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Edited by Vikas Mittal
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Part I

Thermal stability

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Polymer nanocomposites

Layered silicates, surface modifications, and thermal stability

VIKAS MITTAL
The Petroleum Institute

1.1 Introduction

Inorganic fillers have conventionally been added to polymer matrices to enhance their mechanical strength and other properties, as well as to reduce the cost of the overall composites. Layered aluminosilicates, also popularly described as clays, are one such type of filler, which are responsible for a revolutionary change in polymer composite synthesis as well as for transforming polymer composites into polymer nanocomposites. Aluminosilicate particles consist of stacks of 1 nm–thick aluminosilicate layers (or platelets) in which a central octahedral aluminum sheet is fused between two tetrahedral silicon sheets [1, 2]. Owing to isomorphic substitutions, there is a net negative charge on the surface of the platelets that is compensated for by the adsorption of alkali or alkaline earth metal cations. Because of the presence of alkali or alkaline earth metal cations on their surfaces, the platelets are electrostatically bound to each other, causing an interlayer to form in between. The majority of the cations are present in the interlayers bound to the surfaces of the platelets, but a small number of cations are bound to the edges of the platelets. Though the use of layered aluminosilicates has been documented in some older studies [3, 4], indicating their potential for substantially improving polymer properties, reports from Toyota researchers in the early nineties attracted serious attention [5, 6]. In these studies, polyamide nanocomposites were synthesized by in situ polymerization in the presence of clay with organic modifiers.

Polymer nanocomposites are materials in which the filler phase is dispersed in the polymer matrix at nanoscale and at least one dimension of the filler is less than 100 nm. The nanoscale dispersion of the filler leads to tremendous interfacial contact between the organic and inorganic phases, completely changing the morphology of the composite from that of conventional microcomposites where the polymer and inorganic phases are only mixed at macroscale. As a result, the polymer performance is enhanced at much lower filler volume fractions, allowing the polymer matrix to retain its transparency as well as its low density, traits that are completely lost in conventional microcomposites. Apart from this, as the aluminosilicate particles are platelike in nature, with two finite dimensions and thickness roughly 1 nm, these crystalline platelets are more effective in improving gas barrier, and thermal barrier, and other properties, and are also effective in stress transfer

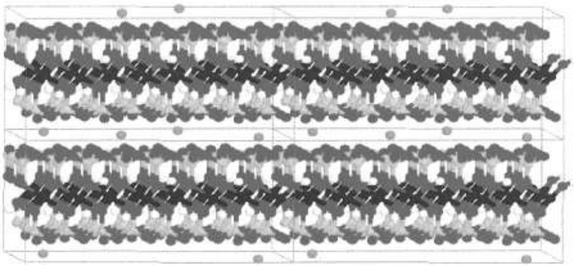

Figure 1.1 Molecular representation of montmorillonite. Reproduced from [16] with permission from American Chemical Society.

when dispersed at nanoscale. Initial studies of polyamide were quickly followed by a large number of studies of other polymers, and significant enhancements in mechanical performance, thermal stability, gas permeation resistance, flame retardancy, and so forth were reported [7–15]. Although different types of aluminosilicates such as mica, vermiculite, and montmorillonite have been incorporated into polymer matrices, the majority of studies have been of montmorillonite. Montmorillonites has a general unit cell formula of $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ [1, 2] and a mean layer charge density of 0.25–0.5 eq.mol^{-1}. The layer charge density is a function of the number of substitutions in the silicate crystals and also indicates the strength of the electrostatic forces holding the platelets together. Figures 1.1 and 1.2 show molecular representations of montmorillonite and mica, respectively [16, 17]. Because of the relatively low mean charge density of montmorillonites, their platelets are held loosely together and can be delaminated in water. This exposes the alkali and alkaline earth metal cations in the aqueous phase and provides the opportunity to achieve exchange of these cations with other organic cations. This type of cation exchange on the surface of the platelets is required because in the pristine form, the surface of the platelets is very polar and possesses high surface energy, hindering their compatibility with the polymers, which are generally hydrophobic and have low surface energies. The exchange of organic cations on the surface of the platelets thus helps in two ways: First, it organophilizes the surface of the platelets, thus lowering the surface energy, and enables more uniform mixture of the fillers with the polymer. Second, the exchange of the long-chain organic ions also increases the interlayer spacing between the platelets by pushing them apart and causing weakening of the electrostatic forces between them. This again helps to intercalate the polymers in the interlayers, allowing the delamination of the filler [18–22]. Conventionally, long-chain alkylammonium ions have been exchanged on the surface of the platelets to organophilize them [18–22]. Alkylammonium ions such as octadecyltrimethylammonium, dioctadecyldimethylammonium, trioctadecylmethylammonium, and benzyldodecyldimethylammonium have been commonly used for the organic modification of silicates. Figure 1.3 shows a representation of the surface modification process [23].

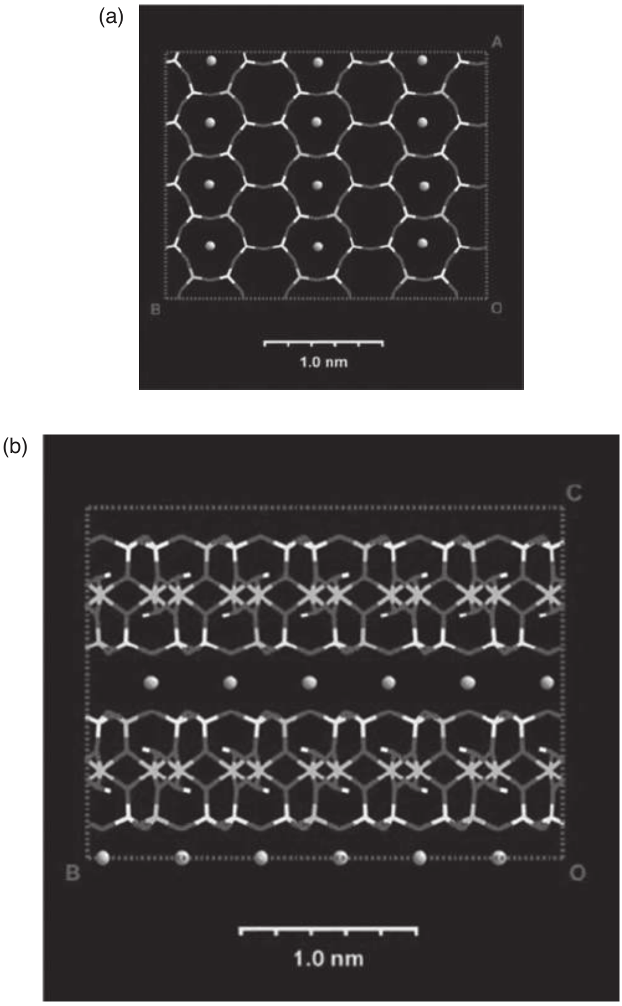

Figure 1.2 (a) Top view of a cleaved mica sheet along the *c* direction and (b) side view along the *a* direction. Reproduced from [17] with permission from American Chemical Society.

As has been mentioned, the montmorillonite substrate has a relatively low charge density, which allows easy delamination in water and subsequent cation exchange, but owing to the presence of a smaller number of ions on the surface of the platelets, less organic matter can be exchanged on the surface, which leads to a lesser expansion of the interlayer spacing. It is possible to employ higher–charge density (1 eq.mol^{-1}) minerals such as mica, which have much smaller area available per cation owing to the presence of a large number of cations on the surface. Exchange on the surfaces of such minerals would lead to much greater basal plane spacing. They also suffer from another limitation: The presence of a large number of cations generates very strong electrostatic forces in the interlayers, which

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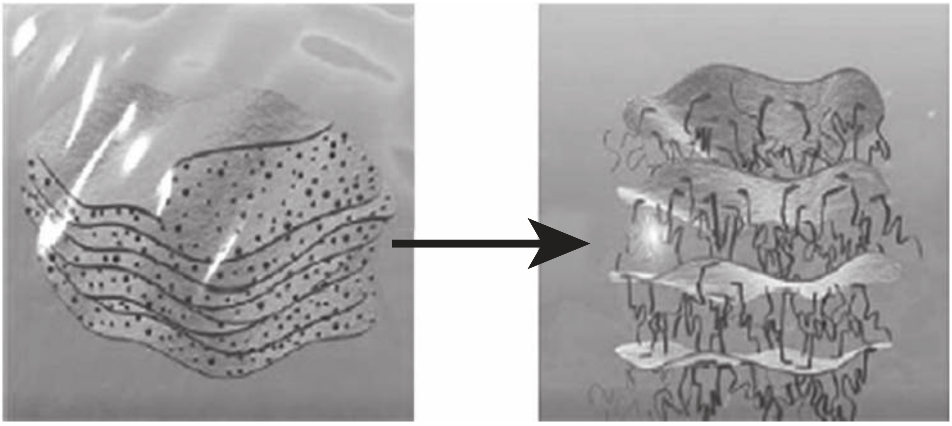

Figure 1.3 Schematic picture of an ion-exchange reaction. Reproduced from [23] with permission from Elsevier.

hinder the complete swelling of these minerals in water and do not allow optimal cation exchange. Aluminosilicates such as vermiculite with medium charge densities of 0.5–0.8 eq.mol^{-1} offer a better alternative, owing to their partial swelling in water and cation exchange causing much higher basal plane spacing in the modified mineral. The chemical constitution of the unit cell of vermiculite is $(Mg, Al, Fe)_3(Al, Si)_4O_{10}(OH)_2Mg_x(H2O)_n$ [24, 25] and the negative charges on the vermiculite layers are compensated for mainly by hydrated Mg^{2+} as interlayer cations. The benefit of the greater interlayer spacing in the modified mineral is that the forces of interaction are further reduced when the spacing between the platelets is increased, providing better conditions for the filler to delaminate in the polymer matrix.

The structural positioning of organic molecules on the surface of the platelets also affects the properties of the organically modified clay. The chemical architecture of the surface modification also significantly affects structure formation on the surface of the platelets. The structure formation and the tilt angles of the modifying molecules estimated from X-ray diffraction and thermal studies as a function of their increasing chain density were reported in a recent study [26]. Figure 1.4 demonstrates these structures for octadecyltrimethylammonium, dioctadecyldimethylammonium, trioctadecylmethylammonium, and tetraoctadecylammonium modifications on the montmorillonite surface. Molecular dynamics studies have also been used to predict the mechanism of monolayer formation on the surfaces of filler platelets. Figure 1.5 shows the formation of surface modification layers for two montmorillonites with different layer charge values as a function of the length of the alkyl chains present in the surface molecules [27].

Polymer nanocomposites are synthesized by a variety of methods, which include in situ polymerization, solution polymerization, and melt intercalation. The route for nanocomposite synthesis suggested by Toyota researchers was also based on in situ monomer polymerization in the presence of filler. Subsequently, Giannelis and co-workers [28, 29]

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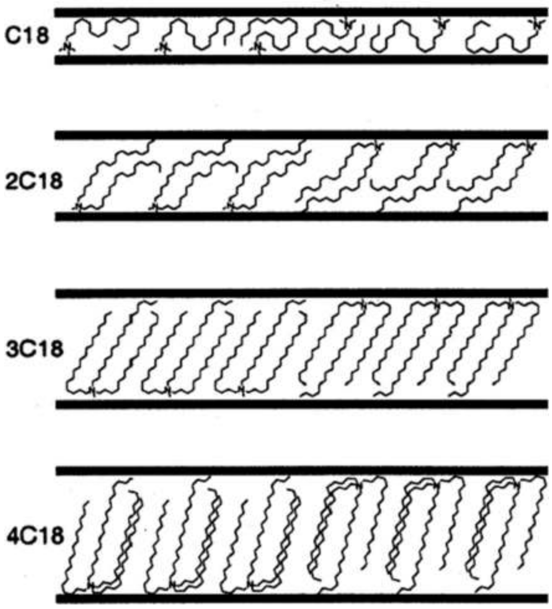

Figure 1.4 Schematic representation of possible structures of the organic modifiers as a function of increasing chain density in the chemical structure. Reproduced from [26] with permission from American Chemical Society.

reported the route of melt intercalation for the synthesis of polymer nanocomposites. In this method the direct use of high–molecular weight polymer can be achieved with mixers and compounders used for the generation of conventional composites. The polymer is melted at a higher temperature and the filler is then added to the polymer melt under shear and kneaded well to efficiently mix it with the polymer. Owing to its simplicity, this method has gained tremendous interest for the synthesis of polypropylene, polyethylene, and polystyrene nanocomposites, to name a few. Figure 1.6 shows a representation of the melt intercalation process. The use of compatibilizer to enhance compatibility between the organic and inorganic phases in the case of nonpolar polymers is also very common, and the compatibilizer is also added along with the polymer for nanocomposite synthesis. However, the melt-compounding approach generally uses high temperatures to achieve optimal mixing of the various components. The use of high operational temperatures can be of concern for the thermal stability of ammonium ion–based organic modifications, as these modifications have an onset of degradation near 200 °C, which is also the temperature commonly used for the melt-compounding of polymers such as polypropylene. It has been observed that the degradation of even a small amount of this modification can have a serious impact on the composite microstructure development and hence properties. The radicals generated during the degradation can also react with the polymer chains, thus lowering the molecular weight and hence impairing the performance. The interfacial interactions

