A pseudo-thermodynamic description of dispersion for nanocomposites

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ABSTRACT

Dispersion in polymer nanocomposites is determined by the kinetics of mixing and chemical affinity. Compounds like reinforcing filler/elastomer blends display some similarity to colloidal solutions in that the filler particles are close to randomly dispersed through processing. It is attractive to apply a pseudo-thermodynamic approach taking advantage of this analogy between the kinetics of mixing for polymer compounds and thermally driven dispersion for colloids. In order to demonstrate this pseudo-thermodynamic approach, two polybutadienes and one polyisoprene were milled with three carbon blacks and two silicas. These samples were examined using small-angle x-ray scattering as a function of filler concentration to determine a pseudo-second order virial coefficient, A_2, which is used as an indicator for compatibility of the filler and polymer. It is found that A_2 follows the expected behavior with lower values for smaller primary particles indicating that smaller particles are more difficult to mix. A_2 is analogous to the excluded volume and long-range interaction potential for non-equilibrated nanocomposites. The measured values of A_2 can be used to specify repulsive interaction potentials for coarse grain DPD simulations of filler/elastomer systems. In addition, new methods to quantify the filler percolation threshold and filler mesh size as a function of filler concentration are obtained. The results represent a new approach to understanding and predicting dispersion in polymer nanocomposites based on a thermodynamic analogy.

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1. Introduction

Processed polymers usually consist of multiple immiscible components such as pigments, fillers, and compounding agents. For complex polymeric mixtures an understanding of relative compatibility or dispersibility of the components on a fundamental level is desirable. Such an understanding could help in the design of polymer nanocomposites and in the control and prediction of behavior. For example, reinforcing fillers such as carbon black (CB) and silica are used in rubber products. The reinforcing ability depends on the structure of the fillers, and the interaction between filler particles and the elastomer matrix as well as the processing history. Aggregated fillers can be quantified by the specific surface

area (and the related primary particle size), the degree of graphitization for carbon, and the hydroxyl surface content for silica. A description of filler structure also includes the fractal aggregate structure that allows access to the surface through spatial separation of primary particles. The fractal structure also contributes a static spring modulus to the composite at size scales larger than the filler mesh size for concentrations above the percolation threshold [1]. Aggregates are often clustered in agglomerates that can largely be broken up during the elastomer milling process.

The affinity for a filler/polymer pair is evidenced by their dispersability and their reinforcing properties in elastomer composites. Since fillers are often nanomaterials, standard characterizations of compatibility focus on the specific surface area. The surface area of fillers is usually measured by iodine adsorption (mg/g of filler), nitrogen adsorption (m^2/g of filler), or cetyltrimethylammonium bromide (CTAB) adsorption (m^2/g of filler) [2,3]. The structure of fillers has been quantified using oil absorption (g/100 g of filler) or dibutyl

phthalate (DBP) absorption (ml/100 g of filler) for CB [2,3], as well as through a variety of surface characterization techniques such as determination of the surface hydroxyl content for silica, and the degree of graphitization for carbon black. In addition, techniques have been applied to study compatibility of filler in the rubber matrix by investigating surface and aggregate structure. Göritz et al. used atomic force microscopy (AFM) and small angle x-ray scattering (SAXS) to study surface structure and fractal dimension of CB [4]. Scanning electron microscopy (SEM) [5] and transmission electron microscopy (TEM) [6] were used to study particle size and morphology of aggregates, Herd et al. [7,8] discovered four types of CB aggregates by TEM: spheroidal, ellipsoidal, linear and branched shapes. Koga et al. investigated hierarchical structure of CB combining techniques of ultra-small angle and small angle scattering of X-rays and neutrons (USAXS, SAXS and USANS) [9]. Abraham et al. introduced a technique of sorption to analyze the compatibility of filler in the rubber matrix by studying transport and diffusion of small molecules through matrix [6].

Silica is the traditional reinforcing filler for polydimethylsiloxane elastomers due to compatibility in chemical structure. Silica was introduced as a reinforcing filler for diene elastomers for tires in the 1990's and showed a lower rolling resistance and higher fuel efficiency compared to carbon black reinforcing filler [2,5]. However, silica is very different compared to CB filled rubbers due to its strong polar and hydrophilic surface. A certain quantity of moisture can be adsorbed on the silica surface and it is difficult to remove. This is especially true of precipitated, colloidal silica and silica gel. Pyrolytic silica has an essentially pristine surface but is rarely used for elastomer reinforcement except for siloxane elastomers. Inter-particle interaction of silica due to hydrogen bonding and Coulombic interactions needs to be considered since it weakens the compatibility of silica and rubber [2].

