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Melt-compounded salt-containing poly(ethylene oxide)/clay nanocomposites for polymer electrolyte membranes

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Abstract

The present study demonstrates the use of a simple and versatile melt-compounding route to prepare $NaClO_4$-containing poly(ethylene oxide) PEO/clay nanocomposites combining excellent mechanical properties with a competitive level of the ionic conductivity. The nanostructure and the resulting thermal, mechanical and conductive properties of the salt-containing PEO/clay nanocomposites were found to be highly sensitive to the clay type, i.e. aspect ratio of the clay, to the presence of an organic modifier in the intergallery spacing, and to the salt concentration. The highest increase of the shear storage modulus is obtained in the presence of single silicate layers, thus an exfoliated nanostructure, having a high aspect ratio. These structures are only obtained with an (polar) organically modified clay (Cloisite 30B), regardless of the presence of salt. The use of non-organically modified clays (Cloisite Na^+ and Laponite) resulted in intercalated nanocomposites, with only a minor improvement in stiffness. A strong interaction between the Na^+ from $NaClO_4$ and the Cloisite 30B silicate layers might be responsible for an increased PEO crystallinity and resultant additional increase in stiffness. A mechanism is proposed whereby the Na^+ ions are drawn away from the PEO phase, to be complexed by the silicate layers, or even ion-exchanged with modifier cations. The addition of clay did not greatly affect the ion conductivity below the melt temperature of PEO. At higher temperatures, the nanocomposites displayed only slightly lower conductivities compared to the $PEO/NaClO_4$ complex, due to the presence of the clay platelets.

Keywords: Clay nanocomposite electrolytes; Poly(ethylene oxide); Mechanical and thermal properties

1. Introduction

Solid-state polymer electrolytes have proven to be an appealing alternative to common liquid based electrolytes because of a highly improved safety, impeding the risk for leakages and fire. They show great potential from a technological and practical point of view, as they can be made compact and highly flexible [1,2]. Poly(ethylene oxide) (PEO) is one of the most known and studied polymers for ion conductive applications since its flexible molecular chain structure ensures a high ionic mobility [3]. In addition, PEO has the ability to act as a solid solvent for many metal salts. Still, PEO/salt complexes often show an insufficient level of conductivity, involving both anions and cations and, not in the least, poor mechanical properties [1–6].

In analogy to conventional composite materials, it is believed that the dispersion of inorganic nanosized components, and more specifically mineral clays, provides an interesting way to improve the polymer electrolyte characteristics. Intercalated, or even exfoliated, structures based on the conductive polymer and various layered silicates are expected to improve the mechanical properties on account of the large interfacial area, as well as the high aspect ratio of the respective clay type used [7–10]. In addition, filled PEO/salt systems generally show improved thermochemical stability and enhanced electrode compatibility [11]. A further innovative possibility is to create single-ion conductive electrolytes where the immobile, negatively charged silicate layers act as counter macro-anions to alkali metal cations [1].

Our previous research [7,10] has been directed towards the preparation and characterisation of PEO/clay nanocomposites based on a low content of various clay types, which differ by the presence of an organic modifier in the intergallery spacing and the aspect ratio of the clay platelets. The main conclusion from these studies was the need for a

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suitable organic modifier in order to improve the compatibility between PEO and the clay platelets, which ultimately results in the formation of exfoliated nanostructures. The presence of exfoliated clay layers, or even a highly intercalated nanostructure, i.e. displaying a large basal spacing increase, Δd, proved essential in order to obtain a strong increase of the stiffness, i.e. shear storage modulus. Presently, thorough studies of the effect of the clay type on the mechanical, thermal and conductive properties of PEO/clay nanocomposites in the presence of salt are quite rare [6,12]. The mechanical properties are especially important in the field of polymer electrolytes, as an improved stiffness and strength would enable a decrease of the electrolyte thickness for membranes.

Most studies found in literature, have focussed on the application of polymer electrolytes in the field of lithium-polymer batteries. Consequently, most results are based on nanocomposites of PEO and Li^+-exchanged clays, i.e. the cations originally present in the intergallery spacing, usually Na^+, have been exchanged for Li^+ [1,3,4,13,14]. The main route to improve the ion conductivity of polymer electrolytes, besides the increase of the number of charge carriers, is to suppress the crystallinity of the polymer. Consequently, most of the research has only focussed on nanocomposites containing PEO in low concentrations (<40 wt%). PEO was found to intercalate between the clay platelets, whereby its crystallisation was greatly suppressed [1,4,15]. Very often, care was taken not to have an excess of PEO as this would allow part of the polymer to be present in the bulk and thus, in the crystalline state. Unfortunately, the resulting mechanical properties are seldom reported. The conductivities of these nanocomposites were not always higher than those of their respective PEO/salt complexes, and in many studies the conductivities of the nanocomposites were actually comparable with the one of the neat clay material [1,3,15]. The addition of salt was found to increase the conductivity in the presence of an excess amount of PEO [6]. The most commonly used preparation techniques for these salt-containing nanocomposites are based on solution [1,3,5,6] or steady-state annealing [4,13,16] processes.

The present study focuses on the preparation of conductive PEO/clay nanocomposites, and the corresponding PEO/salt complexes, via a melt-compounding route. Melt mixing offers a simple and straightforward way of compounding polymer/clay nanocomposites, which is virtually unexploited today. $NaClO_4$ is added as the salt component, and three different clay types are examined. The latter include the natural montmorillonite clay (Cloisite Na^+) and the synthetic Laponite clay, both having Na^+ in the intergallery spacing. Cloisite 30B is the organically modified version of the Cloisite Na^+ clay. The effect of clay type, i.e. aspect ratio and presence of organic modifier, as well as the addition of $NaClO_4$ salt is evaluated by characterising the structural organisation, the mechanical properties, the crystallisation characteristics and the ion conductivity. The study aims to identify the main influential parameters when preparing mechanically stable polymer electrolytes with competitive ion conductivity.

2. Experimental

2.1. Materials

PEO, having a molar mass of 100,000 g/mol, was purchased from Aldrich. The Cloisite clay types were purchased from Southern Clay Products. Cloisite Na^+ is the pure, non-modified form of the montmorillonite clay (MMT-Na^+). Cloisite 30B is organically modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium cations (MMT-30B). The Laponite clay (Laponite® RD) is fully synthetic clay and was kindly donated by Southern Clay Products. PEO and the clays were dried in vacuum before use. $NaClO_4$ was purchased from Aldrich and was handled in an argon filled glove box.

2.2. Melt-compounding

The nanocomposites were prepared in a two-step melt-compounding procedure. The compositions given are based on the weight percentage of the clay silicate, i.e. excluding the modifier content. Firstly, a PEO/silicate master batch, based on 10 wt% silicate, was compounded using a Brabender batch mixer at 120 °C, 40 rpm during 8 min. In the second compounding step, the master batch was diluted with neat PEO using a co-rotating twin screw midi-extruder (capacity of 15 cm^3) at 120 °C, 80 rpm during 10 min. The salt was weighted in the glove box and thereafter fed simultaneously with PEO and the master batch into the extruder. The use of a recirculation channel allows the extruder to be operated as a batch process. The final silicate content of the salt-containing nanocomposites was chosen to be 2.5 wt%. The salt content was based on a molar EO:Na^+ ratio of 20:1 and 40:1. This corresponds to a salt concentration of ~11.9 and ~6.3 wt%, respectively, based on the total blend composition. After melt mixing, the nanocomposites were compression moulded into 1 mm thick samples at 120 °C and left to cool to room temperature. Before characterisation, the samples were dried overnight at 40 °C and kept in a desiccator until measurement.

2.3. Dynamic mechanical properties

The dynamic mechanical properties in shear of the nanocomposites were determined using a torsion pendulum ATM3 Myrenne apparatus. The experiments were performed in the temperature range −90 to 30 °C at a heating rate of 2 °C/min and a frequency of 1 Hz. The samples had a thickness of 1 mm, a width of 9 mm and a measuring length of 50 mm.

2.4. Small angle X-ray scattering (SAXS)

Structural information was gathered from SAXS experiments. They were performed with a Kratky compact camera equipped with a linear position sensitive detector (OED 50M from MBraun, Graz). A Seifert ID 3000 X-ray generator provides the Cu K_α radiation with a wavelength of 1.542 Å. The samples were placed in a sealed solid sample cell between mica sheets and measured during 1 h at 25 °C.

2.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetric measurements were performed using a TA Instruments Q1000 DSC. The nanocomposites were characterised according to a multiple scanning profile. A first heating run was conducted from room temperature to 120 °C, followed by a cooling run down to -70 °C. The second heating run was performed from -70 to 120 °C. The heating/cooling rate was 10 °C/min. The melt temperature (T_m) and crystallisation temperature (T_c) are evaluated from the onset temperature of melting and crystallisation, respectively. The heat of fusion (ΔH_m) is determined by integration of the surface of the melting endotherm after normalisation.

2.6. Electrochemical impedance spectroscopy (EIS)

The ionic conductivity of the salt-containing nanocomposites was investigated with electrochemical impedance spectroscopy (EIS). A Novocontrol High Resolution Dielectric Analyzer V 1.01S equipped with a Novocool temperature system was used to collect the data. The samples were compression moulded at 120 °C, with little or no pressure, into thin circular films to fit within a circular teflon sealing spacer in the sample cell. The measurements were performed every 10 °C, from -10 to 120 °C. The frequency range was varied from 10^{-1} to 10^7 Hz at a measuring voltage of 1.5 V.

3. Results and discussion

3.1. Structural characterisation

The discussion of the structural characteristics of the nanocomposites is based on the SAXS diffraction spectra. Fig. 1(a)–(c) presents the diffraction patterns of the PEO/Cloisite Na^+/$NaClO_4$, the PEO/Cloisite 30B/$NaClO_4$ and the PEO/Laponite/$NaClO_4$ nanocomposites, respectively. Pure Cloisite Na^+ clay commonly displays a basal spacing of 11.5 Å. Upon melt-extrusion with PEO, without $NaClO_4$ addition, a diffraction peak is seen positioned at a basal spacing of 18.3 Å ($\Delta d = 6.8$ Å, Fig. 1(a)). This provides a clear indication that PEO has intercalated in the clay intergallery spacing, an observation that agrees well with previous reports in the literature [2,7,15,17]. The addition of $NaClO_4$ to the melt mixture seems to have an effect on the resulting nanostructure. The nanocomposite with a molar EO:Na^+ ratio of 40:1 displays a peak positioned at a basal spacing of $\sim$18 Å, similar to the pure nanocomposite. However, when increasing the salt content to a molar ratio EO:Na^+ equalling 20:1, it is no longer possible to detect a diffraction peak. Hence, this seems to imply that adding salt above a critical level can have an 'exfoliating effect' on the final nanostructure. This effect may be triggered by a disturbance of the ionic stability of the crystal silicate structure, rather than a difference in shear force during melt-mixing.

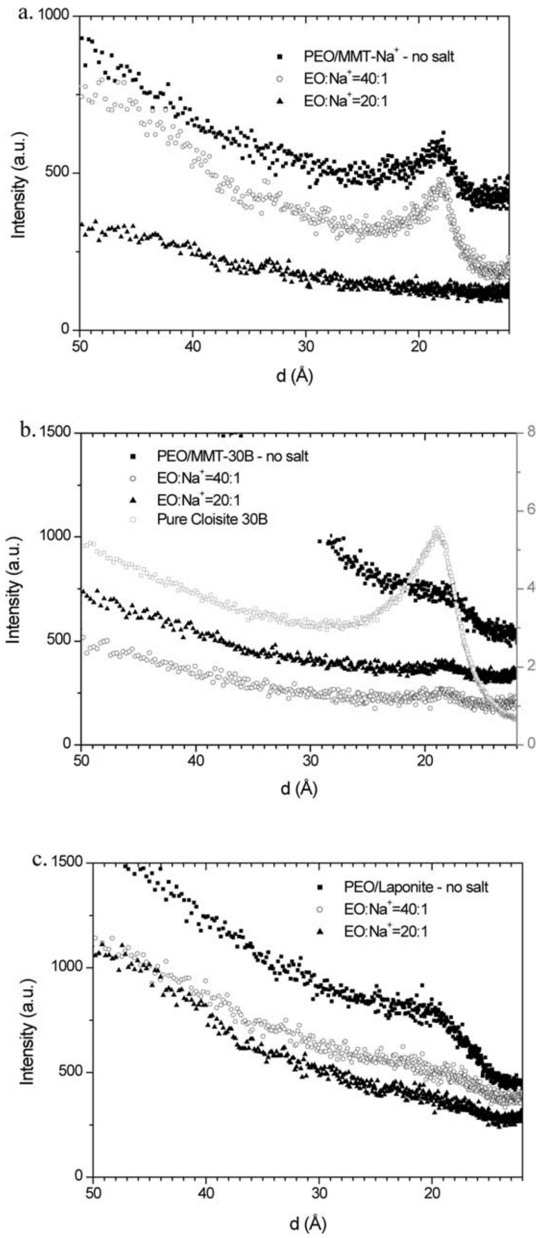

Fig. 1. SAXS diffraction spectra for the PEO/clay nanocomposites at various silicate concentrations for the following clay types: (a) Cloisite Na^+ (MMT-Na^+), (b) Cloisite 30B (MMT-30), and (c) Laponite. The curves have been shifted along the Y-axis for clarity.

Pure Cloisite 30B displays a basal spacing of 18.6 Å, as depicted in Fig. 1(b). Upon melt-extrusion with PEO, without the addition of $NaClO_4$, a very broad and weak diffraction peak can be observed in the SAXS spectra. This observation has been extensively discussed in a previous publication [7]. It is believed that there exists a threshold level for the silicate concentration (~2.5 wt%) above which complete exfoliation can no longer be achieved, resulting in non-intercalated clay tactoids. The actual position of the diffraction peak, at a basal spacing similar to the one of pure Cloisite 30B, indicates that part of the clay did not take part in the intercalation/exfoliation process. The nanostructure is thus believed to be nearly exfoliated. PEO/Cloisite 30B nanocomposites with low silicate contents have been reported to display a completely exfoliated nanostructure [7]. The spectra of the salt-containing nanocomposites show a very weak diffraction peak, with a narrow width, positioned at a slightly lower basal spacing (17.7 Å) compared to the pure clay. In accordance, it can be concluded that also upon addition of salt a nearly exfoliated structure is obtained.

