (Polley and Boonstra 1957) proposed the separation distance between aggregates,

$$d_{a-a} = d_{agg} \{[(200 + \phi_{PHR} / 1.91\phi_{PHR})]^{1/3} - 1\} \quad (12)$$

where, ϕ_{PHR} is the filler loading in parts (by weight) per hundred, and d_{agg} is the diameter of the aggregate. Here the filler to elastomer density ratio was assumed to be 2:1. Caruthers et al. (1976) defined a loading-interfacial area parameter, ψ , that represents the total filler surface area per unit volume, $\psi = \rho\phi S$ where, ρ is the filler density measured in g/cm^3 and S is the specific surface area of the filler measured in cm^2/g . The dimension of ψ is the inverse length and can be related to the inter-aggregate distance, though the authors themselves claimed the idea to be speculative. Tokita et al. (1994) modified the average separation distance between spherical entities by considering the distribution in aggregate size and aggregate arrangement,

$$d_{a-a} = f_{dist} d_{St} \{[(c/\phi_{eff})]^{1/3} - 1\} \quad (13)$$

where, d_{St} is the Stokes diameter for the aggregate and f_{dist} is the distribution factor that can be computed from the median ($\Delta D50$) via a disk centrifuge photo sedimentometer. c , in equation (13), is the atomic packing factor for the aggregates which are considered as equivalent spheres. This parameter is generally considered to be an average of the simple cubic (0.52) and FCC arrangements (0.74). In equation (13), ϕ_{eff} is the effective volume fraction that accounts for rubber

occlusion due to the bound rubber. Wang et al. (1993) argued that the apparent Stokes' diameter in equation (13) exhibits a less meaningful correlation compared with the geometrical diameter of the aggregates and proposed,

$$d_{a-a} = d_{\text{agg}} \{[(c/\phi_{\text{eff}})]^{1/3} - 1\} \quad (14)$$

where the aggregate diameter was normalized by the ratio of the effect to the actual filler volume fraction, β , $d_{\text{agg}} = (6000/\rho S)\beta^{1.43} = d_p z^{0.436}$. The diameter of the primary particle, d_p , or equivalently the Sauter mean diameter, was estimated from the filler density and the specific surface area assuming spherical primary particles (Kraus and Gruver 1965; Wang et al. 1993). Medalia determined the degree of aggregation, z , from the projected areas of the aggregate and the primary particles and found that the effective loading parameter was related to z , such that $\beta = z^{0.3}$ (Medalia 1970). This estimate of d_{agg} has limited use mainly due to the experimentally determined value of the exponent, 0.436 (Medalia 1972). The equation can be generalized using the end-to-end distance of the aggregate, $R_{\text{eted}} = d_p z^{1/d_f}$ as discussed earlier. Here, d_f is the mass fractal dimension of the aggregate. Zhang et al. (2001) proposed a model for the interparticle distance based on simple cubic packing by Wu (1985) that resembles equation (14). However, the radius of gyration of the aggregates, $R_{g,2}$, rather than R_{eted} was considered. Silica aggregates have been likened to prolate spheroids such that d_{a-a} depends on an empirical fit parameter, A , related to the major and minor radii of the spheroids (Staniewicz et al. 2014),

$$d_{a-a} = \frac{A}{\{\phi(1+8\phi)\}} \quad (15)$$

In mean-field systems, the local mesh size, ξ , of the aggregate filler network can be computed from the reciprocal space vector, $\xi = 2\pi/q^*$, corresponding to the point where the horizontal line associated with screening in the RPA equation, $1/\phi v$, intersects the reduced dilute curve, $I_0(q)/\phi_0$. For practical loading levels, the mesh size, representing the pore size of the primary nanoscale network, is expected to scale between the size of the agglomerated super-structure (much greater than the aggregate size) and the primary particle size. This local mesh size can be computed by equating the Unified Function in equation (1) (truncated to structural level 2, that is ignoring the micron-scale network and agglomerates or clusters) to $1/\phi v$ when q satisfies,

$$G_2 \exp\left(\frac{-q^2 R_{g,2}^2}{3}\right) + B_2 (q_2^*)^{-P_2} \exp\left(\frac{-q^2 R_{g,1}^2}{3}\right) + G_1 \exp\left(\frac{-q^2 R_{g,1}^2}{3}\right) + B_1 (q_1^*)^{-P_1} = \frac{1}{\phi v} \quad (16)$$

The above estimate of the mesh size was contrasted against the geometric models developed for the interaggregate distance by Rishi et al. (2018). It was observed that likening, fractal nanofiller aggregates to prolate spheroids (Staniewicz et al. 2014) approximates the mesh size at low concentrations but deviates as the concentration increases (Rishi et al. 2018).

6 QUANTIFYING DISPERSION IN FUNCTIONALIZED NANOPARTICLES

During mechanical mixing of hierarchical nanoparticles in viscous polymers, shear forces break up loosely bound agglomerates into aggregates which are dispersed. These dispersed aggregates re-cluster into agglomerates/clusters, which can be randomly arranged or correlated based on interfacial interactions as discussed earlier. Clustering of filler particles is opposed by the application of mixing energy or accumulated strain. One would expect the energy input or accumulated strain to have a smaller impact at smaller sizes since the lever arm is smaller.