Several groups have considered the impact of surface energy and interfacial modification on dispersion under non-equilibrium processing conditions [10–14]. Stöckelhuber et al. [10] determined the contact angle and surface energy of fillers and elastomer gums to calculate the free energy of emersion of fillers in elastomers. A negative free energy of immersion favors dispersion, and a positive value favors flocculation. The surface energy was broken into a dispersive energy associated with London's dispersive forces and a polar component associated with polar functional groups. These were determined through measurement of the dynamic contact angle. The free energy of immersion depends on the polar component of the elastomer surface energy and the dependence is associated with chemical surface modification. The work of adhesion for filler in polymer can also be calculated from surface energies. This shows a similar dependence on the polar part of the surface energy of rubbers. A large work of adhesion could be associated with good dispersion and poor flocculation. The difference in work of adhesion between the dispersed and flocculated state is related to the formation of a filler network. Evidence from TEM qualitatively supports the approach.

Stöckelhuber et al. [11] further considered the mechanics of elastomer composites in the framework of surface energies. Stöckelhuber developed a plot of surface energy of the filler versus the polar component of the filler surface energy and proposed regimes within this plot where good wetting and good adhesion of the filler would occur in a given elastomer. This mapping enables filler selection for a specific elastomer. TEM and dynamic mechanical measurements were used to verify the approach.

Natarajan et al. [12] studied siloxane polymers of variable polar surface energy, as described by Stöckelhuber [11], filled with surface modified colloidal silica of variable polarity. A comparison was made of the Stöckelhuber plot [11] with TEM micrographs and the glass transition temperature which is sensitive to surface interactions between polymer and filler. The average cluster radius and the average intercluster distance were determined from the micrographs. These showed expected trends in the work of adhesion. Shifts in the glass transition also correlated with a function of the work of adhesion.

Hassinger et al. [13] extended the work of Natarajan et al. towards prediction of dispersion under non-equilibrium processing conditions. They coupled the ratio of the work of adhesion between filler/polymer and filler/filler, developed by Stöckelhuber et al. [10], and a calculated mixing energy to correlate with the interfacial area calculated from TEM images. A model was proposed that correlates the interfacial area reflecting dispersion and a combined term involving the work of adhesion ratio and the calculated mixing energy. Good correlations are found between these parameters.

The prior work based on interfacial energy has had significant success. Coupling of mixing energy with interfacial energies is an appealing approach [13]. However, for the most part this approach has been applied at concentrations below the percolation concentration where TEM analysis and verification is appropriate. The expected primary particle size dependence based solely on surface energy would predict that small particles with high specific surface area that display favorable surface energies should disperse better that larger particles. However, the opposite is often the case for commercial reinforced elastomers above the percolation threshold in the semi-dilute regime for fillers. Further, the measured surface energy is an equilibrium property that reflects local interactions such as those that affect the interfacial T_g [14,15]. These short-range interactions are often attractive and lead to aggregation in many nanocomposites such as pigment dispersions. Despite short-range aggregation that reflects disadvantageous interfacial energies it is still common to disperse aggregates at larger scales through mechanical mixing. A complementary approach is to consider, in addition to short-range interactions that can lead to aggregation, long-range interactions that lead to dispersion based on excluded volume. This approach can lead to the prediction of properties that can not be accessed using short-range surface interactions. For instance, long-range interactions may be responsible for the filler aggregate percolation threshold or overlap concentration and may correlate with the filler network mesh size. Features such as the filler percolation concentration and filler network mesh size may influence the properties of nanocomposites, especially those that are difficult to describe based on short-range interactions and that are related to the emergent structure in semi-dilute concentrations of filler.

In this paper an analogy is made between thermally driven dispersion in colloidal mixtures and mechanically driven dispersion, particularly in aggregated nanocomposites such as carbon black and silica in elastomers. In this pseudo-thermodynamic approach it is possible to obtain an effective long-range repulsive potential that can be used to describe the complex structural result of the interplay between excluded volume, surface energy and mixing kinetics for nanostructures that display an emergent, kinetically frozen, and disperse filler aggregate network structure such as in commercial reinforced elastomers and pigment dispersions in inks, paints and plastics.

The compatibility of colloidal solutions such as mixtures of miscible polymers, solutions of low molecular weight organics and inorganics, and biomolecules is often quantified using the virial expansion to describe the concentration dependence of the osmotic pressure. This approach assumes that molecular and nanoscale motion and the associated dispersion is governed by thermally driven diffusion with a molecular energy of k_BT. Elastomer/reinforcing filler compounds have not been considered equilibrium colloidal mixtures since the materials are highly viscous or solid networks so it is difficult to imagine thermally driven motion