The synthetic Laponite clay commonly displays a diffraction peak positioned at a basal spacing of 10 Å. The PEO nanocomposites based on Laponite, without the addition of $NaClO_4$, show a clearly detectable diffraction peak around 19.4 Å as seen in Fig. 1(c). Hence, PEO is also able to form intercalates with Laponite, leading to a basal spacing typical for nanocomposites of PEO and clays having small cations, e.g. Na^+ and Li^+, in the intergallery spacing [1,7,10,17]. The addition of $NaClO_4$, at a EO:Na^+ molar ratio of 40:1, results in a nanocomposite displaying a clear diffraction peak positioned at a similar basal spacing as observed for the nanocomposite without salt. In contrast to the previously discussed PEO/Cloisite Na^+/$NaClO_4$ nanocomposite, the increase of the salt concentration does not lead to the disappearance of the diffraction peak. This is shown in Fig. 1(c), which reveals the presence of a diffraction peak at a similar position as the other PEO/Laponite nanocomposites, although with a highly reduced intensity. This indicates that the nanostructure of the PEO/Laponite/$NaClO_4$ nanocomposite, with an EO:Na^+ molar ratio = 20:1, consists of partly exfoliated clay platelets, as well as intercalated silicate layers.

Based on the above discussion, it appears possible to control the nanocomposite structure through the clay type, e.g. through the presence of an organic modifier, and the salt concentration. The presence of a polar organic modifier in the clay intergallery spacing has previously been reported to be highly beneficial, as an increased compatibility between the organic modifier and the PEO matrix leads to exfoliated nanostructures [7]. The lack of an organic modifier in the Cloisite Na^+ and the Laponite intergallery spacing can be considered the main reason for the inability to form, at least highly intercalated (high Δd) nanostructures.

3.2. Mechanical properties

As mentioned in the introduction, the addition of mineral clay to polymers is known to have a strong influence on the mechanical properties, dependent on the nanostructure formed [7–10]. The dynamic mechanical shear properties of the PEO/clay nanocomposites, with and without $NaClO_4$, have been investigated by torsion pendulum measurements. The measured shear modulus, in contrast to the elastic modulus, has the distinct advantage of being independent of the distribution of the filler [18].

Fig. 2 presents the shear storage modulus as a function of temperature for the respective nanocomposites. It follows that the mechanical response is highly influenced by two different factors, namely the clay type, i.e. aspect ratio of clay and presence of organic modifier in the intergallery spacing, and the salt addition. Firstly, at temperatures below the glass-transition temperature (T_g) of PEO, the nanocomposites reveal stiffness similar to the one of pure PEO. This is the result of a low relative modulus combined with a possible decrease of the matrix crystallinity in the presence of clays (see below), resulting in the apparent similarity of the respective storage moduli. However, the nanocomposites without the presence of salt show a distinctly different response at temperatures above the T_g of PEO. To evaluate the actual contribution of the clay dispersion, the ratio between the shear storage modulus of the nanocomposite (G'_{nano}) and the shear storage modulus of PEO (G'_{PEO}) needs to be evaluated. Fig. 3 presents the calculated ratios for the respective nanocomposites as a function of the salt concentration. It is found that the addition of the non-organically modified clays (Cloisite Na^+ and Laponite) does not lead to a strong improvement, i.e. increase, of the shear storage modulus. On the other hand, the PEO/Cloisite 30B nanocomposite, without salt, displays a distinctly strong increase of the shear storage modulus.

In our previous publications [7,10], it was concluded that the observed behaviour of the various PEO/clay nanocomposites is a direct consequence of the nanostructure present and the corresponding 'effective' aspect ratio. Using a modified version of the Halpin–Tsai model, the effective aspect ratio of the respective dispersed clay can be evaluated. The model has been corrected for platelet reinforcement by Van Es [9]:

$$\frac{G_{\mathrm{nano}}}{G_{\mathrm{m}}} = \frac{1 + \xi\eta V_{\mathrm{f}}}{1 - \eta V_{\mathrm{f}}} \qquad (1)$$

with

$$\eta = \frac{G_{\mathrm{r}}/G_{\mathrm{m}} - 1}{G_{\mathrm{r}}/G_{\mathrm{m}} + \xi} \qquad (2)$$

$$\xi = \frac{w}{t} \qquad (3)$$

G_{nano}, G_{m} and G_{r} are the shear modulus of the nanocomposite, the matrix and the clay reinforcement, respectively. V_{f} is the volume concentration of the clay silicate and w/t is the aspect ratio of the added clay.

Fig. 4 presents the Halpin–Tsai fittings for the

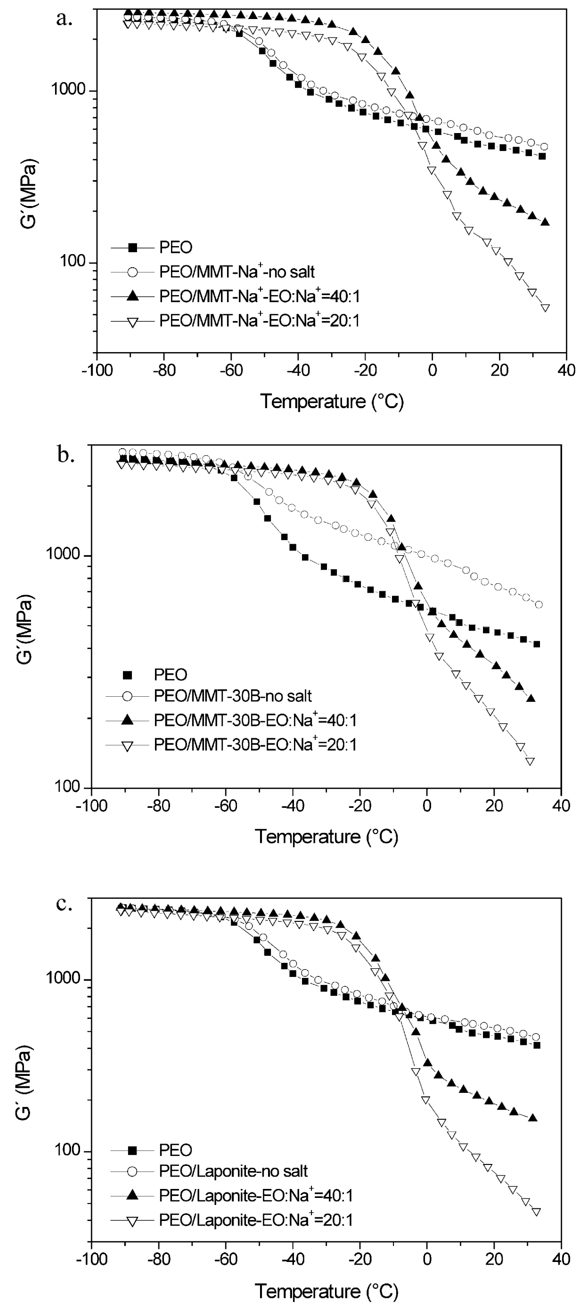

Fig. 2. Shear storage modulus (G') of the PEO/clay nanocomposites for various $NaClO_4$ concentrations as a function of temperature for the following clay types: (a) Cloisite Na^+, (b) Cloisite 30B, and (c) Laponite.

