Composites: Part A 84 (2016) 158–164

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

# Study of nanoparticles aggregation/agglomeration in polymer particulate nanocomposites by mechanical properties

Yasser Zare *

*Young Researchers and Elites Club, Science and Research Branch, Islamic Azad University, Tehran, Iran*

ARTICLE INFO

*Article history:*
Received 6 April 2015
Received in revised form 30 November 2015
Accepted 25 January 2016
Available online 2 February 2016

*Keywords:*
A. Nanocomposites
A. Polymer-matrix composites (PMCs)
B. Mechanical properties

ABSTRACT

A simple approach is described to study the aggregation/agglomeration details in polymer nanocomposites reinforced with spherical nanoparticles. The suggested methodology for mechanical properties can offer the aggregation/agglomeration level as a function of different parameters. In addition, the effective volume fraction of agglomerated nanoparticles in nanocomposite samples ($\phi_{agg}$) is determined by the present technique.

The calculated results for various samples express that the aggregation/agglomeration of nanoparticles is occurred in all reported nanocomposites. Also, both aggregate/agglomerate and nanofiller diameters play important roles in aggregation/agglomeration level of samples. The aggregation/agglomeration extent increases by addition of nanofiller content and reduction of nanofiller size. Moreover, the aggregation/agglomeration decreases the effectiveness of nanoparticles in polymer matrix, which lastly results in the poor properties of samples.



## 1. Introduction

Recently, the attractive features of polymer nanocomposites have involved much attention in academic and industrial fields. The nanocomposites show many substantial properties such as high modulus, large hardness, high thermal stabilization and decreased permeability by little content of nanofiller (below 5 wt %) [1–8]. However, easy-fabricated and low-cost products are the final aims of researches in this field. Also, nanocomposites show various profits such as low cost, high accessibility, easy fabrication and high levels of magnetic, optical and electrochemical properties. Surprisingly, these advantages are achieved without the usual shortages of embrittlement, transparency and lightness in polymer nanocomposites [9–14].

However, nanoparticles can be easily aggregated and agglomerated when added to polymer matrix. The aggregation/agglomeration can be formed during the production process of nanoparticles or incorporating them in polymer. Both aggregation and agglomeration are assemblies of nanoparticles where the strong and dense particle collectives are referred to aggregation. Also, agglomeration is when particles are combined loosely which can be simply broken by mechanical forces. The aggregation/agglomeration prevents the obtaining of improved properties and thus, the achieving of various applications by nanostructured materials [15,16]. The aggregation/agglomeration has been attributed to the direct mutual attraction between nanoparticles via van der Waals forces or chemical bonds. The strategies for avoiding aggregation/agglomeration are mainly attributed to particle coating by a capping agent, application of coupling agent or compatibilizer and charging the filler surface to separate them via electrostatic revulsions [17,18]. Also, using optimal parameters in production process can lead to an effective breaking of aggregates. For example in melt compounding by extruder [16], optimal screw speed and feeding rate apply much stress to melt materials which disrupt the particles aggregates.

The dissimilar effects of aggregation/agglomeration on the final properties of polymer nanocomposites have been reported in previous articles. Although many studies indicated the detrimental effects of particle aggregation/agglomeration on final properties, Dorigato et al. [19] related the effective reinforcement of polymer nanocomposites to primary filler aggregation. In other words, they gave a model for aggregation of nanoparticles, which explains the reinforcing mechanism of polymer nanocomposites by aggregation of nanoparticles, rather than the interfacial adhesion between polymer and nanoparticles. However, the aggregation/agglomeration can produce many defects and stress concentrations in nanocomposites, which all deteriorate the properties of samples.

Many studies in the literature investigated the effects of nanoparticle content and process parameters on the dispersion

* Address: Hesarak, Tehran, Iran. Tel.: +98 21 66454514; fax: +98 21 66547514.
*E-mail address:* y.zare@aut.ac.ir

http://dx.doi.org/10.1016/j.compositesa.2016.01.020
1359-835X/

quality of nanoparticles by manipulating the various parameters such as stress intensity, stress mechanism and stress frequency [20,21]. They aimed to achieve a good dispersion and distribution of nanoparticles in polymer matrix. It was reported that an increasing volume fraction typically leads to smaller aggregate sizes. However, smaller aggregate sizes cause higher re-agglomeration effects during nanocomposite processing [22,23].

Beside the aggregation/agglomeration, nanofiller morphology has a very important role in the overall mechanical behavior of nanocomposites. The effects of morphology have been widely studied in the literature [24–30]. It was shown that the exfoliated/intercalated structure of silicate layers is necessary to obtain good properties in polymer nanocomposites [15,16,31]. Although the morphology of nanocomposites is explicitly assumed in these papers, the nanostructure is implicitly taken into account in the studied models and samples in present paper. Recently, our group has focused on the modeling of nanocomposite behavior to study some important subjects such as interfacial adhesion between polymer and nanoparticles and interphase properties [32–36]. The interphase is defined as a zone of polymer surrounding the nanoparticle with different chemical and mechanical properties from polymer and nanoparticles. The effects of interphase properties such as thickness and strength on the mechanical properties of polymer nanocomposites have been largely discussed in the previous reports [37–48]. Lazzeri and Phuong [49] suggested a direct link between "$B$" interfacial parameter in Pukanszky model and fundamental material parameters for nanocomposites containing nanoclay and carbon nanotubes. They determined the minimum value of "$B$" as 3 which is essential for composite strength to be higher than the strength of matrix.

