

The tensile properties of poly(ethylene oxide)-based segmented block copolymers in the dry and wet state

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Abstract The tensile properties of poly(ethylene oxide)-based segmented block copolymers were studied in the dry and wet state. The hard segments were made up of monodisperse crystallisable tetra-amide segments (T6T6T) comprising terephthalate (T) and hexamethylenediamine (6) groups. The length of the segments making up the soft phase was varied from 600 to 10,000 g/mol. The water absorption of the PEO-based copolymers was found to increase exponentially with the PEO concentration. The modulus and yield strength decreased with water absorption and this effect seemed to be mainly the result of a lowering hard segment content caused by their swelling with water. Upon wetting, the copolymers demonstrated an increased yield strain. Furthermore, the ultimate properties were sensitive to the hard segment content, the molecular weight of the copolymer and whether or not strain-hardening could take place. Upon wetting, the fracture stresses decreased whereas the fracture strains increased. The true fracture stresses of the wet samples were as high as those of the dry samples for reasonable amounts of absorbed water.

Introduction

Poly(ethylene oxide)-containing copolymers are hydrophilic materials that are of interest for numerous application areas, including the fields of textiles, packaging, construction, gas

separation and biomedical. There exist several reports on PEO-based segmented block copolymers with hard segment types such as esters [1–4], amides [5–7] or urethanes (urea) [7–14]. Pure poly(ethylene oxide) (PEO) at room temperature is completely soluble in water, in contrast to other closely related polyethers, e.g., poly(tetramethylene oxide) or poly(propylene oxide), and this solubility can be explained by the strong interaction between water and PEO [15]. The PEO copolymers absorb a considerable amount of water, which affects the material properties. Regardless of the intended use, the knowledge of the mechanical properties of segmented block copolymers in both the dry and the wet state is very important.

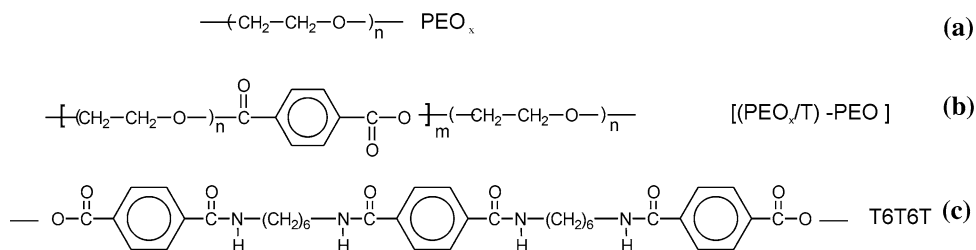
Dry PEO copolymers have been found to display a yield stress at low strains and a strain-hardening at higher strains. In certain cases, an extra hardening can be observed if the PEO segments strain-crystallise at strains above 200%. Upon wetting, the modulus, yield stress, fracture stress and fracture strain become lower as a result of the absorbed water acting as a plasticiser and decreasing the glass transition temperature of the polymer [11, 16–20].

The properties of the segmented block copolymers depend on the morphology. Polyurethane-based segmented block copolymers phase separate through liquid–liquid demixing, and this is often followed by a partial crystallisation of the hard segments. Hard segments that crystallise rapidly, such as polyesters and polyamides, usually phase separate by crystallisation. However, the crystallinity of these hard segments in the segmented block copolymers is generally low and a large amount of non-crystallised hard segments is present in the polyether matrix. The crystallisation and the stability of the hard segments are improved when the segments are monodisperse in length [21–33]. Short monodisperse amide segments crystallise fast and almost completely. With such short monodisperse amide

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Fig. 1 The chemical structures of PEO_x, (PEO₆₀₀/T)_y and T6T6T



segments, the modulus in the dry state of these copolymers has been found to be relatively elevated and the polyether concentration in the copolymer can be high, up to 88 wt% [34, 35].

The water absorption of PEO copolymers increases asymptotically with the PEO content, thus naturally leading to a larger number of water molecules per ethylene oxide unit (H₂O/EO) [36]. With such water absorption, the T_g and T_m of the PEO phase are reduced.

The present article reports on the investigation of segmented block copolymers based on hydrophilic PEO segments and short monodisperse crystallisable tetra-amide (T6T6T) segments comprising terephthalic acid (T) and hexamethylenediamine (6) (Fig. 1).

