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### Macromolecular Nanotechnology

# Heteropolyacid/saponite-like clay complexes and their blends in amphiphilic SEBS

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### ABSTRACT

A synthetic saponite-like clay, Sumecton SA (SSA), was self-assembled with 12-phosphotungstic acid (PTA) heteropolyacid for the preparation of new hybrid nanocomposites for proton exchange membranes. Thermogravimetric analysis (TGA) and Fourier transformed diffuse reflectance spectroscopy (DRIFT) measurements indicate the formation of robust PTA-SSA complexes. The Keggin structure of PTA is preserved within the complexes and is thermally stable up to 450 °C. The amount of PTA incorporated into the clay depends on the PTA-SSA weight ratio used for the complex preparation. PTA incorporation achieved is approximately 2-3 times the PTA content of most reported literature. However, higher PTA incorporation is accompanied by a significant loss of structural clay integrity. Low PTA-SSA weight ratios tend to preserve clay structure, but do not preclude its general amorphization generated by the PTA acidic treatment. PTA-SSA complexes present a low degree of order. Inorganic complexes were blended by melt extrusion with chemicallymodified styrene/ethylene-co-butylene/styrene block copolymer (SEBS). Poly(oxyethylene/oxypropylene)-grafted-SEBS is more efficient than maleic anhydride-grafted-SEBS at dispersing PTA-SSA complexes. For both nanocomposite systems, nanoparticles' size varies between 30 and 300 nm.

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### 1. Introduction

The incorporation of inorganic species into organic polymeric systems leads to hybrid (organic-inorganic) nanocomposites. Polymeric nanocomposites (PNCs) have been an area of intense industrial and academic research for the past 20 years [1,2]. They represent an alternative way to provide value-added properties, such as enhanced mechanical strength, barrier properties and fire resistance, and also to add or increase functionality of the polymer matrix (magnetic, light emitting, ionic properties, etc.).

Heteropolyacids (HPAs), also known as polyoxometalates (POMs), are early-transition-metal oxygen anion clusters that exhibit very strong Brönsted acidity (close to the superacid region); they are also efficient oxidants, exhibiting fast reversible multielectron redox transformations [3,4]. Their acid-base and redox properties can be varied over a wide range by changing the chemical composition [5]. The Keggin-type HPAs have received the most attention due to the ease of preparation and strong acidity [4,6]. Solid HPAs possess a discrete ionic structure comprising fairly mobile basic structural heteropolyanions and countercations (H<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, H<sub>5</sub>O<sub>2</sub><sup>+</sup>, etc.). This unique structure exhibits extremely high proton mobility, while heteropolyanions can also stabilize cationic organic intermediates. Furthermore, HPAs have a very high solubility in polar solvents and a fairly high thermal stability. These properties render HPAs potentially promising acid, redox, and bifunctional catalysts in homogeneous and heterogeneous systems that may require extreme environments [5].

The mobility of Keggin anions even in dehydrated HPA crystals makes them the most preferred structures for

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catalysis than any other form of structures [7,8]. They have been utilized in several new industrial processes, such as vapor-phase oxidation of methacrolein into methacrylic acid, hydration of olefins (propene and butene), polymerization of tetrahydrofuran [9], etc. They also have been used as photocatalysts for the degradation of organic pesticides [10]. Their redox properties and high electron density make them ideal candidates for use as inorganic functional materials in molecular electronics [11], sensing [12], as photochromic or electrochromic materials [13,14], and in energy storage applications [15].

Supported HPAs are important particularly for catalysis applications since bulk HPAs have a low specific surface area  $(1-5 \text{ m}^2/\text{g})$  [5]. Inorganic solids possessing high surface areas such as clays, zeolites, metal oxides, active carbon, acidic ion-exchange resin, have been widely used as suitable support materials for HPAs. More recently, HPAs have been supported on carbon nanotubes to prepare more efficient electrodes for electrochemical capacitors [16].

In nanocomposite systems, HPAs have been widely used to prepare anhydrous proton conducting electrolytes [17]. In recent studies [18], it has been demonstrated that the high proton conductivity of HPAs can be translated into impressive currents in a proton exchange membrane fuel cell (PEMFC) system at room temperature with no external humidification. One of the major concerns in the use of HPAs in open electrochemical systems is their leakage during operation. For the development of stable HPA-based electrolytes, they have been covalently attached to polymer backbones by sol-gel methods [19,20], embedded in sol-gel hybrids [19,21], or immobilized on zeolites [22,23], silica [24], and clays [25]. HPA-polymer nanocomposites have also been used for the preparation of photochromic thin films [26,27].

This paper describes the preparation and characterization of HPA-clay complexes as well as their incorporation by melt extrusion in styrene/ethylene-co-butylene/styrene block copolymer (SEBS), unmodified and grafted with poly(oxyethylene/oxypropylene) (SEBS-g-J) and maleic anhydride (SEBS-g-MA).

