

Influence of chemical crosslinks on the elastic behavior of segmented block copolymers

Martijn van der Schuur¹, Reinoud J. Gaymans*

Department of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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Abstract

Polyether(ester–amide)s (PEEA) segmented block copolymers with di- and tri-functional poly(propylene oxide)s and amide segments were synthesized and the elastic properties studied. The difunctional polyether used had a molecular weight of 2300 g/mol end capped with 20 wt% ethylene oxide. The trifunctional polyether had a molecular weight of 6000 g/mol of which each arm had a molecular weight of 2000 g/mol. The concentration of the trifunctional polyether of the total ether content was varied from 0 to 40 mol%. The amide segments were of a non-crystallizing type with a content in the copolymers of 27 wt%. Phase separation occurred, therefore, only by liquid–liquid demixing. The thermal mechanical properties of the polymers were analyzed by dynamic mechanical thermal analysis and the elastic properties by compression set and tensile set. The materials are model blockcopolymers for the more complex chemically crosslinked polyether(urethane–urea)s (PEUU).

With increasing amounts of chemical crosslinks the glass transition temperature and the modulus did not change noticeably. However, the elastic behavior as measured by compression set and tensile set, improved dramatically. Giving time all materials recovered completely and with increasing amount of chemical crosslinks this recovery happened faster. An explanation is given for the (viscoelastic) deformation in these copolymers.

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1. Introduction

Polyether(ester–amide)s (PEEA) are segmented block copolymers consisting of alternating sequences of mobile polyether and rigid polyamide segments and these copolymers have a thermoplastic elastomer (TPE) behavior. These materials are phase separated, which provide interesting elastic properties, while still be processable as a thermoplast [1]. If the mobile segments of segmented blockcopolymers are volume wise in excess, a dispersion of hard domains in a soft matrix is obtained. Phase separation either proceeds through crystallization and/or liquid–liquid demixing [1,2]. Liquid–liquid demixing occurs when the segments become

incompatible like by increasing the length of the segments [2–4]. In TPE's, the hard domains act as thermo-reversible physical crosslinks and in addition reinforce the material similar to common reinforcing fillers [2].

Segmented block copolymers as the polyether(urethane–urea)s (PEUU) have been extensively studied [5–11] and have found use in numerous applications like: mattresses, cushioning, coatings and clothing [5,6]. For mattresses and in cushioning, PEUU's are used that contain next to physical crosslinks considerable amounts of chemical crosslinks. The physical crosslinks in these block copolymers are partly made up by hard urea aggregates and partly by a crystalline lamellar urea phase [6,9–10]. The chemical crosslinks in these block copolymers are the result of the use of trifunctional polyether segments (triols). The incorporated chemical crosslinks were found to increase the tensile strength and strain at break, but did not affect the hardness, tear strength and glass transition temperature of the polyurethane blockcopolymers [11]. The morphology of these PEUU's is rather complex and unfortunately their thermal stability is low. Amide blocks provide better

* Corresponding author.

E-mail addresses: mvds@oce.nl (M. van der Schuur), r.j.gaymans@utwente.nl (R.J. Gaymans).

¹ Presently at OCE, Venlo, The Netherlands.

thermal stability than urethane or urea groups and have similar hydrogen bonding [2]. We have studied the morphology-properties relationship of liquid–liquid demixed segmented block copolymers (*m*-PEEA), containing amide segments with a similar structure as in PEUU's (Fig. 1) [2].

The amide segments in *m*-PEEA are poly(*m*-xylylene isophthalamide) segments with an irregular structure that do not crystallize and phase separate in the copolymer by liquid–liquid demixing [2]. The dispersed phase of this copolymer has a bimodal particle size distribution, with nano-particles (~5 nm) consisting just of amide segments and sub-micron 'salami type' particles (30–700 nm) containing amide segments and polyether segments [2]. Phase separation is taking place at amide segment length of more than two repeat units [2].

In this study, the influence of chemical crosslinks on the (visco) elastic properties of *m*-PEEA_c is investigated by increasing the amount of trifunctional poly(propylene oxide) (PPO) relative to difunctional PPO, while keeping the amide content constant (27 wt%). The trifunctional polyether had a molecular weight of 6000 g/mol of which each arm had a molecular weight of 2000 g/mol and the difunctional polyether had a molecular weight of 2300 g/mol. In this way, the crosslink density, here a combination of chemical and physical crosslinks, is kept constant. The poly(*m*-xylylene isophthalamide) segments used in this study do not crystallize and have an average amide segment length (*x*) of 3.3–4.5. The thermal mechanical properties of the segmented block copolymers have been studied with DMTA and the elastic properties with compression and tensile set. Some tensile properties are also presented.

