Effect of the presence of excess ammonium ions on the clay surface on permeation properties of epoxy nanocomposites

V. Mittal

Abstract Epoxy nanocomposites with commercially and self-modified montmorillonites of different cation exchange capacities carrying ammonium modifications of various chemical architectures were synthesized using solution casting approach. The commercially treated montmorillonites were observed to contain a large excess of unbound ammonium ions on the surface, which had a negative impact on the permeation properties of the composites owing to the suspected interactions of these unbound ammonium ions with the epoxy polymer. The permeation behavior was significantly improved when self-modified clays free of any excess ammonium modification were used. The microstructure development was unaffected by the physical state of the clay surface indicating that the potential changes in the polymer properties at the interface as well as interfacial interactions in the composites carrying the commercially modified clays may have led to increase in the free volume. Optimal preparation of the clay surface holds the key to achieve enhancement in the composite performance.

Introduction

Recent years have seen the intense research effort to develop polymer-layered silicate nanocomposites to further improve the properties of the neat polymer. Research in nanocomposites have stemmed from the significant property enhancements achieved for polyamide nanocomposites [1–3]. Aluminosilicates, especially montmorillonite, have received much attention as the inorganic filler to prepare such composites owing to their easy swelling in water leading to 1-nm thick platelets [4, 5].

To achieve compatibility among the hydrophilic surfaces of montmorillonite and organic polymer matrix, the inorganic surface cations of montmorillonite are exchanged with the long-chain alkyl ammonium ions [6, 7]. The properties of such composites are synergistically derived from the organic and inorganic components, thus, optimal filler dispersion and distribution in the polymer matrix is necessary. Layered silicate particles with high surface area and geometrical anisotropy lead to increased interactions at the filler–matrix interface bringing about an altogether different morphology, thus, significantly impacting the performance of such composites. This is evident from the remarkable improvements in the mechanical, barrier, and thermal properties of the nanocomposites as reported in literature [8–12].

Epoxies form a special class of thermosetting polymeric materials with a wide spectrum of applications [13–15]. The synthesis of epoxy-clay nanocomposites has been extensively studied, and enhanced mechanical properties were reported [16–24]; however, the permeation properties of these nanocomposites have been neglected. Also, many of the studies employ the commercially treated organo-montmorillonites, which have been generally observed to contain excess of modifier molecules. It has been reported that the presence of excess and unattached molecules of surface modification on the clay surface can have a detrimental effect on the properties of the composites [25–27]. These unattached molecules intercalated between the ionically attached molecules degrade thermally at lower temperature can

V. Mittal (✉)
Department of Chemistry and Applied Biosciences, Institute of Chemical and Bioengineering, ETH Zurich, 8093 Zurich, Switzerland
e-mail: vikas.mittal@chem.ethz.ch

Present Address:
V. Mittal
BASF SE, Ludwigshafen, Germany
e-mail: vikas.mittal@basf.com

specifically interact with the polymer matrix, thus, affecting the performance of the composites, especially the more sensitive permeation properties. In one of the studies, a phenomenon of "degellation" or "deexfoliation" of the organo-montmorillonite, containing bis(2-hydroxyethyl) methyltallowammonium as surface modification, was also reported on addition of polar additives such as amines as crosslinking agents [16]. It was suggested that bifunctional amine molecules may be able to bridge the silicate layers or the N–H groups in the primary and secondary amines may be polar enough to cause re-aggregation of silicate layers. The other possible reason for this behavior may be the presence of excess molecules of surface modifier on the clay surface, which may not be ionically attached to it. These molecules being free on the clay surface may easily interact with the amine or other polar additives thus coagulating the whole dispersion [28]. Thus, the composite properties and morphology are a function of the extent of clean surface.

The goal of the present investigation was to analyze the effect of the presence of excess ammonium ions on the clay surface on the microstructure development as well as the oxygen permeation properties of the epoxy nanocomposites. For comparison, the commercially modified montmorillonites were also either washed or the montmorillonites were self-treated. Ammonium ions of different chemical architecture and montmorillonites of different cation exchange capacities were also employed. The epoxy matrix and the curing agent were chosen to achieve polymer matrix which meets the requirements of the food and health regulations and has low gas permeability on its own. The nanocomposites coatings were drawn on polypropylene substrates and the curing temperatures were kept low to avoid the thermal damage to the substrate foils.