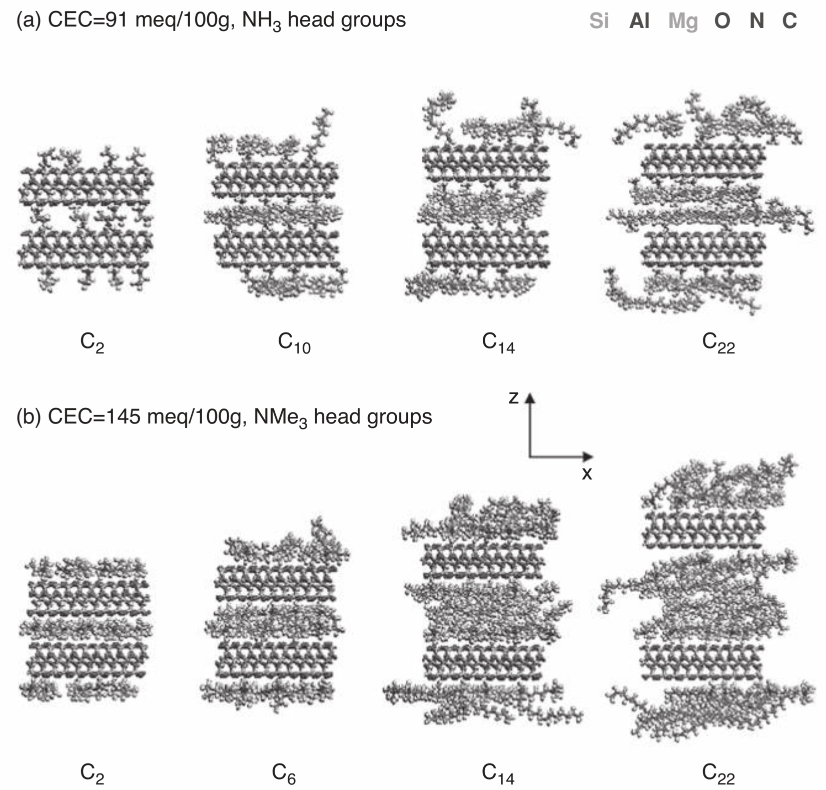

Figure 1.5 Simulation models of alkylammonium montmorillonites modified with different–chain length organic cations, (a) CEC = 91 meq/100 g and (b) CEC = 145 meq/100 g. Reproduced from [27] with permission from American Chemical Society.

of the modified filler with the polymer can also completely change owing to degradation, thus changing the interfacial dynamics that must be achieved to cause filler delamination. Thus, it is important to choose a compounding temperature that is high enough to mix the components by attaining optimal viscosity, but not so high that it severely degrades the organic modification. The compounding time should also be similarly controlled so that it is enough to achieve mixing but not so high as to degrade the modification and polymer. But in many cases, the use of high temperatures and longer compounding times cannot be avoided; it is thus important in these cases to use more thermally stable organic modifications. Also, the commonly used compatibilizers often have very low molecular weights; therefore, consideration should also be given to these molecules similar to that of the organic modifications. It is also important to analyze the thermal behavior of the nanocomposite in order to quantify the effect of compounding on the composite material.

