# Morphology and thermal properties of Poly(methyl methacrylate)/silylated MMTs nanocomposites

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## Summary

In this research, composites based on Poly(methyl methacrylate) (PMMA), and two kind of organomodified montmorillonites, Sodium clay (Dellite HPS) and organo-clay (Dellite 72T) sylilated by using chloro-dimethyl-octadecylsilane, are synthesized by *in situ* intercalative polymerization. Nanocomposites are filled with various amounts of MMTs (1%, 3%, and 5% wt). The influence of montmorillonite contents and type of organic modifier on clay dispersion and thermal properties of PMMA composites are investigated. The structural and morphological characteristics of nanocomposites are verified by XRD, SEM and TEM analyses and confirm that organomodification of Montmorillonite by organosilane is an efficient method to obtain an homogeneous dispersion of the clay in PMMA. Indeed XRD spectra indicate the formation of intercalated structure for silylated Del 72T and intercalated/exfoliated structure for organomodified Del HPS. SEM images of nanocomposites fractured surface show a good dispersion and distribution of montmorillonites in the polymer matrix. Finally TEM analysis of PMMA/silylated Del HPS nanocomposites shows MMT lamellae disorderly exfoliated in submicron domains homogeneously dispersed in PMMA. Nanocomposites glass transition temperatures are measured by differential scanning calorimetry and the thermal stability is measured by thermogravimetric analysis. They present an improvement of thermal properties respect to PMMA, the best result is obtained in presence of silylated Del HPS.

Key words: nanocomposites, montmorillonite, silylation, morphology, thermal properties.

## Introduction

Nanocomposite technology with layered silicate nanoclays as in situ reinforcement has been intensively investigated in recent years (Ray and Okamoto 2003; Tjong *et al.*, 2006; Utracki *et al.*, 2007; Viswanathan *et al.*, 2006). The presence of a limited amount of layered silicates (usually less than 5% wt) has a significant impact on the mechanical, thermal, fire and barrier properties of the polymer (Alexandre and Dubois, 2000; Ray and Okamoto, 2003; Giannelis *et al.*, 1998; Kojima *et al.*, 1993; Zhu *et al.*, 2001). To achieve these properties, mica-type layered silicates, are generally dispersed at the nanoscale in the polymer to yield the so-called nanocomposite. Montmorillonite (MMT) is the most commonly used layered silicate because of its natural occurrences and its properties (high cationic exchange capacity, high surface area, and large aspect ratio) (Tjong *et al.*, 2006; Utracki *et al.*, 2007). Many polymers, such as nylon (Usuki *et al.*, 1993), PS (Weimer *et al.*, 1999), PVC (Gong *et al.*, 2004) and so on are used to obtain novel polymer/layered silicates nanocomposites. PMMA/clay nanocomposites are also reported.

In particular addition of a clay to the PMMA matrix in the nano-scale dispersion can further improve the properties of the virgin polymer. PMMA/clay nanocomposites are of interest for improved thermal and mechanical properties, reduced flammability, reduced gas permeability, as well as their good potential to retain excellent optical clarity.

Nanocomposite can be prepared via several routes including *in situ* polymerization, bulk polymerization, solution blending, or melt blending in high-shear processing environments (extruder or

other molding equipment) (Ray and Okamoto, 2003; Alexandre and Dubois, 2000; Giannelis *et al.*, 1998).

Polymer-clay composites fall in three categories: *Microcomposites*, where the clay tactoids (finite stacks of clay platelets possessing their original platelet-platelet spacing) exist with no penetration of the polymer into the clay lamellae; *Exfoliated Composites* where the individual clay layers are dispersed as single platelets into a continuous polymer matrix; *Intercalated Composites* where the insertion of polymer into the clay structure occurs to swell the spacing between platelets in a regular fashion, regardless of the clay-to-polymer ratio.

In general, in natural-clay filled polymers with favorable thermodynamics for nanocomposite formation, the structure is characterized by a coexistence of exfoliated, intercalated and disordered layers. This behavior is common for most polymer/MMT nanocomposites, and typically the larger – in lateral size – MMT layers create intercalated tactoids, whereas the smaller layers tend to exfoliate. The mixed exfoliated/intercalated structure is intrinsic in MMT-based nanocomposites and originates from the chemical and size inhomogeneities of the MMT layers.

