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Effect of soft segment molecular weight on tensile properties of poly(propylene oxide) based polyurethaneureas

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ABSTRACT

Influence of soft segment molecular weight and hard segment content on the morphology, thermomechanical and tensile properties of homologous polyurethaneurea copolymers based on narrow molecular weight poly(propylene oxide)glycol (PPG) oligomers were investigated. A series of polyurethaneureas with hard segment contents of 12–45% by weight and PPG number average molecular weights $<M_n>$ of 2000 to 11,800 g/mol were synthesized and characterized structurally by SAXS and mechanically by DMA and stress strain analysis. Bis(4-isocyanatocyclohexyl)methane and 2-methyl-1,5-diaminopentane were used as the diisocyanate and the chain extender respectively. All copolymers displayed microphase separation by SAXS and DMA. The critical entanglement molecular weight (M_e) of PPG is reported to be around 7700 g/mol. Our mechanical results suggest that when copolymers possess similar hard segment contents and are compared to those based on soft segments with number average molecular weights (M_n) greater than M_e, they generally displayed higher tensile strengths and particularly lower hysteresis and creep than those having soft segment molecular weights below M_e. These results imply that soft segment entanglements in thermoplastic polyurethaneureas may provide a critical contribution to the tensile properties of these copolymers – particularly in the range where the soft segment content is dominant.

1. Introduction

Segmented thermoplastic polyurethanes and polyureas (TPU) display very interesting composition dependent morphology-property relationships. Specifically, their mechanical properties in particular are highly influenced by several parameters including soft segment molecular weight and chemical make up, hard segment type, content, symmetry, chain extender, etc. [1–7]. TPUs are usually prepared by reacting a hydroxyl terminated aliphatic polyether or polyester oligomer with a number average molecular weight of 1000–2000 g/mol, a diisocyanate and a diol or diamine chain extender [1–7]. In the solid state, TPUs display composition dependent microphase morphologies, which play a dominant effect in determining the overall properties of the polymer. In conventional A-B-A type triblock copolymer systems such as polystyrene-polybutadiene-polystyrene, in order to have microphase separation one has to achieve a sufficient degree of polymerization of each block to promote a sufficient chemical incompatibility in order to induce strong microphase separation, which is needed for these systems to behave as thermoplastic elastomers. Since that system is not highly polar, the critical block lengths that are needed to induce microphase separation are high enough to often exceed the molecular weight between entanglements as well, which means that this added entanglement effect on properties is typically present particularly for the soft rubbery block in these materials [8]. In fact Jerome and co-workers have shown the importance of this soft block entanglement effect [9]. However, in TPUs where strong hydrogen bonding occurs between the hard segments, one might question if this type of entangled soft segment physical network is expected to supersede such a requirement?

Recently, we reported unusually high tensile strengths and low hysteresis values in silicone-urea copolymers based on polydimethylsiloxane (PDMS) soft segments with number average molecular weights above PDMS M_e [10]. We strongly suggested the unexpected improvement in tensile strength and hysteresis performance of silicone-urea copolymers to be due to the contribution from the soft segment entanglements. Similar effects on the improvement in the modulus of PDMS elastomers have also been reported by Cohen and co-workers [11,12]. Cooper [13] discussed

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the effect of PEO soft segment molecular weight (830–3000 g/mol) on microphase separation and melt rheology of polyurethanes, but did not address the issue of M_e. The effect of soft segment molecular weight on morphology and properties of PPG based polyurethaneureas was also systematically investigated by O'Sickey and co-workers [14]. Polyurethaneurea copolymers with PPG soft segment molecular weights in 2000–8000 g/mol range and relatively low hard segment contents of 9–20% by weight were investigated. It was observed that increasing the soft segment molecular weight resulted in better microphase separation as evidenced by small angle X–ray scattering (SAXS), atomic force microscopy (AFM) and thermomechanical analysis. The increase in the molecular weight of the PPG soft segment led to increased microphase separation which also provided greater soft segment mobility and lower T_g of the soft segments. Sheth and co-workers [15] also studied the effect of PPG molecular weight on the morphology and properties of linear and hyperbranched polyurethaneureas. They reported that linear copolymers exhibited long temperature insensitive rubbery plateaus as the hard segment length increased, which also resulted in better hydrogen bonding organization in the hard segments. While not using urethane chemistry, Gaymans and co-workers also reported the influence of PPG molecular weight (1000–4000 g/mol) [16] and PTMO molecular weight (650–2900 g/mol) [17] on the microphase separation and thermal and mechanical properties of segmented polyamides, which also included data on their hysteresis and compression set behaviors. However, the molecular weights of the PPG and PTMO oligomers used were well below M_e.