2. Experimental

2.1. Materials

Diphenyl isophthalate (DPI), tetra-isopropyl orthotitanate (0.05 M Ti(*i*-OC₃H₇)₄ solution in *m*-xylene) and *N*-methyl-2-pyrrolidone (NMP) were purchased from Aldrich. *m*-Xylylene diamine was a gift from Mitsubishi Gas Chemical Company (Japan). Irganox 1330 was obtained from CIBA. These materials were used as received. Poly(propylene oxide) end capped with 20 wt% ethylene oxide (EO tip) with a *M_n* of approximately 2300 g/mol

(PPO₂₃₀₀) and trifunctional PPO with 20 wt% EO tips (PPO₆₀₀₀, *M_n* of 6000 g/mol) were gifts from Bayer AG (Acclaim Polyol PPO-2220 N and Acclaim Polyol PPO-6320 N). Each branched chain of the trifunctional PPO has a number average molecular weight of 2000 g/mol. Before use the polyols were dried in vacuum at 70 °C overnight.

2.2. Synthesis of polyether(ester–amide)s (*m*-PEEA_c)

As an example the synthesis of a blockcopolymer with 31 mol% triol is given (amide content = 26.5 wt%): A 250 ml stainless steel reactor equipped with magnetic coupling stirrer (cylindrical flang flask, cmd 075) was charged with a mixture of diol PPO₂₃₀₀ (10.89 g, 4.73 mmol) and triol PPO₆₀₀₀ (12.68 g, 2.11 mmol), *m*-xylylene diamine (4.31 g, 31.7 mmol), DPI (12.59 g, 39.5 mmol), and 100 ml NMP and 1 wt% Irganox 1330 (based on PPO) under a nitrogen flow. (The magnetic coupled stirring device was important to obtain high vacuum conditions). The reaction mixture was stirred under N₂-flow and heated to a temperature of 120 °C in 1 h and subsequently kept at 120 °C for 2 h. Thereafter, the temperature of the reaction mixture was raised to 250 °C in 1 h. The catalyst (2.0 ml, 0.05 M Ti(OC₃H₇)₄ in *m*-xylene) was added at 150 °C. At 250 °C, a low vacuum (10–1 mbar) was applied for 1 h and finally a high vacuum (0.1–0.08 mbar) for 2 h, during this step a polymer gel was formed. Subsequently, the product was cooled to room temperature while maintaining the high vacuum. The polymers were dried in vacuum at 70 °C overnight before use.

2.3. Compression molding

Samples of blockcopolymers were prepared by compression molding on a Lauffer OPS 40 press at 250–280 °C for 3 min at 100 bar (120 × 120 × 2 mm³). Test specimens were cut from the homogeneous plaques to the desired shape and subsequently dried at 70 °C in vacuum for 24 h before testing.

2.4. Dynamical mechanical thermal analysis (DMTA)

Test samples for dynamical mechanical thermal analysis (70 × 9 × 2 mm³) were used. The storage modulus (*G'*) and loss modulus (*G''*) as function of temperature were measured using a Myrenne ATM3 torsion pendulum at a

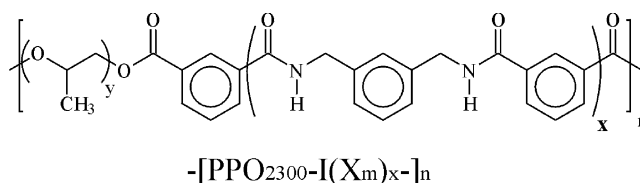


Fig. 1. A *m*-PEEA based on poly(propylene oxide) and non-crystallizable amide segments based on poly(*m*-xylylene isophthalamide) [2].

frequency of 1 Hz and 0.1% strain. The samples were first cooled to $-100\text{ }^{\circ}\text{C}$ and then subsequently heated at a rate of $1\text{ }^{\circ}\text{C}/\text{min}$. The glass transition temperature was taken as the temperature at the maximum of the loss modulus. The flex temperature (T_{flex}) is defined as the temperature at the start of the rubber plateau region, the intercept of the tangents. The storage modulus at $25\text{ }^{\circ}\text{C}$ is given as $G'_{25\text{ }^{\circ}\text{C}}$.