On the nanoscale kinetic mixing has a limited impact. In mechanically-dispersed, immiscible nanocomposites some spontaneous diffusion of nanoparticles is known to occur (Ceccia et al. 2010). At large and intermediate length scales, to the contrary, thermal transport is insignificant and the lever arm for mixing is much larger.

This scale-dependent mixing process is generally observed by monitoring the variation of torque with mixing duration (Cotten 1984; Kondo 2014) or by process conductivity measurements for conductive fillers (Le et al. 2004; 2005). In the mixing process, the matrix is first thermally softened for suitable uptake of fillers followed by incorporation of the filler. A filler wetting process is evidenced by a prominent peak in both the mixing torque (Cotten 1987) and conductivity curves (Le et al. 2004; 2005) as a function of mixing duration. Following wetting and incorporation, the average powder size, initially on the order of several hundred microns, decreases until it reaches the size of nanoaggregates, a few hundred nanometers, and cannot be broken down further under the application of mixing shear forces. The reduction in agglomerate size as a function of mixing time was described by Shiga and Furuta (1982) through Scanning Electron Microscopy (SEM) micrographs. It was observed that the nano-aggregates peel off from the surface of agglomerates in a manner analogous to how an onion would peel. The later stages of the mixing process involve the distribution of these nanoaggregates as shown by Cotton (Cotten 1987). It is hypothesized that although suitable filler wetting is associated with filler-polymer compatibility, the structural emergence is associated with incompatibility which drives local clustering followed by the formation of cluster networks on the micron scale at later stages (Filippone et al. 2010; Filippone and Salzano de Luna 2012; Song et al. 2017; Rishi et al. 2018).

Dispersion encompasses at least four processes: (1) the reduction in agglomerate size into smaller nanoaggregates; (2) their subsequent distribution in the matrix; (3) formation of clusters of dispersed nanoaggregates, and (4) emergence of a micron-scale network of clusters/agglomerates. A size-based quantification of the first two stages was achieved by Leigh-Dugmore (1956) through a series of micrographs. By visual comparison, a dispersion rating based on the percentage of filler agglomerates below a certain size was proposed by Medalia (1961). Coran and Donnet (1992a, b) modeled the change in Medalia's dispersion rating as a function of mixing duration through the DR function,

$$DR(t) = DR(\infty) - \frac{DR(0)}{\exp(\beta t)} \quad (17)$$

The most optimal dispersion, $DR(\infty)$, was based on the critical flaw size of the matrix polymer from Griffith's theory of crack propagation since an improvement in mechanical properties is observed below the flaw size. A higher percentage of agglomerates smaller than the critical flaw size in a micrograph resulted in a better dispersion rating. In equation (17), $DR(0)$ is related to the percentage of agglomerates larger than the critical flaw size prior to incorporation. β is an analogue to the specific rate in a first-order chemical reaction. One would expect β to vary with material and processing properties such as viscosity, mixing rate and temperature as well as mixing geometry. Since the dispersion process commences once all the filler particles have been incorporated into or wetted by the matrix, there exists a time delay known as the wetting time, before which a dispersion rating cannot be assigned (Coran et al. 1994; Leblanc 2002). This characteristic time delay or filler incorporation time can be computed at $DR(t_0) = 0$. Improvements to this model were made by assessing the area ratio of agglomerates of a specific size although the techniques were limited to optical micrographs of these nanofillers (Le et al. 2014; Faraguna et al. 2017) Bohin et al. (1996) proposed a simpler model to monitor the erosion of a filler agglomerate under simple shear flow,

$$DR(t) = \frac{DR(\infty)}{1 + (\gamma t)^{-1}} \quad (18)$$

The rate of agglomerate erosion, γ , indicates a competition between the hydrodynamic shearing force and the cohesive force that holds the agglomerate together and is related to the matrix viscosity and the shear rate. However, Bohin's model assumed a negligibly small incorporation time. Yamada et al. (1998) showed that increased matrix viscosity slowed polymer matrix infiltration into the filler. A slower infiltration process at the same applied shear is associated with longer incorporation time indicating that the characteristic time delay would be longer if the matrix viscosity is higher.

To quantify the distribution of agglomerates and nanoaggregates, optical, SEM and TEM micrographs have been analyzed using numerical, statistical models and advanced computational geometry (Bakshi et al. 2009; Pegel et al. 2009; Khare and Burris 2010; Bray et al. 2012; Li et al. 2012; Lively et al. 2012; Glaskova et al. 2011; Glaskova et al. 2012; Haslam and Raeymaekers 2013; Fu et al. 2013). The strength and weaknesses of quantifying dispersion through these techniques have been reviewed (Krishnamoorti 2007). It has been argued that although the assessment of micrographs depends on a robust statistical method, proper identification of the filler by image thresholding to completely eliminate the inhomogeneous background is generally overlooked (Li et al. 2012). As an alternative, electrical conductivity (or inversely resistivity) could be used to quantify the extent of filler dispersion although the technique is limited to conductive fillers such as carbon black (Kondo 2014). For example, O'Farrell et al. (2000) noticed an increase in volume resistivity with increasing mixing times close to the filler percolation threshold indicating that the number of direct contacts between the filler particles reduced with increasing mixing time. At longer mixing times, the appearance of a plateau in resistivity indicated a state of terminal dispersion such that the number of direct contacts remained unchanged. However, for filler concentrations above percolation, the change in volume resistivity was insignificant indicating that this measure of dispersion is only suitable in the proximity of the global percolation limit.

