Modification of Organosilicate with Silane Coupling Agents for Polymer Nanocomposites

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The effect of organofunctional silane coupling agents on the morpho-structural (XRD) and thermal (TGA) characteristics of the organically modified montmorillonite was examined. The modification of the organosilicates was carried out using organofunctional silane coupling agents in ethanol. The obtained results demonstrate the interaction of the silane-coupling agents with the organosilicate layers. The thermal stability and the basal spacing of the organosilicates increases with silane coupling agent's concentrations. Using organosilicate modified with functionalized coupling agent PP based nanocomposites with enhanced thermal stability and a more disordered lamellar structure were obtained.

Keywords: organically modified montmorillonite, silane coupling agents, polymer nanocomposites

In the last year, the interest for polymer/layered silicate (PLS) nanocomposites increased, because of their enhanced performances compared to classical polymers [1-3]. The most used layered silicate [LS] in the synthesis of nanocomposite is montmorillonite (mmt) based both on the high chemical and mechanical resistances and the low cost. Dispersing layered silicates in a polymer matrix is very difficult and therefore is necessary to achieve a high adhesion at the polymer matrix/ filler interface [4].

It is now well established that small amounts (of about 5%) of exfoliated mmt in polymers enhance their mechanical, thermal and other properties [5]. As it is known, clay layers can be easily exfoliated in hydrophilic polymers [6], but for organophilic polymer organic modification of their surfaces is needed [3].

Even after organic modification of the clays, non-polar (i.e. polypropylene - PP) or weak polar polymer (i.e. polystyrene - PS) do not wet the surface of clays. It is necessary to blend in a functionalized polymer such as maleated PP (PP-g-MA), in the case of PP, or alternate copolymer styrene-maleic anhydride, in the case of PS [7], that wets the modified clay surface more readily and is miscible with the bulk polymer. The interaction between the oxygen atoms on the clay surface and the polymeric compatibilizer must be stronger than the interaction between the clay surface and the surfactant in order to obtain delaminating of the silicates [8].

The coupling between the clay and the matrix can be further enhanced by silane treatment of the clay. Some silane move into the interlayer galleries and react with the gallery faces, leading to stronger intercalated structures [9]. Other silanes react with the edges alone and lead to a higher degree of exfoliation [10].

By reaction of organophylised layered silicate (OLS) with tetraethoxysilane (TEOS), in the presence of some co surfactants type C_6 - C_{12} aliphatique amines, "pillared" hybrids are forming [11]. The water necessary for the sol-gel process of TEOS is that of OLS hydratation. By this experimental solution the formation of the silica on the exterior faces of the OLS layers is avoided. After calcinations of these hybrids was observed that the co-template effect of the aliphatique amines is essential. The interlamelar distance is 14.9 Å for hexylamine and 23.4 Å for octadecylamine.   "Silica-clay heteromaterials"

were obtained by sol-gel process, in acid medium, of OLS with tetra-alkoxysilanes or alkyltrialkoxysilanes [12, 13]. Due to SiO_2 intercalation in OLS there is the possibility of delaminating maintaining the ionic exchange capacity of OLS. SiOH groups existing in the formed network of silica allow the subsequent grafting with aminopropyl-triethoxysilanes. This phenomenon allows the insertion of the $NH_3^+Cl^-$ active groups as ions exchanger, different from those obtained with OLS [12, 13]. Very interesting is that during the sol-gel processing the OLS and silanes mixture is under the form of gel in butanol, in the case of tetra-alkoxysilanes and under form of suspension in the case of alkyltrialkoxy-silanes [12, 13]. In basic medium there is the possibility of silica network grafting by sol-gel process of TEOS with the edges groups of Na-mmt layers [14].

In the presence of trialkoxysilanes the delaminating of the mmt layers is not achieving [15-20].

The high concentration of water allows sol-gel reaction between the silanes molecules and SiOSi- pillars are forming. In this case the mmt layers remain associated.

The effect of reaction of monoalkoxysilane with the surface silicate hydroxyl groups maybe the delaminating of the mmt layers [19, 20].