Many of the properties associated with polymer–clay nanocomposites are a function of the extent of exfoliation of the individual clay sheets that is influenced not only by the synthetic process (Zhao and Samulski, 2005; Truss and Yeow, 2006; Wang *et al.*, 2007) but also by the compatibility between clay and polymer.

Indeed inorganic layered silicates have to be modified to be dispersed into organic matrix. Their structure allows the introduction of specific organic functionalities by ionic exchange between metal cations present in the layers and organic cations and by covalent bond formation on the OH groups present at the broken edges of the clay platelets.

OH groups are often used for the preparation of stable organic derivatives of several silicates using silylating agents (Heinemann *et al.*, 1999; Wanh *et al.*, 2001; Wheeler *et al.*, 2006; Zhang *et al.*, 2006; Zhu *et al.*, 2007). The modification with organosilane may increase the compatibility between clays and polymeric matrix encouraging exfoliation and improving properties of polymer.

Many studies are reported about silylation of clays mainly focusing the attention on the synthe-

sis of organosilane-clays but seldom silylated silicates are introduced in a polymeric matrix to verify if this clay modification is an effective way to improve the nanocomposite processing and properties.

In our study we report the use of two silylated monmorillonites, a sodium montmorillonite (Dellite HPS) and an alkyl ammonium montmorillonite (Dellite 72T) modified by chloro(dimethyl)octadecylsilane to prepare PMMA nanocomposites filled with 1%, 3%, 5% wt of these MMTs.

The main objective of this work is to evaluate the effect of organomodified montmorillonite on clay dispersion and morphology and thermal properties of PMMA nanocomposites.

It should be evident that techniques are needed to characterize the nanocomposite with resolution at the nanoscale.

Due to its easiness and its availability X-Ray Diffraction (XRD) is most commonly used to probe the nanocomposite structure. However, the XRD can only detect the periodically stacked MMT layers; disordered (bunched together but not parallely stacked) or exfoliated layers are not detected. Only the intercalated structures give rise to XRD reflections. To be on the safe side, XRD should be always accompanied by TEM investigations, since generally there is a coexistence of structures and nanocomposite properties can be dramatically affected by the structures that are not manifested in the XRD.

The structural and morphological characteristics of PMMA nanocomposites are so verified by XRD, SEM and TEM analyses. Their glass transition temperature is measured by differential scanning calorimetry and the thermal stability is measured by thermogravimetric analysis.

## Materials and Methods

The fillers used in this study are sodium montmorillonite and organically modified montmorillonite purchased from Laviosa Chimica Mineraria S.p.A. The commercial name of the organoclays are, respectively, Dellite HPS and Dellite 72T (defined in the text as Del HPS and Del 72T), that is modified by dimethyl dehydrogenated tallow ammonium salt. Silylated Dellite HPS (indicated in the text as Del HPS-OS) and Del 72T (Del 72T-OS) are obtained as reported in a previous article

(Borriello *et al.*, 2010).

Methyl methacrylate, chloro-dimethyl-octade-cylsilane, p-toluenesulfonic acid, and 2,20-azo-bis(2-methylpropionitrile) (AIBN) are purchased from Aldrich Chemical Company.

Synthesis of nanocomposites by *in situ* polymerization involved the dispersion of the organoclays in methyl methacrylate, followed by free-radical polymerization initiated by the addition of AIBN. The monomer and desired amount of organoclay (1%, 3% or 5% wt) are mechanically mixed for 24 h at 40°C. The AIBN is then added to the mixture to initiate the polymerization which takes place at 100°C for 4 h. The composites obtained is kept overnight in an oven at 120°C to complete polymerization and to remove the remaining monomer.

The structural characterization is carried out by employing a Philips PW1880 3 kW Bragg–Brentano Diffractometer working with a Cu-target X-ray source (Cu-Ka1; k = 1.54 A°). The X-ray diffraction patterns are recorded in the 2θ angular range between 1.5° and 10° and by using an angular step-size of 0.01° (measurement time: 30 min). Simultaneous STA 449 F3 Jupiter of Netzsch is used for thermogravimetric and differential scanning calorimetry studies. The samples are heated, under dry nitrogen atmosphere, from 25 to 1000°C at a rate of 10°C/min.