In this study we investigated the effect of PPG soft segment molecular weigh, both above and below M_e, and urea hard segment content on the thermomechanical, tensile, hysteresis and creep behavior of poly(propylene oxide) based segmented polyurethaneurea copolymers.

2. Experimental

2.1. Materials

Bis(4-isocyanatocyclohexyl)methane (HMDI) (Bayer MaterialScience) with purity greater than 99.5% was utilized. Poly(tetramethylene oxide)glycol (PTMO) with M_n of 2040 g/mol, was supplied by Du Pont. Narrow molecular weight poly(propylene oxide)glycol oligomers (PPG), which are marketed under the Acclaim® Trade Name were kindly provided by Bayer MaterialScience. They had M_n values of 2,030, 4,040, 7960 and 11,800 g/mol and were all used as received. Table 1 provides the average molecular weights of PPG oligomers utilized in this study. GPC results clearly demonstrate that all PPG oligomers used had very narrow molecular weight distributions with polydispersity (PD) values between 1.04 and 1.09. 2-Methyl-1,5-diaminopentane (DY) (DuPont), reagent grade isopropyl alcohol (IPA) and tetrahydrofuran (THF) (Merck) were used as received. The catalyst, dibutyltin dilaurate (DBTDL) was a product of Air Products.

Table 1
Average molecular weights and polydispersities of PPG oligomers obtained by GPC

Code	M_n (g/mol)[a]	M_w (g/mol)[a]	PD[a]	M_n from OH # (g/mol)
PPG-2K	3040	3210	1.06	2030
PPG-4K	6340	6610	1.04	4040
PPG-8K	11,900	12,800	1.08	7960
PPG-12K	16,700	18,200	1.09	11,800

[a] Calculated from hydroxyl number.

2.2. Polymer synthesis

Polymerization reactions were conducted in 3-neck round bottom flasks equipped with an overhead stirrer, addition funnel, and nitrogen inlet. Copolymers were prepared in two steps, which consisted of prepolymer formation and chain extension. Prepolymer was prepared in THF solution. Chain extension reactions were performed at room temperature in a mixture of THF/IPA. The typical reaction procedure for the preparation of PPG-8K based copolymer with 20% by weight hard segment was as follows: 8.75 g (1.10 mmol) PPG-8K and 1.64 g (6.25 mmol) HMDI were introduced into the reaction flask, dissolved in 6.0 g THF, stirred and heated to reflux at about 65 °C. 250 ppm of DBTDL (0.5% solution in THF) was added as catalyst and the system was reacted for 2 h. Prepolymer solution was cooled down to room temperature and diluted with 10.0 g of THF and 12.0 g of IPA. Isocyanate titration indicated 93% of theoretical NCO remaining, which is typical for these reactions. 7% of the isocyanate was consumed due to side reactions [18]. Following the prepolymer preparation, 0.56 g (4.82 mmol) DY was dissolved in 11.0 g THF and 8.0 g IPA, introduced into the addition funnel and added dropwise into the reactor under strong agitation. During the chain extension step, after about 25% of DY addition dropwise into the reaction mixture, the solution started displaying a milky appearance but it became homogeneous throughout the chain extension reaction and there was no polymer coagulation. This behavior was only observed for copolymers based on PPG-8K and PPG-12K. FTIR spectroscopy was utilized to follow the completion of reactions by monitoring the disappearance of strong isocyanate absorption peak at 2265 cm^{-1}

2.3. Characterization methods

FTIR spectra were recorded on a Nicolet 7600 FTIR spectrometer using solution cast films on KBr discs, which were completely dried using a heat gun before their spectra were measured. 32 Scans were taken for each spectrum with a resolution of 2 cm^{-1}. Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) measurements were performed under ambient conditions by using a Nicolet iS10 spectrometer. The spectrometer was equipped with a flat diamond plate. The spectra of solvent cast and dried films were collected at an angle of 42° and a resolution of 4 cm^{-1}. 16 scans were obtained for each spectrum.

Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPCmax instrument equipped with VE2001 GPC solvent/sample module, Dguard, D2500, D4000, D5000 columns and Viscotek VE3580 refractive index detector. Measurements were made in DMF solutions containing 0.01 M LiBr, at 50 °C with a flow rate of 1.0 mL/min. Narrow molecular weight PMMA standards were used for calibration.