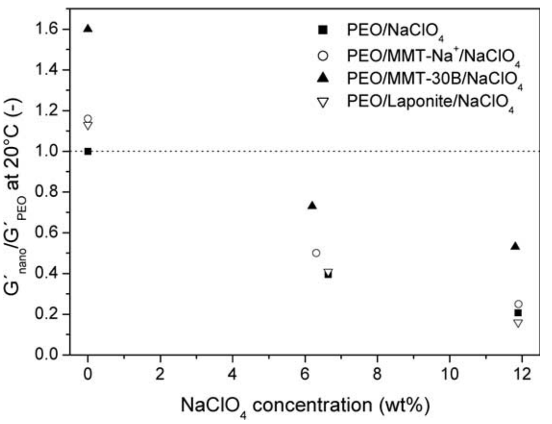

Fig. 3. Ratio between the shear storage modulus G' of the PEO/clay nanocomposite and the G' of PEO as a function of the $NaClO_4$ concentration for the various clay types at 20 °C.

nanocomposites based on (a) the non-organically modified clays (Cloisite Na^+ and Laponite) and (b) the organically modified Cloisite 30B clay, as a function of the $NaClO_4$ concentration. Two different aspect ratios were used as a fitting parameter for each nanocomposite. The supplier provides an aspect ratio (w/t) of 100 for the Cloisite clays, whereas the aspect ratio of the Laponite clay is reported to be 25. It becomes clear that the fitted model offers an explanation to the mechanical properties obtained. A good agreement is obtained between the experimental result of the PEO/Cloisite 30B nanocomposite and the Halpin–Tsai model fit, assuming a completely exfoliated structure (w/t = 100). The PEO/Cloisite Na^+ and PEO/Laponite nanocomposites, however, only revealed a minor intergallery spacing opening which implies a lower effective aspect ratio as

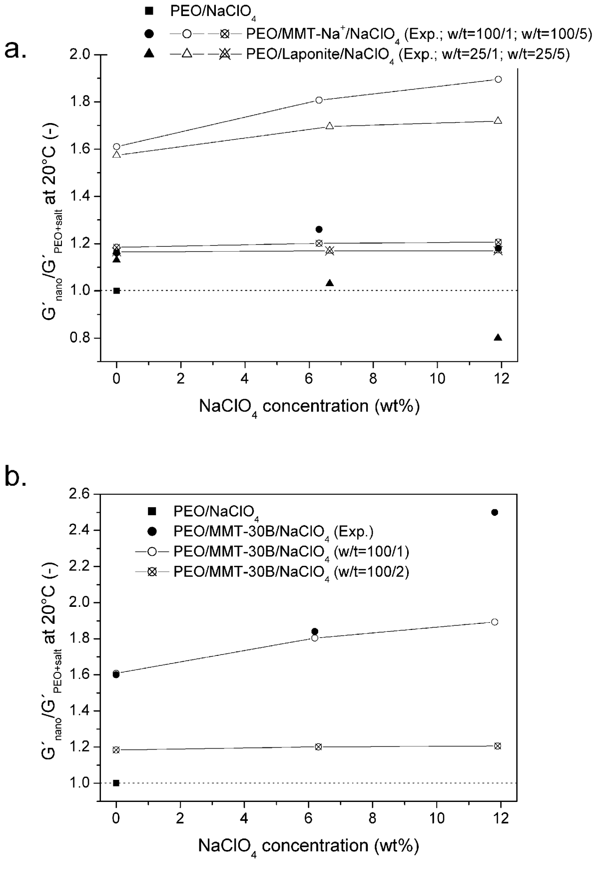

Fig. 4. Ratio between the shear storage modulus G' of the PEO/clay nanocomposite and the G' of the corresponding PEO/$NaClO_4$ complex as a function of the $NaClO_4$ concentration at 20 °C (closed symbols) and the fitted results based on the Halpin–Tsai model using two different aspect ratios (w/t) (open symbols) for the following clay types: (a) Cloisite Na^+ and Laponite, (b) Cloisite 30B.

several clay platelets (∼3–4) remain located in a stacked configuration. This is clearly illustrated by the aspect ratio needed to obtain a reasonable fit. An aspect ratio (*w*/*t*) of 100/5 is required to obtain a good agreement with the experimental results of the PEO/Cloisite Na$^+$ nanocomposite. In addition, the initial aspect ratio of the Laponite clay is significantly lower ($=25$) than the one of the Cloisite clays ($=100$). It has been found that a high effective aspect ratio, thus preferentially single exfoliated silicate layers, is essential to obtain highly stiffened materials [7,9,10].

The effect of the addition of the NaClO$_4$ to the respective clay nanocomposites becomes obvious from Figs. 2 and 3. The T_g of PEO is found to be sharply increased upon the addition of salt, from −50 °C to around −5 °C. The actual salt concentration appears to be less influential. This increase in T_g is often seen upon the addition of salt as a result of a decreased mobility of the PEO chains.

The presence of NaClO$_4$ also has a distinct effect on the shear storage modulus. The G'_{nano} is found to decrease strongly with increasing salt concentration, especially at temperatures above the T_g of PEO. This behaviour is general for all the examined nanocomposites. From Fig. 3, however, it follows that the PEO/Cloisite 30B nanocomposites still display remarkably higher moduli when compared to the corresponding Cloisite Na$^+$ and Laponite nanocomposites. Based on the above observations it would appear that the initial intent of improving the mechanical properties of PEO/salt complexes with the addition of clay was unsuccessful. However, the $G'_{\mathrm{nano}}/G'_{\mathrm{PEO}}$ ratios were based on the G'_{PEO}, without considering the effect of the addition of NaClO$_4$ on the shear storage modulus of pure PEO. Fig. 3 shows that the shear storage modulus of the pure PEO/NaClO$_4$ complexes without clay, undergoes a strong decrease with increasing salt content.

In accordance, both Figs. 4 and 5 present the ratios of the shear storage moduli, based on the G' of PEO in the presence of a corresponding NaClO$_4$ concentration ($G'_{\mathrm{nano}}/G'_{(\mathrm{PEO+salt})}$). This enables the evaluation of the effect of the clay addition, independent of the presence of NaClO$_4$. It immediately becomes clear that the clay type, i.e. aspect ratio and presence of organic modifier and thus the nanostructure also has a strong effect on the mechanical response of the salt-containing nanocomposites. Again, the use of non-organically modified clays does not lead to a strong stiffening effect. Especially the addition of the Laponite clay results in nanocomposites having shear storage moduli, which are highly comparable to those of the corresponding PEO/NaClO$_4$ complexes. From the Halpin–Tsai fits presented in Fig. 4, it clearly follows that the resulting low effective aspect ratio when melt-mixing these non-organically modified clays with PEO, can be held responsible for the low or the lack of improvement of the stiffness. Although the PEO/Cloisite Na$^+$ nanocomposite structure, at a salt concentration of 12 wt%, appeared to be exfoliated from the SAXS data (Fig. 1(a)), this is contradicted by its shear storage moduli. It is more likely that stacks consisting of several silicate layers are making up the main nanostructure, resulting in an only minor increase of G'.

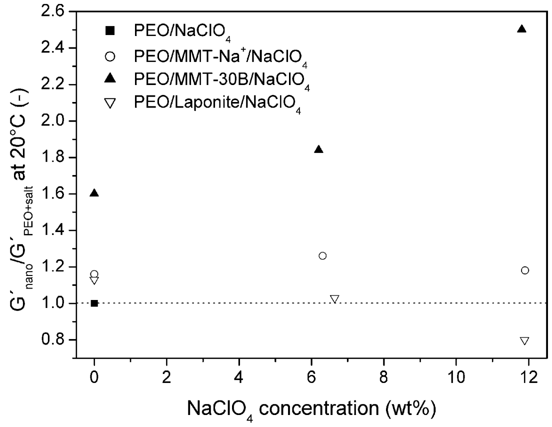

Fig. 5. Ratio between the shear storage modulus G' of the PEO/clay nanocomposite and the G' of the corresponding PEO/NaClO$_4$ complex as a function of the NaClO$_4$ concentration for the various clay types at 20 °C.