In this paper, a simple approach for shear yield strength of polymer particulate nanocomposites is applied to study the aggregation/agglomeration phenomena in nanocomposites. The model can present an "$A$" parameter as a representative of aggregation/agglomeration level depending to nanofiller and aggregates properties such as nanofiller content and density. These parameters affect the state of aggregation during processing as well as the agglomeration due to instable nanoparticles in matrix. In addition, the effective volume fraction of aggregated nanoparticles in polymer matrix ($\phi_{agg}$) is estimated and its effect on the properties of nanocomposites is discussed. In this work, the level of aggregation/agglomeration of nanoparticles is studied assuming the insignificant aggregation of nanoparticles in their synthesis and negligible agglomeration due to instable nanoparticles in matrix by Van der Waals interaction without solid bonds.

## 2. Background

The shear yield strength of nanocomposites ($\tau$) can be expressed [50,51] as:

$$\tau = \tau_m + \frac{Gb_B}{\lambda} \quad (1)$$

where "$\tau_m$" is shear yield stress of polymer matrix, "$G$" is shear modulus, "$b_B$" is Burgers vector and "$\lambda$" is distance between nanoparticles. This equation is applicable for each polymer/-nanoparticle system, but an extremely small "$\lambda$" causes an infinite high "$\tau$". As a result, suitable type and content of nanofiller should be chosen which depend to surface functionalization, aggregate morphology and interface at a similar state of aggregation/agglomeration, etc.

When nanoparticles are aggregated in polymer matrix, this model is given by:

$$\tau = \tau_m + \frac{Gb_B}{A\lambda} \quad (2)$$

where "$A$" is an aggregation/agglomeration parameter which presents the level of nanoparticle aggregation/agglomeration. "$\tau$" can be normally correlated to yield strength ($\sigma_y$) [52] as:

$$\tau = \frac{\sigma_y}{\sqrt{3}} \quad (3)$$

which indicates that "$\tau$" is simply calculated by tensile test. "$G$" is also predicted by tensile modulus ($E$) for isotropic materials [53] as:

$$G = \frac{E}{2(1+\nu)} \quad (4)$$

where "$\nu$" is Poisson ratio. "$\nu$" can be simply measured by tensile properties of isotropic composites [53] as:

$$\sigma_y = \frac{1-2\nu}{6(1+\nu)}E \quad (5)$$

Also, Burgers vector ($b_B$) for polymers is calculated [54] by:

$$b_B = 0.1\left(\frac{60.5}{C_\infty}\right)^{1/2} \quad (6)$$

where "$C_\infty$" is characteristics ratio of polymer [54], given by:

$$C_\infty = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3} \quad (7)$$

where "$d_f$" is nanocomposite structure fractal dimension and "$d$" is dimension of Euclidean space, in which fractal is assumed. "$d$" is equal to 3 for nanocomposites containing spherical nanoparticles. Moreover, "$d_f$" is determined by:

$$d_f = (d-1)(1+\nu) \quad (8)$$

The distance between non-aggregated particles can be calculated [50] by:

$$\lambda = 0.5\left[\left(\frac{4\pi}{3\phi_f}\right)^{1/3} - 2\right]D_p \quad (9)$$

where "$\phi_f$" and "$D_p$" are nanofiller volume fraction and diameter, respectively. According to above equation, the present methodology is only applicable for small volume fraction of nanofiller, since the extremely small "$\lambda$" causes infinite high values of "$\tau$" by Eq. (1).

"$\phi_f$" is attributed to weight percentage ($W_f$) and density ($\rho_f$) of nanofiller as:

$$\phi_f \propto \frac{W_f}{\rho_f} \quad (10)$$

Also, "$\rho_f$" can be correlated to "$D_p$" [50] as:

$$\rho_f \propto D_p^{1/3} \quad (11)$$

which estimates the "$\rho_f$" by:

$$\rho_f = ND_p^{1/3} \quad (12)$$

where "$N$" is a constant parameter attributed to nanofiller type. Using Eqs. (10)–(12) into Eq. (9), we can determine "$\lambda$" as:

$$\lambda = 0.5\left[\left(\frac{4\pi ND_p^{1/3}}{3W_f}\right)^{1/3} - 2\right]D_p \quad (13)$$

Assuming the aggregation/agglomeration diameter ($D_{agg}$), "$A\lambda$" is given by:

$$A\lambda = 0.5\left[\left(\frac{4\pi ND_{agg}^{1/3}}{3W_f}\right)^{1/3} - 2\right]D_{agg} \quad (14)$$

Also, "$A$" parameter can be determined by comparing the latter equations as: