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Filler aggregation as a reinforcement mechanism in polymer nanocomposites

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ABSTRACT

Significant reinforcing effects that are often observed in polymer nanoparticulate composites are usually attributed to strong interfacial interactions over extended interfaces in these systems. Here, we study linear low density polyethylene (LLDPE) reinforced with 1–4% fumed silica nanoparticles. Nanocomposite modulus, evaluated as a function of filler volume fraction, significantly exceeds classical micromechanics predictions. Possible reasons for the observed discrepancy are evaluated experimentally and theoretically. It is concluded that primary nanoparticle aggregation rather than polymer-nanoparticle interaction at the interface is mainly responsible for the observed reinforcement effect. A simple micromechanics-informed model of a composite with primary particle aggregates is presented based on the model of secondary aggregation developed earlier. The model is shown capable of predicting nanocomposites behavior by introducing a single new structural parameter with a straightforward physical interpretation. As nanoparticles are prone to agglomerate, their primary or secondary aggregates may be present in many nanocomposite systems and the aggregation state and its effects need to be thoroughly evaluated, along with the classical interfacial interactions. The described reinforcing mechanism may be responsible for other anomalous property changes in nanoparticulate composites reported in the literature.

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MATERIALS

1. Introduction

Nanocomposites attract rapidly growing interest due to a very broad range of their current and projected applications. In particular, polymer nanocomposites provide an attractive way to utilize unique properties of nanoscale inclusions in bulk applications (Gupta et al., 2010). They often exhibit significant property changes at very small volume loadings of inclusions that allows one to modify and improve material performance without sacrificing excellent polymer processability and light weight. Research on nanocomposites is growing exponentially and some researchers project the long-term impact to be comparable to the impact given by the development of high-perfor-

mance fibers and composites, or even the development of synthetic polymers themselves (Tjong, 2006). Polymer nanocomposites are often classified into layered silicate (clay) nanocomposites, carbon nanotube (CNT) composites, and nanoparticulates (Ajavan et al., 2003). The first two groups received considerable attention due to their demonstrated or projected high mechanical and other properties stemming from the unique characteristics and the extended (2D and 1D) shapes of their inclusions such as clay platelets and carbon nanotubes (CNTs), respectively. By comparison, other nanoparticles received somewhat lower attention as reinforcing agents. At the same time, nanoparticulates have considerable advantages over the platelet- or CNT- reinforced nanocomposites in terms of ease of manufacturing and cost. Moreover, nanoparticles can also be applied for their peculiar magnetic, optical and electrochemical properties in a new generation of multifunctional materials (de Dios and Diaz-Garcia, 2010). In

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addition, unlike platelet- and CNT-reinforced nanocomposites that usually underperform as compared to theoretical predictions of their mechanical properties (due to welldocumented difficulties with dispersion, alignment, interfacial stress transfer, and other problems (Ajayan et al., 2003; Tjong, 2006)), polymer matrix nanoparticulates often exhibit mechanical properties higher than predicted. The addition of relatively small amounts (<3 vol.%) of inorganic particles such as silica, titania, or calcium carbonate having dimension in the nanometer scale was proven to increase both rigidity and toughness of several different thermoplastics (Tjong, 2006). As an example, both tensile modulus and impact strength improvements were observed for high-density polyethylene (HDPE)/silica (Zhang et al., 2003), for nylon-6/silica (Ou et al., 1998), and for poly(vinyl chloride)/CaCO₃ nanocomposites (Xie et al., 2004). Moreover, a remarkable reduction of the creep rate of nylon6,6/titania nanocomposites melt compounded using a twin-screw extruder (Zhang et al., 2004) was reported.

Mechanisms of these improvements are complex and not yet fully understood. Often, the observed significant property changes, especially the increases in mechanical properties, are attributed to nanoparticle interaction with polymer matrix. Intensive research is under way to better understand and control the properties of nanocomposites. It is well known that inorganic nanoparticles can easily aggregate in polymer matrices (Ajayan et al., 2003; Bondioli et al., 2008, 2009; Cassagnau, 2008; D'Amato et al., 2012; Dorigato and Pegoretti, 2010, 2011). These aggregates of primary nanoparticles can be formed during their production process or during their processing into composites. Only an optimal parameter selection of the melt compounding process can lead to an efficient disruption of the agglomerates. However, nanoparticle aggregation was never considered as a key point to explain the stiffness increase associated to the introduction of nanoparticles in polymer matrices.

Therefore, in this paper we analyze variations of elastic moduli of several linear low density polyethylene (LLDPE) nanocomposites reinforced with silica nano- and microparticles. Composites fabricated by melt compounding without additional particle functionalization are tested mechanically and the results are analyzed and compared with classical micromechanics predictions. It is concluded that nanoparticle aggregation is primarily responsible for the anomalous reinforcing effect in the nanoparticulate systems compared to the microparticulate. A simple micromechanics-informed model is presented and used to describe the variations of elastic moduli with nanoparticle volume fractions. The results are discussed in the context of significant recent literature on nanocomposites with unusual mechanical and functional properties. The need for thorough evaluation of nanoparticle aggregation in these systems is emphasized, along with the classical evaluation of interfacial interactions.

2. Experimental

Polymer chips of Flexirene[®] CL10 linear low density polyethylene (LLDPE), kindly supplied by Polimeri Europa

SpA (Mantova, Italy), were used as a matrix in this work. This thermoplastic resin is characterized by a density of 0.917 g cm^{-3} at room temperature, and a melt flow index of 2.6 g $(10 \text{ min})^{-1}$ at 190 °C and 2.16 kg. Two different kinds of fumed silica nanoparticles, supplied by Degussa (Düsseldorf, Germany), were used for the preparation of nanocomposites, i.e. Aerosil[®] 200 (nominal specific surface area of 200 m² g⁻¹) and Aerosil[®] 380 (nominal specific surface area of 380 m² g⁻¹). Traditional microcomposites were prepared by using Cores[®] silica glass microspheres. Relevant physical properties of the selected micro- and nanofillers are reported in Table 1. Density measurements were performed at ambient temperature by using a Micromeritics Accupyc[®] 1330 helium pycnometer, while surface area and porosity measurements were conducted by using an ASAP® 2010 Accelerated Surface Area and Porosimetry machine. Surface properties were evaluated referring to the nitrogen gas physisorption process. Specific surface area (SSA) values of the fillers were evaluated according to the Brunauer-Emmett-Teller (BET) procedure (Brunauer et al., 1938). On the basis of the Barrett-Joiner-Holenda (BJH) method (Barret et al., 1951), the surface area contribution according to pores dimensions was also determined.

Both micro- and nanocomposites were melt compounded with LLDPE in a Thermo Haake internal mixer, at 170 °C for 15 min and 90 rpm. The resulting compounds were then hot pressed in a Carver[®] laboratory press at 170 °C under a pressure of 0.2 kPa. The filler volume fraction was varied between 1% and 4%. In the following figures and the discussion session, the nanocomposites are labeled according to the type of fumed silica nanopowders (for example A200 indicates Aerosil 200 nanoparticles), while glass microspheres are simply denoted as Glass. The full composites label contains the name of the matrix (LLDPE), followed by the name of the filler and its volume content. For example, LLDPE-A200-2 indicates 2 vol.% Aerosil 200 fumed silica nanocomposite.

Uniaxial tensile tests were performed at room temperature with an Instron 4502 tensile machine on ISO 527 type 1BA specimens, tested at a crosshead speed of 0.25 mm min^{-1} . The strain was recorded by using a resistance extensometer Instron model 2620-601 (gage length = 12.5 mm). According to ISO 527 standard, a secant modulus was evaluated between strain levels of 0.05– 0.25%.

Differential scanning calorimetry (DSC) tests were performed by using a Mettler[®] DSC30 apparatus. All measurements were conducted in a temperature range from 0 °C to 200 °C at a heating rate of 10 °C min⁻¹, under a nitrogen

Table 1

Density and surface properties of fumed silica nanoparticles and glass microbeads.

Sample	Density (g cm ⁻³)	BET surface area (m ² g ⁻¹)	Nominal particle diameter (µm)	BJH adsorption cumulative surface area of pores (1.7–
				300 nm) (m ² g ⁻¹)
Glass A200 A380	2.43 ± 0.01 2.27 ± 0.02 2.41 ± 0.02	0.5 ± 0.1 196.6 ± 1.7 320.8 ± 3.4	18 0.012 0.007	0.4 165.2 247.0

flow of 100 ml min⁻¹. DSC tests provided information on the melting temperature (T_m) and the crystallinity content (X_C), derived normalizing the melting enthalpy by the heat of fusion of the fully crystalline polyethylene, taken as 290 J g⁻¹ (Brandrup et al., 1999).

X-ray diffraction analysis was conducted by a Rigaku[®] 3D Max X-ray diffractometer, scanning the sample in a 2θ range between 1° and 67°, at a 2θ step of 0.1°. The wavelength of the X-ray source was 0.154056 nm. From the diffractograms it was possible to determine the dimensional distribution of the crystalline domains, on the basis of a whole powder pattern modeling algorithm (Scardi and Leoni, 2002).

In order to evaluate the dispersion state of the fillers in the matrix, cryogenically obtained fracture surfaces of LLDPE-Glass-2 sample were observed by using a Philips XL30 environmental scanning electronic microscope (ESEM). Ultramicrotomed thin sections of undeformed LLDPE-A380–2 sample were observed by a Philips FEI CM120 transmission electronic microscope (TEM).

3. Results and discussion

3.1. Comparison of experimental elastic moduli with micromechanics predictions

Experimental values of the normalized elastic modulus (E_C/E_M) , where E_C and E_M are the elastic moduli of composite and matrix, respectively) of the prepared composites are plotted in Fig. 1 as a function of filler type and content. For glass-filled microcomposites, the reinforcing effect is very limited, while fumed silica nanocomposites show a very strong improvement of the elastic modulus with the filler content. Furthermore, the elastic modulus enhancement obtained by using fumed silica nanoparticles with the higher specific surface area (A380) is more pronounced than the effect obtained with the lower SSA nanoparticles (A200). The obtained results are compared with predictions of a classical micromechanics model. Christensen (2005) and Christensen and Lo (1979) obtained a closed-



Fig. 1. Normalized elastic modulus data of LLDPE and relative composites from quasi-static tensile tests. (\blacksquare) LLDPE-Glass-x, (\blacklozenge) LLDPE-A200-x, (\blacktriangle) LLDPE-A380-x, and results of calculation according to the Christensen-Lo micromechanics model (continuous line, Eqs. (1)–(11)).

form solution for a model of a composite with isolated spherical inclusions. According to this model, the effective bulk and shear moduli (denoted respectively as K and G) of a polymer filled with hard spherical particles can be calculated as:

$$K = K_m + \frac{V(K_f - K_m)}{1 + \left[\frac{(1 - V)(K_f - K_m)}{K_m + \frac{4}{3}G_m}\right]}$$
(1)

$$G = G_m \left(\frac{-B \pm \sqrt{B^2 - AC}}{A} \right) \tag{2}$$

where:

$$A = 8\left(\frac{G_f}{G_m} - 1\right) (4 - 5\nu_m)\eta_1(V)^{\frac{10}{3}} - 2\left[63(\frac{G_f}{G_m} - 1)\eta_2 + 2\eta_1\eta_3\right] (V)^{\frac{7}{3}} + 252\left(\frac{G_f}{G_m} - 1\right)\eta_2(V)^{\frac{5}{3}} - 50\left(\frac{G_f}{G_m} - 1\right) (7 - 12\nu_m + 8\nu_m^2)\eta_2(V) + 4(7 - 10\nu_m)\eta_2\eta_3$$
(3)

$$B = -2\left(\frac{G_{f}}{G_{m}} - 1\right)(1 - 5\nu_{m})\eta_{1}(V)^{\frac{10}{3}} + 2\left[63\left(\frac{G_{f}}{G_{m}} - 1\right)\eta_{2} + 2\eta_{1}\eta_{3}\right](V)^{\frac{7}{3}} - 252\left(\frac{G_{f}}{G_{m}} - 1\right)\eta_{2}(V)^{\frac{5}{3}} + 75\left(\frac{G_{f}}{G_{m}} - 1\right)(3 - \nu_{m})\eta_{2}\nu_{m}(V) + \frac{3}{2}(15\nu_{m} - 7)\eta_{2}\eta_{3}$$
(4)

$$C = 4\left(\frac{G_f}{G_m} - 1\right)(5\nu_m - 7)\eta_1(V)^{\frac{10}{3}} - 2\left[63\left(\frac{G_f}{G_m} - 1\right)\eta_2 + 2\eta_1\eta_3\right](V)^{\frac{7}{3}} + 252\left(\frac{G_f}{G_m} - 1\right)\eta_2(V)^{\frac{5}{3}} + 25\left(\frac{G_f}{G_m} - 1\right)(\nu_m^2 - 7)\eta_2(V) - (7 + 5\nu_m)\eta_2\eta_3$$
(5)

and:

$$\eta_{1} = (49 - 50v_{f}v_{m}) \left(\frac{G_{f}}{G_{m}} - 1\right) + 35 \frac{G_{f}}{G_{m}}(v_{f} - 2v_{m}) + 35(2v_{f} - v_{m})$$
(6)

$$\eta_2 = 5\nu_f \left(\frac{G_f}{G_m} - 8\right) + 7\left(\frac{G_f}{G_m} + 4\right) \tag{7}$$

$$\eta_3 = \frac{G_f}{G_m} (8 - 10\nu_m) + (7 - 5\nu_m) \tag{8}$$

where K_m , K_f , G_f and G_m are bulk and shear moduli of the matrix and the filler, respectively, V is the filler volume fraction, v_m and v_f represent the Poisson's ratio of the matrix and the filler. Assuming both matrix and filler are isotropic elastic solids, it is possible to determine their bulk and the shear moduli as follows:

$$K_i = \frac{E_i}{3 - 6\nu_i} \tag{9}$$

$$G_i = \frac{E_i}{2 + 2\nu_i} \tag{10}$$

where the index *i* refers to matrix (*m*) or filler (*f*). For the matrix, the elastic modulus of 0.2 GPa was experimentally evaluated, while the Poisson's ratio of 0.44 was adopted from the literature (Meyyappan, 2005). For amorphous silicon dioxide, the elastic modulus of 70 GPa and the Poisson's ratio of 0.17 are commonly reported (Klocek, 1991; Yoder, 1993). These values were used as the properties of both silica nanoparticles and silicate glass. Knowing the effective bulk and shear moduli of the composite (*K*,*G*), the elastic modulus (*E*) can be determined from the expression linking the elastic constants of an isotropic solid:

$$E = \frac{9KG}{3K + G} \tag{11}$$

The calculated model predictions for the effective modulus as a function of volume fraction of the inclusions are plotted in Fig. 1. It should be noted that, as in all classical micromechanics models, the expressions (1-11) do not explicitly depend on the particle size. It can be seen that the classical model successfully predicts the variation of modulus for the glass filled microcomposite. However, the stiffening effects in silica nanoparticulate systems are significantly higher than the predicted values.

3.2. Evaluation of potential effects of interfacial interactions

The discrepancies between the experimentally measured and predicted mechanical properties similar to the ones observed in Fig. 1 are not unusual in polymer nanoparticulates. They are often attributed to the effects of interfacial interactions. Interfaces have been shown to have crucial influence on the mechanical behavior of conventional microcomposites (Pukanszky et al., 1994; Voros and Pukanszky, 1995). For instance, Pan et al. investigated interfacial effects on the viscoelastic characteristics of carbon nanotube polymer matrix composites (Pan et al., 2013). In that work, an effective medium theory was applied to study the effect of interfacial sliding on the time dependent creep, stress relaxation, strain-rate sensitivity, storage and loss moduli of a multi-walled CNT/polypropylene nanocomposite. It was shown how viscoelastic characteristics of CNT nanocomposites were very sensitive to the interface condition, and that continued improvement in surface functionalization was necessary to realize the full potential of CNT reinforcement. In another work of Barai and Weng (2011), a model to describe plasticity of carbon nanotube reinforced composites was presented. It was shown how both the elimination of CNT agglomeration and the improvement of the interfacial interaction were necessary conditions to realize the full potential of CNT reinforcement. Extensive studies in both thermoset and thermoplastic composite systems demonstrated that interaction between the reinforcement (fibers or particles) and polymer could lead to significant changes in polymer composition, structure, and properties in a thin layer near the

interface. It was proposed to account for these changes by introducing a so called interphase, a third phase between the reinforcement and bulk matrix with properties different from the properties of the two primary constituents. Models have been created and the interphase properties have been evaluated, mostly by back-calculation, due to difficulties with direct measurements (Alberola et al., 2001; Colombini et al., 2004; Colombini and Maurer, 2002; Halpin and Kardos, 1976; Ji et al., 2002; Lutz and Zimmermann, 2005; Mori and Tanaka, 1973; Sevostanov and Kachanov, 2007; Shen and Li, 2003; Wang et al., 2003). These properties have been shown to be strongly dependent on the chemical functionalization of reinforcement. Both stiff and soft interphases have been reported depending on the exact nature of the polymer matrix and of the interfacial interactions (Downing et al., 2000; Klein et al., 1995; Marshall et al., 1994; Williams et al., 1990). In advanced composites with "sized" fibers giving rise to strong covalent interactions, the thickness of the interphase layer could be as high as hundreds of nanometers. In thermoplastic composites, in addition to the gradient of chemical composition near the filler surface, filler-matrix interactions could change crystallization behavior and crystal structure, including the degree of crystallinity of the polymer matrix (Ruan et al., 2006; Zhang et al., 2010). Such changes would have crucial effect on the matrix-dominated mechanical properties of composites. The interfacial interaction effects can be further amplified in nanocomposites. Nanoparticles have orders of magnitude higher specific surface area (see Table 1) resulting in extensive interface in the nanocomposite systems. In thermoplastic nanocomposites, such as the LLDPE systems studied, the strongest effect on mechanical behavior can be due to the long-range alteration of polymer crystalline structure. Indeed, nanoparticles have been reported to act as nucleating agents during polymer matrix crystallization, especially in the systems with chemically modified or polymer-grafted nanoparticles (Ruan et al., 2006; Zhang et al., 2010). However, in other thermoplastic systems, negligible effects on crystallization were reported (D'Amato et al., 2012; Dorigato and Pegoretti, 2011, 2010; Dorigato et al., 2010a,b, 2011; La Mantia et al., 2008). To check for possible long-range effects on the crystalline structure of LLDPE, the manufactured composites were analyzed using differential scanning calorimetry (DSC) and X-ray diffraction (XRD). DSC and XRD analyses are sensitive in detecting the presence and the morphology of the interphase layer around the particles. Fig. 2 presents DSC thermograms of pure LLDPE and 2 vol.% filled composites, while melting temperature and crystallinity content are summarized in Table 2. It is evident that neither melting temperature nor crystallinity are affected by the presence of the fillers, regardless of the silica particles size. The same conclusion can be reached if the dimensions of the crystalline domains are considered. X-ray diffractograms of neat LLDPE and 2 vol.% filled composites are represented in Fig. 3(a), while in Fig. 3(b) the distribution of crystallite size computed according to the whole powder pattern model is reported. It is evident that the dimension of LLDPE crystallites (about 20 nm) is not substantially affected by the presence of silica filler, as confirmed by the mean crys-



Fig. 2. DSC plots of pure LLDPE and relative 2 vol.% filled composites.

Table 2 Melting temperature (T_m) , crystalline fraction (x_c) and mean crystallite size of LLDPE and 2 vol.% filled composites.

Sample	T_m (°C)	$x_{C}(\%)$	Mean size of crystallites (nm)
LLDPE	123.0	41.7	20.5 ± 4.8
LLDPE-Glass-2	123.0	41.0	21.1 ± 5.4
LLDPE-A200-2	123.0	42.5	22.9 ± 4.1
LLDPE-A380-2	123.0	42.4	21.2 ± 5.3

tallite size evaluated assuming the lognormal distribution of crystallite diameters (see Table 2). The results of the DSC and XRD analysis show that there were no long-order structural changes in LLDPE in the tested composites. Matrices in all studied composites exhibited crystallization behavior and structure similar to those of the neat LLDPE. This is consistent with the reports on other polyolefin systems with chemically unmodified fillers (Dorigato et al., 2012; Dorigato and Pegoretti, 2012).

There may still be some short-range changes in the polymer matrix in the vicinity of the filler surface. Recently, atomistic simulations have demonstrated changes in polymer density and relaxation behavior at nanometer distances near the surface. Several studies have reported increases in polymer chain mobility as a result of less dense and more ordered polymer chain configurations (Hackett et al., 2000; Sternstein and Zhu, 2002; Zeng et al., 2008). Such increases would manifest themselves in the formation of a softer layer compared to the bulk matrix. Such layer would in turn lead to a reduction of the effective nanocomposite modulus as demonstrated, for example, in Baldi et al. (2007), Dorigato et al. (2009) and Zhou et al. (2008). However, stiffer layers were also reported in the systems with stronger polymer-nanoparticle interactions (Ajayan et al., 2003; Okamoto et al., 2000; Xiao et al., 2001). Mechanical (steric) constraints on macromolecular conformational motion near solid surface can also result in local stiffening of the polymer. The thickness of the short-range layers was estimated by atomistic simulations to be in the range from 1 nm to 2 nm (Sevostanov and Kachanov, 2007). These estimates were also confirmed by



Fig. 3. (a) X-ray diffractograms of pure LLDPE and relative 2 vol.% filled composites, (b) distribution of crystallite size of pure LLDPE and relative 2 vol.% filled composites according to WPPM model.

experimental observations on melts (Sun et al., 2005). These changes in the ultrathin layers confined to the immediate (angstroms) vicinity of the interface might be undetectable by bulk techniques such as DSC. Nevertheless, stiff layers can theoretically be responsible for the additional reinforcing effects in Fig. 1.