The T6T6T segments in segmented block copolymers crystallised near fully (~85%) and had a nano-ribbon morphology with a high aspect ratio [27, 28, 33]. The reinforcing effects of these nano-ribbon crystallites have followed the composite models [28, 33]. Two copolymer series were evaluated, one with PEO_x segments (Fig. 1a), denoted PEO_x-T6T6T [34], and another series containing PEO₆₀₀ segments that were extended with terephthalic units (T) $-(\text{PEO}_{600}/\text{T})_y-$, whereby the x and y values are the segmental molecular weights (Fig. 1b) [35]. The terephthalate units were miscible with the PEO phase and thus increased the soft segment length. The long $-(\text{PEO}_{600}/\text{T})_y-$ segments and T6T6T were found not to phase separate by liquid-liquid demixing upon synthesis, and the crystallinity of the $-(\text{PEO}_{600}/\text{T})_y-$ segments was considered low with respect to the segment length. The physical properties, i.e., the glass transition temperature of the soft phase, the PEO melting temperature and the crystallinity, were determined by differential scanning calorimetry (DSC), and the tensile properties of these hydrophilic copolymers were studied in the dry and the wet state.

Experimental

Materials

The synthesis, analysis and characterisation of various properties of the PEO₂₀₀₀-T6T6T and (PEO₆₀₀/T)_y-T6T6T copolymers have been studied previously and are reported elsewhere [34, 35].

Water absorption

The equilibrium water absorption (WA) was measured on pieces of injection-moulded polymer bars (70×9×2 mm³). The samples were placed in a desiccator filled with demineralised water during a time period of 4 weeks at room temperature. The water absorption was defined as the weight gain of the polymer according to:

$$\text{Water absorption} = \frac{m - m_0}{m_0} \times 100\% \text{ (wt\%)} \quad (1)$$

where m_0 is the weight of the dry sample and m the weight of the sample after conditioning to equilibrium. The measurements were performed in duplicates. After 4 weeks, the samples were dried and m_0 was remeasured so as to exclude weight loss during the experiment. From these data, the number of water molecules per ethylene oxide unit (H₂O/EO) was also calculated.

Differential scanning calorimetry (DSC)

The thermal transitions of the dry and hydrated copolymers were determined by DSC using a Pyris 1 (Perkin Elmer, USA). The analyses were run on small pieces of the injection-moulded polymer bars (5–10 mg). The samples were kept for 1 min at -100 °C and subsequently heated from -100 to 80 °C at a heating rate of 10 °C/min. This first heating scan was followed by a cooling scan from 80 to -100 °C at a rate of 10 °C/min and a subsequent second heating scan under the same conditions as the first. The glass transition temperature was taken as the midpoint of the heat capacity change of the first heating scan. In the case of completely hydrated polymers, the samples were placed in demineralised water for 1 day in order to reach an equilibrium water absorption state. The excess water was gently removed using an absorbing tissue paper.

Tensile testing

Samples for tensile testing were prepared by melt-spinning of the dried polymer into threads on a (4cc DSM res RD11H-1009025-4) co-rotating twin screw mini-extruder. The extrusion temperature was set approximately 40 °C above the flow temperature of the copolymer and the screw

speed to 30 rpm. The titre of the threads (expressed in $\text{tex} = 10^{-6} \text{ kg/m}$) was calculated assuming a polymer density of 1.0 g/cm^3 . Tensile tests were carried out on the threads with a Zwick Z020 universal tensile machine equipped with a 10 N load cell. The strain was measured by clamp displacement, and standard stress–strain curves were obtained at a strain rate of 250 mm/min with a starting clamp distance of 25 mm. The tests were performed in 5-fold, and values of initial modulus, yield stress and yield strain, fracture stress and fracture strain, as well as true fracture stress were determined. The true fracture stress was defined as the fracture stress \times (the fracture strain + 1) assuming that the volume of the sample did not change on straining. The dry polymers had an E/G ratio of three and thus behaved like ideal rubbers. Tensile tests were also performed on hydrated polymer threads that had been placed in demineralised water for 1 day to reach an equilibrium state of water absorption. The observed standard deviation in the data was approximately 10%. For the wet samples the true fracture stresses were also determined assuming that they also behaved like ideal rubbers.

Results and discussion

PEO–T6T6T segmented block copolymers were prepared in a solution-melt process and were found to have high inherent viscosities. The amide copolymers were poorly soluble in most solvents, but could however be dissolved in trifluoroacetic acid and a mixture of tetra-chloro-ethane/phenol. The determination of the M_n values for the amide-containing copolymers was very difficult. GPC was a possible technique, but the values for amide copolymers are often overestimated. Maldi-TOF could not be used as the copolymers did not fly due to the amide segments. NMR can sometimes be used to determine the end-group

content, but for higher molecular weights, this method is inaccurate.