2.5. Compression set

Samples for compression set measurements were cut from the compacted plaques. The compression set was measured according to the ASTM 395 B standard. After 24 h compression at room temperature the compression (25%) was released at room temperature. After half an hour, the thickness of the samples was measured at room temperature. The compression set (CS) is defined as:

$$\text{CS} = \frac{d_0 - d_2}{d_0 - d_1} \times 100\% \quad (1)$$

d_0 , thickness before compression (mm); d_1 , compressed thickness (mm) (here $d_1 = 1.65\text{ mm}$); d_2 , thickness 30 min after release of compression (mm).

The calculated compression sets were taken as the average of three measurements. The compression set was also measured as function of time.

2.6. Tensile test

Stress–strain curves were obtained on compression molded samples, cut to dumbbells (ISO 37 s3), using a Zwick Z020 universal tensile machine equipped with 500 N load cell without extensometers. Standard tensile tests were performed in three-fold according to ISO 37 s3. The strain rate was $3.33 \times 10^{-2}\text{ s}^{-1}$ (test speed of 50 mm/min). The tensile stress at 10% strain, the fracture strain and fracture stress of the blockcopolymer samples were determined.

2.7. Tensile set

Cyclic stress–strain experiments were conducted on samples from compacted plaques, which were cut to dumbbells (ISO 37 s3). A Zwick Z020 universal tensile machine equipped with 500 N load cell was used to measure the stress as function of strain of each loading and unloading cycle at a strain rate of $3.33 \times 10^{-2}\text{ s}^{-1}$ (test speed of 50 mm/min). The strain of each loading–unloading cycle was increased (stair-case loading tensile test) and the tensile set was determined as function of the applied strain. There was no holding time between cycles. The incremental tensile set was calculated from the following relation:

$$\begin{aligned} \text{Tensile set} &= \frac{\Delta \varepsilon_{\text{remaining}}}{\Delta \varepsilon_{\text{cycle}}} \\ &= \frac{\varepsilon_{r, \text{cycle}(i)} - \varepsilon_{r, \text{cycle}(i-1)}}{\Delta \varepsilon_{\text{cycle}}} \times 100\% \end{aligned} \quad (2)$$

With $\varepsilon_{r, \text{cycle}(i)}$ the remaining strain at the end of cycle i and with $\varepsilon_{r, \text{cycle}(i-1)}$ the remaining strain at the end of the preceding cycle $i-1$. Direct after the stress was zero a new cycle was started and the strain steps were 10%.

3. Results and discussion

Segmented polyether(ester–amide)s ($m\text{-PEEA}_c$) based on poly(propylene oxide) (PPO₂₃₀₀) and poly(m -xylylene isophthalamide) segments were synthesized with increasing amounts of trifunctional PPO (PPO₆₀₀₀).

By increasing trifunctional polyether content the chemical crosslink density is increased. The triol content is given as function of the total ether content. However, as the diol ($M_n = 2300$) has almost a similar molecular weight to each polyether arm of the triol ($M_n = 2000$). The molecular weight between crosslinks (M_c), the combined chemical and physical crosslinks, is only changed from 2300 to 2180 g/mol (Fig. 2). Thus, the crosslink density does not change significantly with PPO₆₀₀₀ content, but the amount of physical crosslinks is reduced.

The amide content was kept constant at approximately 27 wt% and the random amide segment length x is thereby increased from 3.3 to 4.5 (Table 1). This increase in amide segment length is expected not significantly affecting the morphology of the copolymers and neither the modulus and elastic properties [2].

