1
Characterization of Nanocomposite Materials: An Overview

Vikas Mittal

1.1
Introduction

Polymer layered silicate nanocomposites are relatively new class of nanoscale materials, in which at least one dimension of the filler phase is smaller than 100 nm [1–9]. They offer an opportunity to explore new behaviors and functionalities beyond that of conventional materials. Owing to nanometer thick platelets in layered silicates, incorporation of such fillers strongly influences the properties of the composites at very low volume fractions because of much smaller interparticle distances and the conversion of a large fraction of the polymer matrix near their surfaces into an interphase of synergistically improved properties. As a result, the desired properties are usually reached at low filler volume fraction, which allows the nanocomposites to retain the macroscopic homogeneity and low density of the polymer.

Montmorillonite has been a layered silicate of choice for most of the studies on polymer nanocomposites. Montmorillonite is an expandable dioctahedral smectite belonging to the family of the 2 : 1 phyllosilicates [10, 11] with a general formula of $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$. The particles in montmorillonites consist of stacks of 1 nm thick aluminosilicate layers (or platelets) held electrostatically with each other with a regular gap in between (interlayer). Each layer consists of a central Al-octahedral sheet fused to two tetrahedral silicon sheets. Isomorphic substitutions of aluminum by magnesium in the octahedral sheet generate negative charges, which are compensated for by alkaline-earth or hydrated alkali-metal cations. Based on the extent of the substitutions in the silicate crystals, a term called layer charge density is defined. Montmorillonites have a mean layer charge density of 0.25–0.5 equiv. mol^{-1}. The layer charge is also not constant and can vary from layer to layer; therefore, it should be considered more of an average value. The electrostatic and van der Waals forces holding the layers together are relatively weak in smectites and the interlayer distance varies depending on the radius of the cation present and its degree of hydration. As a result, the stacks swell in water and the

1 nm thick layers can be easily exfoliated by shearing, giving platelets with high aspect ratio. This thus helps to easily exchange their inorganic cations with organic ions (e.g., alkylammonium) to give organically modified montmorillonite (OMMT) [12, 13]. An exchange of inorganic cations with organic cations renders the silicate organophilic and hydrophobic and lowers the surface energy of the platelets and increases the basal-plane or interlayer spacing (*d*-spacing) [12–16]. This improves the wetting, swelling, and exfoliation of the aluminosilicate in the polymer matrix. Alkyl ammonium ions like octadecyltrimethylammonium, dioctadecyldimethyl-ammonium, etc., have been conventionally used for the organic modification of silicates.

Nanocomposites with practically all the polymer matrices have been reported with varying degrees of property enhancements. Polar polymers have been generally reported to achieve better filler dispersion owing to better match of the surface polarities of filler and polymers. On the other hand, the dispersion of filler in the nonpolar polymers like polyethylene, polypropylene, etc., is challenging owing to the absence of any positive interactions between the organic and inorganic phases. To circumvent these difficulties, either low molecular weight compatibilizers are added to the system or the filler surface is specifically modified by additional chemical or physical processes. The synthesis of nanocomposites has also been reported by a number of different ways, for example, melt compounding, *in situ* synthesis, solution mixing, gas phase processing, living polymerization, etc. All the different techniques to modify the filler surface as well as to synthesize the polymer nanocomposites need to be supplemented with robust characterization of these processes as well as resulting composite properties to gain insights into the various factors affecting the nanocomposite microstructure and properties so as to be able to design them according to the need.

1.2
Characterization of Morphology and Properties

Characterization of the nanocomposite materials is necessary to understand/analyze various facets of polymer nanocomposites. A few of them are listed as follows:

a) quality of dispersion of filler in the polymer matrix along with its orientation or alignment related to the processing method used,
b) effect of filler surface modification on filler dispersion and composite properties,
c) interactions of the filler modification with the polymer chains including chemical reactions between the two,
d) changes in the process parameters on the resulting morphology and properties, and
e) apart from that, analysis of a wide spectrum of properties to ascertain the application potential of the nanocomposites.
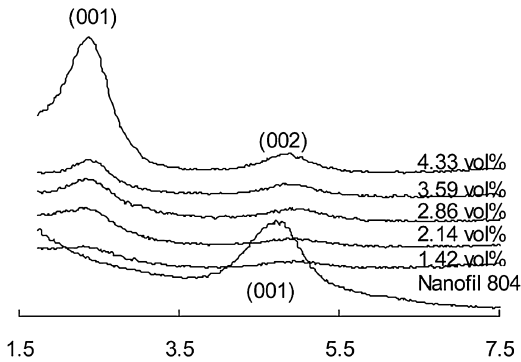
Figure 1.1 X-ray diffractograms of the Nanofil 804 filler as well as polyurethane nanocomposites with different filler volume fractions. Reproduced from reference [17] with permission from American Chemical Society.

It is also, in many instances, necessary to employ more than one characterization technique in order to accurately characterize the nanocomposite material. For example, over the years, it has become common to divide the nanocomposites into intercalated and exfoliated types based on the reflections observed in the detection range of wide-angle X-ray diffraction (WAXRD). However, this classification is arbitrary because the observation of a peak in the diffractogram depends not only on the periodicity but also on other factors, such as the concentration and orientation of the aluminosilicates, and does not exclude the presence of exfoliated part. Its absence also does not exclude the presence of small or randomly oriented intercalated particles and, therefore, does not indicate complete exfoliation as often postulated. Figure 1.1 shows an example of polyurethane nanocomposites generated with montmorillonite filler modified with different surface modifications [17]. The nanocomposites were synthesized by a solution casting method. The X-ray diffractograms of the filler Nanofil 804 (modified with bis(2-hydroxyethyl) hydrogenated tallow ammonium) as well as polyurethane nanocomposites with different filler volume fractions are shown. The diffraction signals of the filler in the composites were shifted to lower angles confirming the intercalation of the polymer in the interlayers; however, the presence of diffraction peaks also signified that the filler was not exfoliated. The extent of filler intercalation or exfoliation could not be quantified. When the same nanocomposites were characterized by transmission electron microscopy as shown in Figure 1.2, extensive filler exfoliation was noticed. The intercalated platelets also had varying thicknesses. Thus, to generate better insights into the nanocomposite microstructures, synergistic combinations of different characterization techniques are useful.

A number of different nanocomposite characterization methods are available which include thermogravimetric analysis, differential scanning calorimetry,

Figure 1.2 TEM micrographs of the 2.86 vol% Nanofil 804-PU composite. Reproduced from reference [17] with permission from American Chemical Society.

transmission electron microscopy, scanning electron microscopy, X-ray diffraction, nuclear magnetic resonance, IR spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, dielectric relaxation spectroscopy, atomic force microscopy, electron spin resonance, continuous-wave and pulsed ESR spectroscopy, etc. Apart from that, numerous characterization techniques to ascertain nanocomposite properties like mechanical performance, fire behavior, barrier performance, biodegradability, rheological properties, PVT characterization, tribo-

logical behavior, etc., are also used. The following section shows the overview examples of nanocomposite characterization performed with a few of these techniques; however, this section is not meant to be exhaustive.

1.3
Examples of Characterization Techniques

Figure 1.3 [18] shows an example of thermogravimetric analysis (TGA) of the modified fillers. The characterization was carried out to ascertain the filler surface cleanliness so as to use them in high-temperature compounding or in *in situ*
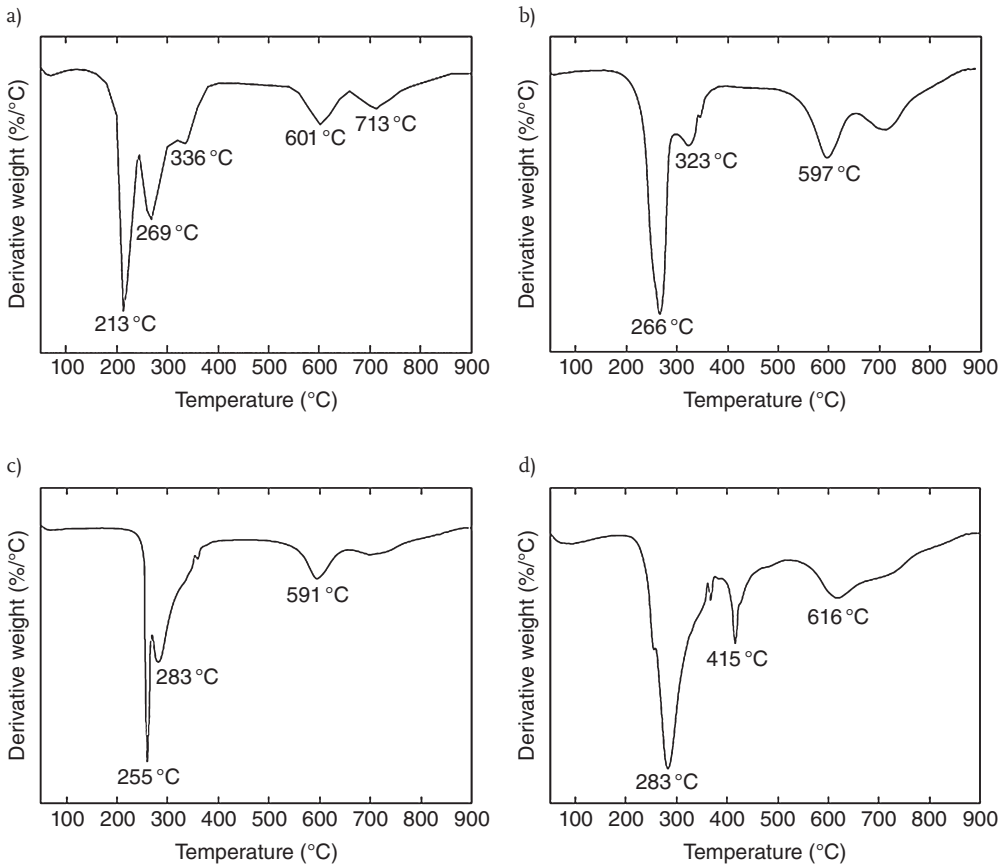
Figure 1.3 TGA thermograms of the (a) commercially modified BzC16; (b) self-treated BzC16; (c) commercially modified 2C18, and (d) self-treated 2C18. Reproduced from reference [18] with permission from Springer.
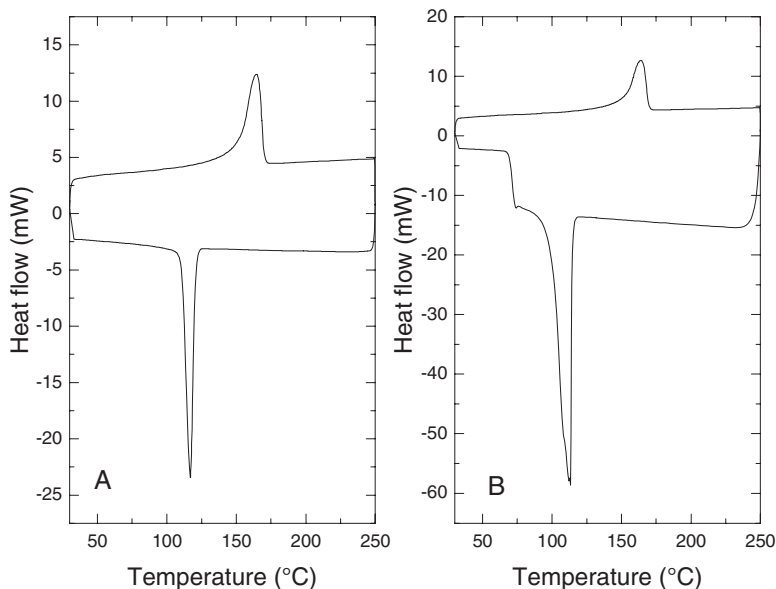
Figure 1.4 DSC thermograms of polypropylene using heating rate of 10°C min⁻¹ and cooling rate of (A) 10°C min⁻¹ and (B) 40°C min⁻¹.

polymerization processes. Fillers modified with sioctadecyldimethylammonium chloride (2C18) and benzylhexadecyldimethylammonium chloride (BzC16) were analyzed. As can be observed, the commercially treated fillers had an additional low-temperature degradation peak, which indicated the presence of excess surface modification molecules in the filler interlayers which were not ionically attached to the filler surface, but were physically trapped in the modification monolayers, thus forming pseudo bilayers. On the other hand, the self-treated fillers were free from any such excess molecules as no low-temperature degradation signal was observed in their thermograms.

Figure 1.4 shows an example of differential scanning calorimetry (DSC) characterization of pure polymer to generate information on the melting and crystallization transitions as well as to obtain information on the extent of crystallinity from the area under the melting transition (melt enthalpy). The nanocomposite materials can be similarly analyzed to know the effect of fillers on the crystallization behavior of the pure polymer. The organically modified fillers are also characterized by DSC in order to obtain information on the phase dynamics and transitions associated with the monolayers present on the filler surface.

Figure 1.5 [19] presents the WAXRD patterns of octadecytrimethylammonium (C18), dioctadecyldimethylammonium (2C18), and trioctadecylmethylammonium (3C18) modified fillers and their 3 vol% polypropylene nanocomposites. The analysis is used to ascertain the increase in interlayer spacing of the fillers after com-
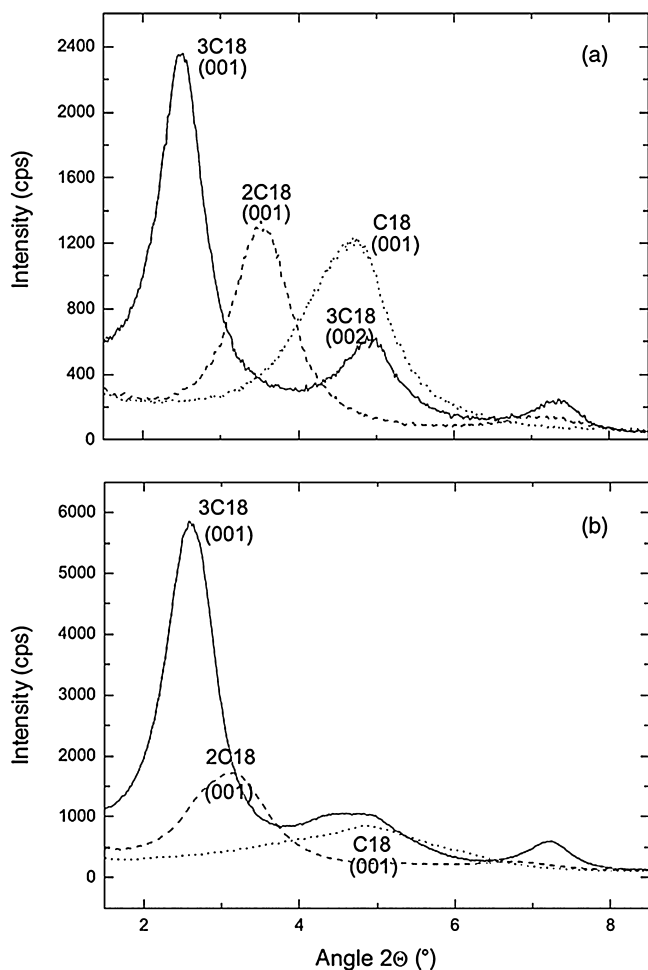
Figure 1.5 Wide angle X-ray diffractograms of (a) 1-3C18 ammonium modified fillers and (b) their PP nanocomposites. Reproduced from reference [19] with permission from Sage Publishers.

pounding with polymers, which is related to the shifting of the diffraction peaks to lower diffraction angles. However, as mentioned earlier, the method does not provide quantification of the extent of intercalation and exfoliation. The filler in the composites in Figure 1.5 was observed to have similar basal plane spacing (as minimal shift in the diffraction peak angle) as the filler powders indicating no intercalation, but the tactoid thickness was observed to be decreased in the microscopy analysis and a partial exfoliation of the filler was achieved. The peak intensity in the diffractograms is also not an accurate indication of the extent of intercalation
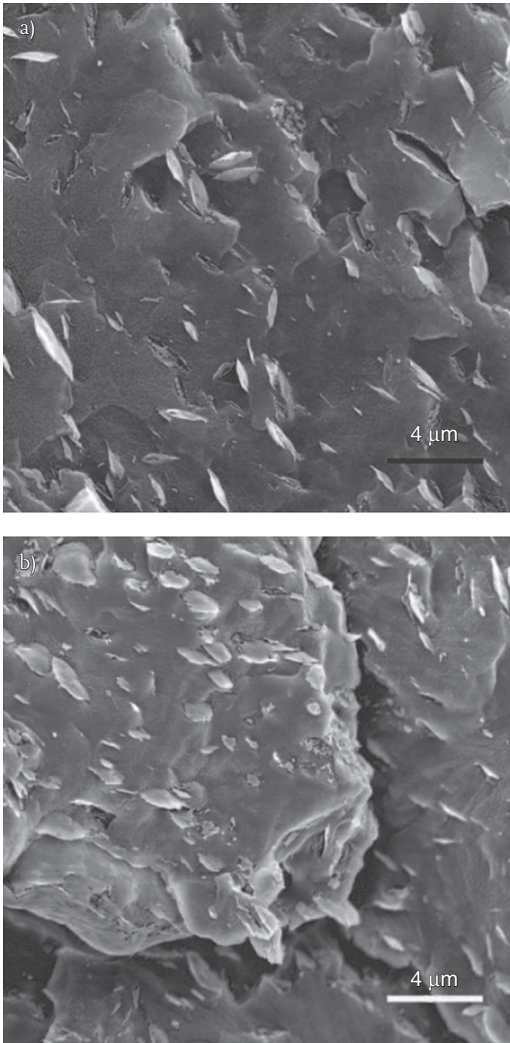
Figure 1.6 SEM micrographs of 3 vol% 2C18 modified filler-PP nanocomposites. The filler platelets are visible in different orientation states. Reproduced from reference [19] with permission from Sage Publishers.

as it depends on other factors like filler concentration, filler orientation, defects in the crystal, and sample preparation methods, etc. Small-angle X-ray analysis is also carried out to analyze the materials in a very low diffraction angle range, which is not possible in the wide-angle X-ray techniques.

Microscopy is commonly used to complement the findings from X-ray diffraction. Figures 1.6 and 1.7 show the scanning and transmission electron microscopy analysis of polymer nanocomposites [19, 20]. It should be noted that the filler
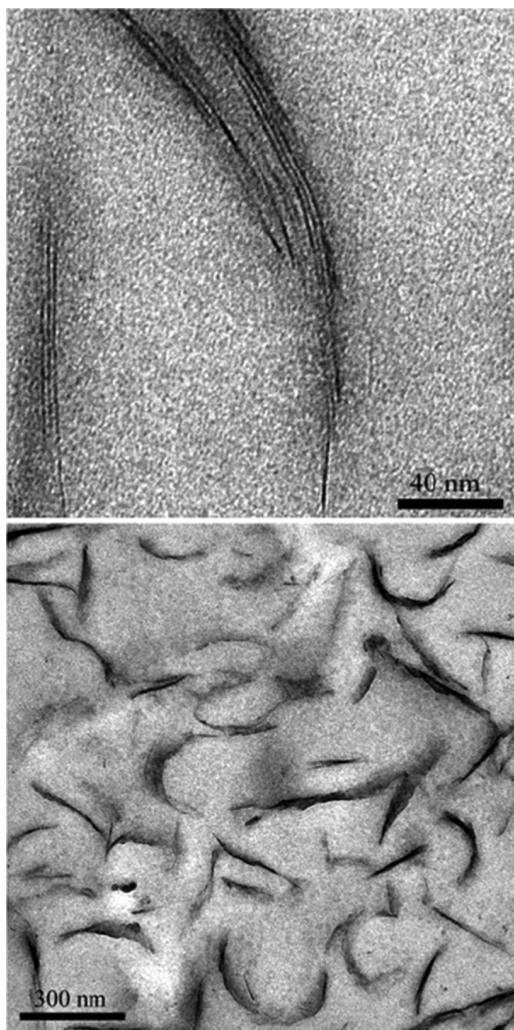
Figure 1.7 TEM micrographs of the 3.5 vol% BzC16 filler–epoxy nanocomposite. The dark lines are cross-sections of aluminosilicate layers. Reproduced from reference [20] with permission from American Chemical Society.

platelets are generally observed to be randomly aligned. Apart from misalignment, the platelets are also occasionally bent and folded. The particles of different thicknesses also indicate that varying degrees of polymer intercalation in the filler interlayers takes place.

Similarly, out of a number of techniques available for characterization of functional properties of nanocomposites, two examples of gas barrier property and mechanical property characterization are shown in Figures 1.8 and 1.9, respectively
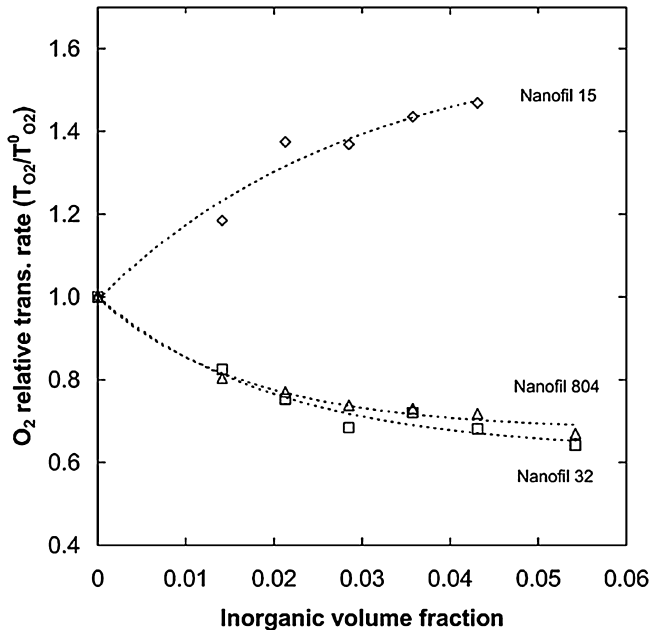
Figure 1.8 Dependence of the oxygen transmission rate through the PU-nanocomposites on the inorganic volume fraction. Reproduced from reference [17] with permission from American Chemical Society.

[17, 21]. The oxygen permeation of the polyurethane nanocomposites as shown in Figure 1.8 is an interesting example as out of the three different fillers, two caused a decrease in oxygen permeation through the polymer, whereas the third filler led to an increase in the oxygen permeation as a function of filler volume fraction. The filler that led to an increase in the permeation was observed to have a least increase in the basal lane spacing as compared to the other two fillers. Also, the microscopy analysis had revealed minimum filler exfoliation in this case. Thus, such microstructure characterizations of the system could also be related to the resulting properties of the nanocomposites. In the example of the mechanical property characterization shown in Figure 1.9 for polypropylene nanocomposites generated with imidazolium modified filler, tensile modulus was observed to increase as a function of filler content, whereas the yield stress was observed to decrease. It indicated that though the load transfer from the polymer chains to the filler particles could take place resulting in an increase in modulus, the filler was still partially exfoliated and the thicker filler tactoids led to reduction in yield stress, which also corresponded with the microscopic characterization of the morphology which was partially exfoliated.

a)

b)
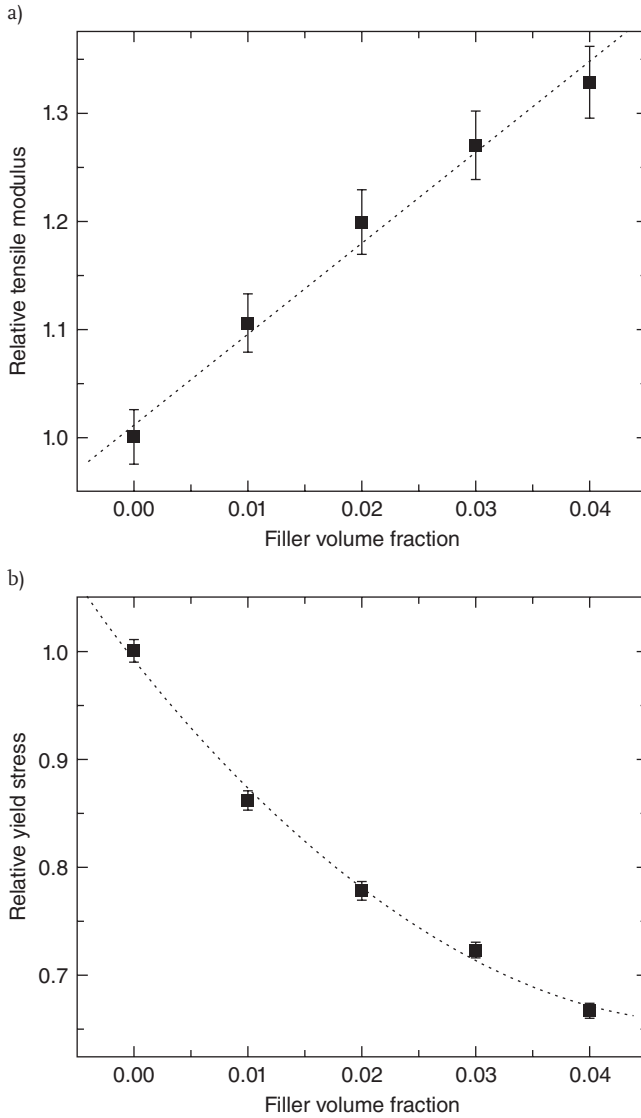
Figure 1.9 Relative (a) tensile modulus and (b) yield stress of polypropylene nanocomposites plotted as a function of the inorganic volume fraction of imidazolium modified filler. Dotted lines serve as a guide. Reproduced from reference [21] with permission from Elsevier.

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