The extent of dispersion depends on the size scale of observation. Macro-dispersion is related to size scales that are large enough so that some key aspects such as aggregate structure and specific surface area are averaged out. At large size scales, the reduction in agglomerate size is a suitable way to quantify dispersion. On the contrary, nano-dispersion involves observation on size scales comparable to the filler aggregate and primary particle sizes. Jin et al. (2017) used an analogy with thermally dispersed colloids to quantify dispersion using the second virial coefficient. Dispersion in colloidal mixtures, such as polymer solutions, printing inks, milk, red blood cells, etc., is dictated by Brownian motion (kT). Generally, such thermally-dispersed colloidal particles have favorable surface interactions with the matrix, i.e., they may be either stabilized by a surfactant or have a natural interfacial compatibility, (Rishi et al. 2019b; Vogtt et al. 2019) although phase separation can be achieved by sedimentation in a centrifuge to overcome the thermally driven Brownian motion. On the contrary, mechanically-dispersed polymer nanocomposites exist in a kinetically locked-in state. The nanoparticles in such systems would normally flocculate, settle or cluster except for the action of shear fields coupled with a viscous, glassy or semi-crystalline matrix phase. Both functionalized and non-functionalized nanofillers in viscous polymers are examples of kinetically dispersed colloids. Nanoparticle dispersion and the resulting properties are tied to the interfacial compatibility between the dispersed phase and the matrix. It is well known that clustering of colloidal particles in thermal equilibrium is opposed by the osmotic compressibility, $d\pi/d\phi$, or the build-up of osmotic pressure, π , with concentration, ϕ . Under dilute conditions, the osmotic pressure is estimated by the van't Hoff equation, $\pi = \rho_{\text{num}} k_B T$. A virial expansion of osmotic pressure can describe deviations from ideality through the second virial coefficient, B_2 as,

$$\frac{\pi}{k_B T} = \rho_{\text{num}} + B_2 \rho_{\text{num}}^2 + B_3 \rho_{\text{num}}^3 + \dots \quad (19)$$

Here B_2 , expressed in cm^3 per particle, reflects deviations in osmotic pressure due to binary particle-particle interactions. The second virial coefficient, B_2 , has been used to determine the stability of colloidal thermal dispersions (Mulderig et al. 2017b). For a stable colloid, with $B_2 > 0$, the dispersed phase remains evenly distributed throughout the solution, whereas particle clustering, sedimentation or flocculation occurs for unstable colloids with $B_2 < 0$. Vogtt et al. (2017) used the mean-field model in equation (10) for a two-level hierarchical worm-like micelle system to obtain B_2 from v ,

$$B_2 = \frac{1}{2}(zV_{pp})^2 v \Delta \rho^2 \quad (20)$$

Here $\Delta \rho^2$ is the squared difference in scattering length density between the nanofiller and the nanocomposite matrix or the scattering contrast, V_{pp} is the volume of the primary subunit and z is the degree of aggregation. The use of equation (20) was extended to hierarchical nanofiller particle systems by Jin et al. (2017). Similar methods to quantify dispersion using interaction parameters that measure filler-polymer compatibility have been explored. For example, Stöckelhuber et al. (2010) proposed the use of the free energy of immersion, ΔG_i , that can be represented as a function of the surface energies of the filler and the polymer-filler interface to quantify the wettability of the filler particles by the polymer. Hassinger et al. (2016) developed a quantitative tool to incorporate mechanical processing conditions to predict interfacial thermodynamics. A set of descriptors to quantify the interfacial energy based on the ratio of the work of adhesion between polymer-filler and filler-filler following Natarajan et al. (2013), the total power consumption during the mixing process, and the volume fraction normalized filler surface area based on TEM micrographs were proposed. Using correlations between the three descriptors resulted in adequate quantification of dispersion under a given set of conditions.

The first derivative of osmotic pressure, in the virial expansion (the osmotic compressibility), is proportional to the second virial coefficient. The temperature dependence of the second virial coefficient, B_2 , for thermally-dispersed, colloidal solutions can be obtained by describing the second virial coefficient of osmotic pressure, with the van der Waals equation of state, $B_2(T) = b - \frac{a}{RT}$, where b is the excluded volume of the colloidal particles and a is the pressure correction term associated with inter-particle attraction. Rishi et al. (2020) considered the overall accumulated strain, γ , to be an analogue to thermal energy for mechanically-mixed, kinetically dispersed filler-elastomer nanocomposites and expressed B_2 as,

$$B_2(t, N, \psi) = b^* - \frac{a^*}{\gamma} = b^* - \frac{a^*}{N\Psi t} \quad (21)$$

Here b^* represents the excluded volume of the nano-aggregates and consequently depends on the degree of aggregation, z , and the primary particle size, d_p . Interestingly, the difference of this experimental estimate of and the actual hard-sphere excluded volume of an aggregate could provide an estimate of the bound rubber layer on the aggregate (Rishi et al. 2019a). N represents the mixing speed whereas, t indicates the mixing duration for batch type geometries and the residence time for continuous mixers such as extruders. Ψ reflects the mixing geometry. For a traditional twin-rotor internal mixer such as a Brabender or Banbury mixer, Ψ can be approximated using simple Couette flow following Bousmina et al. (1999). Similarly, for a single-screw extruder this geometric constant can be approximated following Hassinger et al. (2016). For vortex mixing of nanoparticles in low viscous matrices, this constant can be approximated by an equivalent bob and cup geometry (Mezger 2006). The functions are listed in Table 1.1.

Table 1.1 Instrument geometry-related constants for estimating the accumulated strain

Mixing equipment	Approximate for mixing geometry	Details
Brabender mixer	$\Psi = \frac{4\pi(\beta)^{2/n}}{n\{(\beta)^{2/n} - 1\}}$	β : ratio of wall to rotor diameter; n : power-law index under shear flow (Sadhu and Bhowmick 2005)
Single-screw extruder	$\Psi = \frac{\pi\{d - 2H(L)\}}{H(L)}$	d is the screw diameter and $H(L)$ is the channel depth that depends on the screw length, L (Hassinger et al. 2016)
Vortex mixer	$\Psi = \frac{2\pi(2R^2)}{(R^2 - r^2)}$	R is the cup radius and r is the radius of the bob

These simple estimates for accumulated strain have shown to serve as good approximations for laboratory-scale equipment which are bulk fed. On the contrary, industrial-grade twin-screw extruders are starve-fed and an estimate of the accumulated strain is far more involved due to variations in the fill factor with each rotation. Veigel et al. (2021) estimated $A_2 = (N_A/M^2)B_2$ for carbon black polystyrene nanocomposites by varying the mixing speeds, residence times and the mixing geometries. Note that M is the aggregate mass and N_A is the Avogadro's constant. The functional dependence of nanoparticle dispersion on accumulated strain in equation (21) was manageable as shown in Fig. 1.8.

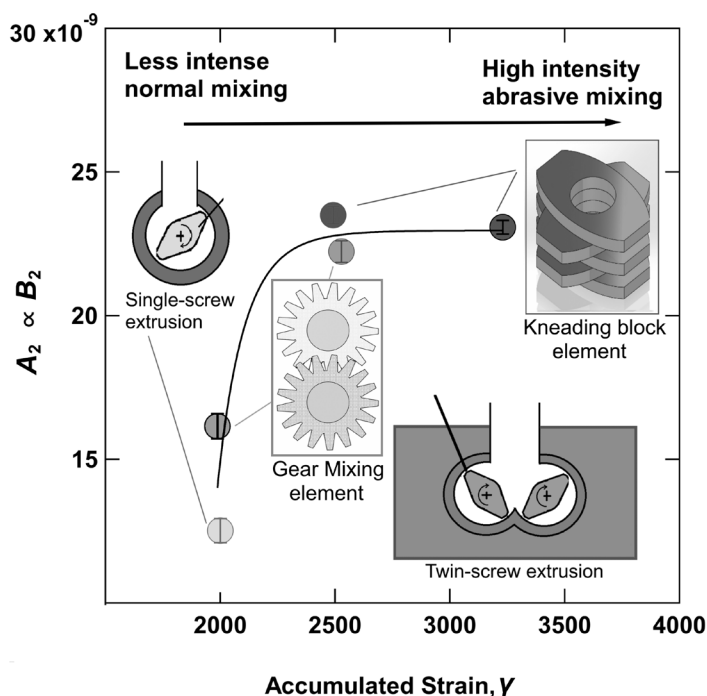


Figure 1.8 Dependence of nanoscale dispersion, quantified via A_2 on the accumulated strain in carbon black-polystyrene nanocomposites for different mixing geometries (single screw vs twin-screw extruder), screw element (gear mixer vs kneading blocks), and mixing speeds (points to the left for a specific screw element represent lower mixing speed). Reprinted (adapted) with permission from Veigel et al. 2021. “Nanocomposite Dispersion in Melt Mixers.” *Bulletin of the American Physical Society*, 2021.

a^* is a measure of the interaction potential and is sensitive to the surface chemistry of functionalized nanoparticles as shown by Rishi et al. (2020). Figure 1.9 shows the dependence of

a^* on the natural log of the surface concentration of silanols and methyl groups for neat, fumed silica (solid symbols) and silane-coupled fumed silica (open symbols) in polystyrene, styrene-butadiene rubber and polydimethyl siloxane compounded using different mixers and processing conditions. A straight-line fit was obtained by varying the constants k' and k'' which represent the relative influence of silanol and methyl functional groups on the interaction potential, whereas C_2 represented a scaling factor. Additionally, the fit parameter, C_1 , was found to be proportional to the total accumulated strain based on the mixing geometry, and the zero-shear rate viscosity of the polymers, η , at the processing temperature. The functional dependence of the interaction energy, ΔG , normalized by the accumulated strain which is an analogue to kT in these viscous nanocomposite systems on the surface chemistry of both neat and modified silica bears semblance to free energy of micellization in surfactant systems.