During polycondensation the melt turned cloudy and the materials were also non-transparent at room temperature. This suggests that during polymerization liquid–liquid demixing had taken place [2]. Furthermore, it was found that with 10 mol% triol or higher, the block copolymers become insoluble in the reaction mixture and formed a gel. Also the copolymers were not soluble in strong solvents like: trifluoro acetic acid, hexafluoro isopropanol, phenol/tetrachloro ethane etc. This indicates the presence of a

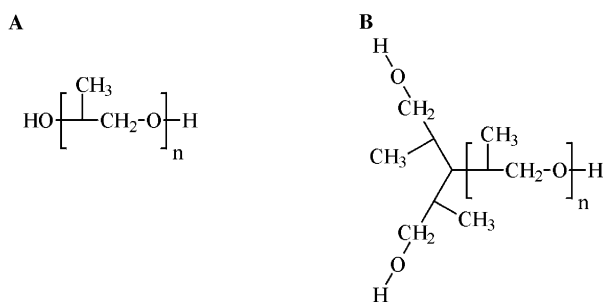


Fig. 2. Structures of poly(propylene oxide) segments: A, diol; B, triol. The value y is the degree of polymerization (≈ 40). The EO groups are not drawn for reasons of simplicity.

Table 1
Properties of *m*-PEEA_c with increased content of trifunctional PPO₆₃₀₀ (triol) segments (amounts are relative to diol)

Triol (mol%)	Triol (wt%)	x^a	$I(X_m I)_x$ (wt%)	M_c (g/mol)	$T_{g, \text{soft}}$ (°C)	T_{flex} (°C)	$G'_{25^\circ\text{C}}$ (MPa)	CS (%)	$\tau_{1/2}^b$ (s)	TS _{50%} ^c (%)
0	0	3.3	27	2300	−55	−35	3.3	51	28,000	37
10	23	3.5	27	2270	−57	−35	2.7	50	65,000	30
14	30	3.5	26	2250	−56	−35	3.3	33	4000	28
18	37	3.6	27	2240	−55	−35	3.9	25	–	30
31	54	4.1	26	2200	−56	−35	2.6	2	–	–
40	63	4.5	27	2180	−54	−30	3.5	8	1200	20

^a Average amide segment length x .

^b Recovery half-time, determined as the time where the CS (at 10 s) is reduced by 50%.

^c TS_{50%} is the tensile set at 50% strain.

chemical network structure and limits the analysis of the materials by NMR and solution viscometry. Another difficulty is the melt processing and the film formation from solution (for TEM analysis). However, test samples for mechanical tests could be prepared by compression moulding.

The morphology of linear *m*-PEEA with non-crystallizable amide segments with liquid–liquid demixed morphologies consist of spherical hard amorphous domains dispersed in a polyether matrix Fig. 3 [2].

This morphology is also schematically given in Fig. 4(a) where the polyether (phase A) is the matrix phase and the amide segments (phase B) the dispersed phase. The dispersion has a bimodal size distribution consisting of nano-particles (~5 nm) and ‘salami type’ sub-micron particles (30–700 nm) [2]. The ‘salami type’ particles most likely contain next to amide segments dispersed PPO particles. The copolymer with triol segments, now also contains chemical crosslinks are present in the polyether phase (Fig. 4(b)).

The thermal and elastic properties of *m*-PEEA_c with increasing triol content measured on compression moulded samples are given in Table 1.

3.1. DMTA measurements

The loss and storage moduli of the chemically crosslinked *m*-PEEA_c polymers were measured as function of temperature by DMTA (Fig. 5, Table 1).

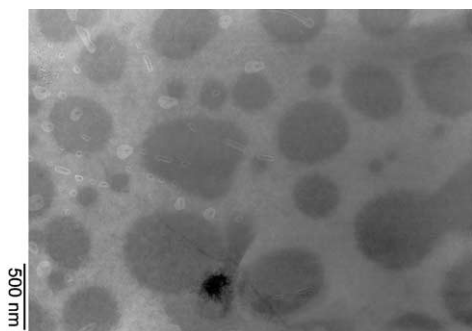


Fig. 3. TEM of *m*-PEEA with 0% Triol [2].

All the polymers have a low T_g (−55 °C), which indicate excellent phase separation of the ether and amide segments. The content of chemical crosslinks has no effect on the T_g . This means that amount of dissolved amide segments in the polyether phase is for all copolymers small. The glass transition temperature can change with molecular weight between crosslink points (M_c) [12].

The M_c did not change significantly in these block copolymers (Table 1) and the change from physical to chemical crosslinks has apparently no effect on the glass transition temperature. The T_{flex} is at a low temperature and independent of chemical crosslink content. In the rubbery region (above the T_{flex}) the modulus decreased gradually with temperature. The modulus at 25 °C ($G'_{25^\circ\text{C}}$) is low and little dependent on chemical crosslink content. The copolymers had such a low modulus that a flow temperature, if existed, could not be determined.