Phosphotungstic acid (PTA) was selected for this study, because it is a strong Brønsted heteropolyacid with a high thermal stability and an interesting intrinsic proton activity (0.18 S/cm in its hydrated crystalline form  $(H_3PW_{12}O_{40} \cdot 29H_2O))$  [18]. The basic structural unit of PTA is the Keggin anion whose schematic representation is shown in Fig. 1. The polyhedral structure of PTA consists of a central PO<sub>4</sub> tetrahedron surrounded by 12 WO<sub>6</sub> octahedra. The octahedra are self-assembled in groups of three, sharing common edges, thus forming (W<sub>3</sub>O<sub>13</sub>) tritungstic units. Four types of oxygen atoms are present in the Keggin structure. O<sub>a</sub> atoms are oxygen connected to the PO<sub>4</sub> tetrahedrons while O<sub>b</sub> and O<sub>c</sub> oxygen atoms link the tungsten atoms from two distinct W<sub>3</sub>O<sub>13</sub> units or from the same unit, respectively. The terminal oxygen atoms, Od, are only bonded to one tungsten atom.

A saponite-like clay, Sumecton SA (SSA), was used for the complexation with heteropolyacids. Sumecton is a trioctahedral smectite clay (Fig. 2) that possesses negatively charged layers neutralized by positively charged counter ions (Na<sup>+</sup> and Mg<sup>2+</sup>). For better compat-



Fig. 1. Schematic representation of the 12-phosphotungstic heteropolyacid Keggin structure.



Fig. 2. Schematic representation of the Sumecton SA smectite structure.

ibilization within polymeric systems, small cations found in the interlayer are most of the time substituted by organic (cationic) surfactants giving the clay a hydrophobic character. In contrast, ion exchange by inorganic counter ions is less common but yet, few studies demonstrated the formation of inorganic-inorganic complexes as, for instance, HPA intercalation into the clay layers [28–31].

The main focus in the preparation of HPA-containing nanocomposites will be the control of their morphology to maximize the interface between the inorganic complex and the organic polymer matrix. It is important to avoid shielding the Keggin structure by large clay aggregates. For this reason, it is essential that the heteropolyacid interacts with exfoliated clay and that the size of aggregates remains as small as possible.

### 2. Experimental part

#### 2.1. Materials

12-phosphotungstic acid was obtained from Aldrich in pure form (99.995%). Sumecton SA a synthetic clay with a saponite-like structure  $((Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03}) O_{20}$  $(OH)_4^{0.77}$ . (Na<sub>0.49</sub>Mg<sub>0.14</sub>)<sup>+0.77</sup>; cation exchange capacity (CEC) of 99.7 meq/100 g), was kindly provided by Kunimine Industries Co. (Japan) and used without further purification. Water used for the dispersion of the clays was purified by a Millipore Milli-Q system (resistance 18.2 MΩ). Styrene–(ethylene–butylene)–styrene triblock copolymer (SEBS) grade used is G1652 supplied by Kraton Polymers contained 30 wt.% styrene and has an average molecular weight  $M_w$  = 125,000. Polystyrene-*b*-(ethyleneran-butylene)-*b*-polystyrene maleic anhydride copolymer (SEBS-g-MA) with ~30 wt.% of styrene and ~1.8 wt.% of grafted maleic anhydride was purchased from Aldrich. Jeffamine XTJ 506 was obtained by the courtesy of Huntsman Holland BV. Jeffamine XTJ 506 is an amino functional oligomeric monoamine based on random distribution of ethylene oxide (EO)/propylene oxide (PO) units (EO/PO = 19/3, Mn ~1000 g mol<sup>-1</sup>). Anhydrous toluene and 2-propanol were purchased from Aldrich.

### 2.2. Preparation and characterization of materials

### 2.2.1. Preparations of the clay and clay-heteropolyacid dispersions

SSA was sonicated in water (400 mL) at a concentration of 0.6% (w/w) for 4 h at 60 °C. The suspension was found to be very stable since no visible flocculation was apparent in at least the following 24 h. To prepare the PTA-SSA complexes, the clay dispersion was added to a concentrated aqueous solution (100 ml) of 12-phosphotungstic acid preheated at 60 °C. Relatively high PTA-SSA weight ratios were used, namely 2, 3 and 5. The large amount of PTA used in the mixture (174 mmol/ 100 g of Sumecton SA for a weight ratio of 5) was higher than the cation exchange capacity of the SSA (99.7 meg/ 100 g). Consequently, most Na ions are expected to be exchanged. The dispersion was sonicated at 60 °C for 1 h and, again a stable aqueous suspension was obtained. Water was rotary evaporated and the obtained white powder was further dried under vacuum at 125 °C for 1 h. The complex was washed by stirring vigorously two times with 100 mL of methanol for 30 min, filtered and dried overnight at 60 °C. A white powder was obtained after the final washing and drying steps.

### 2.2.2. Chemical modification of SEBS

The reactions were performed in the same conditions than described elsewhere [32]. Toluene and 2-propanol were transferred directly from Sure/Seal bottles to the reactive flask via a cannula system. Precursor polymer and polyether (Jeffamine XTJ 506) were dissolved at 80 °C for 1 h and then the temperature was increased to 110 °C for 4 h under slightly positive argon pressure. Reaction of the precursor polymer, SEBS-g-MA (30 g, 0.10 mol) was performed with equimolar amounts (6 g, 0.10 mol) of Jeffamine in a homogeneous toluene/2-propanol (125/14 v/v) solution. After cooling, the organic phase was washed three times with 100 mL of water. rotary evaporated and then dried at 60 °C in vacuo. It was noted that, (amphiphilic) polyether-containing SEBS redissolved easily after drying in dry toluene indicating that chemical modification precludes any cross-linking. The reaction yield was 49%. The content of grafted Jeffamine was obtained from the ratio of the integrated <sup>1</sup>H NMR peak of the methyl units at 0.93 ppm and the methylene groups at 3.52 ppm. The weight amount of Jeffamine was estimated to 5.9% (w/w).

### 2.2.3. Nanocomposite preparation

Samples were prepared on a MiniLab Rheomex CTW5 laboratory twin-screw extruder equipped with a cooling circulation for air and liquid operating at 200 °C, 100 rpm and under nitrogen atmosphere. A recirculation time of 5 min was used to ensure good melt-blending of the different components.

### 2.3. Characterization

### 2.3.1. NMR Spectroscopy

Spectra were obtained with a 500-MHz Bruker AVANCE 500 spectrometer. <sup>1</sup>H chemical shifts,  $\delta$ , are given in ppm relative to the solvent residual resonance fixed at <sup>1</sup>H: 2.03, 6.98 (H-1), 7.00 (H-3), 7.09 (H-2) ppm for deuterated toluene (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>).

# 2.3.2. Fourier transformed diffuse reflectance spectroscopy (DRIFT)

Infrared spectra were recorded on a Nicolet Magna 860 FT-IR from Thermo Electron Corp. (DTGS detector, resolution 2 cm<sup>-1</sup>, accumulation of 128 scans). Diffuse reflection was measured with a Praying Mantis accessory from Harrick Scientific Corp. Samples were dried at 125 °C, grounded very finely with dried KBr and dried again under vacuum at 60 °C for 2 hours and finally stored under dried nitrogen atmosphere for 2 days before recording the spectra. Diffuse reflectance spectra were converted to absorbance by the Kubelka-Munk method. Maxima were obtained after smoothing the data by the Fourier function. DRIFT experiments were also carried out for complexes heated overnight at 110 and 280 °C (under dynamic vacuum), 450 °C (under static vacuum) and 600 °C (under air atmosphere). PTA was dried at 60 °C under vacuum overnight. Infrared (IR) spectra of nanocomposites were measured by transmission on thin films (50  $\mu$ m) obtained by compression moulding using a Carver press at 195 °C for 10 min under a maximum pressure of 1.5 tons.

### 2.3.3. Energy-dispersive X-ray spectroscopy (EDX)

Elemental characterization of the clay (SSA), heteropolyacid (PTA) and PTA–SSA complexes were performed by EDX using a Hitachi S-4700 scanning electron microscope. Microanalysis was performed at three points using a voltage of 10 KeV. Absorption spectra were collected with an Oxford spectrometer (Model 7200) with a detector area of 20 mm<sup>2</sup> and a resolution of 136 eV at 5.9 Kev.

### 2.3.4. Scanning electron microscopy (SEM)

FEG-SEM Hitachi S-4700 microscope was used at low voltage for examination of the morphology of selected PTA–SSA complexes and nanocomposites. Clay and complexes were dried overnight at 60 °C under vacuum and then dispersed in diluted methanol  $(10^{-3} \text{ g/L})$  by sonication for 30 min. Drops of the dispersion were deposited on a porous polycarbonate membrane (SPI<sup>®</sup>, pore size = 0.22 µm), air-dried, coated with Pt before observation. Nanocomposite samples were cryofractured in liquid nitrogen. As samples are characterized by domains with different atomic compositions and therefore different sig-

nal magnitudes, observations of backscattered electron images were also performed on platinum-sputtered surfaces at 10 kV acceleration voltage and 10 mA. Secondary electron images were also obtained for nanocomposites at 1 kV and 10 mA.

### 2.3.5. Transmission electron microscopy (TEM)

TEM observations of extruded PTA–SSA containing nanocomposites were performed on unstained cryo-ultramicrotomed sections using JEOL JEM-2000FX operating at 160 KV.

### 2.3.6. Atomic force microscopy (AFM)

AFM analysis of PTA–SSA containing nanocomposites was also performed on cryo-ultramicrotomed sections using tapping mode with a Nanoscope IV controller (Beeco) operated under ambient atmosphere. The tips had spring constants between 21 and 78 N m<sup>-1</sup> and oscillation frequencies between 250 and 390 KHz.