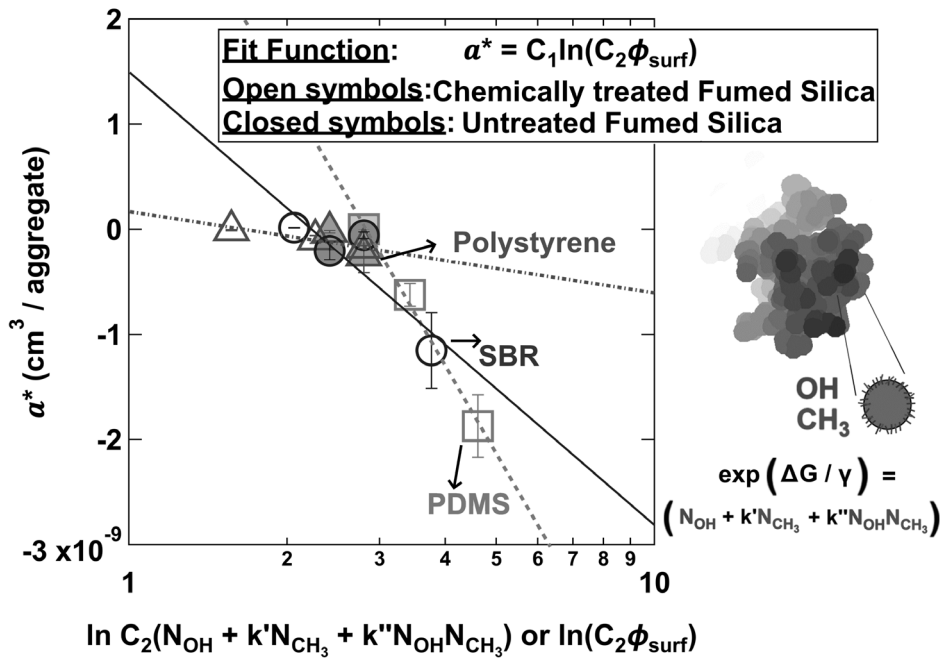


Figure 1.9 The dependence of the binary interaction potential, a^* , on the surface concentration of chemical species (N_{OH} and N_{CH_3}) for surface-functionalized and bare silica nanofiller grades in SBR (solid line), polystyrene (dot-dash line), and PDMS (dashed line) matrices. The constants, k' and k'' describe the relative effects of different surface functionalities whereas, C_2 is a scaling constant. C_1 is directly related to the accumulated strain sensitive to the mixing conditions and the zero-shear rate viscosity of the matrix. A logarithmic dependence of a^* normalized by the accumulated strain ($\gamma \propto C_1$) on ϕ_{surf} is analogous to the free energy of micellization. Reprinted from Rishi et al. 2020. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. *J. Appl. Phys.* 2020, 127(17): 174702, with the permission of AIP Publishing.

Quantification of dispersion through the pseudo-second-order virial coefficient, B_2 (or A_2), accounts for the material-specific variables viz. particle size, the degree of aggregation, the interaction potential which is sensitive to the surface chemistry of the nanofillers and the matrix viscosity. The dependence of B_2 on the accumulated strain, which accounts for the mixing duration, mixing speed, viscosity and the instrument geometry presents a large phase-space within which the effects of processing on polymer nanocomposites can be specified. B_2 is a direct, quantitative measure of the dispersion with larger values indicating better dispersion. Negative B_2 indicates phase segregation and $B_2 = 0$ is a critical value. Understanding the dependencies of B_2 in different polymer-filler systems are important to developing predictive techniques for control of structural

emergence in polymer-filler systems. B_2 can be used to calculate binary filler interaction potentials for coarse-grained computer simulations of complex multi-level hierarchical filler mixtures. Control over this complex multi-hierarchical structure can be achieved through manipulation of filler-polymer interactions such as by varying the silanol surface density, by chemically-tailoring the surface and by grafting low molecular weight polymers. It is expected that these modifications can control dispersion and the associated emergent multi-hierarchy.

7 THE IMPACT OF EMERGENT STRUCTURES ON THE DYNAMIC RESPONSE OF FUNCTIONALIZED NANOPARTICLE POLYMER COMPOSITES

In commercial products such as tires, specific properties such as traction, wear-resistance and rolling resistance depend on the filler morphology, the filler-elastomer surface chemistry as well as the degree of filler dispersion. With the increase in filler concentration, well-dispersed nanoparticle aggregates in polymers form a continuous network (Warring 1950; Fletcher and Gent 1954). The presence of this filler network has been evidenced in the dynamic mechanical response with varying strain amplitude (Payne 1962; Payne and Watson 1963; Payne 1963; Payne and Whittaker 1971). This network is associated with the Payne effect and bulk conductivity is on the micron-scale (Karásek et al. 1996; Yurekli et al. 2001) and commences at the global percolation limit, ϕ^{cc} in the structural hierarchy discussed earlier. For many types of nanofillers, ϕ^{cc} can be estimated from the dibutyl phthalate (DBP) absorption number (Janzen 1975) although, only conductive fillers like carbon black with lower DBP numbers agree experimentally (Li et al. 2016).