Experimental

Materials

The epoxy resin, bisphenol A diglycidyl ether (4,4′-isopropylidenediphenol diglycidyl ether, epoxide equivalent weight 172–176), was procured from Sigma (Buchs, Switzerland). Dioctadecyldimethylammonium chloride (2C18), tetraethylenepentamine (TEPA), and tetrahydrofuran (THF) were supplied by Fluka (Buchs, Switzerland). Benzylhexadecyldimethylammonium chloride (BzC16) was purchased from Acros Organics (Basel, Switzerland). Corona-treated substrate polypropylene (100 μm thick) foils were kindly supplied by Alcan Packaging (Neuhausen, Switzerland). A surfactant (trade name BYK-307), used to achieve better wetting of the neat epoxy coating to the substrate foils, was obtained from Christ Chemie (Reinach, Switzerland). Sodium bentonites with two different cation exchange capacities (680 and 880 μeq g^{-1}) as well as modified bentonites were commercially procured from Southern Clay Products (Gonsalez, TX) and Süd Chemie (Moosburg, Germany), respectively. The modifications on these bentonites of two different cation exchange capacities included dioctadecyldimethylammonium (2C18), benzylhexadecyldimethylammonium (BzC16), and bis(2-hydroxyethyl) methylhydrogenatedtallowammonium (C182OH).

Filler surface modification and nanocomposite preparation

To compare the performance of commercially treated montmorillonites with the self-treated minerals, the sodium bentonites of both CECs were exchanged with dioctadecyldimethylammonium chloride (2C18) and benzylhexadecyldimethylammonium chloride (BzC16) following the processes as reported earlier [29]. To a slurry of suspended unmodified clay in water and ethanol, a solution of desired ammonium salt corresponding to 100% of the CEC of the clay in ethanol was added dropwise. The degree of exchange and the purity of the product were monitored by Hi-Res TGA [28]. If the mass loss in the TGA did not correspond to full ion exchange, the exchange reaction was repeated. The modified clay was finally suspended in 500 mL of dioxane, sonicated, and freeze-dried. All other details of nanocomposite synthesis have also been reported earlier [29]. The procedures adopted for the determination of density and thickness of substrate and nanocomposite films have also been reported [29].

Characterization techniques

High-resolution (Hi-Res) thermogravimetric analysis (TGA) of the modified clays, in which the heating rate is coupled to the mass loss, i.e., the sample temperature is not raised until the mass loss at a particular temperature is completed, was performed on a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE). The microstructure of the composite films was studied by bright-field TEM using a Zeiss EM 912 Omega (Leo, BRD) microscope. Small pieces of coated foils etched with oxygen plasma were embedded in an epoxy matrix (Epon 812 + Durcopan ACM 3:4, Fluka, Buchs, Switzerland) and 50- to 100-nm thick sections were carefully microtomed with a diamond knife (Reichert Jung Ultracut E). The sections were supported on 100-mesh grids sputter-coated with a 3-nm-thick carbon layer. The oxygen (23 °C and 0% RH) transmission rate through substrate foils coated with the neat epoxy and the nanocomposites was measured using OX-TRAN 2/20 (Mocon, Minneapolis, MN). The procedure adopted for the normalization of the transmission rates and the calculation of permeation of the

nanocomposite film from the combined value of nano-composite film and the substrate foil can be found elsewhere [29].

Results and discussion

The excess ammonium ions present on the clay surface can form the local bilayer in which the free ammonium ions are present in tail-to-tail arrangement with the ionically bound ammonium ions as shown in Fig. 1 [30]. The presence of local bilayer owing to the free ammonium head groups can negatively interact with the epoxy prepolymer thus induc-ing the system instability or changing matrix interactions with the filler at the interface and subsequent loss of composite properties. To confirm and quantify this notion, the composites were synthesized with montmorillonites with and without the excess of these ammonium ions and the composites properties along with microstructure were elucidated. The polypropylene substrate was selected to draw the nanocomposite composites and was selected on the basis of its high transmission rate to oxygen so that it does not hinder measuring the permeation through the coated films. An inorganic volume fraction (i.e., inorganic silicates without considering the organic modification) of 3.5% was used in all the composites.

Commercially modified clays of specifications 2C18 · M680, BzC16 · M680, 2C18 · M880, BzC16 · M880, and C182OH · M880 were selected for the synthesis of nanocomposites (M680 and M880 represent the montmo-rillonites with corresponding cation exchange capacities of 680 and 880 μeq g^{-1}). Table 1 details these abbreviations along with the cations exchanged on the surface of the montmorillonites. Various chemical architecture of the ammonium ions as well as different CEC were chosen to study the effect of these parameters on the composite

properties along with excess ammonium ions. To ascertain the state of ammonium ions on the surface, high-resolution TGA was first performed on these modified clays. Figure 2 shows the first derivative curves of the TGA signal of weight% (not reported), which also reports the degradation rate of the organic matter on the mineral. Figure 2a and c shows the TGA thermograms of BzC16 · M680 and 2C18 · M880 modified clays, the rest being also of similar nature. The presence of two thermal degradation peaks between the temperature range of 200 and 300 °C clearly confirmed that the excess of ammonium ions were present on the surface whose degradation occurs at lower temper-ature than the ions ionically bound on the surface. It was observed from the amount of weight loss in this low-tem-perature TGA peak that 15–20% of the total organic weight loss is attributable to the unbound ammonium ions in these commercially available modified montmorillonites. In the self-treated clays, care was taken to avoid using the large excess of ammonium ions for exchange and the clays were rigorously washed after exchange to eliminate any pres-ence of unattached ammonium ions thus avoiding the formation of local bilayer. Apart from the clean surface, it was also necessary to obtain a satisfactory extent of surface exchange, which was quantified by using the amount of weight loss in the TGA. Exchanges above 90% of the number of available cations on the surface were achieved in the present study, whereas exchanges in the range of 100–110% of the CEC were estimated in the commercially treated montmorillonites confirming the presence of excess ammonium modification. The TGA thermograms of self-treated BzC16 · M680 and 2C18 · M880 clays are shown in Fig. 2b and d for comparison with their commercially modified counterparts. Only one major thermal degradation peak was observed in the temperature range of 200–300 °C. Absence of any lower-temperature peak owing to the degradation of the unbound ammonium ions confirmed

Fig. 1 Schematic of the excess molecules of the surface treatment present in the clay interlayer as local bilayer
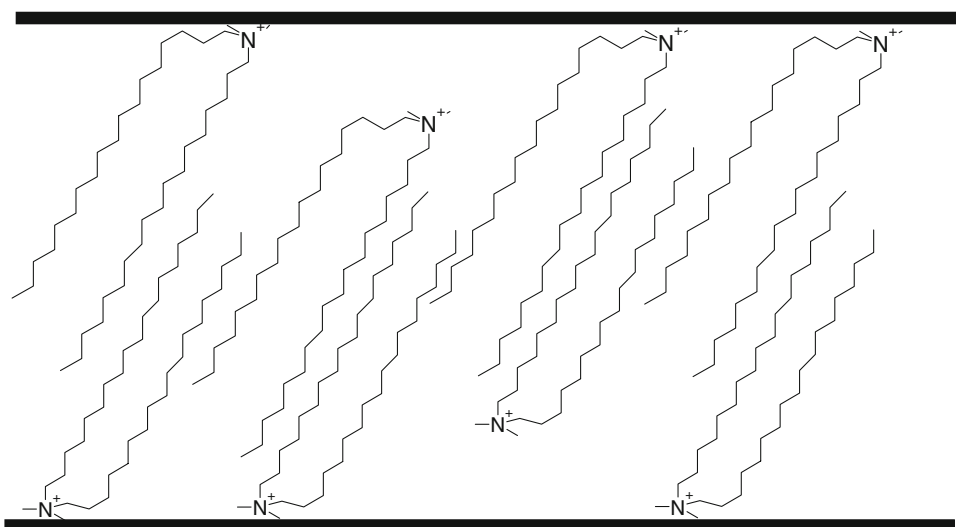
Table 1 Abbreviations of the cations used for ion exchange and the modified montmorillonites

Cation	M680[a]	M880[a]
Dioctadecyldimethylammonium	2C18 · M680	2C18 · M880
Benzylhexadecyldimethylammonium	BzC16 · M680	BzC16 · M880
Bis(2-hydroxyethyl)methylhydrogenatedtallowammonium	C182OH · M680	C182OH · M880

[a] M680 and M800 represent the montmorillonites with CEC values of 680 and 880 µeq g^{-1}, respectively

Fig. 2 TGA thermograms of the (**a**) commercially modified BzC16 · M680; (**b**) self-treated BzC16 · M680; (**c**) commercially modified 2C18 · M880, and (**d**) self-treated 2C18 · M880
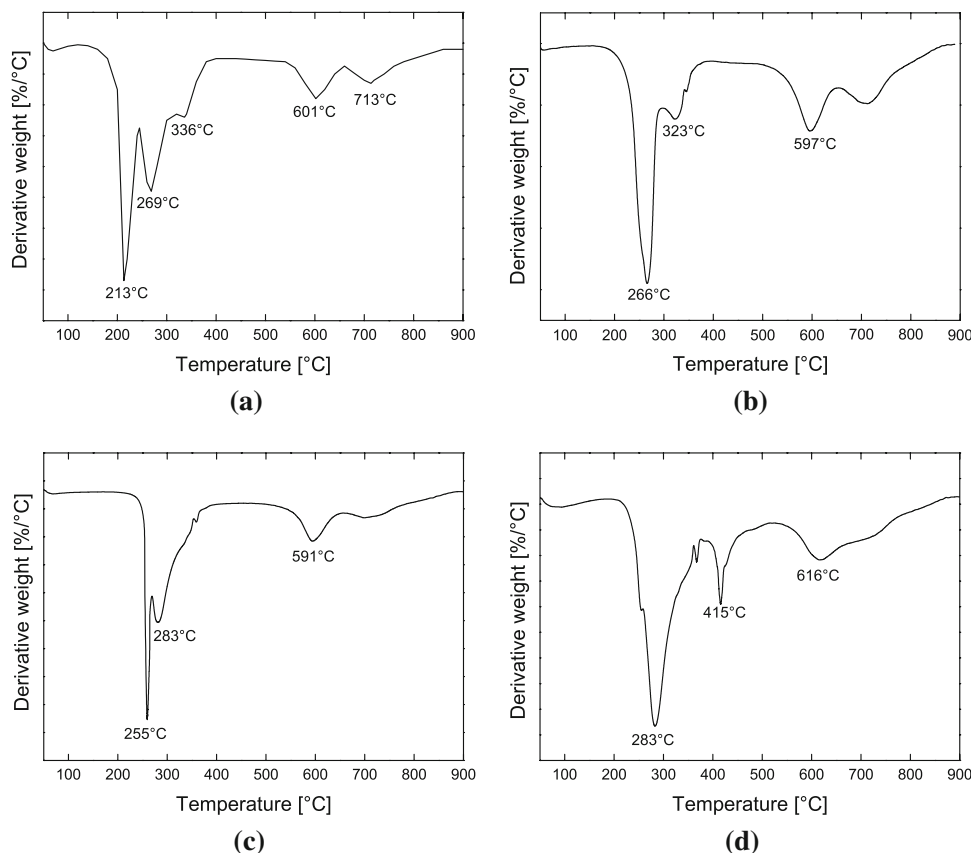
that modified clays with much more cleaner surface were achieved. It is also worth mentioning that even 4–5 rounds of cleaning cycles may be necessary to clean the excess of ammonium ions [31]. It is also worth mentioning the smaller peaks at 336 °C and 323 °C in Fig. 2a and b, respectively, which can still be attributed to the thermal degradation of the organic ions because the ammonium ions do not completely volatilize in the first major degradation step, and small amount of carbonaceous residual remains which burns at higher temperatures [28]. Similar is true for the other modifications performed in the study. Also visible in the TGA degradation curves are the peaks around 600 °C and 700 °C, which are attributable to the chemical dehydration, i.e., dehydroxylation of the mineral which is accompanied by a change in the crystal structure [28].

Oxygen permeation properties through the composite films drawn on polypropylene substrates were measured to quantify the effect of optimization of the surface modification on the composite properties. Table 2 details the oxygen transmission rates through the composite films synthesized using the modified clays with large excess of unbound ammonium ions on the surface. A value of 2 cm^3 µm/(m^2 d mmHg) was observed for the pure polymer, which was significantly increased to high values in the composites containing 3.5 vol.% of filler indicating that incorporation of clay in fact had a negative impact on the properties. Especially, high were the transmission rates in C182OH · M680 and C182OH · M880, where the values were enhanced to 5.9 and 5.5 cm^3 µm/(m^2 d mmHg), respectively. Also, no observable effect of chemical architecture of the ammonium ions as well as the CEC

Table 2 Oxygen transmission rates through the nanocomposite films containing 3.5 vol.% commercially modified clay

Composites	Oxygen permeability coefficient [cm^3 μm/(m^2 d mmHg)]
Neat epoxy	2.0
2C18 · M680	4.8
C182OH · M680	5.9
BzC16 · M680	2.9
BzC16 · M880	2.8
2C18 · M880	4.6
C182OH · M880	5.5

Table 3 Oxygen transmission rates through the nanocomposite films containing 3.5 vol.% of washed or self-treated montmorillonites

Composites	Oxygen permeability coefficient [cm^3 μm/(m^2 d mmHg)]
Neat epoxy	2.0
BzC16 · M680	1.8
2C18 · M680	3.9
BzC16 · M880	1.6
2C18 · M880	3.7
C182OH · M880 (washed)	1.5

could be observed on the transmission rates through the nanocomposite films. As the polymer itself had low permeation on its own, therefore, the increase in transmission rates can only be linked to the interactions of the polymer with the filler. Table 3 describes the oxygen transmission rates through the 3.5 vol.% composites synthesized with the self-treated clays. The composites were also prepared with commercial C182OH · M880 after rigorous washing. Totally different behavior toward the oxygen permeation was observed in these composites as evident from much lower permeation values. Values of 1.8 cm^3 μm/(m^2 d mmHg) was observed for BzC16 · M680 which was much lower than 2.9 observed earlier. Further lower value of 1.6 cm^3 μm/(m^2 d mmHg) was observed for BzC16 · M880, indicating much better permeation properties when the clay surface was properly optimized. The composite films drawn with washed clay of C182OH · M880 had a remarkable decrease in oxygen permeation of 1.5 cm^3 μm/(m^2 d mmHg) as compared to 5.5 when drawn with commercially modified clay. In 2C18 composites, the permeation values though decreased from the earlier observed with commercial clays, but were still higher than the pure polymer itself. This phenomena has been earlier described to be the result of negative interactions between the polar polymer and the nonpolar alkyl chains inducing enhancement of free volume at the interface [12, 29]. The effect of ammonium ion chemical architecture and the CEC