### 2.3.7. X-ray diffraction (XRD)

SSA, PTA and PTA-SSA complexes were analyzed by XRD to evaluate their structural characteristics. The dspacings were determined from the diffraction peaks using Bragg's relation,  $d = \lambda/(2 \cdot \sin \delta)$ . Samples were previously dried at 60 °C, gently pressed for the analysis but exposed to the moisture of air during the experiment. The first set of data covered angles between 3° and 70°. The diffraction patterns were recorded on a Bruker Discover 8 diffractometer operating at 40 kV, 40 mA with Cu K $\alpha$  radiation in reflection mode using a horizontal Bragg Brentano focussing geometry. For a greater precision in the measurement of the Bragg spacing of clay and selected complexes as well as investigation of the heated complexes for which small amounts of samples were available, experiments were carried out in transmission mode over a range between  $2^{\circ}$  and 15°. The samples were placed in 1.5 mm i.d. Lindemann capillaries (Charles Supper) then sealed. The diffraction patterns were recorded by a Bruker AXS two-dimensional position-sensitive wire-grid detector. The sampleto-detector distance was fixed at 10 cm and collimation was obtained by a graphite monochromator and a 0.8 mm pinhole. No background correction was performed on the profiles obtained. Maxima observed were obtained after smoothing the data using the Savitsky Golay algorithm.

# 2.3.8. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

Thermal analysis was performed using a Setaram TG96 (ATG Thermogravimetric analyzer), operating under constant argon flow (50 mL/min) and a heating rate of  $10 \,^{\circ}$ C/min over a temperature range varying between 25 and 1000 °C.

### 3. Results and discussion

# 3.1. Structural characterization of powdered PTA–SSA complexes

Elemental characterization and semi-quantitative composition of heteropolyacid–clay complexes were obtained by EDX. Table 1 compares the data obtained for SSA and PTA as well as PTA–SSA complexes prepared at different weight ratios. EDX spectra are presented in Fig. 3. The PTA spectrum (Fig. 3a) is characterized by peaks which are assigned to elements W, O and P. The W peaks are easily identified at 1.38, 1.79, 8.4 and 9.68 keV while those corresponding to both P and O are also visible at 0.52 and 2.03 keV respectively. In the SSA spectrum (Fig. 3b),



**Fig. 3.** EDX spectra for (a) PTA; (b) Sumecton SA and (c) PTA–SSA complex prepared at a weight ratio of 5.

### Table 1

Elemental composition obtained from semi-quantative EDX analysis for the heteropolyacid (PTA), the clay (SSA) and their complexes (PTA–SSA) formed at different weight ratios (*r*). Calculated data are given in parenthesis.

| Materials    | Elemental composition (w/w%) |           |             |           |             |             |           |     |      |            |  |
|--------------|------------------------------|-----------|-------------|-----------|-------------|-------------|-----------|-----|------|------------|--|
|              | 0                            | Na        | Mg          | Al        | Si          | W           | Р         | S   | Si/W | Si/Al      |  |
| SSA          | 45.3 (49.9)                  | 3.9 (1.9) | 16.5 (19.3) | 2.6 (2.9) | 29.4 (25.5) | -           | -         | 2.5 | -    | 11.3 (8.8) |  |
| PTA-SSA(r=2) | 34.2                         | -         | 8.5         | 1.6       | 15.8        | 39.3        | 0.6       | -   | 0.40 | 9.9        |  |
| PTA-SSA(r=3) | 31.9                         | 0.3       | 4.7         | 1.3       | 14.1        | 48.6        | 1.2       | -   | 0.29 | 10.8       |  |
| PTA-SSA(r=5) | 33.7                         | -         | 3.1         | 0.9       | 8.5         | 52.3        | 1.5       | -   | 0.16 | 9.4        |  |
| PTA          | 18.8 (22.2)                  | -         | -           | -         | -           | 79.6 (76.6) | 1.6 (1.1) | -   | -    | -          |  |

the usual distinct peaks are observed for O, Si, Al, Mg and Na at 0.52, 1.74, 1.49, 1.26 and 1.04 keV, respectively. S appears also as an impurity (at 2.31 keV) in the SSA spectrum, but disappears after the clay was dispersed and treated with HPA.

The spectrum of the clay complex (prepared from a solution which contained a PTA-SSA weight ratio of 5 and washed extensively in methanol (Fig. 3c)) unambiguously shows the presence of P, Si and W signals. Elemental analysis (Table 1) confirms the changes in the complex composition. A significant amount of W is incorporated in the complexes, depending on the PTA–SSA weight ratio. High weight ratios allow the incorporation of higher W amounts and at a weight ratio of 5, approximately 52 wt.% of W is incorporated. This accounts for approximately 25 mol% clay coverage, and it is approximately 2-3 times the PTA content of most reported literature [33-35]. As expected, the immobilization of W onto the clay results in a marked decrease in the Si/W weight ratio. The Si/Al weight ratio (see Table 1) is apparently not significantly affected by the amount of PTA used for the preparation thereby confirming that the smectite structure of the clay is not affected by the PTA treatment. Similar results were obtained for PTA-SSA weight ratios 2 and 3. On the other hand, the disappearance or the marked decrease in the intensity of both the Na and Mg peaks confirms that a large fraction of counter ions (Na<sup>+</sup> and Mg<sup>2+</sup>) found primarily at the interlayer region are exchanged as the complex is formed.



**Fig. 4.** X-ray diffractograms of (a) PTA; complexes prepared at PTA–SSA weight ratios of (b) 5; (c) 3; (d) 2; (e) pristine (non-sonicated) SSA; (f) sonicated SSA (same conditions as for complex preparation).

The effect of the acidic treatment on the structure of the SSA clay by PTA can be analyzed by powder X-ray diffraction (XRD). Diffractograms of pure SSA and PTA as well as complexes self-assembled at various PTA–SSA weight ratios are shown in Fig. 4. The associated data is given in Table 2. For the pristine (non-sonicated) SSA clay, diffractogram (Fig. 4e) shows a rather broad Bragg peak associated to the (001) reflection at  $2\theta = 6.95^{\circ}$ . The derived basal spacing, 12.7 Å, is in agreement with other studies [36]. Other major reflections observed at larger angles ( $2\theta = 19.4, 27.9, 34.8$  and  $60.5^{\circ}$ ) reveal the crystalline order existing within the layers. The medium (060) reflection seen at  $60.5^{\circ}$  (1.53 Å) reflects the trioctahedral nature of the SSA clay [37].

The diffractogram of the sonicated SSA clay (Fig. 4f) shows some clear differences with the one obtained for the pristine SSA. The two reflections seen at  $2\theta$  = 7.66 and 27.9° are much more intense while the others are considerably broadened. On the other hand the numerous reflections observed for the pure PTA acid reveal its crystalline nature (Fig. 4a) at room temperature.

Complexes formed at low PTA–SSA weight ratios (2 and 3) give similar diffractograms (Fig. 4c and d). However, it is interesting to note that although the intensity of the (001) reflection decreases in comparison to the sonicated SSA, the peak remains relatively intense, thus inferring that some long range periodicity along the platelet direction is maintained. However, diffractograms in the wide-angle region appear to be noticeably modified after PTA treatment, even at low PTA–SSA weight ratios. Broad reflections in the range 12–40° are observed for the clay complexes and the (060) reflection peak is barely visible (Fig. 4c and d). These features suggest a loss of crystalline order or an increase of the amorphous behaviour in the clay's in-plane direction.

A small shift to a higher  $2\theta$  in the (001) or basal reflection is also observed for clays treated with PTA. Although this increase is not significant, it does suggest that a decrease in the clay's *d*-spacing, and therefore a decrease in the interlayer distance, has taken place. The decrease in the interlayer region appears to increase with increasing PTA weight ratio (Table 2). Previous work has shown that upon complexation of the activated clay material with HPA, the interlayer compensating cations are partly exchanged by protons of the PTA hereby, reducing the interlayer distance, and hence, the basal spacing measured by XRD [25].

Fourier transformed diffuse reflectance spectrometry (DRIFT) spectra of PTA, SSA and PTA–SSA complex formed in excess of PTA (PTA–SSA weight ratio of 5) attest the

### Table 2

20 angles and Bragg spacings,  $d_B$  (first reflections), obtained from the X-ray reflection data (unless otherwise mentioned) for the clay (SSA) and its complexes (PTA–SSA) formed at different weight ratios (r).

| Materials       | SSA (pristine)    | SSA (sonicated) | PTA-SSA |       |       |  |
|-----------------|-------------------|-----------------|---------|-------|-------|--|
|                 |                   |                 | r = 2   | r = 3 | r = 5 |  |
| 2θ (°)          | 6.95 <sup>a</sup> | 7.66            | 7.34    | 7.66  | 8.50  |  |
| $d_{\rm B}$ (Å) | 12.7              | 11.5            | 12.0    | 11.5  | 10.4  |  |

<sup>a</sup> Obtained in transmission mode (see Experimental part for details).

inclusion of PTA into the clay (Fig. 5). The spectrum shown in Fig. 5a is typical for PTA. It is characterized by four major bands at 1081, 986, 892 and 812 cm<sup>-1</sup> which correspond to P-O<sub>a</sub>-W, W=O<sub>d</sub>, W-O<sub>b</sub>-W and W-O<sub>c</sub>-W pure or mixed (bending/stretching) vibration modes, respectively [38]. Two other bands with weaker intensity were also found at 596 and 527 cm<sup>-1</sup>, the former being assigned to the O-P-O vibration mode of the PTA moiety [39]. The spectrum shown in Fig. 5c is typical for pure SSA clay. The peaks observed at  $\sim$ 1006, 659 and 462 cm<sup>-1</sup> are characteristic vibration bands of the tetrahedral silicate sheets in the clay structure [40]. The broad and intense band observed at 1006 cm<sup>-1</sup> can be assigned to Si–O–Si stretching vibration mode. The presence of another band at  $\sim$ 813 cm<sup>-1</sup> is consistent with that reported on Saponite clay and it is believed to be also related to Si-O vibration [41,42]. The spectral features of PTA-SSA complex (Fig. 5b) in the 1200–400 cm<sup>-1</sup> region are, however, quite different from those of the two pure components. The major feature of the complex spectrum concerns the shape of the strong Si-O-Si vibration envelop which is clearly affected by the acidic PTA treatment. The change appears as a broad shoulder, near  $1290 \text{ cm}^{-1}$  (Fig. 5b) but the subtraction of the clay spectrum from that of the complex (see the inset, Fig. 5d) allows a better visualization of the position of this new peak, broadened and shifted to higher wavelengths near 1185 cm<sup>-1</sup>. Similarly, the peak seen at 462 cm<sup>-1</sup> for the complex presents a broad shoulder at  $\sim$ 530 cm<sup>-1</sup> (Fig. 5d).