Eventually, solution viscosities could be determined in tetra-chloro-ethane/phenol mixtures and these measurements proved to be very reproducible. The inherent viscosities were determined at low polymer concentrations, and the inherent viscosity values at low concentrations were virtually the same as those of the intrinsic viscosity. For amide polymers and copolymers, the inherent viscosities usually increase linearly with the molecular weight [15]. For polyethers, the relationship of M_n (as determined by NMR) and the inherent viscosity, according to [37, 38]:

$$M_n = 10.700\eta_{\text{inh}} \quad (2)$$

can be applied to polymers for which the molecular weights are not too high. This relationship corresponded well with that for polyamides. Under the assumption that this relationship was permitted, the molecular weights of the copolymers could be approximated. Moreover, the number of hard segments (HS) in the chain for these multi-block copolymers could be estimated. Table 1 presents these and various other properties of the $\text{PEO}_x\text{-T6T6T}$ and $(\text{PEO}_{600}/\text{T})_y\text{-T6T6T}$ copolymers.

PEO-based segmented block copolymers

The water absorption (WA) of two series of PEO-based copolymers, i.e., the $\text{PEO}_x\text{-T6T6T}$ and $(\text{PEO}_{600}/\text{T})_y\text{-T6T6T}$ series, was investigated (Table 1).

Because of the high T6T6T crystallinity in the copolymers ($\sim 85\%$) and the fact that crystalline nylon does not absorb water [39], it was assumed that water was only absorbed in the PEO phase of the copolymers (Fig. 2).

As can be seen in Fig. 2, the water absorption at 100% relative humidity (RH) increased exponentially as a function of the PEO content. This strong increase in water

Table 1 Various properties of $\text{PEO}_x\text{-T6T6T}$ and $(\text{PEO}_{600}/\text{T})_y\text{-T6T6T}$ copolymers

x or y (g/mol)	Conc. T6T6T (wt%)	Conc. PEO (wt%)	Conc. T (wt%)	η_{inh} (dL/g)	HS per chain	WA (wt%)	H ₂ O/EO	T_g PEO dry (°C)	T_g PEO wet (°C)	T_m PEO dry (°C)	T_m PEO wet (°C)	T_m T6T6T (°C)
<i>PEO_x-T6T6T</i>												
600	51.0	49.0	0	1.4	12	18	0.9	−42	−58	np	np	219
2000	23.8	76.2	0	1.9	7.7	91	2.9	−53	−70	14	−39	167
<i>(PEO₆₀₀/T)_y-T6T6T</i>												
600	51.0	49.0	0	1.4	12	18	0.9	−42	−58	np	np	219
1250	33.3	60.4	6.3	1.6	9.0	30	1.2	−40	−60	np	np	208
2500	20.0	69.0	11.0	1.7	5.8	49	1.7	−44	−55	−6	−26	187
5000	11.1	74.8	14.1	1.5	2.8	69	2.2	−43	−63	−3	np	171
10000	5.9	78.1	16.0	1.5	1.5	75	2.3	−44	−	−2	−	158

np not present

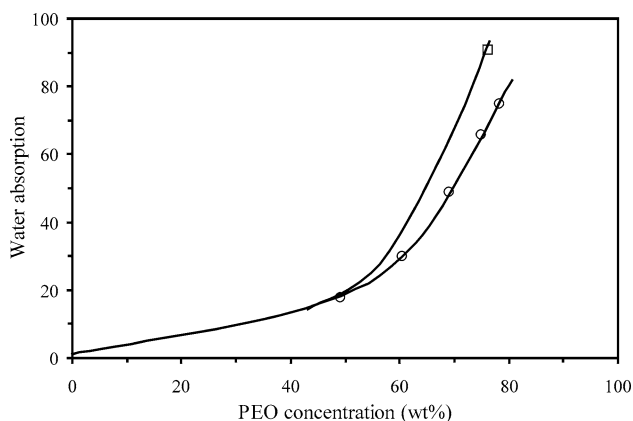


Fig. 2 The equilibrium water absorption (WA) as a function of the PEO concentration for: □ PEO₂₀₀₀-T6T6T, ○ (PEO₆₀₀/T)_y-T6T6T

absorption can be explained as being due to both the PEO content and the decreasing density of physical crosslinks, i.e., the length of polyether between T6T6T segments [36]. The water absorption for the (PEO₆₀₀/T)_y-T6T6T copolymers was lower than for PEO_x-T6T6T, indicating that the presence of terephthalic units in the amorphous phase reduced the water absorption. Moreover, the number of water molecules per ethylene oxide unit (H₂O/EO) was calculated and this value was found to vary from 0.9 to 2.9 between the various copolymers.

