Macromol. Symp. ***194****, 155–160 (2003)*

Tailored Interfaces in Nanocomposites

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Summary: Different kinds of clays based on sodium montmorillonite have been modified i) by cationic exchange of alkylammonium ions and ii) by covalent grafting of organosilane. We have prepared organophilic clays with different gallery heights (due to alkylammonium ions with alkyl chain length varying from 8 to 18 carbon atoms) and with a specific functionalisation (due to the organosilane). We have generated organoclays with different kind of organic layer properties: ionically bonded or physically adsorbed alkylammonium ions and covalently grafted organosilane. These different organoclays have shown various specific behaviours when dispersed in monomers or in a reactive mixture, proving the influence of the surfactant on the nanocomposite final properties.

Introduction

In the past twenty years, many studies have been focused on the incorporation of inorganic clay platelets in organic polymers in order to obtain hybrid materials [1]. These nanostructured composites are of great interest because they present attractive behaviours in terms of stiffness [2], thermal resistance [3] and barrier properties [4]. These properties are related to the high aspect ratio of silicates and to their layered structure. Clays exhibit a specific multi-scale organization. At the angström scale, is the platelet, which is 7 Angström thin and several hundred nanometers long and wide. At the micron scale, these platelets are stacked into primary particles. At a higher scale, these primary particles are stacked together to form aggregates.

In order to get optimal properties for the nanocomposite, the platelets must be randomly dispersed, *i.e.* exfoliated, in the matrix to obtain a large contact area with the matrix. However, the hydrophilic nature of the silicate surface primarily limits its dispersion. In order to facilitate exfoliation, surface treatment of the platelets is necessary in order to change their nature from hydrophilic to hydrophobic [5]. Other parameters also govern the dispersion of the layered silicates in the polymer: the type of silicate (which determines the swelling capacity) [6], the way of mixing the clay with the polymer [7], and the curing treatment of the final nanocomposite [7-8].

The easiest way to make clay minerals hydrophobic is to exchange the intercalated cations with alkylammonium ions [9]. The swelling of clay in an aqueous alkylammonium ion solution leads to an extension of the interlayer galleries due to the hydration of inorganic cations (Na^+, Ca^{2+}) contained in these galleries allowing the alkylammonium ions to intercalate between the platelets.

Organosilane grafting on the hydroxyl groups present on platelets edges is another way to functionalise the clay. Modification of silica with variable geometry such as divided particles for chromatographic applications or silicon wafers for elaborating molecular devices has been investigated extensively [10], however much less work deals with grafting reactions with clay mineral [11-13]. The grafting of hydroxyl groups on platelets edges by organosilanes with

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different functionalities facilitates production of organically modified clays where organic moieties are covalently bonded and chosen in accordance with matrix.

In this paper, we report the building of organic layers of different types: i) ionically bonded by the cation exchange process ii) physically adsorbed iii) covalently bonded by grafting. We have searched to prepare organophilic clays with well-controlled surface properties (clay modified with specific functions, stable layers with an extended conformation in the galleries) in order to generate different kind of interfaces as a function of the properties (mechanical, thermal and barrier) requested for the nanocomposite material. We introduced some of these organoclays in monomers and in a reactive mixture to put into evidence the effect of surfactant on the final properties of the nanocomposite.

Experimental part

Materials

Na^+-clay (Optigel EX0255 subsequently called OPT) was obtained from Société Française des Bentonites et Dérivés, based in Le Tréport, France. Its Cationic Exchange Capacity (CEC) is around 100 meq/100g and its d-spacing is about 12.6 Å (hydrated clay).

A commercial organophilic clay (Tixogel, subsequently called TIX) supplied from Société Française des Bentonites et Dérivés was taken as a reference organophilic clay. This clay is modified with dimethyl- benzyl-tallowalkyl-ammonium ions and its d-spacing is about 20 Å.

The different amines used were octadecylamine CH_3-$(CH_2)_{17}$-NH_2, hexadecylamine CH_3-$(CH_2)_{15}$-NH_2, dodecylamine CH_3-$(CH_2)_{11}$-NH_2 and octylamine CH_3-$(CH_2)_7$-NH_2. The silane was γ-aminopropyltriethoxysilane $H_2N(CH_2)Si(OC_2H_5)_3$ (subsequently noted γ-APS). All these products were purchased from Aldrich and used without further purification.