The morphology of cross section of nanocomposites is examined by scanning electron microscopy (SEM, ZEISS EVO MA 15) equipped with EDS microanalysis. In order to prepare cross sectional samples exposing the interfacial structure of the nanocomposites, the samples were first frozen in liquid nitrogen, fractured and coated with carbon. Transmission electron microscopy (TEM) observations is performed using an FEI Tecnai F20 ST transmission electron microscope operated at 200 kV accelerating voltage. Thin sections (about 90 nm thick) of the specimens were cut at room temperature using a Pabish Top Ultra 170A ultramicrotome without inclusion in resin, and then deposited on copper grids. A low dose irradiation was used during the observations in order to avoid overheating of the samples.

## Results

Nanocomposites are successfully synthesized by *in situ* intercalative polymerization of Methyl methacrylate in presence of both silylated MMTs. Indeed changes in the interlayer distance of the clays after polymeritazion are observed by XRD analysis. For PMMA/Del 72T-OS nanocomposites XRD analysis shows a shift of d(001) peak at lower 2θ values (Figure 1), indicating expansion of the clay structure due to the polymer insertion into the silicate galleries. No influence is observed increasing clay concentration from 1 to 3% wt, while at 5% wt there is a shift of the diagnostic peak at lower 2θ value.

In PMMA/Del HPS-OS XRD spectra (Figure 2), the total absence of Del HPS-OS peaks for nanocom-
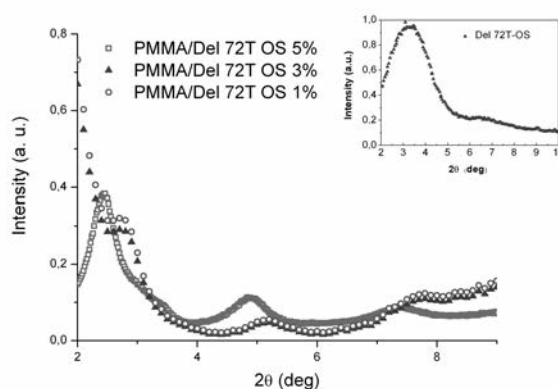


**Figure 1. XRD spectra of nanocomposites PMMA/Del 72T-OS containing 1,3,5 % of loading. In the inset d(0,0,1) peak of Del 72T-OS. We observe a shift of this peak at lower 2θ value in nanocomposites.**
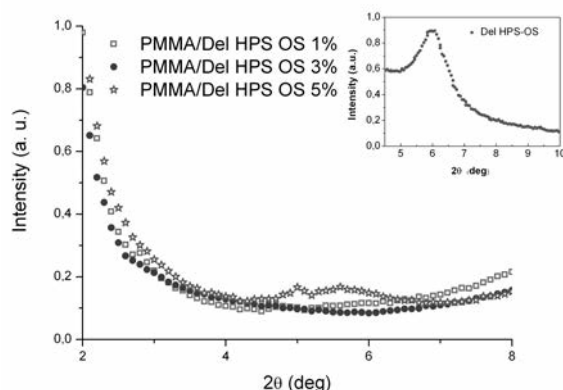


**Figure 2. XRD spectra of nanocomposites PMMA/Del HPS-OS containing 1,3,5 % wt of loading. In the inset d(0,0,1) peak of Del HPS-OS. We observe disappearance of this peak for nanocomposite at 1 and 3% wt and the presence of broaden peaks in 2θ range 4.5-6 for nanocomposites at 5% wt of Del HPS-OS.**

posites with 1% and 3% wt of clay suggest an exfoliated structure (or an interlayer distance lower than detection limit of measuring system) while the presence of broaden peaks in 2θ range 4.5-6 for nanocomposites with 5% wt indicates a probably mixture of both intercalated and exfoliated structures.

Figure 3 shows Secondary electron images of pure PMMA and its nanocomposites where clay particles do not appear at micro level. This indicates that the mineral domains are submicron, well-adherent to the polymer, homogenously dispersed in the polymer matrix and also that the PMMA is intercalated in the interlayer of clays. Furthermore is noted that the roughness of nanocomposites with silylated clay is lower than Del 72T nanocomposites one, in particular in the case of Del HPS-OS, that so shows the best compatibility with polymer matrix and the best distribution of the clay within PMMA.