Effect of water on the PEO phase transitions

Water is known to act as a plasticiser in PEO copolymers and depress the glass transition temperature of the PEO phase [40–42]. The glass transition temperatures of dry and completely hydrated PEO copolymers were measured by DSC (10 °C/min) and the results are summarised in Table 1. The PEO₆₀₀ displayed a relatively elevated T_g and this can be explained by the high density of physical crosslinks. The T_g values of the copolymers with a (PEO₆₀₀/T)_y increased a bit with the soft segment (SS) length. The T_g for (PEO₆₀₀/T)_y with a y -value corresponding to about 2000 g/mol was, in the dry state, approx. 9° higher than the value for PEO₂₀₀₀. This 9 °C shift in T_g caused by the presence of the terephthalate groups corresponded to previous observations [27, 43]. Upon wetting, the T_g values shifted to lower temperatures, and this phenomenon was due to the plasticising effect of water on the PEO segments. The difference in T_g between dry and wet copolymers for PEO₂₀₀₀ and PEO₆₀₀ was 22–25 °C for both copolymers and thus almost independent of the amount of absorbed water as well as of the H₂O/EO ratio.

The PEO melting temperature increased with increasing PEO segment length, but was lowered in the presence of terephthalate groups [35]. In the dry state, PEO₂₀₀₀

demonstrated a melting temperature of 14 °C whereas that of (PEO₆₀₀/T)_y ranged from –2 to –6 °C. Upon wetting, the PEO₂₀₀₀ copolymer displayed a decrease in T_m to –39 °C, and the T_m of the (PEO₆₀₀/T)₂₅₀₀ segment was –26 °C. On the contrary, for the other (PEO₆₀₀/T)_y samples in the wet state, no T_m could be detected, possibly due to an overlap between peaks. The lowering of the T_m of PEO in the presence of water was due to the solvent effect of water on the PEO crystallites.

With increasing water content, the reduction in the PEO melting temperature was stronger than that of the glass transition temperature. Thus, upon wetting, the T_g/T_m ratio increased from 0.77 to 0.81 for the PEO₂₀₀₀-T6T6T copolymer. Generally, a higher T_g/T_m ratio results in a reduced crystallisation rate and crystallinity [44].

Tensile properties

The choice was made to analyse the tensile properties of the copolymers on threads instead of dumbbell-shaped bars for two reasons. The first was that the amount of available material was limited, and the second was that threads have very smooth surfaces, thus resulting in the data being less influenced by surface inhomogeneities.

The tensile properties of the PEO-T6T6T segmented copolymers were studied on dry and wet samples and typical stress–strain curves can be seen in Fig. 3. At small deformations, the stress displayed a linear increase with the strain. No necking was observed at the yield point and the samples deformed homogeneously. Above the yield point, the stress continued to gradually increase with the strain.

The increase in strain was due to a strain-hardening process. In certain cases, such as for the PEO₆₀₀-T6T6T, an extra increase in stress was observed at strains above 200%. This extra strain-hardening was believed to have been due to a strain-induced crystallisation of the polyether segments. The strain-hardening stabilised the deformation and increased the fracture stress [18]. Both the basic strain hardening as well as the strain-induced PEO crystallisation process decreased with increasing segment length of (PEO₆₀₀/T)_y, thereby decreasing the T6T6T concentration. For stress-induced crystallisation, the melting temperature of the soft (oriented) phase should be above the test temperature. However, the isotropic melting temperature of the polyether phase did not have to be above room temperature since, upon orientation, the melting temperature could increase by several tens of degrees [43]. Since water reduced the melting temperature of PEO, the strain-induced crystallisation of the PEO segments should become more difficult. In order to study the influence of water on the tensile properties of the PEO-T6T6T copolymers, an investigation was carried out on copolymers with a PEO

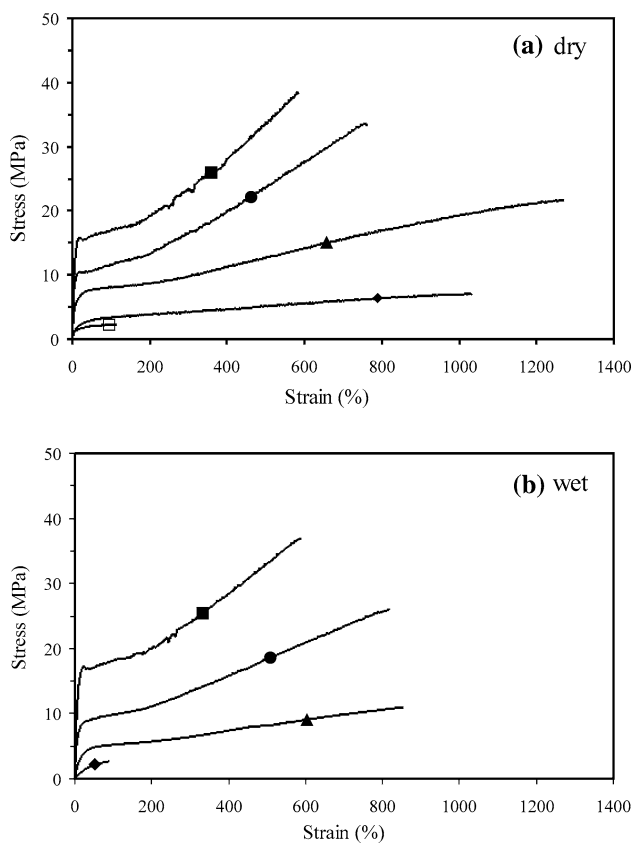


Fig. 3 Typical stress–strain diagrams of **a** dry and **b** wet samples of $(\text{PEO}_{600}/\text{T})_y\text{-T6T6T}$: ■ 600, ● 1250, ▲ 2500, ◆ 5000, □ 10000

melting temperature in the isotropic state below room temperature. The results of these tensile tests are summarised in Table 2.