The complex dynamic modulus for a nanocomposite is estimated by applying an oscillatory perturbation, $\gamma(t) = \gamma_0 \sin(\omega t)$, with a fixed strain amplitude, γ_0 and monitoring the subsequent stress response. In the linear viscoelastic regime at low strain, the stress varies linearly as

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) = \gamma_0 \{G' \sin(\omega t) + iG'' \cos(\omega t)\} \quad (22)$$

In equation (22), $G'(\omega) = G \sin \delta$ and $G''(\omega) = G \cos \delta$ represent the storage and loss shear moduli, respectively. The phase difference between the applied strain and the resulting stress, δ , varies between 0° (Hookean elastic response) and 90° (Newtonian viscous response) (Ferry 1980). The ratio of the two moduli is the damping factor, $\tan \delta = G''(\omega)/G'(\omega)$.

Most commercially available instruments are limited in the accessible frequency range. Accessing the response over a wider frequency range necessitates the use of the time-temperature superposition principle. The William-Landel-Ferry (WLF) equation (Williams et al. 1955), is one such example that allows for estimation of this inaccessible frequency range through horizontal shifting (a_T) of isothermal frequency curves at different temperatures to a reference temperature, T_{ref} . The logarithm of the horizontal shift factor, $\log a_T = -C_1(T - T_{ref})/(C_2 + T - T_{ref})$ such that C_1 and C_2 are constants for a particular polymer. In practice, least-square fitting methods are used to arbitrarily shift the isothermal response curves and the estimated a_T is fit to the WLF equation to determine C_1 and C_2 . The construction of the moduli master curves for polymer nanocomposites requires both frequencies, a_T , and moduli, $b_T = \rho_{ref} T_{ref} / \rho T$, shift factors.

The addition of nanofillers to a polymer matrix increases the shear modulus, although a_T is expected to be independent of the filler loading. The Einstein-Smallwood equation (Smallwood 1944), written in analogy to the Einstein equation for the viscosity of colloidal suspensions, is used to describe the enhancement of modulus under dilute conditions such that, $G = G_0(1 + K\phi)$. Here, G and G_0 are the moduli of the filled elastomer and neat elastomer, respectively whereas, ϕ is the volume fraction of filler, and K is a factor related to filler structure (analogous to the intrinsic viscosity $[\eta]$). For mono-disperse rigid spheres under dilute conditions, K is 2.5 (using the Einstein equation for $[\eta]$ of spheres). This linear dependence on volume fraction arises from

amplification of the observed strain rate due to volumetric displacement of elastomer by rigid filler. For mass-fractal nanofiller aggregates, a larger effective volume is displaced as compared to a sphere for a given volume fraction, so values of K greater than 2.5 can be used. Additionally, under semi-dilute filler concentrations, the modulus enhancement can be generalized by a Taylor series expansion,

$$G = G_0(1 + K\phi + K'\phi^2) \quad (23)$$

where, the coefficients, K and K' are related to the filler structure and interactions. For low structure carbon blacks, that are more compact and allow closer packing, K equals 2.5 and K' equals 14.1, as described by Guth (1945). For mass-fractal nanoparticles, the ratio of excess modulus to the bare polymer modulus, $(G/G_0) - 1$, was found to vary linearly with filler concentration until aggregate overlap, ϕ^* , based on linear elastic theory (Huber and Vilgis 1999; Huber and Vilgis 2002). It was predicted that beyond percolation, ϕ^* , this dependence on volume fraction would change to a power-law which is not necessarily 2 (equation (23)).

Increasing filler-elastomer interaction by surface functionalization could result in the formation of a bound polymer layer. The amount of bound polymer is related to the amount of occluded polymer owing to the fractal nature of the fillers (Robertson et al. 2007). Medalia (1970) postulated that the amount of occluded polymer within the interstices of the filler aggregates would increase the effective filler volume fraction. The ratio of effective to actual filler volume fraction, $\beta = (1 + e)/(1 + \varepsilon)$, was directly related to the effective loading parameter, e , that represented the void space in a single aggregate divided by the volume of the solid aggregate. The void space is related to the volume of DBP (dibutyl phthalate) that fills the aggregates during a crushed DBP absorption, (Kraus 1971; Medalia 1972) such that $e = \rho DBPA$. ρ is the filler density whereas, ε is the aggregate packing factor ranging from 0.35 to 0.92. It was experimentally determined that a part of the occluded polymer volume, $\phi_{\text{eff}} - \phi$ deformed under the application of stress, (Medalia 1972) necessitating the need to introduce an occlusion effectiveness parameter, F , to adequately account for the effective filler volume fraction in the nanocomposite as,

$$\phi_{\text{eff}} = \phi\{F(\beta - 1) + 1\} \quad (24)$$

F is approximately 0.5 under low-strain conditions meaning that only 50% of the occluded rubber remains immobilized and contributes to modulus enhancement and is independent of the carbon black structure (Medalia 1972).