The epoxy prepolymer is Diglycidyl ether of bisphenol A (subsequently called DGEBA) with n=0.15, purchased from Ciba-Geigy. The curing agent is Jeffamine D2000 from Hunstman. These monomers have been used without further purification.

Organoclay preparation

-Cation exchange process: The alkylamine (10^{-2} mol) is dissolved in 1 liter of 0.01 M hydrochloric acid solution (based on deionized water). The solution is stirred at 80°C during 3 hours. Five grams of OPT are then added to the solution, which is then stirred at the same temperature for 3 more hours.

The solution is then filtered and washed with hot deionized water or a hot ethanol: water (1:1) mixture until no chloride is detected when adding 0.1M aqueous $AgNO_3$. The resulting organoclay is then dried at 85°C during 36 h and kept dry in a dessicator.

-Covalent grafting: The organosilane (0.3% wt) is introduced in a water:ethanol mixture (25:75). The solution is stirred at 80°C for 1 hour. Ten grams of TIX are added to the silane solution, which is stirred at the same temperature during 6 hours. The solution is then filtered and washed with a hot ethanol-water mixture. The grafted organoclay is then dried at 85 °C during 1 h.

Characterisation

X-Ray diffraction (XRD) spectra were obtained with a Siemens D500 diffractometer with a back monochromator and a Cu anticathode. The 2θ angles were varied between 1 and 10° in order to measure the d_{001}-spacing of the modified montmorillonites.

Thermogravimetric analysis experiments were performed using a TGA2950 from TA Instruments. The samples were brought from 25°C to 800°C at a scanning rate of 20°C/min under helium atmosphere in order to evaluate the thermal stability of the modified clays and the quantity of intercalated alkylammonium ions.

Wetting measurements were completed on a GBX device. From contact angles measurements performed with water and diiodomethane as test liquids, we have determined polar and dispersive components of surface energy by using Owens-Wendt theory.

Viscosity measurements were performed on an ARES system with an air convection oven from Rheometric scientific between 50mm parallel plates at a frequency of 6.28 rad.s-1 and with an applied strain of 10%.

Results and discussion

Organoclay preparation

We have generated organoclays by cationic exchange and organosilane grafting.

The organoclay synthesized by cationic exchange can present different structure depending on the cation exchange process parameters (temperature, washings, amine/clay ratio, alkyl chain length).

The alkyl chain length was varied from octyl (OPTC8), to dodecyl (OPTC12), hexadecyl (OPTC16) and octadecyl (OPTC18). We have chosen primary amines because Zilg et al. [17] demonstrated that organoclay modification with protonated primary amines gives a much better toughness/stiffness balance with respect to those modified with protonated secondary and tertiary amines or quaternary ammonium cations, respectively.

As shown by the data in Table 1, basal spacings measured by XRD increase in proportion to the alkyl chain length of the ammonium cations.

Table 1: *Interlayer distance (d_{001}, Å) of alkylammonium exchanged montmorillonites*

Sample Name	Alkylammonium ion	d_{001} spacing (Å) ^{a}	Calculated value, l_t (Å)	Tilt angle α (°)
OPT	none	12.6	-	-
OPTC18	CH_3-$(CH_2)_{17}$-NH_3^+	31.6	24.5	50
OPTC16	CH_3-$(CH_2)_{15}$-NH_3^+	29.6	22	50
OPTC12	CH_3-$(CH_2)_{11}$-NH_3^+	22.3	18.2	32
OPTC8	CH_3-$(CH_2)_7$-NH_3^+	13.6	11.9	4

^{a} Measured by XRD at 0.1 °/min

To evaluate the chains conformation in the clay galleries, we have reported the theoretical length when the chain adopts an all-trans conformation. The theoretical extended chain length, l_t, can be calculated as follows:

$$l_t\,(\text{Å}) = 1.265\,(n_c-1) + 3.0$$

where (n_c-1) is the number of methylene groups in the alkyl chain, 1.265 Å is the contribution due to the $-CH_2-$ chain segments by assuming that the chains adopt an all-trans configuration and we add the dimension of the methyl end group (3 Å) as proposed by Lagaly [14].