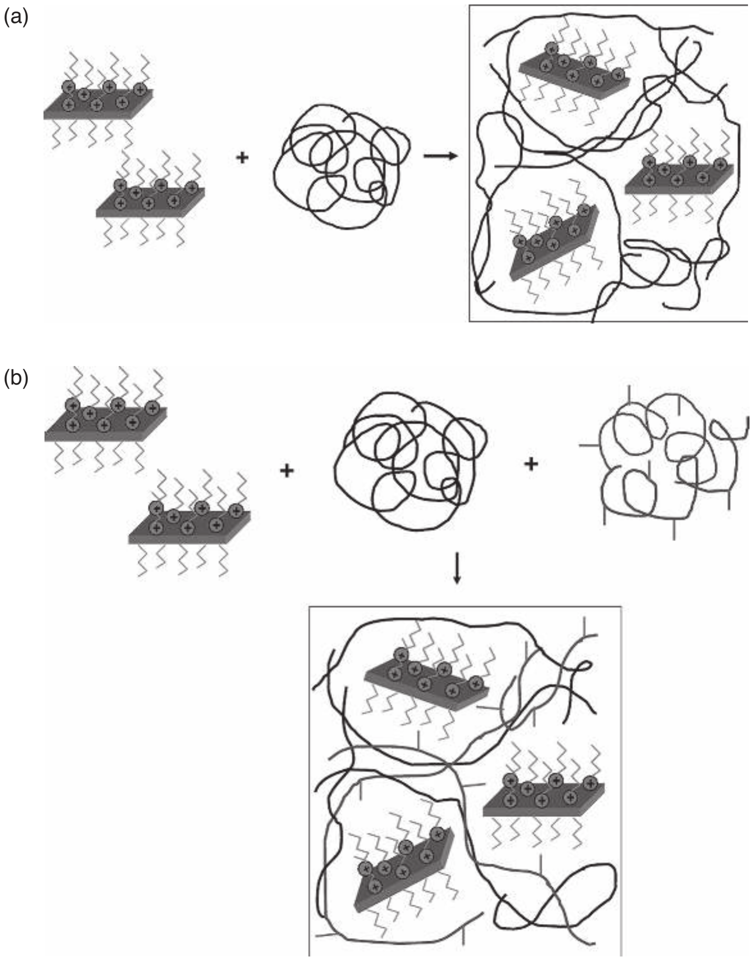

Figure 1.6 Representation of melt intercalation of (a) polymer with clay and (b) polymer in the presence of compatibilizer with clay.

1.2 Evaluation of thermal behavior

As has been mentioned, evaluation of the thermal performance of the surface-modified filler, as well as of composite materials, is important, because it affects the properties of the final nanocomposites significantly. High-resolution (Hi-Res) thermogravimetric analysis (TGA), in which the heating rate is coupled to the mass loss, that is, the sample temperature is not raised until the mass loss at a particular temperature is completed, is the method most commonly used for analysis of the thermal performance of materials.

First, the use of TGA is beneficial in quantifying the amount of organic matter present in the filler interlayers, thus generating an idea of the extent of ion exchange on the surface. If the amount of organic matter does not correspond to a satisfactory extent of

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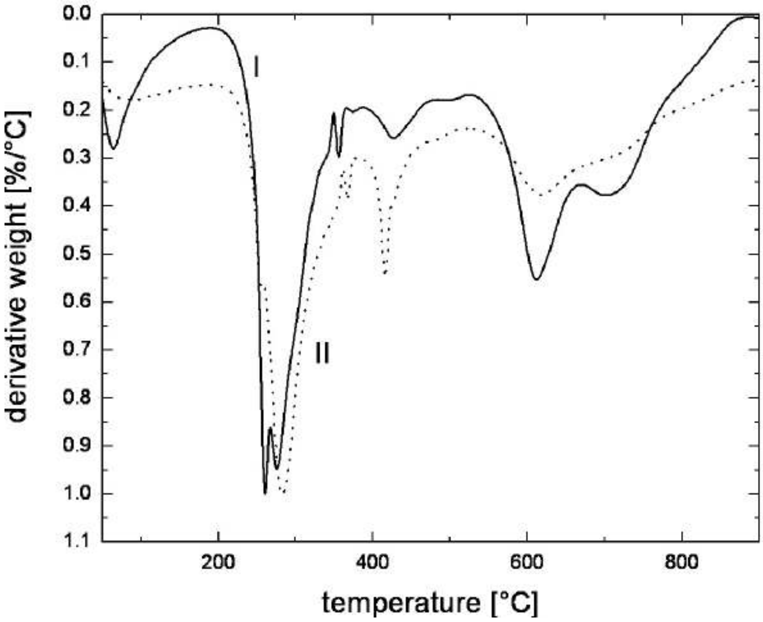

Figure 1.7 TGA thermograms of montmorillonite with a cation-exchange capacity of 880 μ.eq/g modified with (I) octadecyltrimethylammonium and (II) dioctadecyldimethylammonium.