The enhancement in modulus based on equation (23) considers the hydrodynamic effect and the binary filler interactions whereas, equation (24) accounts for the immobilization layer and the effective volume fraction. However, the contribution due to filler network formation is not considered in equation (24), and thus, a deviation in the predicted relative modulus, G/G_0 , is expected when the filler network emerges above ϕ^* . Rishi et al. (2018) attempted to relate the dynamic response in the plateau and terminal flow regions at very low-strain amplitudes in the linear viscoelastic regime to features of the hierarchical network obtained from static X-ray scattering. The nanoscale mesh size discussed previously was found to relate to a characteristic transition frequency in the dynamic spectrum. Figure 1.10(a) shows a plot of storage modulus for a semi-dilute carbon black polybutadiene nanocomposite and bare polymer after correction for the hydrodynamic reinforcement and effective filler volume fraction of the filler. Since the semi-dilute filler concentration is on the order of 20 volume percent, a nano-scale network based on the hierarchical model discussed previously has developed. In the high-frequency plateau region, the response follows the Einstein-Smallwood equation (Smallwood 1944) with modifications based on the effective filler content (Medalia 1972). A clear deviation in the two master curves is observed at low frequency and the transition frequency between the two opposing regimes is related to the mesh size from scattering as shown in Fig. 1.10(b). This simple frequency-length relationship was found to depend on the spectral dimension (Vilgis and Winter 1988) which is associated with the network connectivity (Rishi et al. 2018). The static aggregate connectivity dimension

has been described as an intrinsic measure of the aggregate structure with a value of 1 for linear aggregates and greater than 1 for branched aggregates (Meakin et al. 1984). For homogenous percolation clusters, the spectral dimension is predicted to be $4/3$ (Alexander and Orbach 1982). In Fig. 1.10(b), this spectral dimension, $c \sim 1/0.8 \sim 1.25$ was in agreement with the aggregate connectivity dimension from scattering.

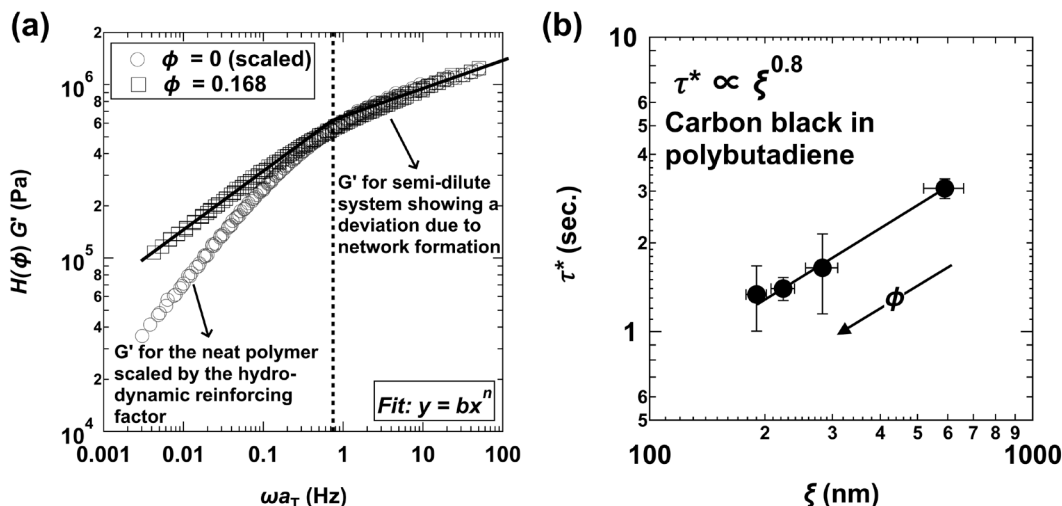


Figure 1.10 (a) Storage modulus master curve for a semi-dilute (squares) compatible nanocomposite (carbon black in polybutadiene) compared to a master curve for the same nanocomposite based on the modulus of the neat polymer, the hydrodynamic reinforcement and effective filler content (circles). The dashed line indicates the transition frequency (time) associated with the filler network. (b) Dependence of this characteristic time scale, τ^* and the network mesh size, ξ that are related by the spectral dimension. Reprinted (adapted) with permission from Rishi et al. 2018. Impact of an Emergent Hierarchical Filler Network on Nanocomposite Dynamics. *Macromolecules* **2018**, 51(20), 7893–7904. Copyright 2018 American Chemical Society.

Wet grip, described as the handling efficiency of an automobile tire on the road, and rolling resistance, defined as the energy loss induced by the deformation over the contact area of an automobile tire with the road, are two essential properties that dictate tire performance (Sae-oui et al. 2017). The dynamic response parameter, $\tan \delta$ is generally employed in the evaluation of wet grip and rolling resistance. The hysteresis of the polymer compound during continuous deformation at various temperatures is the underlying principle behind the functionalities of these parameters, which are directly related to driving safety and fuel economy (Araujo-Morera et al. 2019). In the industry, the dynamic response at 60 to 70°C is a measure of the tire rolling resistance whereas, the response at about 0°C is associated with tire braking/grip. $\tan \delta$ values at these temperatures are used to parameterize the performance (Lee et al. 2013). Elastomeric nanocomposites with relatively lower $\tan \delta$ values at 60°C have reduced rolling resistance while higher $\tan \delta$ values at 0°C improve wet grip. Consequently, reaching a compromise between reducing the $\tan \delta$ values at 60°C and increasing the $\tan \delta$ values at 0°C becomes an elusive goal in tire research (Lei et al. 2016). $\tan \delta$ measures the combined effect of energy lost and stored owing to the viscoelastic nature of the silica SBR nanocomposites. A lower rolling resistance is characterized by a reduction in $\tan \delta$ or a relative increase in the storage modulus whereas, a better-wet grip is achieved at larger $\tan \delta$ values or a relative increase in the energy lost. To achieve this synergistic effect, tire compounders use both carbon black and silica (Sattayanurak et al. 2019; Gabriel et al. 2019). Figure 1.11(a) shows how the wet grip changes with the surface silanol content in carbon-coated and surface silanized pyrogenic silica in SBR rubber. A lower surface silanol content resulted in an improved wet grip. Similarly, a lower surface carbon content resulted in lower rolling