For OPTC8 and OPTC12 the measured basal spacing is somewhat smaller than the value calculated with an extended chain perpendicular to the platelet, suggesting that this shorter chain ions do not adopt a paraffin-like structure.

For alkylammonium ions with $n>12$, the basal spacing is very near the theoretical extended chain length which puts into evidence that the chains adopt a paraffin like structure in a tilted arrangement with respect to the silicate surface.

Moreover, TGA experiments reveal that after the cation exchange process, part of the alkylammonium ions is physisorbed outside the galleries (cf. Figure 1.). A TGA spectrum which reports the weight loss first derivative as a function of temperature, performed on a modified montmorillonite usually shows three main peaks. The first peak, located in the 25-150°C range, is linked to the vaporization of water. The weight loss in the 150-300°C range can be attributed to the vaporization of physisorbed alkyammonium ions or alkylamines. The last peak located from 300 to 500°C is linked to the vaporization of the ionically bonded species.

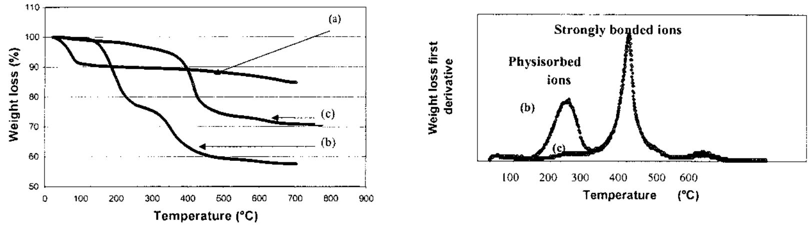

Figure 1: *TGA experiments on the pristine clay OPT (a), after exchange before washing (b) and after repetitive washings (c): weight loss and weight loss first derivative as a function of temperature*

Washing of the organoclay with hot ethanol/water mixture allows to eliminate this physisorbed ions layer and to obtain organoclays in paraffin-like organization with a good thermal stability (cf Fig.1). This kind of organoclay is likely to be incorporated in a melt polymer in an extruder or during curing of a thermoset without being degraded.
To summarize, we have synthesized by cationic exchange organoclays with distinct galleries structure and d-spacings depending on the alkyl chain length and with or without physorbed ions depending on the washing treatment.

We have functionalized a commercial organoclay with amino groups to make the organoclay reactive towards an epoxy matrix. The tixogel already exchanged with dimethyl-benzyl-tallowalkyl-ammonium allows us to have intercalated clay with a d-spacing about 20 Å. After surface modification, the organic chains are covalently bonded to the clay minerals, and the surface properties are changed. The results in Table 2 show that the polar component of surface energy after treating increases because of polar functions, i.e. amino functions. The surface energy values are quite similar to values determined on a γ-APS grafted glass fiber.

Table 2: *Polar and dispersive components of surface energy of a commercial organoclay (Tixogel) before and after aminosilane grafting*

Modified clay	θ water (°)	θ CH_2I_2 (°)	Polar component ($mJ.m^{-2}$)	Dispersive component ($mJ.m^{-2}$)
Tixogel	64.8±1.2	50.4±0.6	14.9±1.1	27.3±0.9
Aminosilane grafted Tixogel	39.8±0.4	44.4±1.0	31.3±0.8	27.4±0.7
Aminosilane grafted glass fiber	37.6±1.1	32.8±0.4	30.6±0.7	30.3±0.3

The silane grafting takes place on the hydroxyl groups situated on the platelets edges, which explains why there is no effect on d-spacing of gallery. The X-ray spectra performed on Tixogel before and after grafting are similar, which means that the conformation of the chains in the galleries is not affected.

Nevertheless, after grafting, the TGA spectrum of Tixogel is modified (Figure 2). The peak significant of physisorbed dimethyl-benzyl-tallowalkyl-ammonium ions of Tixogel nearly disappears. By considering the excess of ions adsorbed on hydroxyl groups or around the primary particles, this is not surprising to note their removal during grafting since the grafting process in a water:ethanol mixture is similar to repetitive washings as explained previously. The two other peaks (about 300 and 380 °C) are related to the degradation of intercalated modifying ions of Tixogel. A distinct knee at 420 °C appeared after grafting can be attributed to silane covalent coupling.

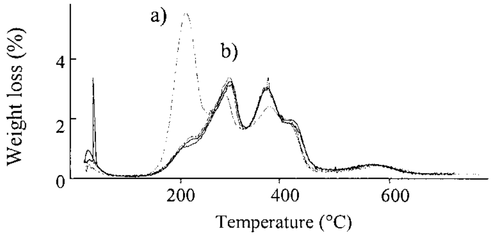

Figure 2: *TGA experiments on Tixogel: a) before γ-APS grafting and b) after γ-APS grafting*

Role of the surfactant on nanocomposite properties

In order to confirm that interface nature and structure are key parameters in nanocomposite synthesis and properties, we have introduced Tixogel (commercial organoclay) and OPTC18 (home-made organoclay based on Na-montmorillonite exchanged with octadecylammonium ions) in the monomers of our epoxy/amine system and in the reactive mixture. The filler have been dispersed with a high shear mixer (Five cycles of 1 minute at 11000 rpm).

In Table 3, one can note that the viscosity of the monomers is increased by the incorporation of organoclay. The organoclay is swollen by the monomers, the d-spacing increases as a function of the organoclay/monomer affinity and leads to an uptake in viscosity.

Table 3 : *Complex viscosities at 25°C of organoclay dispersions in monomer*

Monomer	Complex viscosity without filler at 25°C (in Pa.s)	Complex viscosity with OPTC18 at 25°C (in Pa.s)	Complex viscosity with Tixogel at 25°C (in Pa.s)
D2000	0.3	6.3	2.5
DGEBA	26.3	33.5	124

In D2000, the highest viscosity is obtained with OPTC18 whereas it's obtained with Tixogel in DGEBA. These observations reveal that the nature of the interface plays a role in the ability for an organoclay to be dispersed in a monomer. The long aliphatic chains of D2000 develop more interactions with the alkyl chains of OPTC18 and swell it easier than Tixogel. Reciprocally DGEBA is more likely to swell Tixogel, which has benzyl groups on its platelet surface.

These observations confirm that the inorganic/organic interface plays a key role in the dispersion process. Tailoring of interface nature and structure leads to a better dispersion in the monomers before polymerisation.

When the evolution of viscosity during curing is followed, one can note another effect of the organic/inorganic interface on the final nanocomposite properties. As shown in Figure 2, ionic surfactants present on the clay platelets have got an effect on the curing kinetics.

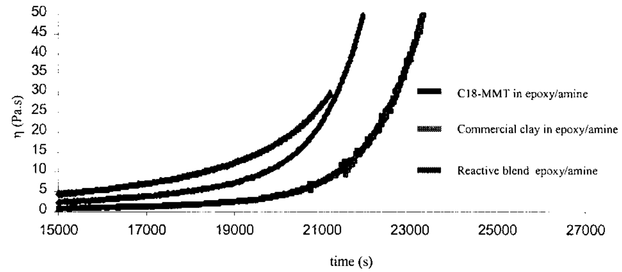

Figure 3: *Evolution of viscosity during curing for DGEBA/D2000 systems*

The organic cations catalyse the epoxy/amine polycondensation. The catalytic effect is more important with OPTC18 than with Tixogel. It's known that there is a competition during curing between monomers diffusion into the galleries and polymerisation of the reactive mixture. This competition rules the final state of dispersion of the platelets in the matrix. That is why the catalytic effect of the surfactant is of great interest. Properties of nanocomposites based on the same matrix but with different organoclays differ because of different reinforcing effects but also because of this modification of cure kinetics by the surfactant.

Conclusion

We are able to elaborate organoclays with various properties by tailoring the quantity and the organisation of alkylammonium ions in the galleries. We are also able to regulate the quantity of ions physisorbed outside the galleries and to create functionalized layers. We have put into evidence the fact that this organic layers in and outside the galleries have an important effect on the organoclay dispersion in the monomers and on the curing kinetics and by the way affect the properties of the nanocomposite. The study of the influence of the inorganic/organic interface on nanocomposite properties is complex because this interface does not affect only the reinforcing effect at a macroscopic scale but affects also the primary dispersion and the cure kinetics of the thermoset.

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