cation exchange, the ion-exchange reaction has to be repeated. Thus, TGA provides an efficient tool for determining the organophilization of the filler surface. One has to be careful in treating the total weight loss achieved in a TGA analysis. Mass loss due to high-temperature dehydroxylation of the mineral has to be subtracted from the total mass loss to obtain information on the mass loss corresponding to the organic layer. The weight loss between 50 and 150 °C, corresponding to the evaporation of physisorbed water and solvent molecules, should also be subtracted from the total weight loss. The total exchanged moles of ammonium cations per gram of clay, φ_{amm}, is then calculated using the expression

$$\varphi_{\text{amm}} = W_{\text{corr}}/[(1 - W_{\text{corr}}) * M_{\text{amm}}],$$

where W_{corr} is the corrected mass loss, corresponding to organic weight loss owing only to alkylammonium ions, and M_{amm} is the molecular mass of the organic cation exchanged on the surface. Figure 1.7 shows the TGA thermograms of montmorillonite (with a cation-exchange capacity of 880 μ.eq/g) with octadecyltrimethylammonium and dioctadecyldimethylammonium modifications. The increase in the overall organic matter attached to the filler can be observed from the increasing chain density of the surface modification. Increasing chain density also led to better thermal stability of the modified filler on the surface, in that the peak degradation temperature for the dioctadecyldimethylammonium-modified montmorillonite was higher than that for the octadecyltrimethylammonium-modified montmorillonite.

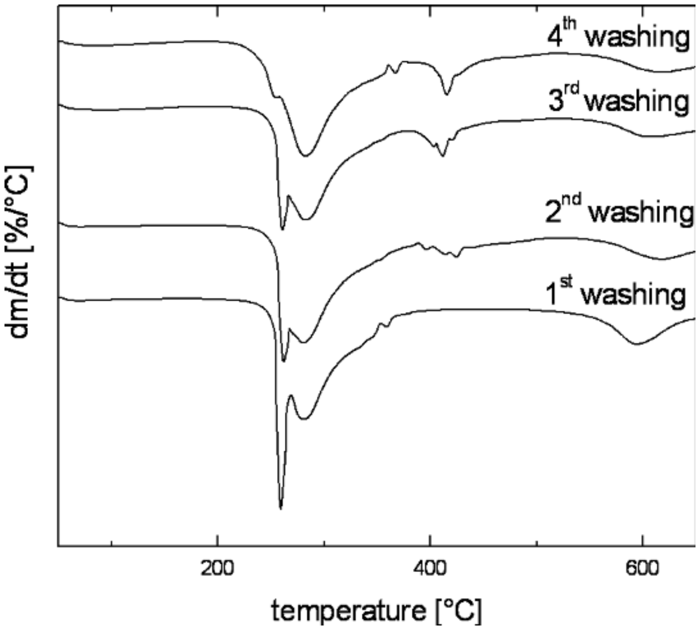

Figure 1.8 Effect of washing protocols on the thermal behavior of the surface-treated montmorillonite modified with dioctadecyldimethylammonium. Reproduced from [32] with permission from Wiley.

Second, high-resolution TGA also helps to ascertain the presence (or absence) of excess surface modification in the interlayers. Excess surface modification is not ionically bound to the surfaces of platelets, but is present as a pseudo-bilayer in the interlayers. The presence of such an excess of surface modification is important to ascertain, and such excess needs to be cleaned off before the filler is compounded with polymer. The reason is the low thermal stability of such pseudo-bilayers as compared with surface-bound molecules. The lower thermal degradation is much more problematic when the filler has to be compounded with the polymer at high temperatures. This low-temperature degradation of the unbound surface modification molecules can cause unwanted interactions with the polymer, leading to a reduction in the molecular weight as well as a deterioration of the interface between the polymer and filler phases [30, 31]. It is also worth noting that it is only high-resolution TGA that is able to detect the presence of such an excess, because other methods like X-ray diffraction are blind to it. Figure 1.8 shows the thermograms of surface-treated montmorillonite modified with dioctadecyldimethylammonium [32]. It is obvious that in the initial washing stages, there was excess surface modification that degraded at a lower temperature, represented by a sharp degradation peak. The montmorillonite after the fourth washing was observed to be relatively free from this excess, as the low temperature degradation peak is almost eliminated. As reported earlier, X-ray diffraction carried out for all four montmorillonite samples obtained after subsequent washing cycles had similar basal plane–spacing