SAXS experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-ray with a wavelength of 0.154 nm (Cu Kα). The sample-to-detector distance was 1603 mm, and q-range was calibrated using a silver behenate standard. Two-dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector, with an exposure time of 1 h. The raw SAXS data was corrected for sample thickness, sample transmission and background scattering. Then absolute intensity was obtained using a type 2 glassy carbon sample as a standard that had been calibrated in Argonne National Laboratory. All SAXD data were analyzed using the SAXSGUI software package to obtain radically integrated SAXS intensity versus scattering vector q, where $q=(4\pi/\lambda)\sin(\theta)$, θ is one half of the scattering angle and λ is the X-ray wavelength. In this report, the profiles were vertically shifted to facilitate a comparison of the peak positions. And thus no numerical values or units are shown for the intensity in the SAXS profile plots.

Dynamic mechanical analysis (DMA) was performed on a TA Model Q800 instrument. The test specimens (approximately 9 × 5 × 0.5 mm) were cut from solution cast films. Measurements were performed in tensile mode between −100 and +250 °C. The frequency was 1 Hz and the heating rate was 3 °C/min. Tests were conducted under a dry nitrogen atmosphere.

Stress-strain and hysteresis tests were performed on an Instron model 4411 tester, controlled by Series IX software. Polymer films with final thicknesses of 0.3–0.5 mm were cast into Teflon molds from solution and kept at room temperature overnight to slowly evaporate the solvent. Then they were transferred into a 50 °C vacuum oven and kept there until the solvent was completely evaporated and the films reached a constant weight. Visually these films were quite optically clear indicating that no structural variation occurred on the scale of the wavelength of light. Dog-bone shaped specimens (ASTM D-1708) were cut from these films. The initial sample length (L_o) was 24.0 mm. Tensile tests were performed with a crosshead speed of 25.00 mm/min 10 Cycle hysteresis behavior of the materials were investigated by stretching them to 300% elongation and then immediately reversing the crosshead at the same speed of 25.0 mm/min. Tests were conducted at room temperature and for each polymer at least three specimens were tested. Test conditions were similar to those of polydimethylsiloxane-urea copolymers reported earlier [19].

Constant initial stress creep behavior of PPG based polyurethaneureas was tested at room temperature. A dog-bone shaped specimen (ASTM D-1708) was clamped on a sample holder which was attached to a metal frame. A constant weight was loaded on the free end of the specimen through a metal grip. A metric scale bar was used to measure the time dependent extension of the specimen. The change in the specimen length was measured for up to 10 days (240 h). Three different measurements on each polymer sample were performed.

3. Results and discussion

Recently we demonstrated a significant effect of soft segment molecular weight on improving the tensile properties and hysteresis behavior of silicone-urea copolymers [10,19]. Silicone-urea copolymers are unique materials, which display excellent microphase separation due to major differences in the solubility parameters of siloxane matrix and urea hard segments. On the other hand in conventional polyether or polyester based polyurethanes or polyureas although microphase separation is achieved, significant hydrogen bonding interaction between hard and soft segments is also possible. Therefore, in this study our aim is to understand if we could generalize the effect of soft segment molecular weight/entanglement on tensile properties and hysteresis behaviors of the polyether based polyurethaneureas based on different molecular weight PPG oligomers. The critical entanglement molecular weight (M_e) of PPG is reported to be 5800 g/mol by Krevelen [20], 7700 g/mol by Zang and Carreau [21] and 7750 g/mol by Aharoni [22]. In this study four different PPG oligomers with (M_n) values of 2030, 4040, 7960 and 11,800 g/mol and with very narrow molecular weight distributions (Table 1) were utilized. The former two oligomers have (M_n) values below (M_e), which we take as 7700 g/mol, whereas the latter two have (M_n) values above (M_e). The reader should recall that since the PPG oligomers have very narrow polydispersities, M_n is not far below M_w – the latter which is often the parameter used to compare with M_e values.

Using these PPG oligomers a large number of thermoplastic segmented polyurethaneureas with hard segment contents ranging from 12% to 45% by weight were prepared. All polymers formed uniform, strong and transparent films, including PPG-8K and PPG-12K based copolymers, which were cast from milky solutions. For comparison of the tensile properties and hysteresis behaviors, PTMO-2K based polyurethaneureas with 20 and 30% hard segment contents were also synthesized.