The particles are much easily identified in TEM observations because of the difference in their atomic weight with respect to the matrix. TEM analysis (Figure 4) supports XRD and SEM data. Indeed PMMA/Del HPS-OS nanocomposite, containing 3 wt% of Del HPS-OS shows the formation of domains (Figure 4a) of montmorillonite that are generally below 1 μm size. These domains have irregular shape and are homogeneously distributed in the polymer matrix. All domains present disordered/exfoliated stacks of layers (Figure 4b) that have no periodic stacking and thus remain XRD silent. PMMA/Del HPS-OS nanocomposite at 1% wt of loading presents the same morphology (not shown in the article) but the domains are generally smaller (about 500 nm) and their concentration in the polymer matrix is lower with respect to the 3% wt sample.

The thermal properties of nanocomposites and homopolymers have been studied by DSC and TG analyses, which show that the glass transition temperature ($T_g$) and thenanocomposites decomposition temperature ($T_d$), measured to 5% wt loss, present higher values than homopolymer ones.

In Figure 5 percentage increase of $T_g$ versus filler weight percentage in PMMA nanocomposites is reported. The best results are realized in presence of Del HPS-OS, in particular $T_g$ of 3% by weight is 16.8% higher than homopolymer one.

Thermogravimetric analysis and percentage increase of $T_d$ versus filler weight percentage in PMMA nanocomposites are reported in Figure 6.
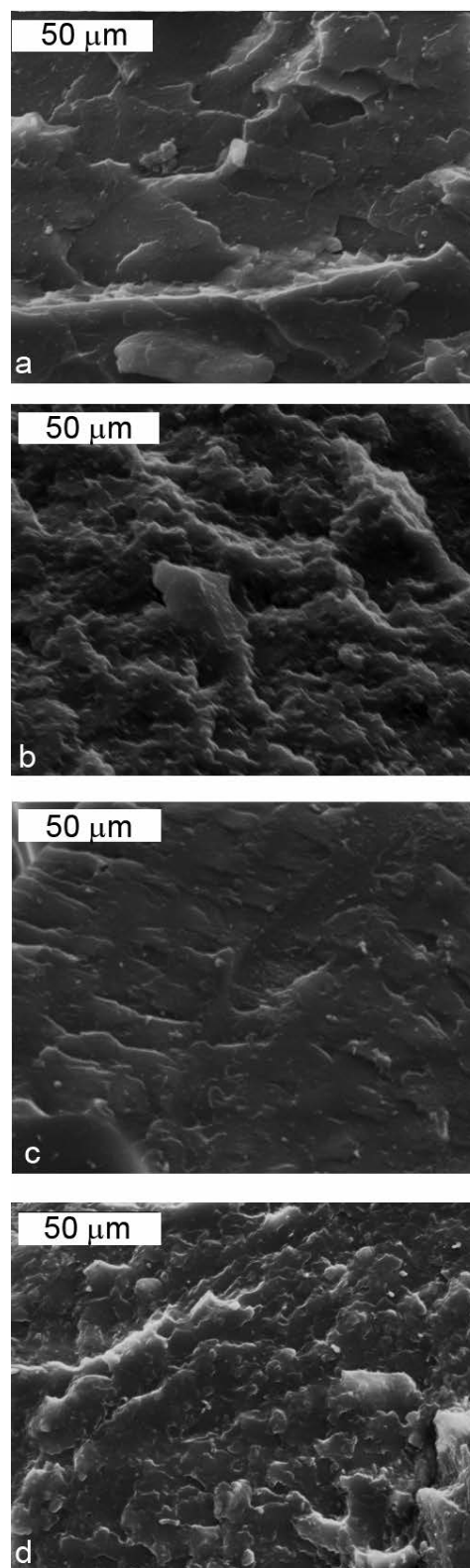


**Figure 3. Secondary Electron fracture section of a) PMMA, b) PMMA/Del 72T, c) PMMA/Del HPS-OS d) PMMA/Del 72T-OS 3% by weight**

For PMMA Del 72T-OS nanocomposites decomposition temperature shifts toward higher values as the amount of the filler increases.

PMMA/Del HPS-OS nanocomposites, show the best thermal stability in the presence of lower clay content. In the presence of 1% Del HPS-OS the $T_d$ is 17.4% higher than homopolymer one.