In contrast, the dispersion of Cloisite 30B results in a marked increase of the shear storage modulus of the salt-containing nanocomposites, especially at a high salt concentration, The exfoliated nanostructure of the Cloisite 30B nanocomposites, and thus the corresponding effective aspect ratio, are considered the main reason for the observed stiffening effect. The Halpin–Tsai model again provides a perfect fit when using an aspect ratio equal to single clay platelets ($w/t=100$), at least for the lower salt concentrated nanocomposite. The high increase of the shear storage modulus at the high salt content can only partly be explained by the presence of an exfoliated nanostructure. Also in the presence of salt, the clay type is found to be crucial to obtain a nanostructure, which provides the desired mechanical properties.

3.3. Crystallisation characteristics

Besides the obvious beneficial effect of clay addition on the mechanical properties, an additional influence is anticipated, namely that on the crystallisation behaviour of the semi-crystalline PEO matrix. Table 1 summarises the main thermal characteristics of the various PEO nanocomposites, with and without NaClO$_4$. Fig. 6 presents the heat of fusion, as measured during the second DSC heating run, as a function of the salt concentration, both for the nanocomposites and pure PEO.

The thermal characteristics of the respective nanocomposites, without the presence of salt, have been described and extensively discussed previously [7,10]. In general, it can be stated that the added clay does not act as a nucleating agent for the PEO crystallisation, as follows from the decreased crystallisation temperatures when compared to pure PEO [7,10,17]. This means that a higher degree of undercooling is needed to initiate crystallisation. The

Table 1
Thermal characteristics, determined via DSC measurements, of the various salt-containing PEO/clay nanocomposites and the PEO/$NaClO_4$ complexes at different salt concentrations

Salt concentration (wt%)	Cooling, $T_{c,onset}$ (°C)	Second heating	
		ΔH_{m2} (J/g PEO)	$T_{m2,onset}$ (°C)
PEO			
0	52	162	58
6.8	49	131	55
12.2	45	94	47
Cloisite Na^+			
0	52	154	60
6.3	50	133	55
11.9	44	93	47
Cloisite 30B			
0	51	150	53
6.2	50	136	55
11.8	47	117	51
Laponite			
0	51	150	56
6.6	49	132	55
11.9	43	91	47

addition of clay actually inhibits the PEO crystallisation process. Consequently, the nanocomposites display a clearly decreased heat of fusion compared to pure PEO [7,10,19,20]. The presence of the dispersed clay platelets disturbs the crystal growth [17,20], mainly as a result of the restricted chain mobility due to the limited space available. This hinders part of the polymer chain of entering the crystalline structure. The inhibition of crystallisation does not appear to be directly related, nor to be proportional, to the incorporation of the chain in the intergallery structure, as no distinct difference in the crystallisation behaviour between the intercalated (Cloisite Na^+ and Laponite) and the exfoliated (Cloisite 30B) nanocomposites could be observed [7,10]. The decrease of the melt temperature of the nanocomposites illustrates the formation of less perfect, disrupted crystalline structures [7,10,17].

Fig. 7 shows the melt endotherms of pure PEO with and without $NaClO_4$, as well as the respective PEO nanocomposites with a high salt concentration, EO:Na^+ = 20:1 corresponding to ~12 wt%. When adding $NaClO_4$ to PEO, in the absence of clay, the PEO/salt complexes formed display a strong decrease of the heat of fusion. This is a well-known phenomenon, often observed with PEO/salt complexes [21,22]. It finds its origin in the hindrance of crystallisation (decrease of T_c, Table 1), commonly attributed to the presence of the 'bulky' anionic part of the salt acting as a crystallisation inhibitor [22]. Furthermore, the salt increases the T_g, and thus the viscosity, leading to a lower chain mobility. This inevitably results in a lower degree of crystallinity, i.e. decrease of ΔH_m, and less perfect crystals, i.e. decrease of T_m. The effect is strongly influenced by the salt concentration, as seen in Fig. 6 and Table 1.

The PEO/clay nanocomposites all display a similar trend of the main thermal characteristics (T_c, T_m and ΔH_m) with increasing salt concentration. The actual clay type does not appear to have a strong effect at a low salt content (EO:Na^+ = 40:1 or ~6 wt%). However, at a higher salt concentration, a marked difference between the non-organically modified clay nanocomposites and the one based on Cloisite 30B becomes quite apparent. The PEO/Cloisite 30B/$NaClO_4$ nanocomposite is found to display a distinctly higher ΔH_m and corresponding T_m. From Table 1, it can also be seen that the T_c of this Cloisite 30B nanocomposite is higher when compared to the T_c of the other nanocomposites and the corresponding PEO/$NaClO_4$ complex.

Chen et al. have previously reported on the influence of salt addition on the crystallinity of PEO nanocomposites [6,12]. They studied PEO nanocomposites based on a montmorillonite clay, modified with acidified poly(oxypropylene) diamine, and various concentrations of $LiCF_3SO_3$ salt. The addition of clay to PEO, without the $LiCF_3SO_3$ salt, also resulted in a decrease of the matrix crystallinity.

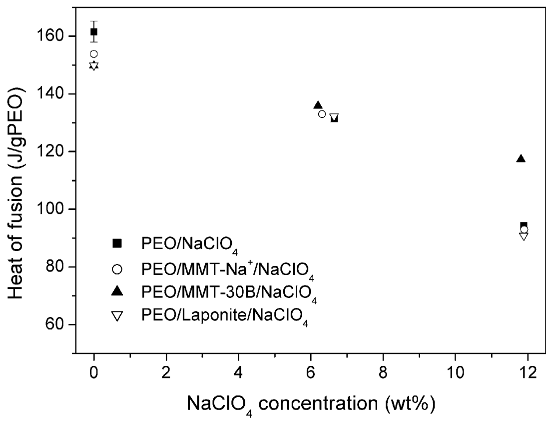

Fig. 6. Heat of fusion of the various PEO/clay nanocomposites, as determined from the second heating DSC run, as a function of the $NaClO_4$ concentration.

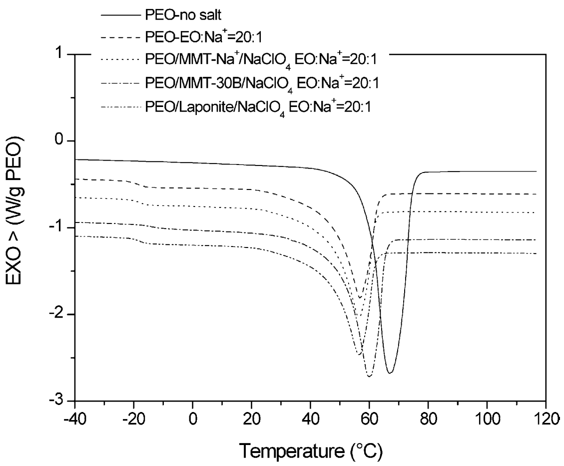

Fig. 7. DSC second heating run endotherms of the different PEO/clay/$NaClO_4$ nanocomposites having a high $NaClO_4$ concentration, EO:Na^+ = 20:1 or ~12 wt%, and the respective PEO/$NaClO_4$ complex, and pure PEO.