If the properties of such stiff modified layers of resin were known, a theoretical prediction of their effect on the properties of nanocomposites could be made using one of the micromechanics models with interphases (Alberola et al., 2001; Colombini et al., 2004; Lutz and Zimmermann, 2005; Wang et al., 2003). Such an analysis was performed for example in Odegard et al. (2005) using a range of interphase properties derived from atomistic simulations. Atomistic simulations for the polymer/nanoparticulate systems studied here are not available and the measurement of mechanical properties in the ultrathin interphases is currently impossible. In absence of such properties, a simple estimate of the possible extent of additional reinforcement produced by a stiff interphasial layer can be made for the limiting case of infinite interphase stiffness. If the interphase layer is infinitely stiff, then the composite nanoparticle comprising the original nanofiller particle and the interphasial layer will be also infinitely



Fig. 4. Normalized elastic modulus data of LLDPE and relative composites from quasi-static tensile tests. (\blacksquare) LLDPE-Glass-x, (\blacklozenge) LLDPE-A200-x, (\blacktriangle) LLDPE-A380-x, and results of calculations according to the Christensen-Lo model (Eqs. (1)–(11)) with an infinitely stiff interphasial layer having different thickness.

stiff, even if the layer is thin. This can be checked using micromechanics models (Christensen, 2005; Christensen and Lo, 1979). Variation of modulus of a composite with infinitely stiff inclusions can be then computed using a regular micromechanics model such as the model (1-11). The effective volume fraction of the composite nanoparticles will be higher as a result of added interphase. Results of calculations using the above approach are shown in Fig. 4 for two interphase layer thicknesses, 1 nm and 2 nm. The smaller nanoparticles diameter of 7 nm (A380) was utilized. As can be seen, even the interphase with highly exaggerated ultimate stiffness cannot explain the observed dramatic increases in moduli of the polymer nanocomposites. Note that the calculations for the nanofiller A200 with larger nanoparticles further reduces the observed interphasial effect. The calculated values for glass microparticles are practically undistinguishable from the classical micromechanics predictions without the interphase due to the negligible increase in the overall volume fraction of large particles. It is important to note that possible stiffness increases in the interphasial layers in composite systems are usually referencing low polymer matrix modulus. These increases are never expected to reach the elasticity of the rigid inorganic inclusions, not to speak of becoming infinite. Based on the results of experimental and theoretical evaluations in this section, it can be concluded that the observed stiffening effect of silica nanoparticles in LLDPE cannot be attributed to the presence of interphase surrounding the nanoparticles.

3.3. Phenomenon of nanoparticle aggregation and its effect on properties of nanocomposites

Note that the exact solution (1-11) for the model of stiff particles embedded in a softer matrix is very close to the lower variational bound on the elastic moduli of an isotropic composite derived by Hashin and Strikman (Hashin and Shtrikman, 1963). This means that the isolated stiff particles in a soft continuous matrix represent the least stiff mutual phase configuration of this two-phase system (Torquato, 2002). Similar analysis shows that the upper bound can be interpreted as a solution for the soft inclusions in the stiff continuous matrix (Hashin and Shtrikman, 1963). From the analysis of Fig. 1, the nanocomposite samples are characterized by the effective moduli that are in between the lower and upper variational bounds. This might be the result of nanoparticle phase morphology deviating from the collection of isolated particles dispersed in the continuous polymer matrix. Nanoparticles have very high specific surface area and are prone to agglomerate due to strong interparticle interaction. Nanoparticle aggregation and network formation are known to have significant effects on polymer rheology (Cassagnau, 2008; Dorigato et al., 2010b). Phenomena such as Payne effect are well documented and are usually attributed to particle network formation (Payne, 1962). Aggregation also has strong effects on transport properties of nanocomposites (Pedrazzoli et al., 2012a,b; Traina et al., 2007). When conductivity of the discontinuous phase is significantly higher than the corresponding property of the matrix, strong percolation effects are observed at the critical particle volume fraction called percolation threshold. Aggregation or agglomeration of nanoparticles can theoretically affect composite elastic properties. Some controversial results can be found in literature on the role played by nanofiller aggregation on the final properties of nanocomposites. In many reports, nanofiller aggregation negatively affected mechanical behavior of the resulting composites. For instance, in a work of Barai et al. it is reported that preventing CNT aggregation is a fundamental condition to realize the full potential of CNT reinforcement (Barai and Weng, 2011). Most aggregation phenomena described in the literature occur during nanocomposite processing. However, it is important to remind that some nanoparticles can form strong aggregates during their synthesis. These aggregates may or may not survive nanocomposite processing conditions. It is well-known that fumed nanoparticles, including silica, can form extended aggregates during their manufacturing (Cassagnau, 2008). Fig. 5(a) shows a TEM image of A380 fumed silica nanoparticles used in this work. Near spherical primary nanoparticles with diameters between 7 nm and 20 nm are clearly seen, consistent with the producer's data. However, these nanoparticles appear to be fused together to form extended 3D aggregates. Moreover, TEM image of the cryofractured surface of the LLDPE-A380-2 nanocomposite (Fig. 5(b)) also shows the presence of isodimensional silica aggregates homogeneously dispersed within the matrix. The mean diameter of these aggregates is about 200 nm. These microscopic observations clearly show that silica nanoparticles used in this study are indeed aggregated and their aggregates appear to have survived the nanocomposite processing. This is consistent with the general poor compatibility between silica and polyolefins. The fact that the initial aggregates survived nanocomposite melt processing testifies to the relatively strong nature of their bonded contacts. Despite frequent mentioning of the importance of aggregation of rigid nanoparticles in the literature on polymer nanocomposites, little is currently known about its quantitative impact on properties. The effect of particle clustering has been studied in several papers. It has been shown that