Nanocomposites with greater contents of clay have comparable $T_d$ values for both silylated dellites.
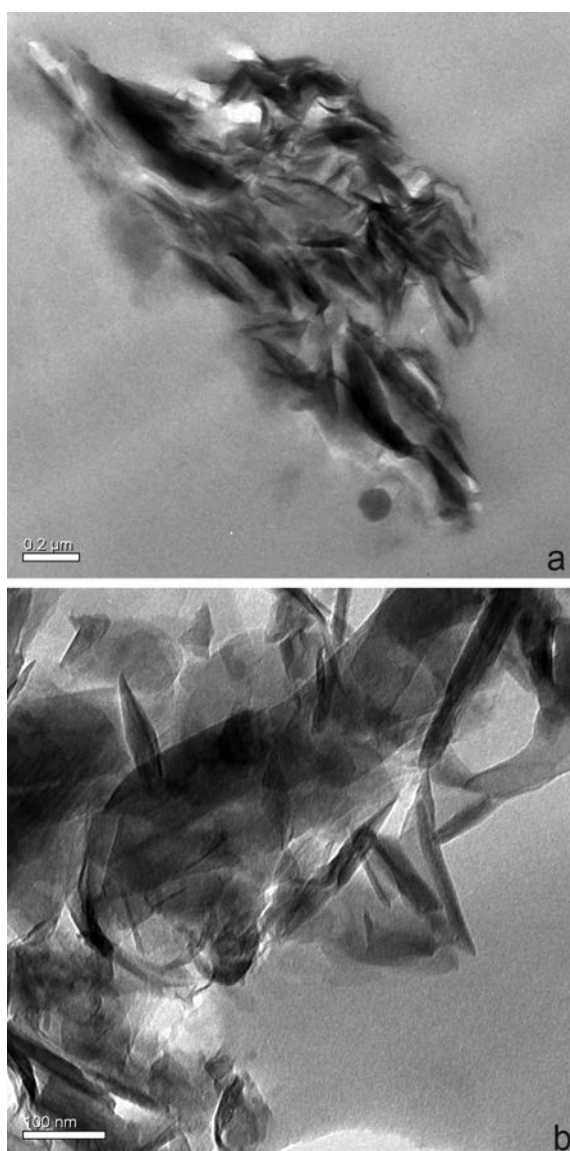


**Figure 4. Bright field TEM images of PMMA/Del HPS-OS 3% by weight. The montmorillonite is found to form domains as the one imaged in (a). The enlargement in b shows the disordered distribution of the layers inside the domains.**

## Discussion and Conclusions

Silylated dellites (Del HPS-OS and Del 72T-OS) are dispersed in PMMA to obtain nanocomposites with different structures, depending on the filler and the percentage of loading.

XRD and SEM nanocomposites characterizations show an intercalated structure for PMMA/Del 72T-OS at all percentage of loading and a possible exfoliated structure for PMMA/Del HPS-OS is observed at low clay loading (1% and 3% wt). Indeed TEM analysis of PMMA/Del HPS-OS at 1 and 3% wt shows the loss of periodic stacking of MMT lamellae which are disorderly exfoliated in submicron domains homogeneously dispersed in PMMA.

Instead as the content of Del HPS-OS is increased at 5% wt some silicate layers aggregated and ordered intercalated structures developed partially: in XRD characterization (Figure 2) weak broaden peaks in $2\theta$ range 4.5-6 are developed.

The discrepancy in the behavior of the two silylated clays is probably due to the different interactions PMMA clay in presence of the ammonium salt of Del 72T-OS. Probably in this case there is the formation of a long-range electrostatic interactions which hinder the complete exfoliation of the clay.

Nanocomposites with organosilylated montmorillonites have better thermal properties than PMMA and PMMA/Del 72T. It is observed an increase of glass transition temperature in all cases but the best result is realized in presence of Del HPS-OS. Indeed $T_g$ of PMMA/Del HPS-OS at 3% wt shows an
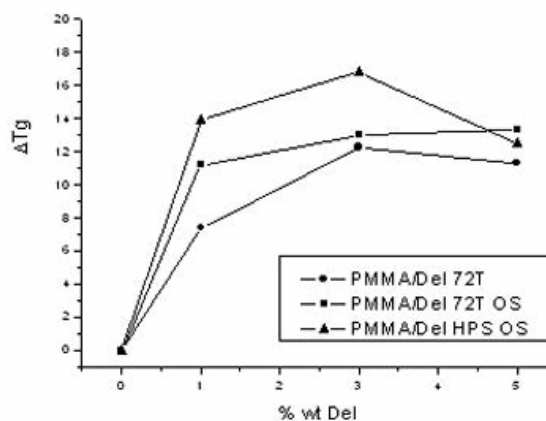