A list of polyurethaneurea copolymers prepared, their various structural and compositional properties and average molecular weights are provided on Table 2. Since the prepolymers are obtained by the reaction of hydroxyl terminated PPG and HMDI, the covalent bonds that connect the soft and hard segments are “urethane” linkages. On the other hand since a diamine (DY) is used as the chain extender, chemical bonds connecting the hard segments are “urea” linkages, as shown in Fig. 1. This leads to the formation of “urethaneurea” hard segments.

As can be seen from Table 2, GPC results indicated the formation of high molecular weight polyurethaneurea copolymers in all cases. In order to understand the effect of PPG chain length on the morphology and properties of the resultant materials, a series of copolymers with constant hard segment contents of 20 and 30% by weight were prepared. In order to investigate the effect of hard segment length on properties, a series of copolymers with constant hard segment length of 1680 ± 10 g/mol were also prepared. Hard segment contents, average molecular weights (M_n) of the (urethaneurea) hard segments and average urea hard segment chain lengths (which also provide the average number of urea linkages

Table 2
Average hard and soft segment chain lengths and polymer compositions.

Sample code	PPG $\langle M_n \rangle$ (g/mol)	Hard segment[a]				Polymer MW[b]	
		(wt %)	$\langle M_n \rangle$ (g/mol)	(n) urea link in HS	urea mole frac. in HS	$\langle M_n \rangle \times 10^{-3}$	$\langle M_w \rangle \times 10^{-3}$
PPG-2-20	2030	20.0	510	0.66	0.40	33.0	54.5
PPG-2-30	2030	29.2	870	1.61	0.62	31.0	51.5
PPG-2-45	2030	45.3	1680	3.75	0.79	58.5	73.5
PPG-4-20	4040	20.4	1035	2.04	0.67	99.0	136.5
PPG-4-30	4040	29.3	1675	3.74	0.79	125.0	177.0
PPG-8-18	7960	17.5	1690	3.78	0.79	86.5	127.0
PPG-8-20	7960	19.9	1980	4.54	0.82	92.0	120.0
PPG-8-30	7960	28.8	3220	7.83	0.89	47.0	85.6
PPG-12-12	11,800	12.4	1670	3.72	0.79	55.0	90.5
PPG-12-20	11,800	20.1	2970	7.16	0.88	52.0	88.0
PPG-12-30	11,800	29.9	5040	12.6	0.93	61.0	98.5
PTMO-2-20	2040	19.8	505	0.64	0.39	84.0	166.0
PTMO-2-30	2040	29.8	865	1.60	0.62	150.0	310.0

[a] Calculated from the reaction stoichiometry.
[b] Determined from GPC measurements.

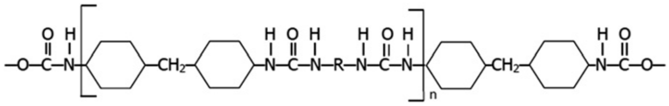

Fig. 1. Chemical structure of the urethaneurea hard segments in PPG based copolymers synthesized. (R) denotes 2-methyl-pentane backbone in the chain extender.

per hard segment (n) in the hard segment structure) were calculated from the reaction stoichiometry.

At this point it is also important to note that for PPG based polyurethaneureas with identical hard segment contents, as the average molecular weight of the soft segment increases, hard segment length and the fraction of urea groups in the hard segment also increases, as displayed in the 5th and 6th columns in Table 2. This also plays a critical role on the extent of microphase separation and properties of the copolymers.

3.1. FTIR studies

FTIR spectroscopy is a simple and reliable technique to understand the hydrogen bonding in polyurethanes by investigating various peak positions. The nature and extent of hydrogen bonding, on the other hand is closely related to the microphase separation in polyurethanes. The 1800–1400 cm^{-1} region of the ATR-FTIR spectra of copolymers containing 30% by weight hard segment but based on different molecular weight PPG oligomers, are reproduced in Fig. 2.