Fig. 5. TEM image of (a) A380 fumed silica nanoparticles and of (b) the cryofractured surface of LLDPE-A380-2 nanocomposite.

clustering can result in a slight increase of modulus and decrease of the ultimate strain and fracture toughness (Ajayan et al., 2003). However, clustering in these works was simply inhomogeneous distribution of particle volume fractions within the composites. Particle contacts, particularly strong fusion-type contacts that appear to have been created during high-temperature fuming were not studied.

Quantitative analysis of a polymer composite with aggregating microparticles was performed by Dzenis (1986). In that work, mineral calcite filler was mechanically activated just before mixing it with high density polyethylene (HDPE). Mechanical activation significantly increased interparticle interactions in the composite and led to the formation of strong cement-like bridges at particle contacts that were observed microscopically. By analogy with Fig. 1, the HDPE/calcite composite outperformed classical micromechanics predictions, but the difference between the measured and predicted moduli appeared to increase with the increasing filler volume fraction. At percolation threshold, continuous calcite particle network caused the effective modulus to reach the upper Hashin-Strikman bound, indicating phase inversion in the composite to the stiffest possible phase configuration. As mentioned above, this stiffest configuration is micromechanically equivalent to the stiff continuous phase with soft inclusions. Formation of continuous particle network at percolation threshold was confirmed experimentally in Dzenis (1986) by thermal removal of the polymer matrix and observation of the resulting mineral skeleton retaining the shape of the original composite specimen.

A simple model was developed in Dzenis (1986) to describe the effective moduli of the aggregating system. The original discrete particles were assumed to form aggregates of gradually increasing size as the filler volume fraction increased. A schematic representation of this situation can be found in Dzenis (1986). Deformation of the matrix confined within these rigid aggregates was constrained due to the aggregate reinforcing effect, as opposed to the unconstrained (bulk) matrix outside the aggregates. All polymer matrix was therefore divided into two parts constrained matrix and unconstrained bulk matrix (Fig. 6(a)). The rigid aggregates with the constrained matrix were described as composite particles whose properties were calculated using the upper variational bound expressions, taking into account the reinforcing effect. The overall effective properties of the composite with such reinforced particles were then computed using the lower bound expressions. Evolution of the aggregation state with the filler volume fraction was evaluated using the average number of contacts between the particles. Based on statistical analysis, this number was found to be proportional to the square of the filler volume fraction. The relative content of the constrained matrix was assumed to vary nonlinearly from 0 to 1, proportionally to the average number of contacts between the particles and reaching unity at the percolation threshold. The latter assured that the effective composite modulus reached the upper bound at the percolation threshold as was observed earlier experimentally. The developed model was shown capable of describing significant increases in the elastic moduli of polymer composites as a result of filler aggregation (Dzenis, 1986). A single new structural parameter, the percolation threshold could be determined independently experimentally or evaluated from the best fit between the predictions and the experimental data. The model was later generalized for particle-fiber hybrid composite and expanded to predict other effective properties such as thermal expansion, creep, and dynamic loss factors (Dzenis, 1989; Dzenis et al., 1989). Systematic experimental validation showed that the single new structural parameter, the percolation threshold, was capable of describing a variety of effective properties. Aggregation effects, similar to the ones described in Dzenis (1986) can be responsible for the high effective elastic modulus of nanocomposites studied in the present work. A successful model prediction of this effect would indirectly confirm the proposed mechanism. The model would also provide a tool for further analysis and optimization of other nanoparticulate composites. Such a model, based on the aggregation modeling approach described above, is presented in the next section.

3.4. A model with nanofiller aggregation as reinforcing mechanism

The aggregation model presented in Dzenis (1986) needs to be modified in order to be applied to the



Fig. 6. Schematic representation of (a) the model of particulate nanocomposite with primary particle aggregation and (b) the mechanically equivalent composite with solid composite inclusions.

nanocomposites studied in this work. Unlike the HDPE/calcite composite where aggregates formed dynamically during composite processing, fumed silica aggregates were formed during nanoparticle manufacturing. They therefore preexisted before mixing with the polymer. We will call this type of aggregation the primary aggregation, as opposed to the secondary dynamic aggregation that was studied in Dzenis (1986). For the primary aggregation, the amount of matrix whose deformation is constrained by the stiff reinforcing aggregates will depend on the aggregate geometry. In absence of additional secondary aggregation, the fraction of such constrained matrix will be directly proportional to the filler content. The exact 3D shape of nanoparticle aggregates is very complex and may vary from particle to particle. Some geometric characteristics of aggregates may be obtained by numerical simulations (Brasil et al., 1999). However, the parameter of interest for modeling, i.e. the average volume of the constrained matrix associated with the unit fraction of the nanofiller may be simply evaluated from the best experimental fit. If our assumptions are correct, and there is no secondary aggregation, this single new structural parameter should be able to describe the nanocomposite elastic modulus at all volume fractions of nanoparticles. The model reported in Dzenis (1986), modified for the primary filler aggregation is presented below.

