Evaluation of Nanoparticle Dispersion in Polypropylene by Small-Angle X-Ray Scattering

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ABSTRACT: A small-angle X-ray scattering method has been developed for the quantitative evaluation of the effectiveness of nanoparticle dispersion in polymer matrices; it is termed the nanoscale dispersion index. This method was applied to dispersions of nanosized TiO_2 fillers in polypropylene. Master batches prepared with lower filler contents showed better dispersion as evaluated by the nanoscale dispersion index. The addition of 1,3:2,4-di(3,4-dimethylbenzylidene) sorbitol to the compounds did not affect the degree of nanoscale dispersion as estimated by the nanoscale dispersion index. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 350–354, 2008

Key words: nanotechnology; poly(propylene) (PP); SAXS

INTRODUCTION

Blending additives within polymeric matrices, particularly nanosized ones, can provide beneficial functions with minimal disturbance of the polymer's properties. However, the adequate dispersion of nanoparticle agglomerates in the compounded polymer is an ongoing challenge. The main obstacle is achieving a uniform dispersion while maintaining the small dimensions of the dispersed particles and avoiding their tendency to agglomerate into larger structures. Much effort has been expanded on enhancing the ability to control and direct this dispersion. Among the methods that have been employed toward these goals are solid-state shear pulverization,[1] utilization of surface-active agents,[2] melt compounding, and so on.[3] Dimethyl benzylidene sorbitol (DBS), often used as a gelator in organic liquids and as a nucleator and clarifier for polypropylene (PP), was reported to interact with dispersed colloidal silica within poly(ethyl methacrylate), so that the interface created between the molten polymer and the DBS fibrillar structure could enhance and direct the dispersion of the particles.[4]

An alternative method for nanoparticle dispersion in the polymer matrix is to synthesize the particle within the polymer. This may be especially useful in thin polymer films. When bulk applications are of interest, another approach may be to synthesize the particles within the voids of a porous polymer solid before its melt compounding.

Despite the efforts toward tackling these problems, the ability to correctly evaluate the degree of the nanoscale dispersion remains illusive, and it is often based only on electron microscopy imaging. It is therefore the objective of this article to present a small-angle X-ray scattering (SAXS) method to evaluate the degree to which the nanoscale dispersion of the particles has been achieved in a compounded polymer.

EXPERIMENTAL

Materials

Commercial grades of PP [high-molecular-weight Capilene QB (a random propylene copolymer with 4% ethylene), Carmel Olefins, Ltd. (Haifa, Israel), and Accurel PP, Membrana GmbH, Wuppertal, Germany] were used. 1,3:2,4-Di(3,4-dimethylbenzylidene) sorbitol (DMDBS; Millad 3988) was acquired from Milliken, Inc. (Spartanburg, SC), and used as received. TiO_2 nanoparticles were *in situ* prepared by a sol–gel method with titanium tetraisopropoxide (TTIP; 99.99%; Aldrich, Wilmington, DE). TTIP in isopropyl alcohol solutions was impregnated onto the polymer pellets and within their inner pore surface *in vacuo*. Subsequent exposure to humidity facilitated TTIP hydrolysis, which was followed by condensation to TiO_2 nanoparticles with a size of about 25 nm. Master batches (MBs) at different particle concentrations were made from these pellets by

melt compounding, as described later. Compounds of desired compositions were made through dry blending at room temperature and subsequently melt blending in a Thermo Haake Rheomix batch melt mixer (Battenfeld Co., Guangdong, China) for 10 min at a set point of 180°C at 50 rpm. The operating temperature exceeded the set point by about 20–30°C. Polymer plates were prepared from this compound either by compression molding with a Collin hydraulic press (Ebersberg, Germany) at 180°C or by injection molding with a Battenfeld injection-molding machine. Samples were punched from these plates and used for X-ray scattering measurements.

SAXS

SAXS measurements were conducted with a small-angle diffractometer (KFF CU 2 K-90, Bruker Nanostar, Karlsruhe, Germany) with Cu Kα radiation from a sealed tube, two Göbel mirrors, two-pinhole collimation (which resulted in a beam ca. 300 μm in diameter on the sample), and a 10×10 cm^2 two-dimensional position-sensitive wire detector positioned 65 cm behind the examined sample. The samples were placed in a vacuum chamber perpendicular to the incident beam. Each sample was subjected to an 18-h exposure time in this apparatus to ensure sufficient data collection and to reduce the noise-to-data ratio. The scattered intensity was recorded in the interval of 0.13 nm$^{-1} < h <$ 3.20 nm^{-1}; the wave vector is defined as $h = 4\pi/\lambda \sin\theta$, where 2θ is the scattering angle and λ is the wavelength. The samples (1.6–2 mm thick) were placed between thin polyimide films within a metal holder. The measured intensities were circularly averaged after azimuthal integration at a constant value of θ to give the scattered intensity as appropriate for an isotropic material. The intensity was then normalized to the time, primary beam intensity, and sample thickness and transmission. The scattering of the polyimide films (as well as the parasitic scattering and the low electronic noise) was subtracted from the normalized intensity to give the normalized and subtracted intensity $[I(h)]$. The sample temperature was maintained at the desired value (180°C) with a restive heating sample chamber (KHR, A. Paar, Ltd., Graz, Austria). The variation of the sample thickness (d) with the temperature (T) was evaluated on the basis of its measured X-ray transmission [$Tr(d)$]:

$$Tr(d) = e^{-\mu\rho(T)d(T)} \quad (1)$$

where μ is the mass transmission coefficient and ρ is the sample density. μ of PP was experimentally obtained with eq. (1), and the values of Tr, ρ, and d were measured at 25°C. The T (°C) dependence of the melt density was approximated with the following equation:[5]

$$\rho(T) = 0.862 \times \exp(-6.7 \times 10^4 T) \quad (2)$$

Electron microscopy

The instrument used was a Leo 982 high-resolution scanning electron microscope (Carl Zeiss SMTAG, Oberkochen, Germany) operated at an accelerating voltage of 4 kV with a working distance of 3 mm. Rectangular samples with a thickness of about 2 mm were cut from compression-molded plates. From these, thin slices ($\sim$ 50 nm thick) were sectioned with a Reichert-Jung FC 4E cryo-ultramicrotome (Buffalo, NY) at 190 K. The stump was glued to an aluminum sample holder and used for high-resolution scanning electron microscopy (HRSEM) imaging after the sputtering of a thin gold layer.

RESULTS AND DISCUSSION

Nanoscale dispersion index (NSDI)

The assessment of the extent of nanoscale dispersion within polymer matrices often uses imaging by electron microscopy. Although this technique provides information on the size and shape of particles and indicates their state of agglomeration, it requires much effort for suitable sample preparation and covers a relatively small sample area, so it often does not provide quantitative and statistically significant information. Utilization of X-ray scattering, in particular SAXS, promotes data acquisition from a significantly larger volume with minimal sample preparation.

The total scattered intensity from an examined material, such as the polymer/nanoparticle samples studied, is termed the scattering invariant (Q), and it is defined as follows:[6]

$$Q = \int_0^\infty I(h) \cdot h^2 dh \quad (3)$$

For a two-phase system of well-defined particles with sharp interfaces, Q can be calculated from the particle volume fraction (ϕ_F) and the difference in the electron densities of the filler (ρ_F) and matrix (ρ_m) as follows:[6]

$$Q_{calc} = 2\pi^2(\rho_F - \rho_m)^2\phi_F(1 - \phi_F) \quad (4)$$

where Q_{calc} is the calculated scattering invariant. Data collection in our experiments is limited to scattering vectors in the interval of 0.13 nm$^{-1} < h <$ 3.20 nm^{-1}, as described previously. This poses a limitation on the dimensions of the particles that contribute to the measured intensity. This is particularly important for the larger agglomerates that are not dispersed to the desired extent. We make use of this effect for comparative evaluation of the extent to which the particles are dispersed in nanoscale dimensions.

TABLE I
NSDI Evaluation for Compounds with About 2% TiO₂ Made from MBs of Different Concentrations

TiO$_2$ in the MB (%)	TiO$_2$ in the final composition (%)	NSDI (%)
4.8	2	62
11	2	61
20	1.9	51
41	1.8	29

The experimentally measured invariant (Q_{exp}) is obtained with eq. (3) by numerical integration of the data in the measurable h interval. The data are extrapolated beyond the high h limit with Porod's law:[6]

$$I(h) = (\Delta\rho)^2 \frac{K}{h^4} + I_b \qquad (5)$$

where K is Porod's constant related to the specific interfacial area and I_b is a background constant. Extrapolation to low values of h uses Guinier's law:[6]

$$I(h) = A \exp\left(-\frac{1}{3}R_g^2 h^2\right) \qquad (6)$$

where A is Guinier's constant and R_g is the radius of gyration. The intensity of the molten polymer is finally subtracted from $I(h)$. Thus, we can define NSDI as the ratio of Q_{exp} [eq. (3)] to Q_{calc} [calculated from the known volume fraction and electron densities of the components; eq. (4)]:

$$\text{NSDI} = 100 \times (Q_{exp}/Q_{calc}) \qquad (7)$$

To evaluate the maximal particle size that is accounted for by this evaluation procedure, model calculations were performed for various particle sizes and shapes (spheres and ellipsoids of revolution). The simulated patterns were cut off at the low and high h interval limits of the experimental SAXS measurements. NSDI values were calculated for the simulated particle scattering following the appropriate Guinier and Porod extrapolations. NSDI values of over 90% were estimated for the different simulated particles for which the largest dimension was 70 nm. These results indicate the significance of the NSDI evaluation as a rapid, nondestructive method providing the extent to which nanoparticles have been successfully dispersed in the polymer matrix to dimensions smaller than 70 nm.

As described previously, TiO₂ nanoparticles were synthesized by impregnation of precursor solutions into granular PP raw materials, which were subsequently diluted by compounding with the same polymer grade. These PP grades included a porous grade (Accurel; specific surface ≈ 13 m²/gr) for which a higher particle loading could be achieved,

enabling the preparation of a concentrated MB containing over 40% (w/w) filler. NSDI evaluations were used to compare the effectiveness of the nanoparticle dispersion in these polymeric systems. Furthermore, PP containing DMDBS was also evaluated to examine possible effects on the dispersion.

The effect of the MB concentration was examined with the Accurel/TiO₂ composite polymers. Four different initial MB concentrations, 4.8, 11, 20, and 41% (w/w), were taken and compounded to give roughly the same TiO₂ concentration (2%). As can be seen in Table I, the reduction of the nanoparticle concentration within the MB (down to ca. 10%) has a pronounced effect on particle dispersion, as shown by the NSDI value. Reducing the MB concentration from 41 to 11% more than doubles the amount of TiO₂ that is dispersed on the nanoscale (<70 nm). It is assumed that the higher concentration of the precursor, required for the preparation of a concentrated MB, provides more pathways for agglomerate formation during particle synthesis. These agglomerates are not dispersed upon subsequent compounding, thus reducing the evaluated NSDI.

Table II compares the NSDI estimations for different particles embedded in different PP grades with and without DMDBS. SAXS measurements of the compounded samples were performed at 180°C, which is above the melting temperature of PP. The status of the DMDBS fibrils in the samples measured at this temperature depended on the way in which it was reached. This was achieved with two procedures: (1) heating from room temperature and (2) cooling from 250°C. In the former, the PP crystals melted, but the DMDBS fibrils were intact, whereas in the latter, both PP and DMDBS were in a miscible melt.[7] As can be noted, the extent of the nanoscale dispersion seems to be independent of the temperature protocol. The maximum error estimated for these calculations is about 6%, as evaluated from several measurements of the same system (Accurel/TiO₂) and by model calculations. The negligible effect of temperature on the evaluated NSDI may be due to the low signal from DMDBS fibrils with

TABLE II
NSDI and Size Evaluation for Different Compounds With and Without DMDBS During Heating and Cooling

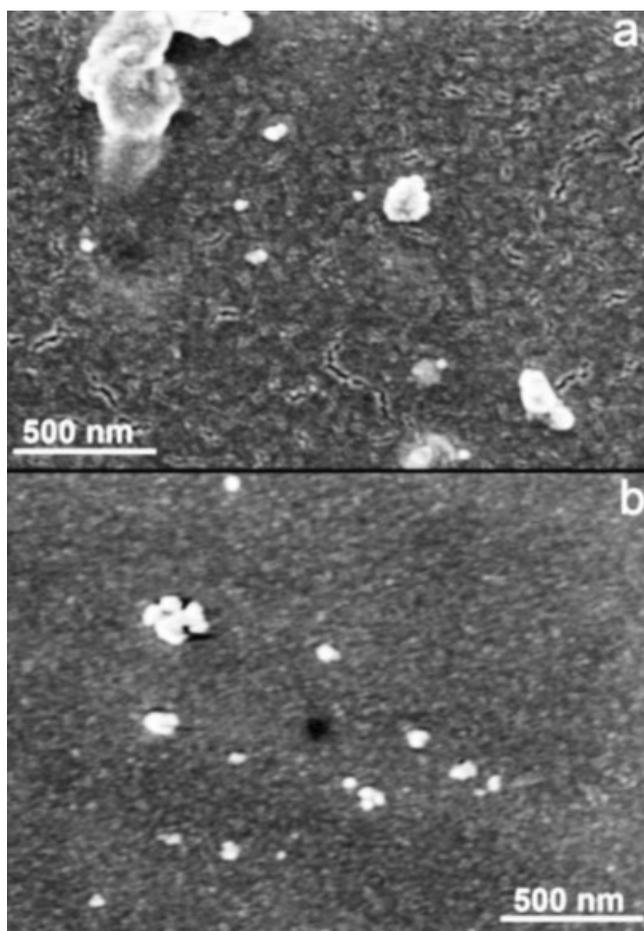| PP grade	DMDBS (%)	Temperature protocol	TiO$_2$ (%)	NSDI (%)
QB	0	Heating	2	44
QB	0	Cooling	2	43
QB	1	Heating	2	37
QB	1	Cooling	2	38
Accurel	0	Heating	2	56
Accurel	0	Cooling	2	62
Accurel	1	Heating	2	58
Accurel	1	Cooling	2	59

Figure 1 HRSEM micrographs of PP with 2% TiO$_2$ made from a 5% MB: (a) without DMDBS and (b) with 1% DMDBS.

respect to that from the dispersed TiO$_2$ because of the lower contrast and content. Moreover, the presence of DMDBS does not change the value of NSDI, and this implies no specific interactions either between these additives or between the DMDBS/PP interface and the TiO$_2$ particles, which may affect the dispersion. A comparison of the NSDI values for compounds with Accurel and QB-grade PP indicates that in both cases rather high levels of dispersion were achieved (ca. 60 and 40%, respectively). These results are encouraging with respect to the use of the sol–gel method in PP with some porosity. This is even somewhat surprising in the case of the QB grade, which has a specific surface of only 0.4 m^2/g. This suggests that in the current method of particle fabrication, the usage of a porous polymer substrate is not of prime importance, although it has some effect on the ultimate particle dispersion and also on the initial quantity of titania in the polymer MBs.

HRSEM images obtained from microtomed surfaces of compounded samples are shown in Figures 1 and 2. Figure 1 shows TiO$_2$ particles of different sizes, mostly less than 70 nm in diameter, as well as

some larger agglomerates. This is in accord with the SAXS measurements. The micrographs also do not indicate any difference between samples compounded with and without DMDBS. In a few cases, HRSEM imaging of DMDBS fibrils could be achieved in the microtomed surfaces, as shown in Figure 2, and this likely occurred when the fibril was nearly parallel to the sectioning plane. Rarely, particles attached to the fibrils were observed, as shown in Figure 2(b).

CONCLUSIONS

A SAXS-based method is presented for the comparative evaluation of the extent to which dispersions of nanoscale particles have been successfully achieved in a polymeric matrix. NSDI is evaluated as the ratio of the measured total scattering intensity to that calculated from the material composition. Utilization of this method was demonstrated for PP/nanofiller systems, some of which included the clarifier DMDBS. Nanoparticle fabrication was performed with precursor solutions via a sol–gel method by impregnation of a TTIP/isopropyl alcohol solution into the polymer pellets *in vacuo*. This method demonstrated high dispersion levels: up to 60% of the filler was dispersed, so the dimensions were below about 70 nm. The NSDI evaluation of porous PP (Accurel) with 2% TiO$_2$ compounded from MBs of 4.8–41% indicated that above about 10%, the higher the MB concentration was, the lower the nanoscale dispersion was that was achieved in the final compound. This observation is attributed to the fact that during nanoparticle fabrication, usage of a concentrated precursor solution will enhance the likelihood of
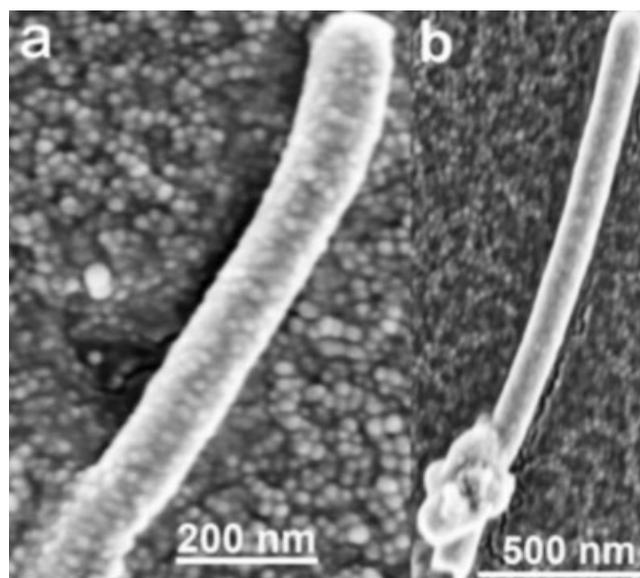

Figure 2 HRSEM micrographs of DMDBS fibrils in a PP/DMDBS compound containing nanoparticles.

agglomeration. As these agglomerates are not broken during master-batching or compounding, the dispersed particles in the final compound will be of larger size. An investigation of similar compounds with a relatively nonporous PP indicated that a decrease of more than an order of magnitude in the specific surface area of the pellets used to prepare the MBs results in a decrease of NSDI of only about 30%. The influence of DMDBS, which forms a network of nanofibrils in the polymer melt, on the nanoparticle dispersion was also investigated. However, the NSDI values remained practically unchanged for samples with and without DMDBS.

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