Background corrected spectrum of the clay complexes in Fig. 6 also shows the dramatic effect of using high PTA



**Fig. 6.** DRIFT spectra after background subtraction measured for (a) PTA; (b–d) PTA–SSA complexes; (e) exfoliated SSA. Complexes were prepared at a PTA–SSA weight ratio of 5 (b), 3 (c), 2 (d).

concentration (PTA–SSA weight ratio of 5) on the crystalline integrity of the SSA clay. Indeed, such asymmetric broadenings, reported elsewhere for acidified (HCl) Sapo-



**Fig. 5.** DRIFT spectra measured for (a) pure PTA; (b) PTA-SSA complex (prepared at weight ratio of 5); (c) pure SSA (non exfoliated). The inset shows the 1125–400 cm<sup>-1</sup> region of the pure PTA spectrum (A; dashed line) and the PTA-SSA complex spectrum after subtracting SSA spectrum (D; in solid line). In the inset, vibration wavenumbers of PTA and the new bands visible in the complex spectrum. Asterisks indicate the new bands observed in the PTA-SSA complex.

nite clay [41,43], have been associated with the vibration of Si–O–Si and Si–O–Mg bonds in amorphous silicate that originate from the partial destruction of the ordered crystalline tetrahedral sheet by the PTA acidic treatment. This confirms the coexistence of an ordered tetrahedral silicate structure and amorphous silica phases as discussed earlier by XRD (Fig. 4).

In contrast to PTA and natural clays complexes reported in the literature [25], the bands found at 534, 593, 809, 880, 958, 1077 cm<sup>-1</sup> (see Fig. 5b and d) indicate that the PTA in the complexes under investigation have preserved their Keggin-like structure. Indeed, no significant shift (±1 cm<sup>-1</sup>) was observed for the bands associated with the W-O<sub>b</sub>-W and W-O<sub>c</sub>-W vibrations. In addition, the vibration band at 1081 cm<sup>-1</sup> appears only to be slightly shifted to  $1076 \text{ cm}^{-1}$ . This contrasts with the W–O<sub>d</sub> vibration at  $984 \text{ cm}^{-1}$  which is markedly shifted to  $960 \text{ cm}^{-1}$  (see Fig. 5b and d). This shift downwards by about 24 cm<sup>-1</sup> indicates that external oxygen atoms (Od) of PTA are involved in the interactions with the clay while bridge oxygens  $(O_b, O_c)$ and O<sub>a</sub> are particularly insensitive. One possible explanation is that hydronium ions  $H_5O_2^+$  could electrostatically bridge the terminal O<sub>d</sub> oxygen atoms of PTA and the silanol anionic surface of the clay. This conclusion seems reasonable since silanol groups are known to interact with PTA [44] and that acidic protons are claimed to be located in the terminal oxygen positions in PTA heteropolyacid [45].

In addition to the dramatic changes reported above, we observed upon complexation with low PTA excess (PTA-SSA weight ratios of 2 and 3) a slight shift upwards (Fig. 6c and d) of the maximum of the Si-O-Si vibration band. It is noteworthy that the shape of the Si-O-Si band envelop appears to be very similar to that of the pure exfoliated clay (Fig. 6e), suggesting that the crystalline structure of the clay is preserved although a small amount of amorphous (free) silicate is somewhat indicated by the presence of the broad peak detected at  $\sim 1200 \text{ cm}^{-1}$ . On the other hand, the intensity of the bands found at 693 (Al-OH vibration bond) and 659 cm<sup>-1</sup> (Mg-OH vibration bond) clearly decreases in intensity with the increase in the PTA-SSA weight ratio, indicating that Al and Mg cations are partially removed when a low excess is used during the complexation process.