Three major peaks centered at 1716, 1630 and 1558 cm^{-1} are clearly observed in the FTIR spectra. The peak at 1716 cm^{-1} corresponds to non-hydrogen bonded urethane carbonyl group. It also has a shoulder at 1695 cm^{-1} which indicates the presence of a small amount of hydrogen bonded urethane carbonyl groups in the copolymers. PPG-2-30, which has the shortest hard segment length and the highest fraction of urethane groups as shown in Table 2, also has the highest amount of non-hydrogen bonded urethane groups, as shown by the relative absorbances of 1716 cm^{-1} peaks in the FTIR spectra. As the PPG molecular weight increases, the intensity of the 1716 cm^{-1} peak decreases significantly. This is expected since the urethane content of the hard segments also decreases. The strong absorption peak at 1630 cm^{-1} is due to hydrogen bonded and ordered urea groups. The skewed shape of the peaks toward higher wavenumbers indicates that there may be other less intense peaks underneath these absorption bands. These are most probably due to urea groups, which are less ordered and weakly hydrogen bonded. This may be due to the interaction of the ether oxygen in the PPG segments with the urea groups, which disturbs the hydrogen bonded urea network. The absorption band at 1558 cm^{-1}, which is usually designated as the amide II peak, is due to the combination of N–H bending and C–N stretching modes of the urethane and urea groups. The spectra in Fig. 2 were normalized using this peak as the reference.

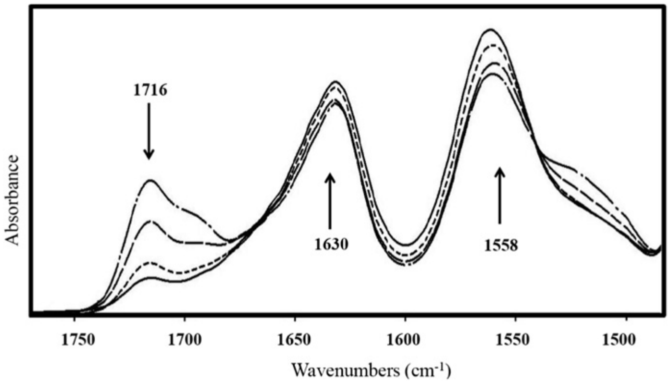

Fig. 2. Carbonyl region of the ATR-FTIR spectra of polyurethaneureas with 30% by weight hard segment content. PPG-12-30 (—), PPG-8-30 (- - - - -), PPG-4-30 (– – –) and PPG-2-30 (— ● — ● —).

3.2. Dynamic mechanical analysis

Comparative storage modulus-temperature and tan δ–temperature curves for copolymers with 30% by weight hard segment content are reproduced in Fig. 3a and Fig. 3b, respectively. As can be seen from Fig. 3a, the PPG segment molecular weight plays an important role on the modulus-temperature behavior of polyurethaneureas with identical hard segment contents. All copolymers display fairly sharp and well defined soft segment glass transition, the value of which is strongly dependent on the molecular weight of the PPG oligomer incorporated into the copolymer as also observed by O'Sickey and Wilkes [13]. Glass transition temperatures of the copolymers based on PPG-2K, 4K, 8K and 12K are determined respectively to be −42, −49, −53 and −55 °C from the peak maxima of the temperature dependent tan δ curves. As reproduced in Fig. 3b, tan δ peaks are very symmetrical and sharp, which is another indication of good microphase separation in the copolymers. Moreover, the breadth of the tan δ peak also decreases with increasing soft segment molecular weight. The dramatic effect of PPG soft segment (SS) molecular weight is also observed on the behavior of the rubbery plateau. As shown in Fig. 3a, PPG-2-30 displays a rather short and quite temperature sensitive rubbery plateau as the temperature

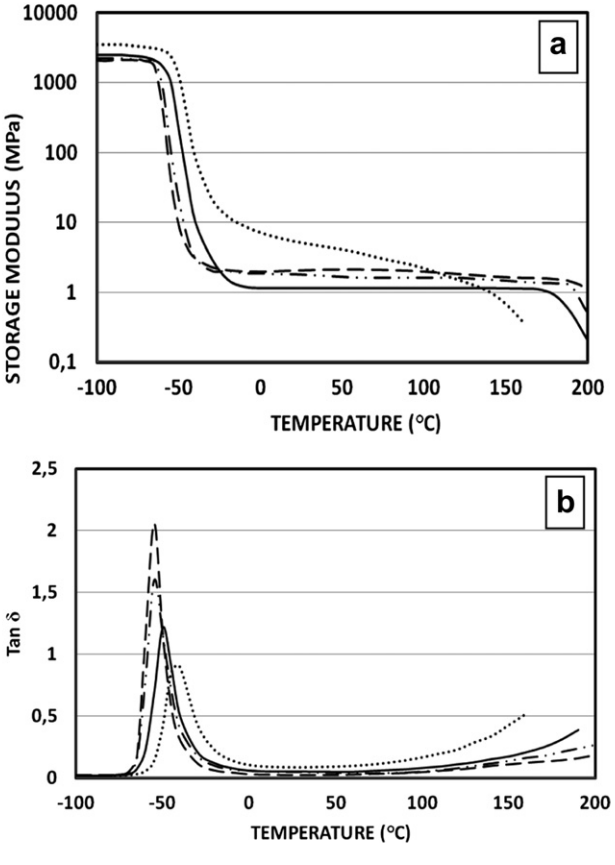

Fig. 3. (a) Storage modulus-temperature and (b) tan δ–temperature curves for PPG-2-30 (●●●●●●), PPG-4-30 (——), PPG-8-30 (– ● ● – ● ● –) and PPG-12-30 (– – –).