The modulus of a particle filled polymer system can be described by Eq. (3) [12,13]:

$$G = G^0(1 + 2.5\phi_h + 14.1\phi_h^2) = \frac{\rho RT}{M_c}(1 + 2.5\phi_h + 14.1\phi_h^2) \quad (3)$$

With G^0 the storage modulus of the matrix phase, ϕ_h the filler content, ρ the polymer density and M_c the molecular weight between crosslinks (chemical+physical). In this model it is assumed that the modulus of the filler particles is large compared to the modulus of the matrix. This composite model can also be used to describe the increase in modulus for linear liquid–liquid demixed segmented block copolymers [2].

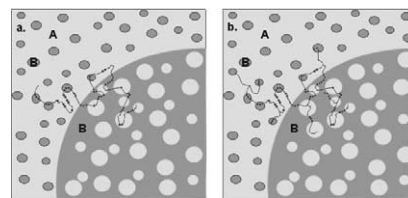


Fig. 4. Schematic representation of the morphology of *m*-PEEA with phase A is PPO and phase B is amide phase: (a) linear polymer; (b) chemically crosslinked *m*-PEEA_c.

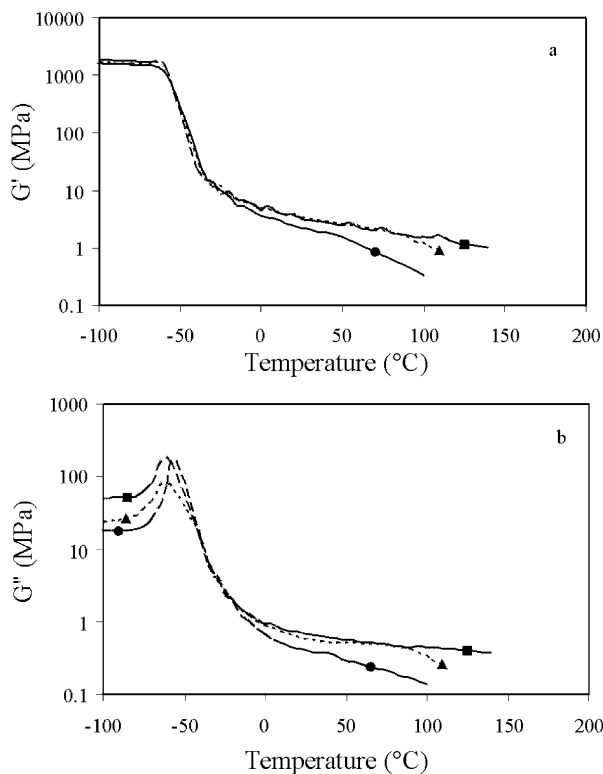


Fig. 5. Storage (G') and loss modulus (G'') as function of temperature of m -PEEA_c with increasing chemical crosslink content. Triol content mol%: (●), 0; (▲), 14; (■), 40.

In our system, chemical crosslinks are introduced without changing the M_c (Table 1). As the amide content was kept constant at ~ 27 wt%, the ϕ_h is expected to remain constant as well. Therefore, it seems logical that the modulus of our m -PEEA_c remained constant with increasing amounts of triol (Table 1).

3.2. Elastic behavior

3.2.1. Compression set

Compression set (CS) is a standard test for evaluating the elastic behaviour of segmented block copolymers and was studied as function of triol content (mol% ether) (Fig. 6, Table 1).

With increasing amount of triol (chemical crosslinks) the CS values decreased considerably. By increasing the triol content several changes have taken place. As the triol content is increased the number of chemical crosslinks increase and chemical crosslinks suppress the flow of polymer chains. Furthermore, with increasing the triol content and a constant concentration of network point (constant M_c) the number of the deformable physical crosslinks is reduced. The decrease in physical crosslink points decreases the possible plastic and/or viscoelastic deformation of these physical crosslink points. An extra effect of decreasing physical crosslink points at a constant amide content is that the amide segment length (x) increases