Modulus

The modulus of segmented block copolymers depends on the modulus of the soft phase, the network density and the reinforcement of the matrix by the HS crystallites [45]. Figure 4 presents the E - and G' -moduli as functions of the T6T6T content in the $(\text{PEO}_{600}/\text{T})_y\text{-T6T6T}$ copolymers, and as can be seen from the figure, the E -modulus of the studied PEO copolymers in the dry state increased significantly with increasing T6T6T concentration, as did the G' -modulus.

As previously observed, the type of soft segment, i.e., PEO_{2000} or $(\text{PEO}_{600}/\text{T})_y$, had little effect on the modulus [35]. The increase in E -modulus with HS content was thus mainly caused by the reinforcing effect of the HS crystallites. The E -modulus is related to the storage modulus (G') according to Eq. 3.

$$G' = \frac{E}{2}(1 + \nu) \quad (3)$$

where ν is the Poisson constant. In the case of an ideal elastomer, the Poisson constant equals 0.5 and thus $G' = 3E$. According to the E - and G' -modulus values from Fig. 4, G' could be approximated with $3E$ for a majority of the copolymers and thus behaved like ideal rubbers. Upon wetting, the E -modulus was found to decrease with increasing water content (Table 2). As water was absorbed, the PEO phase was plasticised and the T6T6T concentration in the system reduced. The samples thus became swollen and the concentration of the HS was lowered (Table 2). In order to single out the T6T6T concentration effect obtained from the water absorption on the

Table 2 Tensile properties in the dry and wet state of the $\text{PEO}_{2000}\text{-T6T6T}$ and $(\text{PEO}_{600}/\text{T})_y\text{-T6T6T}$ copolymers

SS length (g/mol)	η_{inh} (dL/g)	WA (wt%)	Conc. T6T6T (wt%)	$\text{H}_2\text{O}/\text{EO}$	G' (Mpa)	E (MPa)	σ_y^a (MPa)	ϵ_y^a (%)	σ_f (MPa)	ϵ_f (%)	σ_{true}^b (MPa)
<i>PEO₂₀₀₀-T6T6T</i>											
2000	1.9	0	23.8	0	38	117	6.3	27	27	920	275
		91	12.5	2.9	–	20	5.4	67	14	490	100
<i>(PEO₆₀₀/T)_y-T6T6T</i>											
600	1.4	0	51.0	0	160	263	15.5	17	32	490	189
		18	43.2	0.9	–	216	16.8	16	36	520	223
1250	1.6	0	33.3	0	68	233	10.8	13	27	710	219
		30	25.6	1.2	–	130	8.7	21	26	780	229
2500	1.7	0	20.0	0	32	81	5.9	24	19	1080	224
		49	13.4	1.7	–	22	4.2	40	9.6	650	72
5000	1.4	0	11.0	0	12	66	3.2	35	7.7	900	77
		66	6.6	2.2	–	9	2.4	63	2.6	90	26
10,000	1.5	0	5.9	0	5	21	1.5	38	2.1	100	4
		75	3.4	–	–	–	–	–	–	–	–

^a Yield stress and strain as determined by the Considère method [43]

^b The true fracture stress (σ_{true}) as calculated according to $\sigma_f \times (1 + (\epsilon_f/100))$

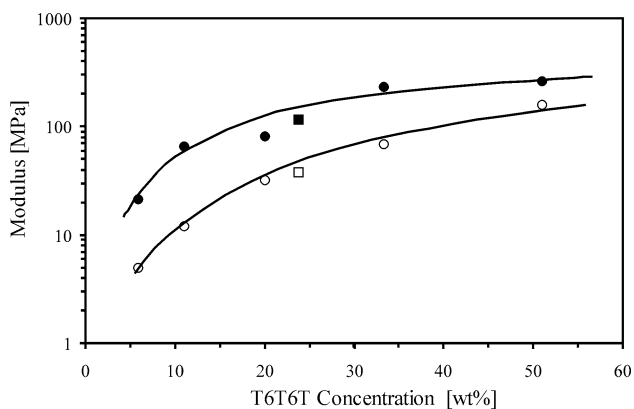


Fig. 4 The E-modulus (filled symbols) and storage modulus (G') (open symbols) of dry PEO copolymers as functions of the T6T6T content: ■ and □ PEO₂₀₀₀, ● and ○ (PEO₆₀₀/T)_y

mechanical properties of the copolymers, the E -modulus was plotted as a function of the actual T6T6T concentration, the concentration in the dry and the wet samples, respectively (Fig. 5).