However, in the presence of a high amount of salt, EO:Li$^+$ molar ratio $\leq$12:1, an increase of the PEO crystallinity was observed in the presence of a low amount of clay ($<$9 wt%). The authors explained this increase by assuming that part of the added Li$^+$ was co-ordinated by the clay layers. In this way, added Li$^+$ were drawn into the clay region and were thus only partly, or not all, co-ordinated by the PEO oxygens. This then induces a higher polymer chain flexibility, and thus higher crystallinity. This increase was only observed in systems highly concentrated with salt.

In view of our results, it appears valid to assume a similar interaction between the silicate layers and the added Na$^+$ for the PEO/Cloisite 30B/$NaClO_4$ nanocomposite, at high salt concentration. The observed increase in the heat of fusion, melt temperature and crystallisation temperature suggest that the crystallisation of PEO is less hindered by the presence of $NaClO_4$, compared to the other PEO nanocomposites and the PEO/$NaClO_4$ complex at the same salt content. We propose that this observation is caused by interactions between Na$^+$ ions and the clay surfaces. The clay can complex and co-ordinate the Na$^+$. Consequently, it is not unlikely that an ion exchange has taken place between the modifiers quaternary ammonium cations (QA$^+$) and the Na$^+$ from the salt. It has been reported that the cations in the intergallery spacing are located very close to the outer boundary of the oxygen layer of the silicate crystalline structure [23], which implies that they are out of reach of the bulk PEO and no longer influence the polymer chain mobility.

Fig. 8 presents a simplified scheme illustrating the proposed interactions. In the early stage of the melt-compounding process ($t\sim0$ s), the modifier cations are positioned in between the silicate clay layers, while the Na$^+$ are complexed by the ether oxygens of PEO. During the melt-mixing, the modifier cations are partly ion-exchanged with the Na$^+$ from the salt, causing the latter to be partially or fully co-ordinated by the silicate clay layers. The modifier cations are proposed to be partly co-ordinated by the ether oxygens of PEO and to interact with ClO_4^-. Because of the exfoliated nanostructure of the PEO/Cloisite 30B/$NaClO_4$ nanocomposite and the cationic modification of the clay, the situation described above is limited to this system. It is obvious that the exfoliated nature provides a high interfacial surface area, highly increasing the co-ordinating and the level of ion-exchange capability of the clay.

3.4. Correlation between crystallisation characteristics and mechanical properties

Since the matrix crystallinity is known to have a significant effect on the mechanical properties, it is important to take this effect into account in order to establish the main stiffening mechanism of the examined PEO/clay nanocomposites. Accordingly, Fig. 9 presents the heat of fusion as a function of the shear storage modulus for the nanocomposite with and without $NaClO_4$, as well as the PEO/$NaClO_4$ complexes without clay. When considering the results of the nanocomposites without salt, as shown on the right-hand side of Fig. 9, it can be clearly seen that there is no direct correlation between the matrix crystallinity and the storage modulus. The observed stiffening effect, i.e. increased shear storage modulus, can be fully attributed to the nanostructure present, whereby the exfoliated PEO/Cloisite 30B nanocomposite clearly displays the strongest stiffening effect. In the presence of $NaClO_4$, it follows that

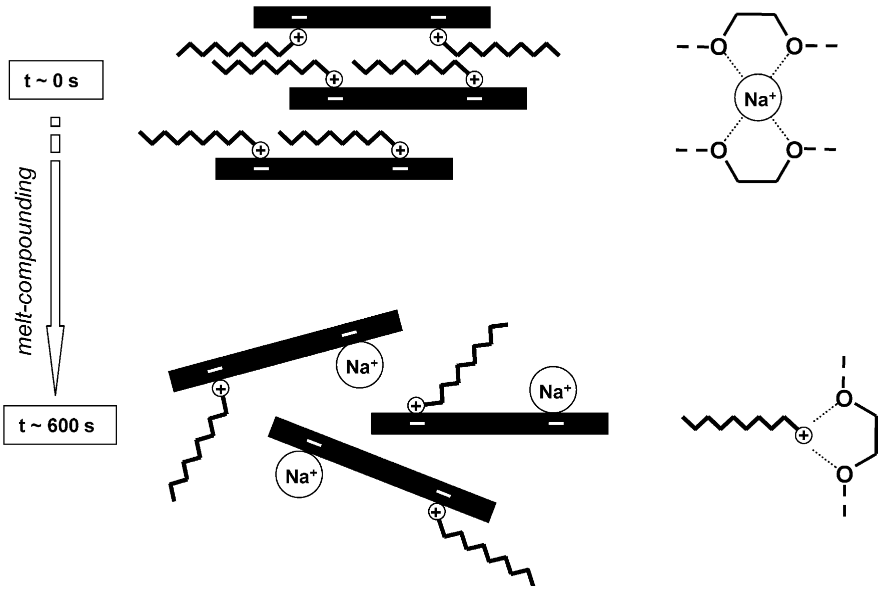

Fig. 8. Simplified illustration of the interactions between the silicate clay layers and the ether oxygens from PEO with the modifier cations and the Na$^+$ from the salt in the early ($t\sim0$ s) and final ($t\sim600$ s) stages of melt-compounding.

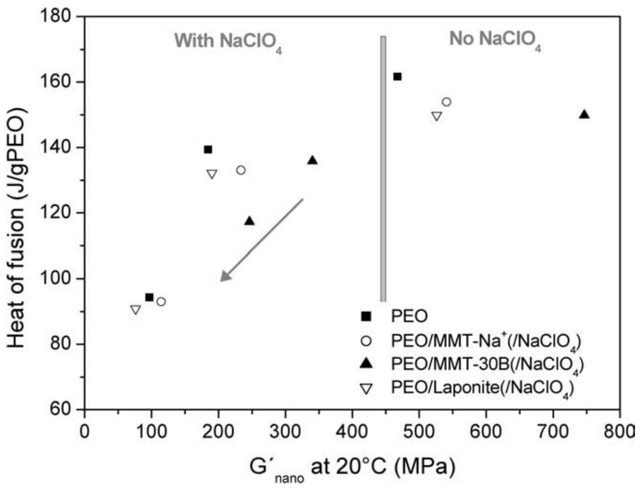

Fig. 9. Heat of fusion of the various PEO/clay nanocomposites at different $NaClO_4$ concentrations as a function of the shear storage modulus at 20 °C. The right-hand side presents the values for the nanocomposites without $NaClO_4$, while the left-hand side presents the values of the salt-containing nanocomposites.

the storage modulus decreases with decreasing heat of fusion, shown on the left-hand side of Fig. 9. Hence, it would appear liable to conclude that there exists a direct correlation between the degree of crystallinity of the PEO matrix and the shear storage modulus for the salt-containing nanocomposites. However, it is essential to distinguish between the actual influence of the degree of crystallinity and the nanostructure on the final mechanical properties. In order to do so, both the heat of fusion and the shear storage modulus of the nanocomposites need to be corrected for the presence of $NaClO_4$.