of the montmorillonite substrate also became clearer when self-treated clays were used owing to the elimination of the effect of excess ammonium ions. More polar ammonium ions were observed to perform better owing to better interactions with the polar epoxy polymer. Higher CEC clay was also observed to perform marginally better owing to smaller area per cation and hence higher filler basal plane spacing values. It is obvious from these results that the properties were significantly affected with the cleanliness of the surface. The excess ammonium ions present on the
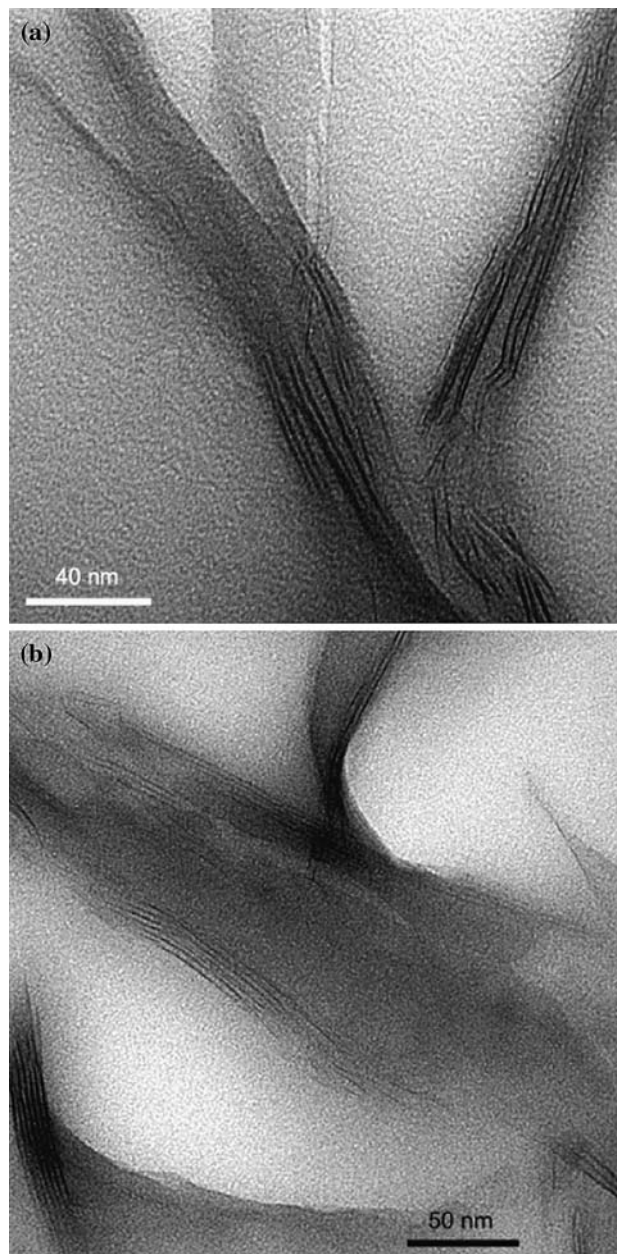
Fig. 3 TEM micrographs of 3.5 vol.% composites with (**a**) commercially modified BzC16 · M680 and (**b**) self-modified BzC16 · M680. The dark lines are cross sections of aluminosilicate platelets

surface are suspected to interact with epoxy prepolymer thus changing the polymer characteristics at interface by inducing plasticization or by reducing the crosslinking or affecting polymer filler interfacial interactions, which severely affect the permeation properties. Thus, this changed nature and possibly structure of the polymer matrix after crosslinking at the organic–inorganic interface owing to the interactions between the prepolymer and excess of ammonium salt is to be hypothesized for significant effect on barrier properties.

As the physical state of the montmorillonite surface impacted the properties of the composites significantly, it was of interest to analyze the corresponding microstructure in these composites to further understand the system. Surprisingly, WAXRD and TEM investigation of the composites synthesized both with commercial and self-treated clays did not show any significant distinctions from each other. For instance, Fig. 3 shows the TEM micrographs of composites with commercially modified BzC16 · M680 and self-modified BzC16 · M680. All other composites had similar microstructure and are thus indistinguishable. It is clear that both the micrographs in Fig. 3 point toward the presence of mixed morphology in the composites with the presence of single layers and intercalated tactoids with varying thicknesses as generally seen indicating that the microstructure development was unaffected irrespective of physical state of clay surface. It thus indicates that the intercalation and subsequent exfoliation of the clay layers may not be generally affected by the presence of excess surface ions; however, the specific interactions of these ions with the polymer chains in the interlayer do change the polymer characteristics and the interfacial interactions to generate possible higher free volumes significant enough to impact the sensitive permeation properties.

Conclusions

Comparison of the microstructure and the permeation properties of the epoxy nanocomposites synthesized with commercially modified and self-treated clays was performed. The presence of a large excess of ammonium ions on the clay surface was confirmed in the commercially modified clays, which could be totally washed off when the montmorillonites were treated and washed more optimally. The clays with large excess of surface ions on the surface deteriorated the permeation properties of the composites with a 2- to 3-fold increase in the transmission rates. The permeation behavior was tremendously improved when the self-treated clays were used or the commercial clays were used after washing. The microstructure development was unaffected by the state of clay surface indicating that the suspected interactions of the free ammonium ions with the prepolymer affect the polymer characteristics (reduction of crosslinking, plasticization, and increase of free volume) and interfacial interactions which in turn may lead to deterioration of the properties. A careful optimization of the clay surface is of utmost importance to achieve the optimum enhancement in the composite properties.

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