At low water contents (i.e., for high values of the actual T6T6T concentration) the modulus–T6T6T relationship in the wet state was similar to that in the dry state. However, at high water contents, the modulus–T6T6T relationship in the wet materials was appreciably lower than in their dry counterparts. This was most evident for the PEO₂₀₀₀ copolymer that had absorbed a large quantity of water. It was assumed that the crystalline T6T6T phase was not affected by the water and that the reinforcing effect of the T6T6T crystallites remained unchanged. The reinforcing effect of the T6T6T crystallites (nano-ribbons) followed the fibre reinforced composite models [28, 33]. Most likely, the modulus of the polyether phase, as can be observed by the extrapolated modulus at zero T6T6T concentration, was

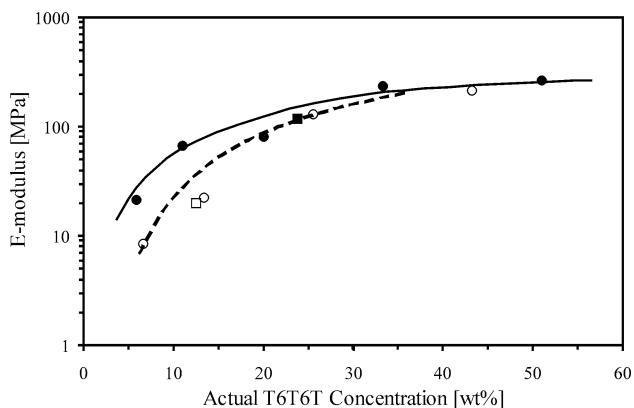


Fig. 5 The E-modulus of the PEO₂₀₀₀–T6T6T (■, □) and (PEO₆₀₀/T)_y–T6T6T copolymers (●, ○) as a function of the actual T6T6T content: ■, ● dry; □, ○ wet

lowered by the plasticisation with water. Thus, as water was absorbed, the PEO phase became plasticised and at the same time the T6T6T concentration was lowered.

Yield properties

The yield point of segmented block copolymers is regarded as the onset of a large-scale deformation of the crystalline phase. Before the yield point, i.e., at low stresses, the crystallites are not (or very little) plastically deformed and the material has a highly elastic nature. In segmented block copolymers, the yield stress generally displays a linear increase with the crystallite concentration and the properties of the soft segments apparently have no effect on the yield stress [26, 45, 46].

The yield stress of the studied block copolymers increased linearly with the actual T6T6T concentration in both the dry and the wet states (Fig. 6a). Moreover, the wet copolymers displayed identical relationships of yield stress versus actual T6T6T concentration. The observed variations in yield stress upon wetting were solely due to the changing T6T6T content whereas the plasticisation of the PEO phase had no effect.

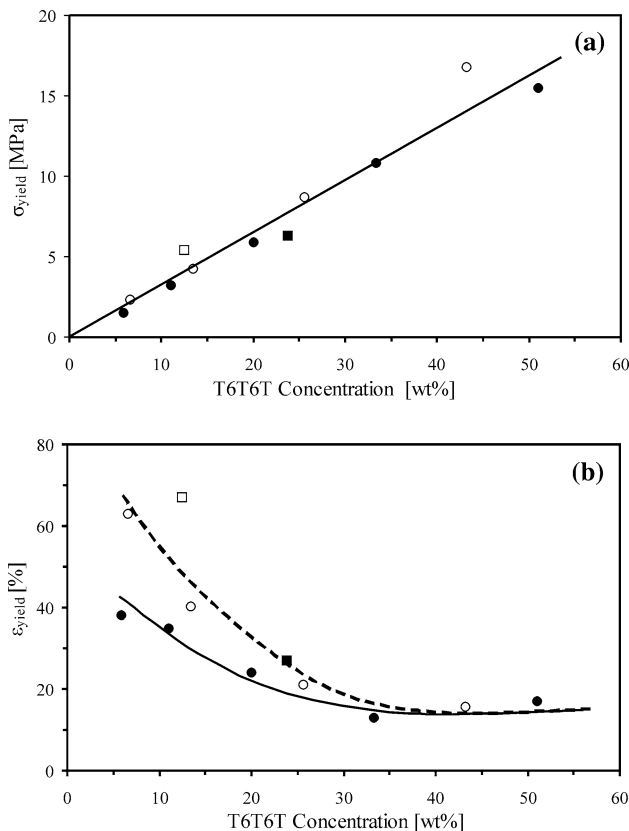


Fig. 6 a The yield stress and b the yield strain as functions of the actual T6T6T content for the PEO₂₀₀₀–T6T6T (■, □) and (PEO₆₀₀/T)_y–T6T6T copolymers (●, ○): ■, ● dry; □, ○ hydrated