**Figure 5. Percentage increase of $T_g$ versus filler weight percentage in PMMA nanocomposites.**
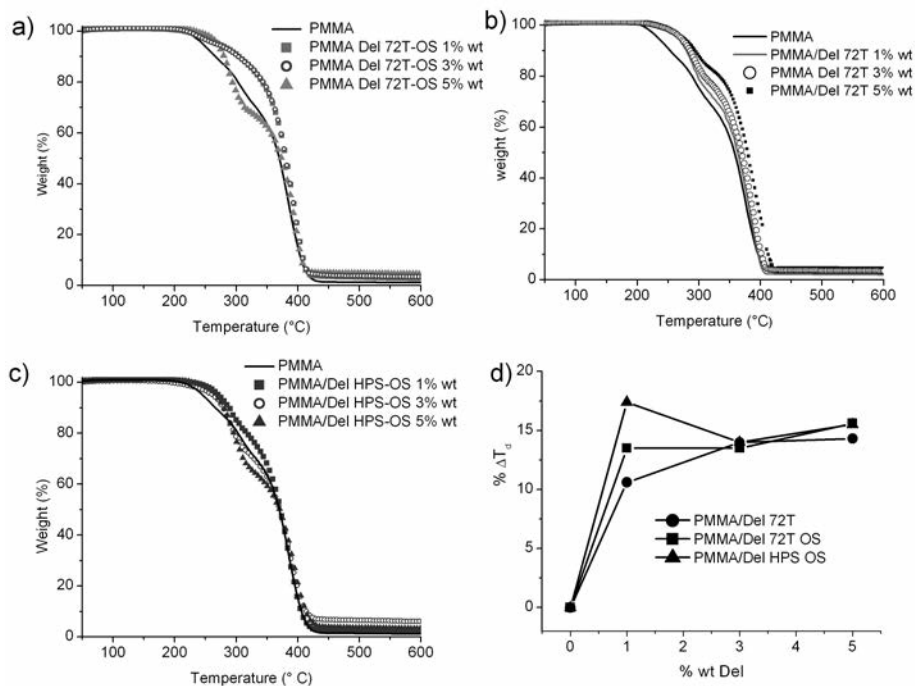
**Figure 6. Thermogravimetric analysis of nanocomposites a) PMMA/Del 72T-OS, b) PMMA/Del 72T, c) PMMA/Del HPS-OS, d) Percentage increase of $T_d$ versus filler weight percentage in PMMA nanocomposites.**

increase of 16.8% respect to PMMA one. The nanocomoposites glass transition temperatures tend to a plateau with the increase of the clay content. This result probably could be attributed to a lowering of polymer molecular weights due to the increasing viscosity of the reaction medium with montmorillonite clay loading. This inhibits the diffusion of initiator molecules and the chain propagation during polymerization (Greesh *et al.*, 2009; Fu and Qutubuddin, 2001; Usuki *et al.*, 1993).

Silylated MMTs improve also decomposition temperature. $T_d$ of PMMA/Del HPS-OS at 1% wt is 17.4% higher than PMMA one. The improvement in thermal stability due to the presence of clay is generally attributed to the formation of a char which hinders the volatilization of the decomposition products (Gilman *et al.*, 1997). The clay layers function as a diffusion barrier and delay the decomposition process, even without the enhanced char formation. We observe an increase of $T_d$ at higher percentage

of loading in PMMA/Del 72T-OS and a decrease of $T_d$ in PMMA/Del HPS-OS. We remember that thermal stability is influenced not only by clay loading but also by their structure: generally exfoliated nanocomposites have higher thermal stability than intercalated structures and nanocomposites with 1% of Del HPS-OS present a disordered/exfoliated structure. However, contradictory results are also reported (Giannelis *et al.*, 1996).

In conclusion we report the preparation of PMMA/silylated MMTs nanocomposites that shows an improvement of thermal properties. This result can be attributed to the better compatibility between silylated MMTs and polymeric matrix which favors an homogeneous distribution of the filler in the polymer and the separation of silicates lamellae during the polymerization process. Indeed structural and morphological characterizations confirm the formation of intercalated or disordered exfoliated nanocomposites.

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