The reaction between the mmt and silanes performed in ethylic alcohol with delaminating of the OLS layers was demonstrated in many published articles [21].

The effect of silane coupling agents on the morpho-structural (XRD) and thermal (TGA) characteristics of the organically modified montmorillonite represents the essential aim of this work. Polypropylene/silane modified organosilicate nanocomposites were obtained.

Experimental part
Materials
Commercially available alkoxysilane structures bearing various organic functions were utilized as coupling agents, without modification: trimethylethoxysilane (TMES), triethoxymethylsilane (MeTES), tetraethylortosilicate (TEOS), triethoxyvinylsilane (VTES), triethoxyoctylsilane (OTES), 3(trimethoxysilyl)-1propanthiol (HSTMS), 3(triethoxysilyl)-propylamine (H_2NTES) (Merck Schuchardt), (3-glycidyloxypropyl) trimethoxysilane (GMPS), 3(trimethoxysilyl) propyl methacrylate (MPTS), (3-isocyanatopropyl) triethoxysilane (NCOTES) (Fluka), phenyltriethoxysilane (PTES) (Aldrich).

Organically modified montmorillonite (Southern Clay Products S.U.A.): Cloisite 20A, Cloisite 30B, and Cloisite 93A. These contain as organically components: dimethyl, diydrogenated tallow, quaternary ammonium chloride (Cl 20A), methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride (Cl 30B), methyl, diydrogenated tallow ammonium hydrogen sulfate (Cl 93A). Tallow composition is: fatty acids with ~65% C_{18}; ~30% C_{16}; ~5% C_{14}.

Absolute ethyl alcohol (EtOH) (CHIMOPAR-Romania) was used as received.

Polypropylene (PP), type MOPLEN HP 501 H (MFI: 2.1 g/ 10 min), grafted copolymer (PP-g-MA) (Polybond 3200-MAH index: 2.2; MFI: 120 g/10 min, Uniroyal Chem.Co.Inc.) utilized as compatibilization agent.

Treatment of organosilicate with silane
The treatment of OLS with silane was made at room temperature (25°C) by adding to the Cloisite powder, under stirring, an ethanol solution of silane derivatives with 16% silane. After 24 h, the solvent was removed at room temperature. For Cl 20A three concentrations of silanes were used: 5.5, 36 and 55-mmoles silane/100 g OLS, with 10/1, 1.5/1 and 1/1 water/ silane ratio (w/w). For Cl 30B and Cl 93A only maximum concentration was used: 55-mmoles silane/100g OLS. The silane modified organosilicates were dried at 4 h at 105°C before characterization.

Nanocomposites preparation
For PP nanocomposites preparation Cloisite 20 A was used. From the obtained silane modified silicates were selected those having substituents compatible with PP matrix. Therefore, Cloisite 20 A-OTES and Cloisite 20 A-MPTS were used for PP nanocomposites obtainment.

The nanocomposites were obtained in dynamical conditions, in a Brabender Plastograph, by using a masterbatch of PP with silane modified organosilicate, which was diluted with PP until the final concentration of 4 % mmt, at 190°C, 100 rpm, and 15 min. Thus were obtained the PP /compatibilizer agent/ silane modified organosilicate (100/14.3/6.1) nanocomposites: PP/PP -g-MA/ Cloisite 20 A; PP/PP -g- MA /Cloisite 20 A-OTES and PP/PP -g- MA /Cloisite 20 A-MPTS.

Characterization
The basal spacing, d_{001}, was determined by means of X-ray diffraction (XRD) on a DRON-2, 0 X-ray diffractometer with horizontal goniometer; it was utilized the CuKα radiation source (λ= 1.5418Å) filtrated with Ni for K_β component removing, in Bragg-Brentano system (by reflection); the patterns were automatically recorded at small angles (2θ = 2÷30 °).

The weight losses of the analyzed samples were determined by thermal gravimetric analysis (TGA), made with the THERMAL ANALYSIS 2100 Du Pont system at the 20°C/min heating rate, in air. The temperature at the maximum rate of weight loss was determined by DTA curves.

Results and discussions
The influence of the number of alkoxy groups on the silanes
The results obtained by TGA, DTA and XRD (table 1) reveal that for the alkoxysilanes modified Cloisite 20 A (concentration of silanes: 55-mmoles silane/100g OLS), compared with Cloisite 20 A, the thermal stability increases swith 4 - 12°C, the basal spacing slightly decreases (0.4 - 0.9 Å) and the half-maximum breadth, $\beta_{1/2}$ increases, suggesting a disorder in the stacking of the organosilicate layers. Regardless of the number of alkoxy groups, the silanes not intercalate between the silicate layers but interact with the organosilicate. This is confirmed by the values obtained for the half-maximum breadth, $\beta_{1/2}$. The hybrid obtained with MeTES has a more disordered structure than that obtained with TEOS and a higher thermal stability.

The influence of the length of the hydrocarbon substitute chain
The values for the d_{001} and the half-maximum breadth, $\beta_{1/2}$ presented in the table 2 reveal that the tri-alkoxysilanes modified Cloisite 20 A (concentration of silanes: 55-mmoles silane/100g OLS) presents more disordered structures ($\beta_{1/2}$ increase with 6 ÷ 14 % compared to Cloisite 20 A). The degree of the order in the structure and the basal spacing (d_{001}) increases with the increasing of the length of the hydrocarbon substitute chain.

The length of the hydrocarbon substitute chain does not influence the thermal stability of the tri-alkoxysilanes modified Cloisite 20 A.

Table 1
THE TGA AND XRD RESULTS FOR THE MONO, TRI AND TETRA-ALKOXYSILANES MODIFIED CLOISITE 20 A

Crt. No.	Sample	T_{vmd} (°C)	d_{001} (Å)	$\beta_{1/2}$ (°)
1	Cloisite 20 A	310	25.2	1.40
2	Cloisite 20 A - TMES	314	24.3	-
3	Cloisite 20 A - MeTES	322	24.8	1.59
4	Cloisite 20 A - TEOS	315	24.4	1.44

Note:
d_{001}: The basal spacing;
T_{vmd}: The temperature at the maximum rate of decomposition;
$\beta_{1/2}$: The half-maximum breadth.

Table 2
THE TGA AND XRD RESULTS FOR THE TRIALKOXYSILANES MODIFIED CLOISITE 20 A

Crt. No.	Sample	T_{vmd} (°C)	d_{001} (Å)	$\beta_{1/2}$ (°)
1	Cloisite 20 A - MeTES	322	24.8	1.59
2	Cloisite 20 A - VTES	318	25.5	1.53
3	Cloisite 20 A - PTES	320	28.0	1.27
4	Cloisite 20 A - OTES	320	27.3	1.48

Table 3

THE TGA AND XRD RESULTS FOR THE FUNCTIONALIZED ALKYLTRIALKOXYSILANES MODIFIED CLOISITE 20 A

Crt. No.	Sample	T_{vmd} (°C)	d_{001} (Å)	$\beta_{1/2}$ (°)
1	Cloisite 20 A - HSTMS	336	25.7	1.35
2	Cloisite 20 A - GMPS	325	28.2	1.15
3	Cloisite 20 A - MPTS	331	30.8	0.99

Table 4

THE TGA AND XRD RESULTS FOR THE ALKYLTRIALKOXYSILANES MODIFIED CLOISITE 20 A

Properties	Cloisite 20 A	Cloisite 20 A + alkyltrialkoxysilanes		
		mmol/ 100 g	MeTES	OTES
T_{vmd} (°C)	310	5.5	311	316
		36	312	317
		55	322	320
d_{001} (Å)	25.2	5.5	25.2	25.5
		36	24.7	27.1
		55	24.8	27.3
$\beta_{1/2}$ (°)	1.40	5.5	1.68	1.63
		36	1.68	1.53
		55	1.59	1.48

The influence of the functionalized non-hydrolysable groups: propanthiol, glycidyloxypropyl, propylmethacrylate

The results presented in the table 3 reveal that, compared to Cloisite 20 A, the thermal stability of the resulted products increases with 15 - 25°C (concentration of silanes: 55-mmoles silane/100g OLS). With GMPS and MPTS the basal spacing, d_{001}, increases from 25.2 Å for Cloisite 20 A, with 3 Å for GMPS and with approximate 6 Å for MPTS. These results demonstrate the adsorption of the silanes on the silicate surface and increasing of basal spacing, either because of the interactions with surface silicate hydroxyl groups, or probably because of some favorable interactions between the non-hydrolysable groups (glycidyloxypropy, propylmethacrylate) and alkyl chain of quaternary ammonium salt from Cloisite 20 A. The hybrids obtained with silanes have a more ordered structure than those obtained with Cloisite 20 A ($\beta_{1/2}$ decreases from 1.40° for Cloisite 20 A to 1.15° and 0.99° for GMPS and MPTS respectively). With HSTMS the basal spacing remains practically unmodified, but $\beta_{1/2}$ decreases suggesting some interaction between silicate and silane and an ordering of the layers. The hybrid with HSTMS presents the biggest thermal stability because of the stabilization effect of the thiol derivatives.

The influence of the alkoxysilanes concentration

The influence of silane derivatives concentration (Table 4) was estimated only for two derivatives with hydrocarbon substitute with eight carbon atoms (OTES) and with one carbon atom (MeTES). In both cases is observed that d_{001} value increases with trialkoxysilane concentration. The maximum value is obtained for OTES, the derivative with longer hydrocarbon chain. The basal spacing, d_{001}, increases from 25.2 Å for Cloisite 20A, with approximate 2 Å for Cloisite modified with 36 mmoles and 55 mmoles OTES/100g OLS. The values obtained for the half-maximum breadth, $\beta_{1/2}$: 1.40° - for Cloisite 20 A; 1.59 - 1.68° for Cloisite 20 A-MeTES and 1.48 - 1.63° for Cloisite 20 A-OTES suggests a disorder in the stacking of the organosilicate layers. The order in the structure increases with increasing of trialkoxysilane concentration. The hybrid obtained with MeTES has a more disordered structure than that obtained with OTES.

The value T_{vmd} increases with the silane derivative concentration.

Similar results were obtained with the other two

alkoxysilanes modified OLS (Cloisite 30 B and Cloisite 93 A - concentration of silanes: 55-mmoles silane/100g OLS). The thermal stability of the alkoxysilanes modified Cloisite 30 B and Cloisite 93 A is enhanced compared to Cloisite 30 B and Cloisite 93 A (fig. 1). The higher thermal stability was obtained for PTES modified Cloisite 30B (fig. 1a), either because of the interactions with the surface silicate hydroxyl groups, or probably because of some favorable interactions between the phenyl group and the 2-hydroxyethyl substitutes of the quaternary ammonium salt from Cloisite 30 B.
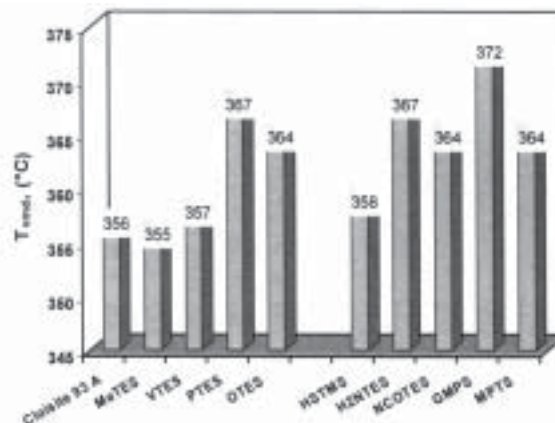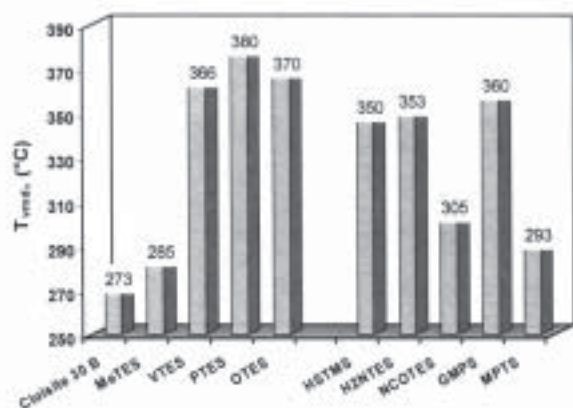

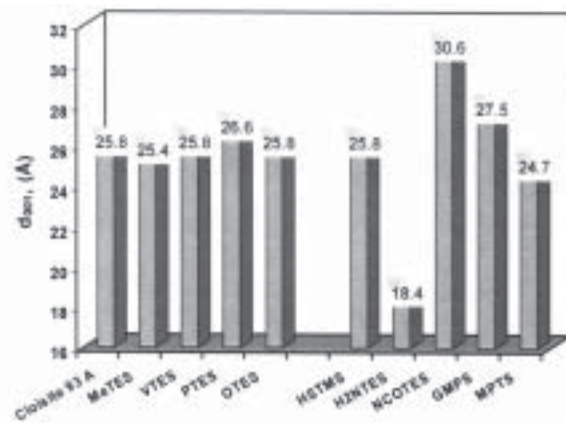Fig. 1 The thermooxidative stability of the alkoxysilanes modified Cloisite 30 B (a) and Cloisite 93 A (b)
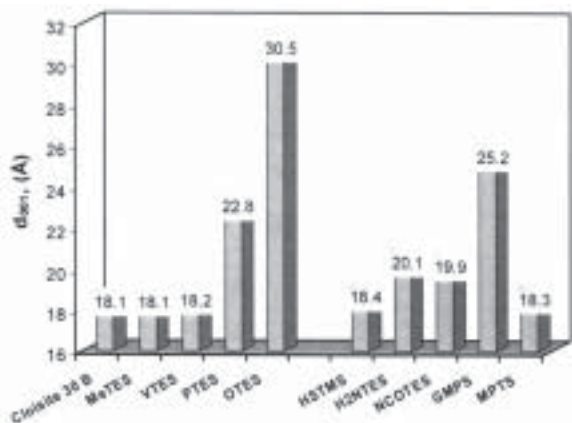
Fig. 2 The basal spacing, d_{001} for silane coupling agents modified Cloisite 30 B (a) and Cloisite 93 A (b)
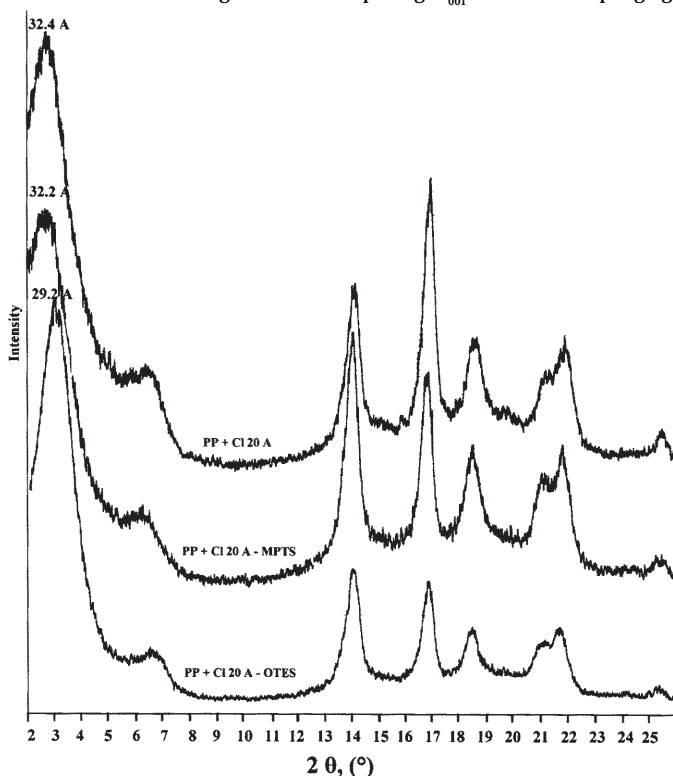

Fig. 3 X-ray diffraction patterns for the nanocomposites with Cloisite 20 A modified

The values presented in the figure 2a reveal that with silane coupling agents the basal spacing d_{001} increases from 18.1 Å for Cloisite 30 B, with approximate 5 Å for PTES, with approximate 7 Å for GMPS and with approximate 12 Å for OTES modified Cloisite 30 B. In the case of alkoxysilanes modified Cloisite 93 A (fig. 2b) the basal spacing d_{001} increases from 25.8 Å for Cloisite 93 A, with approximate 2 Å for GMPS and with approximate 5 Å for NCOTES modified Cloisite 93 A.

These results demonstrates the intercalation of the organical products between the organosilicate layers.

The existing of the organic substitutes from trialcoxysilanes on the OLS surface was emphasized by the XPS studies [22].

The X-ray diffraction patterns for nanocomposites obtained with the organosilicate modified with silane coupling agents, in presence of compatibilizer agent are presented in figure 3. Compared to the organosilicate modified with silane coupling agents, the basal spacing (d_{001}) for nanocomposites increases with approximate 1.5

Å for PP/PP -g- MA /Cloisite 20 A-MPTS, with approximate 2 Å for PP/PP -g- MA /Cloisite 20 A-OTES and with approximate 7 Å for PP/PP -g- MA/ Cloisite 20 A. For nanocomposites with Cloisite 20 A-OTES, the diffraction peak has a narrow and sharp shape compared to diffraction wider-rounded peaks for Cloisite 20 A-MPTS. This suggests a disorder in the stacking of the organosilicate layers. The nanocomposite obtained with Cloisite 20 A-MPTS has a more disordered structure than that obtained with Cloisite 20 A-OTES and with Cloisite 20 A.

The nanocomposites obtained with the modified organosilicate exhibit a better thermal stability, and the inorganically residue determined at 700 °C is with approx. 90 % greater (table 4). These results reveal the interaction between the polymer and the modified organosilicate: the stronger the polymer matrix-organosilicate modified interaction is, the greater the inorganically residue value is. The strongest interaction is obtained with MPTS modified Cloisite 20 A; the nanocomposite obtained shows the highest thermal stability also: the sample

Table 5

TGA RESULTS FOR PP/SILANE MODIFIED CLOISITE 20 A NANOCOMPOSITES

Sample	Decomposition temperature (°C)						T_{vmd} (°C)	R_{700} %
	I-st step		II-nd step		III-rd step			
	T_{id}	T_{fd} (°C) / % loss	T_{id}	T_{fd} (°C) / % loss	T_{id}	T_{fd} (°C) / % loss		
PP/ Cl 20 A	224	375/27	375	426/67	426	445/96	435(III)	2,4
PP/ Cl 20 A-MPTS	230	380/26	380	428/65	428	445/95	437(III)	4,5
PP/ Cl 20 A-OTES	232	374/24	374	423/66	423	437/93	429(III)	4,6

Note:

T_{id}: The initial temperature of decomposition;

T_{vmd}: The temperature at the maximum rate of decomposition;

R_{700}: The inorganic residue at 700 °C.

decomposition begins at 230 °C and decomposes with maximum rate at 437 °C.

Conclusions

The obtained results demonstrate the interaction of the silane-coupling agents with the organosilicate layers.

The modification of the organosilicate with silane coupling agents diminishes the interactions of the alkyl-ammonium chains with the silicate, creating potential sites for the interaction with the polymer matrix.

The thermal stability and the basal spacing of the organosilicates increases with silane coupling agent's concentrations. The degree of the order in the structure and the basal spacing (d_{001}) increases with the increasing of the length of the hydrocarbon substitute chain. The length of the hydrocarbon substitute chain does not influence the thermal stability of the tri-alkoxysilanes modified Cloisite 20 A.

Similar results were obtained also with the alkoxysilanes modified Cloisite 30 B and Cloisite 93 A.

Using organosilicate modified with functionalized coupling agent nanocomposites with enhanced thermal stability and a more disordered structure than that obtained with Cloisite 20 A were obtained.

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