# 3.2. Thermal characterization of powdered PTA–SSA complexes

It is of practical importance for applications using heteropolyacids to investigate whether the temperature can affect the stability of the PTA–SSA complexes. Thermogravimetry (TGA) and differential thermal (DTA) spectra were recorded for pure clay, heteropolyacid and their complexes (Fig. 7). For PTA (Fig. 7a), heating leads immediately to dehydration according to a two-step process in the 25–100 and 120–230 °C temperature ranges. It is wellknown that heteropolyacid hydrates lose water molecules even at room temperature and are transformed to lower hydrates [46]. The corresponding DTA curves showed two endothermic peaks at 40–60 and 185 °C which probably involve the loss of crystallisation (lattice water) and constitution water (structure water) [47]. The total weight loss of



water was around 6%. An additional transition was observed at higher temperature (594 °C) which, in contrast with the others two, was not accompanied with a weight loss, suggesting a phase transformation. DTA and TGA thermograms above 600 °C (not shown) were essentially featureless. The TGA trace of SSA (Fig. 7b) was characterized by a single initial weight loss occurring between 25 and 110 °C and observed as a broad endothermic peak in the corresponding DTA curves. The PTA-SSA complex (Fig. 7c) was characterized by a slight and monotonic weight loss from 25 until around 280 °C corresponding to a weight loss of  $\sim$ 12%, and observed in the DTA traces as a broad endothermic peak. As observed for PTA, this broad transition is followed by an exothermic peak at 551 °C which does not correspond to any weight loss in the TGA trace.

In agreement with DTA/TGA experiments, DRIFT measurements confirm that no major structural changes occurred for the complex heated up to 450 °C. DRIFT spectra of PTA–SSA complex formed at high PTA–SSA weight ratio of 5, exposed at different temperatures, are presented in Fig. 8. In contrast with other natural montmorillonite and kenyaite clays [25], PTA immobilized on SSA surface preserves its Keggin structure and forms a robust and stable complex in this temperature range. At higher temperatures (650 °C), dramatic changes are observed in the complex spectrum, as can be seen by the disappearance of the vibration bands associated with the Keggin structure in the 1000–800 cm<sup>-1</sup> range. This result suggests the presence of a structural transition





**Fig. 8.** DRIFT spectra for the PTA–SSA complex formed at a weight ratio of 5 at (a) 125 °C; (b) 280 °C; (c) 450 °C; (d) 650 °C.

consistent with the DTA analysis. In consequence, these experiments indicate that PTA–SSA complexes can be manipulated over a broad range of temperature, namely 25–450 °C.

#### 3.3. Characterization of nanocomposites

It is well-known that hydrophilic (unmodified) smectite clays are poorly dispersed in hydrophobic (co)polymers such as SEBS. PTA immobilization at the surface of the clay probably increases the hydrophilic character of the clay and precludes even more its efficient dispersion into the SEBS matrix. In the present work, nanocomposites have been fabricated by blending 5% (w/w) of the PTA–SSA complex prepared at a weight ratio of 5 in the SEBS matrix (Kraton 1652). The poor dispersion of the complex is confirmed by SEM examination as illustrated in Fig. 9a. The composite contains a large number of aggregates (white areas in Fig. 9a) whose sizes vary between 10 and 100 µm.

In past studies, the weak propention of unmodified clays to disperse in classical polymer was circumvented by using hydrophilic polymers [48–50] as well as amphiphilic block copolymers [51] having a hydrophilic poly(ethylene oxide) block. In the present study, commercially available maleated-SEBS (SEBS-g-MA) and poly(oxyethlene/propylene)-grafted SEBS (SEBS-g-J) were used to prepare hybrid (nano)composites. SEBS-g-J grafted block copolymer was prepared by a simple chemical modification of SEBS-g-MA. The structure was confirmed by <sup>1</sup>H NMR and FT-IR. Spectra can be found in Supplementary information.

Dispersion of PTA-SSA complexes within chemicallymodified SEBS (SEBS-g-MA and SEBS-g-J) was also evaluated by SEM at low magnification (×1000). Representative SEM images of hybrid composites (prepared from PTA-SSA complexes formed at a weight ratio of 5) are presented in Fig. 9b and c. At low inorganic content (5 w/w%), the presence of maleic anhydride or poly(oxyethylene/propylene) segments grafted onto the SEBS backbone promotes the dispersion of PTA-SSA complexes. Indeed, Fig. 9b and c show that for both systems, the size of the largest inorganic clusters has been reduced to less than 10 µm. Although still inhomogeneous, it is clear that the complex dispersion is significantly enhanced in the SEBS-g-J based nanocomposite (Fig. 9c). The inset of Fig. 9c confirms the presence of particles with nanometric dimensions, and indicates qualitatively that hybrid composites are a heterogeneous mixture of small proportion of micrometric aggregates and a large proportion of nanoparticles (<300 nm). At higher inorganic content (16 w/w%),



**Fig. 9.** Representative SEM images ( $\times$ 1000, backscattered electron detection) of 5 wt.% PTA–SSA nanocomposites based on (a) SEBS; (b) SEBS-g-MA; (c) SEBS-g-J. PTA–SSA complex was formed at a weight ratio of 5. Arrows point to the largest aggregates seen for each sample. Inset represents the magnification of a part of the image allowing the observation of the improved dispersion of the PTA–SSA complex in the matrix.



**Fig. 10.** Representative images of SEBS-g-J/PTA-SSA (95/5% (w/w)) nanocomposites obtained from (left) TEM (×41,000) (middle) AFM phase and (right) AFM height measurements.