The original model used the variational bounds on the effective elastic constants of heterogeneous materials derived by Hashin and Shtrikman (1963) based on the theorems of minimum complementary energy and minimum potential energy. For a bi-component isotropic composite, under the condition that $K_2 > K_1$, $G_2 > G_1$, the following inequalities for the effective bulk and shear moduli were derived:

$$K_{1} + \frac{V_{2}(K_{2} - K_{1})}{1 + V_{1}R_{1}(K_{2} - K_{1})} \leqslant K \leqslant K_{2} + \frac{V_{1}(K_{1} - K_{2})}{1 + V_{2}R_{2}(K_{1} - K_{2})}$$
(12)
$$G_{1} + \frac{V_{2}(G_{2} - G_{1})}{1 + V_{1}Q_{1}(G_{2} - G_{1})} \leqslant G \leqslant G_{2} + \frac{V_{1}(G_{1} - G_{2})}{1 + V_{2}Q_{2}(G_{1} - G_{2})}$$
(13)

where:

$$R_i = \frac{3}{3K_i + 4G_i} \tag{14}$$

$$Q_i = \frac{6(K_i + 2G_i)}{5G_i(3K_i + 4G_i)}$$
(15)

and i = 1, 2 are indices of the phases. The model assumed that the filler particles underwent spontaneous aggregation (secondary aggregation) that caused part of the matrix to become mechanically constrained within the aggregates. The composite was then viewed as an unconstrained matrix reinforced with composite inclusions formed by the aggregated particles and constrained matrix. This is schematically illustrated in Fig. 6(a), where the two types of matrix are denoted (m_1) or unconstrained (bulk) matrix and (m_2) or constrained matrix within the aggregates. The deformation of the constrained matrix is influenced by the presence of a rigid network of nanoparticles within the aggregates. The amount of constrained matrix was quantified in Dzenis (1986) by introducing a material parameter (β), equal to the ratio of the amount of matrix (m_2) in the constrained state to its total content $(m = m_1 + m_2)$. According to the secondary aggregation hypothesis, it was found that this parameter changed non-linearly with the volume fraction of the filler.

For the primary nanoparticle aggregation considered in this study, a new structural parameter of the medium, i.e. constrained matrix ratio (α), equal to the ratio between the constrained matrix fraction and the filler volume fraction, is introduced:

$$\alpha = \frac{m_2}{V} \tag{16}$$

where $m = 1 - V = m_1 + m_2$. Realizing that the total content of the polymer is equal to m = 1 - V, the quantity of the constrained matrix is $m_2 = \alpha V$. The content of the soft phase in the material of the composite inclusion (V_{m2}) can be determined as:

$$V_{m2} = \frac{m_2}{m_2 + V} = \frac{\alpha}{1 + \alpha}$$
(17)

Taking into account that the volume content of such inclusions is $V' = V + m_2 = V (1 + \alpha)$, the effective moduli of the composite can be calculated using the two-step approach described above. After some simplifications, the following expressions were obtained for the bulk (*K*) and shear (*G*) moduli of the nanocomposite:

$$K = K_m + \frac{V'(K_f - K_m)}{1 + (1 - V')R_m(K_f - K_m) + R}$$
(18)

$$G = G_m + \frac{V'(G_f - G_m)}{1 + (1 - V')Q_m(G_f - G_m) + Q}$$
(19)

where:

$$R = \frac{\alpha}{1 + R_f(K_m - K_f)} \tag{20}$$

$$Q = \frac{\alpha}{1 + Q_f(G_m - G_f)}$$
(21)

In Eqs. (18)–(21), the terms Q_m , R_m , Q_f and R_f refer to the definitions reported in Eqs. (14) and (15). The Young's modulus of the nanocomposite can be determined from the expression linking the elastic constants of an isotropic medium (Eq. (11)). It is important to underline that the expressions obtained for *K* and *G* for the primary aggregation conditions are similar to those developed by Dzenis



Fig. 7. Normalized elastic modulus data of LLDPE and relative composites from quasi-static tensile tests. (\blacksquare) LLDPE-Glass-x, (\blacklozenge) LLDPE-A200-x, (\blacktriangle) LLDPE-A380-x, and fitted data according to the proposed model under primary aggregation conditions (Eqs. (18) and (19)).

under the hypothesis of secondary aggregation (Dzenis, 1986), but in the present work *R* and *O* do not depend on the filler volume fraction and can be determined from the elastic properties of the two constituents and the α parameter. Considering Eqs. (20) and (21), it is evident that the elastic properties of the nanocomposites are strongly related to the constrained matrix ratio (α). This ratio is determined by the 3D aggregate geometry that in turn can depend on a variety of factors such as the dimensions of the primary nanoparticles, their manufacturing or synthesis conditions, etc. A direct experimental determination of α is difficult, so it is proposed to evaluate this parameter a posteriori from the best experimental fit. If our assumptions are correct, a single new structural parameter (α), associated with the average shape of the nanoparticle aggregates, would describe the dependency of the elastic modulus of the investigated composites on the filler content.