As shown in Fig. 6b, the yield strain increased with decreasing T6T6T content. Furthermore, the hydrated copolymers demonstrated a higher yield strain than their dry counterparts. This can be explained by the plasticising effect of water on the PEO segments. One should also notice the higher yield strains of the PEO₂₀₀₀ copolymer in both the dry and the wet state.

Ultimate properties

The ultimate properties of segmented block copolymers depend strongly on whether strain-hardening as well as a strain-induced crystallisation of the flexible segments can take place. Segments with a melting temperature above or just below its testing temperature can undergo strain-induced crystallisation. Upon orientation, the melting temperature of the polyether as well as its crystallinity increases [43]. Thus, even polyethers with melting temperatures (in the isotropic state) below the test temperature can in some cases undergo strain-induced crystallisation. A copolymer displaying a strain-induced crystallisation effect at room temperature has been known to lose this effect as the test temperature was increased to above the melting temperature of the oriented segments [46]. However, at high temperatures, a certain amount of strain hardening was still observed. The fracture properties of the segmented block copolymers depend on the hard segment content and the number of (physical) crosslinks per chain. In the present study, the number of T6T6T segments per chain decreased with an increasing soft segment length of the copolymers (Table 1).

Fracture properties are known to be strongly dependent on the molecular weight of the copolymer [27, 43]. For copolymers of higher molecular weight, the strain-hardening is usually more significant. Among the studied block copolymers in the dry state, the stresses increased above the yield stress and this increase was more significant at strains above 200% (Fig. 3a). However such strain-hardening processes generally diminish with increasing (PEO₆₀₀-T)_y segment length and this was also the case for the samples tested in the wet state (Fig. 3b). The fracture stresses of the copolymers in both the dry and wet states were found to increase linearly with the actual T6T6T concentration, as can be seen in Fig. 7a.

Besides the changing T6T6T concentration, the decreasing number of amide segments per chain was also believed to be of importance. At a low T6T6T concentration, the number of amide segments was small. The fracture stress values of PEO₂₀₀₀ were higher than for the (PEO₆₀₀/T)_y copolymers and this might be due to the higher molecular weight of the copolymer. The fracture strains for the dry copolymers seemed to increase with decreasing fracture stress (Fig. 7b). However, for the copolymers with

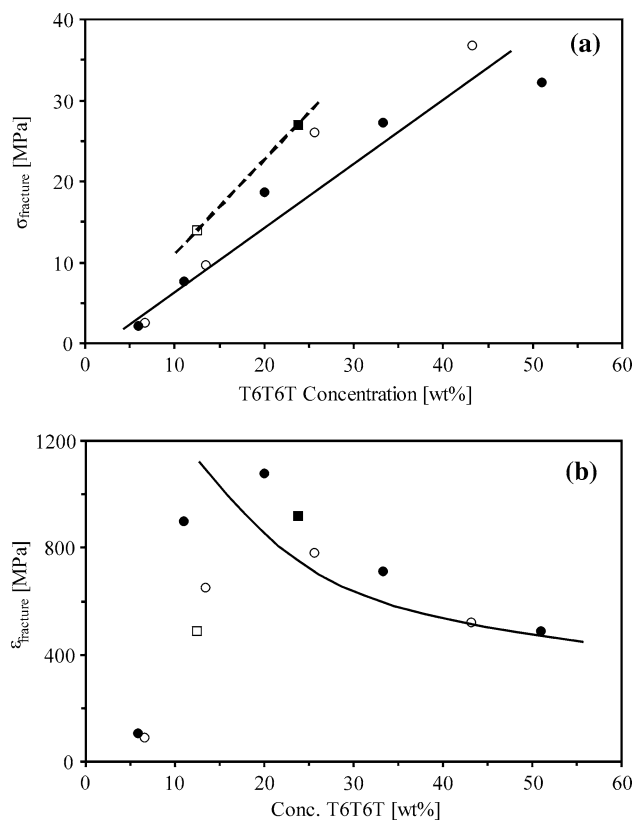


Fig. 7 The fracture **a** stress and **b** strain of PEO₂₀₀₀-T6T6T (■, □), and (PEO₆₀₀/T)_y-T6T6T copolymers (●, ○) as a function of the actual T6T6T content: ■, ● dry; □, ○ wet

very few T6T6T segments per chain, the fracture strains were low. In the wet state, the fracture strains were especially low for high H₂O/EO values.