Table 2 provides the ratios between the heat of fusion of the nanocomposite and the heat of fusion of the corresponding PEO/$NaClO_4$, complex as well as the ratio of the G' of the nanocomposite, and the G' of the respective PEO/$NaClO_4$ complex. When considering the nanocomposites based on Cloisite Na^+ and Laponite, it follows that the ultimate shear storage modulus appears to be independent of the PEO crystallinity. The ratios of the heat of fusion reveal that the nanocomposites display a slightly lower crystallinity, while the shear moduli are similar or slightly higher, as compared to the one of the corresponding PEO/$NaClO_4$ complex. The addition of these clays is found to have no or only a minor stiffening effect. On the other hand, the PEO/Cloisite 30B/$NaClO_4$ nanocomposites having a low $NaClO_4$ content ($\leq$6.2 wt%) clearly reveal that the observed stiffening can be completely attributed to the clay addition and the resulting exfoliated nanostructure. However, in the presence of a high salt content it has already been mentioned that the crystallinity was distinctly higher compared to the corresponding PEO/$NaClO_4$ complex. It can be calculated that the crystallinity increases with 16% when increasing the salt concentration from 6 to 12 wt%. An increase of 26% is found for the respective shear storage modulus. Taking the experimental error into account, the respective increases appear to be highly correlated. Hence, the improved shear storage modulus of this nanocomposite can be attributed to two co-operating effects: the exfoliated nanostructure of the clay (see Halpin–Tsai fit, Fig. 4) and the increased PEO crystallinity.

3.5. Ionic conductivity

As discussed above, the shear storage modulus has been found to display a significant improvement upon the addition of clay, depending on the clay type (Fig. 5). It is obviously very interesting to investigate the influence on the ion conductivity of the respective salt- and clay-containing systems. The ion conductive behaviour of the salt-containing nanocomposites, as well as the PEO/$NaClO_4$ complexes, was studied with impedance spectroscopy. Before discussing the results obtained, it is important the address the issue of water contents. The sample preparation via compression moulding, as described in the experimental section, prevents the preparation in a completely water-free environment. Although the samples were dried afterwards, it was not possible to completely remove all the water. Thermogravimetric analysis revealed a weight loss of 0.9 wt% up to 150 °C in a PEO/Cloisite 30B/$NaClO_4$ sample with a high salt content, EO:Na^+ = 20:1. If this weight loss should be completely attributed to H_2O, it accounts for 0.9 wt% of the total composition. The water molecules will most probably, together with PEO, take part in a hydration shell around the ions [23].

Table 2
Ratio between the heat of fusion of the PEO/clay nanocomposite and the heat of fusion of the corresponding PEO/$NaClO_4$ complex, and the ratio of the shear storage modulus G' of the PEO/clay nanocomposite and the G' of the respective PEO/$NaClO_4$ complex, for the different nanocomposites

Clay type	Salt concentration (wt%)	$\Delta H_{m(nano)}/\Delta H_{m(PEO+salt)}$ (-)	$G'_{nano}/G'_{PEO+salt}$ (-)
Cloisite Na^+	0	0.95 ± 0.02	1.16
	6.3	1.01	1.26
	11.9	0.99	1.18
Cloiste 30B	0	0.93 ± 0.02	1.60
	6.2	1.03	1.84
	11.8	1.24	2.50
Laponite	0	0.93 ± 0.02	1.13
	6.6	1.00	1.03
	11.9	0.96	0.80

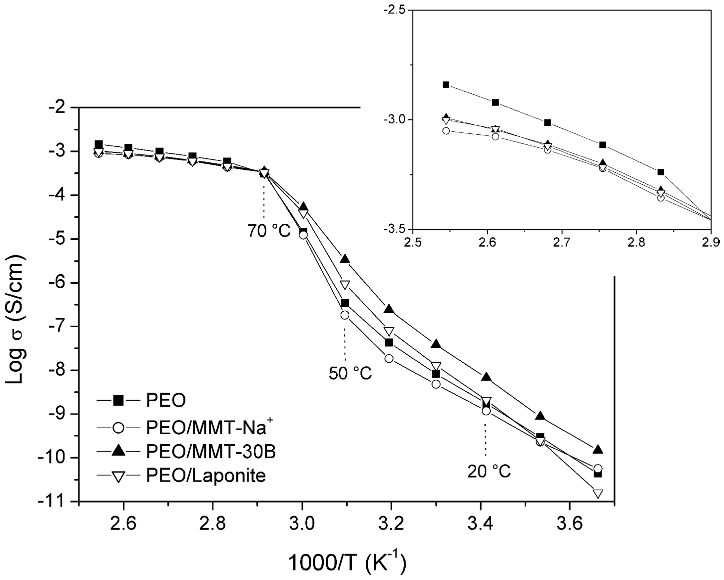

Fig. 10. Arrhenius plots of the conductivity for the PEO/clay/$NaClO_4$ nanocomposites having a low $NaClO_4$ concentration, EO:$Na^+ = 40{:}1$ or ~6 wt%, and the corresponding PEO/$NaClO_4$ complex.

A single semi-circle could be observed in the respective Cole–Cole plots of the various salt-containing systems, and the intercept at the low frequency region was taken as the ionic resistance. Figs. 10 and 11 present the Arrhenius plots for the PEO nanocomposites and the corresponding PEO/$NaClO_4$ complex, for a salt concentration of 6.3 wt% (EO:$Na^+ = 40{:}1$) and 12 wt% (EO:$Na^+ = 20{:}1$), respectively. Inserted is a magnification of the conductivity in the high temperature region. It should be noted that on account of the compression moulding, albeit performed with little or no pressure application, it is very likely that the clay platelets have a tendency to be oriented parallel to the film surface. First, the conductivity at temperatures below the melt temperature of PEO will be considered. It is quite obvious that the conductivity increases upon an increase of the salt concentration. This is a direct consequence of the increased number of charge carriers, i.e. ions. The conductivity behaviour strongly depends on the thermal history of the sample, especially at $T < T_m$. Accordingly, it can be concluded that the conductivity of the salt-containing nanocomposites is very similar to the conductive behaviour of the respective PEO/$NaClO_4$ complex. This is quite apparent for samples having a salt concentration of 12 wt%. At a lower salt content, it is observed that the PEO/Cloisite 30B/$NaClO_4$ nanocomposite displays a higher conductivity compared to the other nanocomposites and the respective PEO/$NaClO_4$ complex.

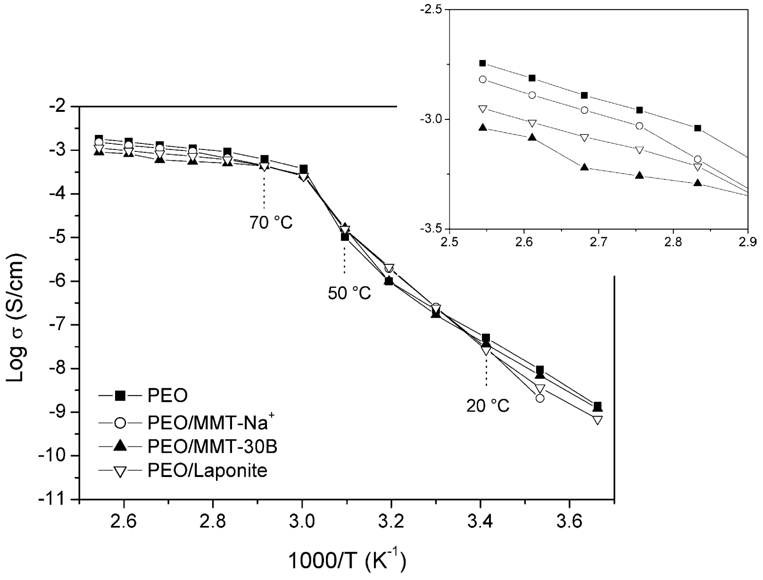

Fig. 11. Arrhenius plots of the conductivity for the PEO/clay/$NaClO_4$ nanocomposites having a high $NaClO_4$ concentration, EO:$Na^+ = 20{:}1$ or ~12 wt%, and the corresponding PEO/$NaClO_4$ complex.