In Fig. 7, the experimental data for the LLDPE nanocomposites are fitted with the proposed model (Eqs. (18) and (19)). It is evident that the model is capable of accurate description of the elastic modulus of nanocomposites in the whole range of filler volume fractions studied. Strong correlation of the constrained matrix ratio (α) and the reinforcing effect with nanofiller surface area is observed. Nanoparticles with higher specific surface area exhibit higher stiffness.

4. Discussion

The analysis above shows that the mechanism of nanofiller aggregation can explain the anomalous stiffening effects observed in the nanocomposites systems. Moreover, the developed model predicted the elastic behavior of nanocomposites with primary aggregates using a single new parameter (α) that has a straightforward structural interpretation. By analogy with the earlier works (Dzenis, 1989; Dzenis et al., 1989), the developed model can be further generalized and applied to describe other effective properties, such as coefficients of thermal expansion, dynamic mechanical properties, and creep behavior. All these properties can be strongly affected by nanofiller aggregation mechanism. It is expected that the same structural parameter (α) will describe various effective properties of the particulate nanocomposite with aggregated filler.

The proposed model can be applied to the primary aggregation in both micro- and nano-composites. However, it is expected to be especially beneficial to nanocomposites where nanoparticles tend to agglomerate and where it is often impossible to obtain a composite with well dispersed isolated nanoinclusions. Most of these systems will exhibit secondary aggregation, but some may show primary aggregation as well. As the volume fraction of the nanoparticle aggregates increases, the nanocomposites with primary aggregates will eventually exhibit secondary aggregation between the primary nanoparticle aggregates. Note that the model above can be combined with the previously developed model (Dzenis, 1986) to describe the combined primary-secondary aggregation. Care should be taken of the particle and primary aggregate contacts. It is important to note that either primary or secondary aggregation might be present in many nanoparticulate systems. Even carbon nanotube composites often exhibit aggregated morphologies in which nanotubes are strongly entangled (Spitalsky et al., 2010). Aggregation or agglomeration has been reported in numerous other nanocomposite systems (Ajavan et al., 2003). It is therefore possible that aggregation might have contributed to the unusual changes in nanocomposites properties reported in the literature.

It is also interesting to note that the computed α parameter appears to be proportional to filler specific surface area (see Fig. 8). If further confirmed (we only have 2 data points at this time), this may mean that there is a connection between the state of agregation achieved during fumed nanoparticle synthesis and the SSA. Such a fact might be important for controlled manufacturing of nanoparticle aggregates. It may also explain some reported empirical correlations of the nanocomposite properties



Fig. 8. Correlation between the immobilized matrix ratio (α) and the filler specific surface area (SSA).

with the SSA of their nanofillers that are currently routinely attributed to the interfacial interactions. However, more studies are needed to confirm the aggregation-SSA correlation.

Polymer matrix nanoparticulate composites have been recently reported to exhibit a host of unique and unusual properties. It was widely demonstrated that the incorporation of inorganic nanoparticles into a polymer matrix can significantly improve its physical properties, such as dimensional stability, thermal degradation, and chemical resistance, while significantly decreasing the gas or solvent permeability and avoiding the typical drawbacks (embrittlement, loss of transparency, loss of lightness) associated with the addition of traditional microfillers (Dorigato et al., 2011). These properties, combined with enhanced mechanical performance of nanoparticulate systems open up a wide platform for the development of novel structural and multifunctional materials. Our results call for thorough evaluation of the aggregation state of nanoparticles while analyzing nanocomposite properties, in addition to the usual interfacial analysis. The presented simple micromechanics-informed model will allow quantitative evaluation and further nanocomposite optimization.

Finally, unusual ultratough behavior of fused nanoparticle chains has been recently demonstrated experimentally and modeled numerically (Dalis and Friedlander, 2005; Friedlander et al., 1998). This behavior was attributed to the ability of particle chains to rotate about the contacts between nanoparticles. The nanoparticle chains studied were essentially linear primary aggregates, a particular case of the primary aggregates considered here. These results on the nanoparticle chains combined with the stiffening effects reported here open up promising avenues for simultaneous enhancements of stiffness and toughness in the nanocomposites. Recent observations of the reorientation and stretching of the primary aggregates in the direction of the plastic polymer deformation (Dorigato et al., 2012; Dorigato and Pegoretti, 2012) is very promising in this context.

5. Conclusions

Variation of elastic modulus with filler volume fraction was studied on several LLDPE-silica composites prepared by melt compounding process. DSC and XRD analyses did not show any influence of silica fillers on polymer crystallization and crystallinity. The observed high elastic moduli were attributed to nanoparticle aggregation that was confirmed microscopically. A modified model of primary particle aggregation was presented and a good agreement between theoretical predictions and experimental data was demonstrated.

Potential correlation between the filler surface area and the new structural parameter describing the state of nanoparticle aggregation was observed and discussed. It is expected that the proposed model can be extended to other nanocomposite systems filled with fused nanoparticles such as carbon black, fumed metal oxides, etc. The described reinforcement mechanism and the developed model can be further generalized and used to analyze a variety of other effective properties, such as coefficients of thermal expansion, thermal and electrical conductivity, creep, dynamic losses, etc.

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