resistance in Fig. 1.11(b). It was argued that although the reduction in the surface hydroxyl groups by silanization could improve the wet grip of the resulting nanocomposite, it would concomitantly result in an increase in the surface carbon or surface methyl content (Okoli et al. 2021). An optimal solution could result if the surface of silica were coated with a critical number of carbon monolayers that would also result in improved dispersion.

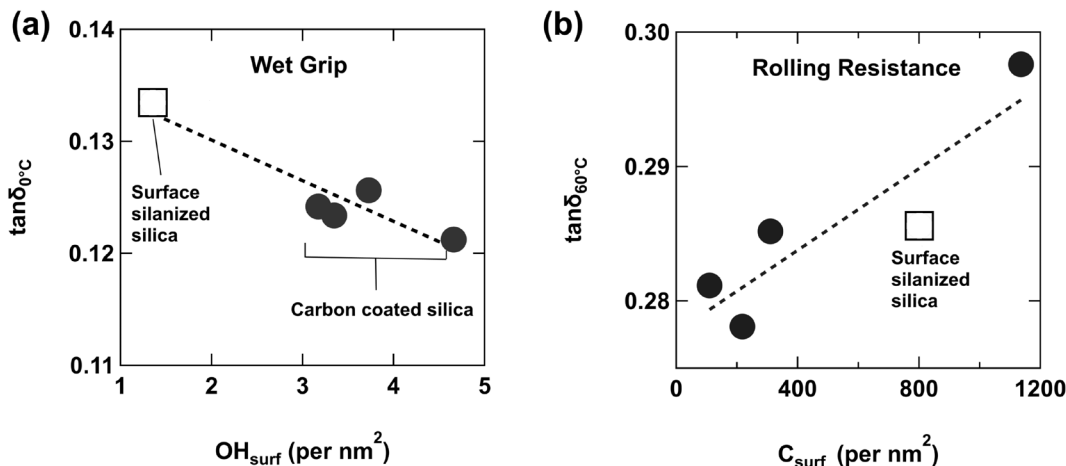


Figure 1.11 (a) Plot of $\tan \delta$ at 0°C as a function of surface silanol content and (b) $\tan \delta$ at 60°C as a function of surface carbon content for functionalized fumed silica in SBR rubber. Reprinted (adapted) with permission from Okoli et al. 2021. “Dispersion and Dynamic Response for In-Flame and Chemically Modified Fumed Silica Nanocomposites.” In *Bulletin of the American Physical Society*, 2021.

8 CONCLUSION

Surface functionalization of nanoparticles can be used to manipulate the complex structural emergence that leads to control over mechanical, electrical and viscometric properties of polymer nanocomposites. For industrial filled materials containing immiscible aggregated nanoparticles, a balance between compatibility and immiscibility is needed to influence the emergence of a robust macroscopic network, while retaining accessible nanoscale surface area at low volume fractions of the filler. The emergent structure with a multi-hierarchy can influence both high-frequency response (rolling resistance) and moderate frequency (wet grip) as well as low frequency (bulk modulus and tear resistance). Dramatic advances have been made in the past 5 years in this area that have allowed the direct correlation for the first time of the mechanical frequency spectrum with the structural spectrum as measured with X-ray scattering and X-ray tomography. This multi-hierarchical approach shows promise for the design of new materials for solid electrolytes, paints, inks, flame retardants and filled elastomers among other areas where features on the macroscopic scale are desired from nanoscale polymeric additives. Some general observations have been found associated with the influence of the Debye screening length coupled with concentration for polar additives such as silica. A critical concentration was found for aggregated nanoparticles to display correlated organization. Dispersion on the nanoscale is improved for larger particles if the mixing is dominated by kinetics, while it is improved for smaller particles if the mixing is dominated by thermal diffusion. A quantitative function has been reviewed that relates specific surface functionality to nanoscale dispersion. This function predicts how surface organic and polar content will influence mixing at a specified accumulated strain which is related to polymer viscosity and mixing time and geometry. The impact of accumulated strain on nano-dispersion for polar and non-

polar fillers was also described. It is generally understood that compatibilization can be important to nanocomposites. In simple model systems composed of spherical, monodisperse particles mixed in monodisperse polymers by solvent blending from single phase colloidal suspensions, idealized mappings of phase behavior have been reported. These predictive tools are of little use in the commercial setting where incompatible, aggregated, polydisperse multi-component melt blended materials are encountered. This chapter has indicated some of the fundamental tools that have been made available in the past few years to predict and design these commercial materials which are of increasing importance to the advancement of a wide range of fields.

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