The presence of the highly crystalline PEO matrix is considered the main reason for the observed conductivity behaviour at $T<T_m$. The addition of clay did not lead to a further decrease of the PEO crystallinity, which would have resulted in an increased ion transport rate. However, it has been stated in the literature that the conductivity perpendicular to the surface of the sample ($\sigma_\perp$), as measured here, is generally one order of magnitude lower than the conductivity parallel to the surface of the sample ($\sigma_\parallel$) as a result of the platelet orientation [3,4]. It is, therefore, not unreasonable to assume that the higher conductivity observed for the PEO/Cloisite 30B/$NaClO_4$ nanocomposite at low salt content, is a direct result of the exfoliated nanostructure, which should provide a less diffusion hindered system in the measuring plane.

The effect of the nanostructure appears to be minimised at a higher salt concentration. It has been suggested in our previous discussion that the Na^+ of the salt may be complexed by the clay platelets, or even ion-exchanged with the modifier cations at these high salt concentrations (Section 3.3). Furthermore, the conductivity is only partly governed by the cations of the salt. It is well known that anions usually provide the major contribution to the resulting conductivity of salt-containing polymer electrolytes. Assuming an ion exchange between the Na^+ from the salt and the large quaternary ammonium cations of the modifier (QA^+), the mobility of the ClO_4^- anions can be seriously decreased by association with the QA^+ cations. This provides a further indication of the assumed interaction between the Na^+ of the salt and the Cloisite 30B clay. Several papers in literature have reported on the difficulty of improving the conductivity above the value of the corresponding PEO/salt complex [1,3,15].

A comparison of the results presented in Figs. 10 and 11 reveals that the melt transition is shifted towards a lower temperature when increasing the salt concentration. This has been observed previously from in the DSC study (Table 1). The effect is not influenced by the addition of clay, and can thus be completely attributed to the addition of salt and the consequent decreased crystallinity (and melting temperature). The curves display a sharp increase of the conductivity from an initial low level at temperatures below T_m.

The conductivity at temperatures above the PEO melt temperature, reach a high level and show a less steep increase with temperature. The nanocomposites having a low salt content (Fig. 10) all display a similar behaviour. Their conductivities are lower than the one of the respective PEO/$NaClO_4$ complex. In addition, the activation energy seems to be lower which can be indicative of a different mechanism of conduction, as the T_g remains largely unaffected by the presence of the clay at a similar salt concentration. The observed behaviour most likely results from the presence of the stiff clay platelets. Their absence in the corresponding PEO/$NaClO_4$ complex ensures a higher degree of freedom for the ionic mobility in this material.

The nanocomposites also display a lower conductivity compared to the respective PEO/$NaClO_4$ complex at the higher salt concentration. However, the difference between the various clay types is much more obvious. The PEO/Cloisite Na^+/$NaClO_4$ nanocomposite reveals the best results. The lower conductivity of the Laponite clay can most probably be attributed to the lower cation exchange capacity (CEC) of this clay. From calculations based on the actual CEC of the clay, the clay concentration and the $NaClO_4$ concentration, it follows that the intergallery Na^+ make up 1.5% of the total Na^+ content in the Laponite-based composites. In contrast, the ratio of intergallery Na^+ increases to 2.3% for the Cloisite clay on account of its higher CEC. The clay cations, e.g. Li^+ or Na^+, are known to contribute to the total conductivity [1,3,15]. The PEO/Cloisite 30B/$NaClO_4$ nanocomposite clearly displays the lowest conductivities. This partly results from the total absence of small intergallery cations, lowering the total concentration of Na^+. In addition, the proposed interaction between the Na^+ of the salt and the Cloisite 30B clay, and the possible salt formation between the ClO_4^- anions and the QA^+ cations, are considered responsible for the lower conductivities.

The ion conductivity might be further increased by increasing the clay concentration, as this would decrease the crystallinity of PEO. The use of this approach is, however, limited, as it would imply a corresponding deterioration of the mechanical properties. The shear storage modulus is known to level off if the clay concentration is increased due to a decrease of the effective clay aspect ratio [7,9,10]. Chen et al. reported on the appearance of a maximum in the conductivity as a function of the clay content, after which the conductivity shows a steep decrease [6].

In general, it can be stated that the clay addition did not greatly affect the conductivity of the PEO/$NaClO_4$ complex. However, the corresponding mechanical properties, especially of the PEO/Cloisite 30B/$NaClO_4$ nanocomposite, displayed a strong improvement.

4. Conclusions

The study revealed that the nanostructure and the resulting thermal, mechanical and conductive behaviour of the melt-compounded, salt-containing PEO/clay nanocomposites was highly sensitive to the clay type, i.e. aspect ratio of the clay and the presence of an organic modifier in the intergallery spacing, and the $NaClO_4$ concentration.

The addition of non-organically modified clays, that is Cloisite Na^+ and Laponite, resulted in the formation of intercalated PEO nanocomposites, regardless of the presence of $NaClO_4$. As a consequence, their mechanical properties, i.e. shear storage modulus, only showed a minor or no improvement compared to the corresponding PEO/$NaClO_4$ complex. The low effective aspect ratio, due to the presence of stacks of silicate layers rather than individual platelets, is considered the main reason for the minute stiffening effect. In contrast, the $NaClO_4$-containing PEO/Cloisite 30B nanocomposites displayed an exfoliated nanostructure, which in turn resulted in an impressive improvement of the material stiffness. The presence of the exfoliated, single silicate layers results in a high effective aspect ratio, and consequently an improved shear storage modulus. At a higher salt content, the Cloisite 30B nanocomposite displayed a distinctly higher crystallinity, compared to the other nanocomposites, which was found responsible for an additional increase of the stiffness. A strong interaction between the Na^+ of the salt and the silicate layers is considered responsible for the increased crystallinity. The proposed mechanism of interaction is based on two effects: the complexation of Na^+ by the silicate layers and the ion-exchange between Na^+ and the organic modifier.

The addition of clay to PEO/$NaClO_4$ complexes did not have a strong effect on the ion conductivity below the PEO melt temperature. However, the PEO/Cloisite 30B/$NaClO_4$ nanocomposites having a low salt content, revealed an increased conductivity attributed to the exfoliated structure. That effect was minimised at higher $NaClO_4$ content due to the interaction between Na^+ and the silicate layers. At temperatures above T_m, the nanocomposites display slightly lower conductivities compared to the corresponding PEO/$NaClO_4$ complex. This is due to the presence of the clay platelets, hindering the ion transport.

In general, the present study illustrated the possibility to use a simple and versatile melt-compounding route to prepare salt-containing PEO/clay nanocomposites with excellent mechanical properties and a competitive level of the ion conductivity.

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