PTA–SSA complex can be still seen under the form of nanometric aggregates within the matrix but a higher proportion of large particles (>1  $\mu$ m) can be observed compared to the nanocomposite containing lower amount of inorganic species (see Supplementary information).

Topographic and bulk features at a sub-micro level were also examined by TEM and AFM in PTA-SSA nanocomposites prepared from SEBS-g-J. In both techniques, samples were examined from cryo-ultramicrotomed sections and representative images are presented in Fig. 10. In the TEM images, PTA/SSA particles with spherical-like morphology dispersed homogeneously in the polymer matrix can be easily seen (Fig. 10, left). Similar observations were reported for PTA/polyacrylamide hybrid films [52]. Particle diameter varies between 30 and 150 nm although a small number of larger particles (~300 nm) are also visible. These observations are in good agreement with those obtained from AFM experiments (Fig. 10, middle and right), with the exception that the shape of nanoparticles was found somewhat less spherical in the AFM images than in the TEM images, probably due to the mechanical constraint induced by the tip. Additionally, as observed by SEM, no exfoliated clay structure could be observed in the samples.

Finally, the structural integrity of the inorganic acid after incorporation by melt extrusion in the polymer matrix was evaluated using DRIFT/transmission spectroscopy. Fig. 11 presents a comparison of the spectra of the PTA-SSA complex (weight ratio of 5), the two chemically-modified SEBS and the corresponding PTA-SSA nanocomposites. The nanocomposite blends were prepared with 5 w/w% of the PTA-SSA complex. As mentioned above, the 750-1050 cm<sup>-1</sup> region of the PTA–SSA complex spectrum presents three major bands (986, 896, 812 cm<sup>-1</sup>) associated with the PTA and one related to the Si-O-Si vibration of the clay  $(1016 \text{ cm}^{-1})$  (Fig. 11a). For the nanocomposites based on SEBS-g-MA (Fig. 11d), these bands are clearly absent from the spectrum. It is also worth mentioning that the introduction of higher amounts of inorganic complexes (up to 15 w/w%; data not shown) did not reveal the Keggin bands neither, confirming that their absence is not related to insufficient amount of PTA in the complex but most likely to an instability of the Keggin structure within the SEBS-g-MA matrix at high temperature. On the other hand,



**Fig. 11.** IR spectra of (a) PTA–SSA complex (weight ratio of 5) measured in diffuse reflection, mixed with potassium bromide; (b) SEBS-g-J/PTA– SSA composites; (c) SEBS-g-J; (d) SEBS-g-MA/PTA–SSA composites; (e) SEBS-g-MA. Composites have a composition of (95 (modified SEBS)/5 (PTA–SSA) w/w%). IR spectra of the composites (b–e) were measured in transmission mode.

the spectrum of the SEBS-g-J/PTA-SSA complex (Fig. 11b) shows new vibration bands at 819, 885 and 955 cm<sup>-1</sup> coincides well with the position observed for PTA. The other band associated with the Si-O-Si vibration is barely detectable but appears as a slight shoulder near 1020–1030 cm<sup>-1</sup>. These results confirm that melt extrusion can provide new hybrid nanocomposites integrating relatively well-dispersed (immobilized) PTA while preserving its Keggin-like structure.

### 4. Conclusions

12-phosphotungstic acid has been successfully immobilized on Sumecton clay. The Keggin structure on the clay complex was maintained and was stable up to 450 °C. The content of PTA in the complex could vary from 39.3 to 52.3 wt.% by increasing the weight ratio of PTA from 2 to 5. This content of PTA corresponds to approximately a 2- to 3-fold increase in PTA content in comparison to that reported in the literature with the Keggin structure of the PTA still preserved after the inclusion into fillers. Although high concentration of PTA in the reaction could lead to higher loading of PTA in the clay, spectroscopic data indicate that these conditions could lead to a partial destruction of the crystalline nature of the tetrahedral silicate sheets in the clay and a gradual decrease of the clay galleries (i.e. from 12.7 to 10.4 Å with PTA weight ratios from 2-5). The collapse of the clay gallery is perhaps attributed to the exchange of bigger sodium ions by smaller PTA protons at the interlayer region.

Microscopic images reveal that PTA-SSA complexes dispersed as a mixture of nanoparticles were (30-300 nm) and microparticles  $(1-50 \mu \text{m})$  in the polymer composite. Although, still inhomogeneous, the complex dispersion appeared to be enhanced in the SEBS-g-J matrix in contrast to the SEBS-g-MA matrix. Vibrational bands corresponding to the Keggin structure in the SEBS-g-J nanocomposite confirms their inclusion. Their absence in SEBS-g-MA nanocomposite even at higher loading suggests for the possibility of a negative interaction between the PTA and SEB-g-MA matrix which degrades the PTA Keggin structure. Nonetheless, these results confirm that melt extrusion can provide a new way for integrating immobilized PTA to a polymer matrix while preserving its Keggin-like structure.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.eurpolymj.2009.01.001.

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