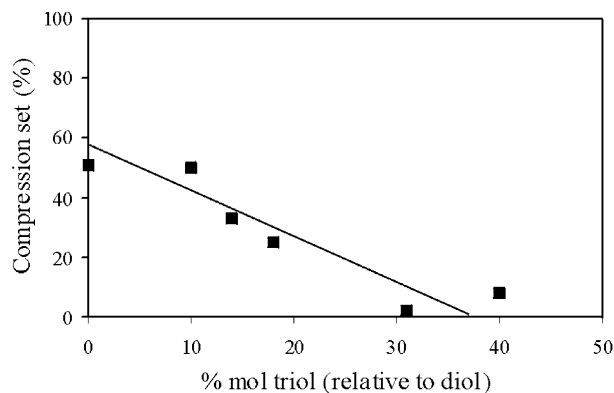


Fig. 6. Compression set of m -PEEA_c as function of the triol content.

(Table 1). However, the effect of increasing the segment length from 3.3 to 4.5 (Table 1) on the CS is expected to be minimal [2].

In a standard ASTM compression set experiment the compression set (CS) is measured 30 min (1800 s) after the sample is unloaded. As the recovery of polymers and particular TPE's is a time dependent (viscoelastic) process the recovery of several copolymers was monitored as function of time over a period of several weeks ($30\text{--}1 \times 10^6$ s) (Fig. 7). The compression set values after 30 s (the first measurement) differed greatly with the crosslink content. With time (recovery time) the compression set values of most samples decreased to zero and thus fully recovered.

This time dependent recovery is a viscoelastic process, which also has an S-type relationship with log time. The recovery half times ($\tau_{1/2}$) of the viscoelastic process decreases with increasing degree of crosslinkings (Table 1).

These materials have thus an elastic response occurring instantaneously on unstraining and a viscoelastic recovery [2]. With increasing amounts of chemical crosslinks the elastic recovery is stronger and the viscoelastic recovery faster. The lower elastic recovery and slower viscoelastic recovery of the linear polymer must be due to the

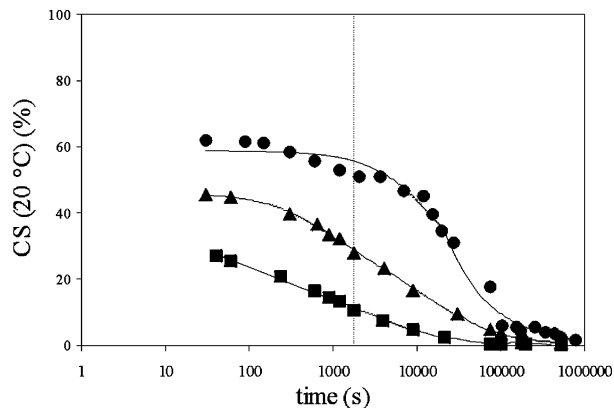


Fig. 7. Compression set as function of recovery time of m -PEEA_c. Triol content (mol% ether): (●), 0%; (▲), 14; (■), 40% (Dashed line indicates the compression set at 30 min).

deformation of the physical crosslinks. The physical crosslinks are the dispersed particles and these dispersed particles must have deformed appreciably on straining, but it is difficult to see how this is possible. The deformation of the dispersed domains depends on the ratio of the moduli of the particles and matrix phase. As the dispersed amide particles are in the glassy state they have a much higher modulus than the PPO ($E_{\text{amide}} \approx 2000$ MPa [14], $E_{\text{PPO}} \approx 1.2$ MPa). The deformation of glassy particles is expected to be only a fraction of the 25% applied strain. At very low strains (well below the yield strain) the glassy amide particles are expected to behave fully elastic. The less elastic and slower viscoelastic effects with physical crosslink content can be explained by the suggestion that not the whole amide particle deforms but that individual polymer chains are pulled out of these glassy particles [2]. The amide domains have glass transition temperatures well above room temperature and retraction of these polymer chains, after releasing the compressive strain, back into the hard domains may therefore be slow. The PPO-triols are expected not to interfere with what is happening in the glassy amide phase. The CS and the viscoelastic properties are directly related to the amount of physical network points.

3.2.2. Tensile set

The incremental tensile set (TS) as function of applied strain of PEEA's with increasing amounts of chemical crosslinks was studied (Fig. 8, Table 1). In the region of 0–30% strain, the TS increases strongly and thereafter only a gradual increase is observed. With an increasing concentration of chemical crosslinks the TS-values are lowered. These results are in line with the trends observed in the compression set experiments (Fig. 6). However, the TS values are higher than the CS values, this probably due to the absence of a 30 min relaxation time in the TS. The increase in TS with strain is somewhat stronger for the chemical crosslinked materials.