Upon increasing the fracture stress, the fracture strain often decreases, and since both these factors are important they can be combined into a single parameter: the true fracture stress. The true fracture stresses of the strain-hardened segmented block copolymers have been found to increase with increasing inherent viscosity [46]. In the present case, Fig. 8 displays the true fracture stress as a function of the actual T6T6T content in the copolymers. It can be seen that in the dry state, the true fracture stresses were elevated at high T6T6T concentrations and depend very little on concentration.

It was a possibility that the true fracture stresses increased when going from PEO₆₀₀ to PEO₂₀₀₀, and this might have been due to the increase in molecular weight. Such high values are typical for strain-hardened materials, and consequently, the low values of true stress at low T6T6T content in the dry state must have resulted from the absence of strain-hardening, as can be seen in Fig. 3. Thus, for non-strain-hardened systems with few T6T6T segments in the chain (<3), the true fracture stresses were low and increased with T6T6T content. For the wet copolymers

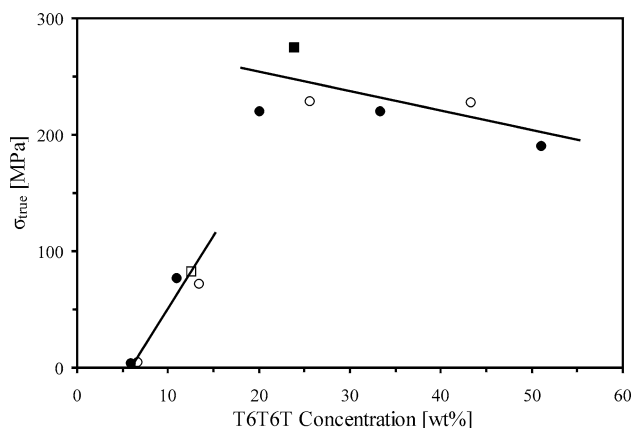


Fig. 8 The true fracture stress of the PEO₂₀₀₀-T6T6T (■, □) and (PEO₆₀₀/T)_y-T6T6T copolymers (●, ○) as a function of the actual T6T6T content: ■, ● dry; □, ○ hydrated

with low H₂O/EO values (<1.5), the true fracture properties were as high as for the dry materials, whereas they were low at H₂O/EO values >1.5. A typical behaviour with regard to the true fracture stresses was observed for PEO₂₀₀₀ that displayed a high value in the dry state and a low value in the wet state. Since the wet PEO₂₀₀₀ had a very low melting temperature (−39 °C), no strain-induced crystallisation was expected to have occurred in this case.

Conclusions

The influence of water on the physical and tensile properties of segmented block copolymers, containing flexible hydrophilic poly(ethylene oxide) segments and monodisperse high-melting T6T6T segments, was investigated. The copolymers showed an exponential increase in water absorption with increasing PEO content and also the H₂O/EO ratio was significantly raised. The presence of terephthalate groups in the PEO phase reduced the H₂O/EO ratio.

Upon wetting, both the T_m and T_g of PEO were lowered as a result of the solvent effect of water on the PEO crystallites and the plasticising effect on the PEO amorphous segments. The modulus and yield strength of the copolymers increased with T6T6T concentration while, at the same time, the yield strain decreased. Upon wetting, the modulus and yield stress decreased and the yield strain increased. This effect could partly be explained by the lowering of the T6T6T concentrations on wetting and at high water contents also by the plastisation of the PEO amorphous phase. The T6T6T nano-ribbon like crystals act as reinforcing fibres.

The ultimate properties of the segmented block copolymers were sensitive to several parameters: the T6T6T

concentration, the molecular weight of the copolymer, the number of HS per chain and whether or not strain-hardening was possible. The fracture stresses in the dry state increased with T6T6T concentration, and this effect was possible partly due to the increase in the number of T6T6T segments per chain. Upon wetting, the fracture stress varied as the actual T6T6T concentration was altered. The fracture strains in the wet state also changed with the actual T6T6T concentration. However, the fracture strain for the wet PEO₂₀₀₀ was significantly reduced, probably due to the high H₂O/EO value giving rise to a strong reduction in the T_m of PEO and thereby reducing the possibility of strain crystallisation.

The true fracture stresses in the dry state were high for all copolymers if at least three T6T6T segments were present in the polymer chain. Moreover, they were independent of the T6T6T concentration and seemed to increase with molecular weight. Upon wetting, the true fracture stresses remained high for H₂O/EO values <1.5. Consequently, PEO₂₀₀₀ displayed low true fracture stresses as this material had a high H₂O/EO value, which was expressed in a significant lowering of the T_m of the copolymer and a reduced possibility of strain-induced crystallisation.

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