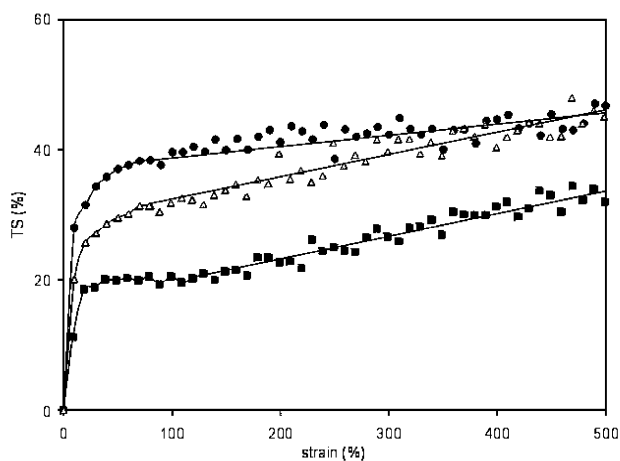


Fig. 8. Tensile set (TS) as function of strain of *m*-PEEA_c. Triol content (mol% ether): (●), 0%; (△), 18%; (■), 40%.

3.3. Stress–strain behavior

The tensile properties were measured on compression moulded samples (Fig. 9). Although the samples looked good, a good flow of the highly crosslinked materials was not possible. The tensile stress at 10% strain of the studied blockcopolymers is in the order of 0.1–0.4 MPa. These *m*-PEEA_c are very soft materials, like already observed with the $G'_{25\text{ }^\circ\text{C}}$ values (Table 1). The stress–strain behavior is up to 300% strain independent of the chemically crosslink content.

At high strains a strain hardening behavior is observed for the linear polymer (0% triol). The chemical crosslinks seem to suppress the strain hardening. The fracture strains of all the samples are high despite the poor flow during compression moulding and the 14% crosslinks sample has a fracture strain of even 1700%. The true fracture stress of the 0 and 14% triol is thereby the same at ~ 170 MPa.

4. Conclusions

Polyether(ester–amide)s (*m*-PEEA_c) with difunction PPO₂₃₀₀, trifunctional PPO₆₀₀₀ segments and non-crystallizable amide segments (27 wt% amide) were synthesized. During the polymerization liquid–liquid demixing was taking place and with triols present the polymers formed gels. The morphology of the *m*-PEEA copolymers has nano and submicron particles. With increasing chemical crosslinking the PPO T_g and the $G'_{25\text{ }^\circ\text{C}}$ were unaffected, however, the compression set and tensile set (at strains below 300%) decrease strongly. The lower sets with increasing triol contents can be explained by the lower contents of physical crosslinks. The recovery of compressive strain of the PEEA's shows a viscoelastic process. This must be due to rearrangements in the amide phase [2]. The recovery proceeds at a considerable higher rate when the triol content in the PEEA_c is above 10 (mol%) and giving time the materials with the liquid–liquid demixed morphology recovered completely. The viscoelastic deformation process

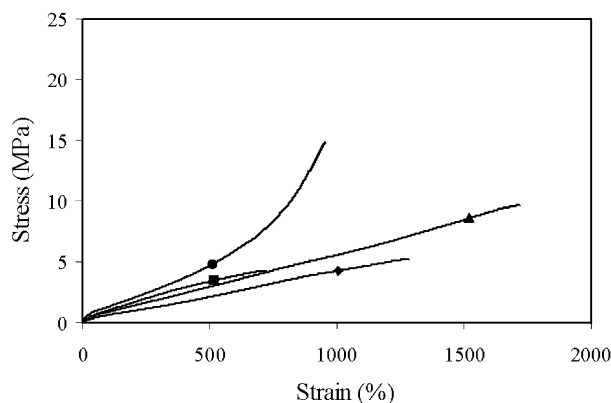


Fig. 9. Stress–strain curves of PEEA_c. Triol content (mol% ether): (●), 0%; (◆), 10%; (▲), 14%; (■), 40%.

has been explained as being due to deformation of single amide segments and not whole amide particles.

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