increases. On the other hand PPG-4-30, PPG-8-30 and PPG-12-30 display much longer and much less temperature sensitive rubbery plateaus. Likely, this is primarily due to higher hard segment length and higher urea content of the "urethaneurea" hard segments (HS) leading to improved extent of microphase separation in these samples. As will be given later in this paper, SAXS results support this latter statement as does the observation of the tan-delta behavior from the DMA. Note that these latter data in Fig. 3 show a higher peak temperature than the materials with high SS molecular weight and also the breadth of the peak is distinctly greater implying a broader Tg region which we believe is due to poorer microphase separation. Another interesting observation is that the rubbery plateaus of PPG-8-30 and PPG-12-30 is longer and has higher modulus than that of PPG-4-30. This may possibly be due to the contribution of the soft segment entanglements in PPG-8-30 and PPG-12-30 and/or stronger hydrogen bonding between longer urea hard segments in this copolymer as indicated on Table 2. Recall that the critical entanglement molecular weight of PPG is 7700 g/mol [21,22].

3.3. SAXS analysis

To obtain further evidence for the microphase separation of the SS and HS components, SAXS profiles were obtained from the same cast film materials. SAXS profiles of copolymers are reproduced in Fig. 4. The reader should note that as stated in the experimental section, these SAXS profiles have been shifted vertically relative to one another and hence the log intensity scale is not provided with units. Only the general shape and the peak positions that relate to structural features of each material will be compared. It might also be added that the profiles were arranged such that the lower most profile has the smallest interdomain or interference spacing (7.5 nm) (obtained by a Bragg analysis) while the uppermost profile possesses the largest spacing (16.5 nm). All respective values of the interdomain spacings obtained from the SAXS data are listed in Table 3.

Table 3
Interdomain spacings for the copolymers calculated from the SAXS data.

Copolymer description	Interdomain spacing (nm)
PPG-2-20	7.5
PPG-2-30	8.8
PPG-2-45	10.4
PPG-4-20	10.6
PPG-4-30	11.2
PPG-8-20	12.3
PPG-8-30	13.6
PPG-12-12	13.6
PPG-12-20	14.0
PPG-12-30	16.5

It is first noted that each sample does display a single first order interference peak indicating that microphase separation does occur in all materials and that the breadth of the peaks does vary. Recognizing that peak breadth does not represent a truly linear relationship with domain spacing distribution, it still does at least suggest that, in general, as the SS molecular weight increases from 2K to 12K, there is a narrowing of the peaks which may indicate a more homogeneous interdomain size or texture. This is not surprising since as the incompatibility of the HS and SS increase, whenever an increase in SS molecular weight occurs at constant HS content, it results in an increase in the HS molecular weight (Table 2) as well. One further observes that at a constant SS molecular weight, an increase in HS content also tends to lead to a narrowing of the interference peak and a similar argument for this behavior can be given as just presented, i.e., there will be further incompatibility between the SS and HS due to the greater average molecular weight of the HS as well. What particularly stands out is the very systematic behavior of the interdomain spacings, when either SS molecular weight is held constant and HS content is increased, or SS molecular weight is increased and HS content is held constant by also increasing the HS length, as noted in Table 3. In the case of the former, note in either Fig. 4 or Table 3 how the respective peak spacings systematically shift in the profiles for PPG-2-20, PPG-2-30 and PPG-2-40 as a function of their HS content. Likewise, as an example of the increase in domain spacing with SS molecular weight at constant HS content, the interdomain spacings calculated from the interference peaks of samples PPG-2-20, PPG-4-20, PPG-8-20 and PPG-12-20 can be compared. As the SS molecular weight increases the interdomain spacings also increase from 7.5 nm, to 10.4 nm, 12.3 nm and to a final value of 14.0 nm. Similar results are observed when the comparison is undertaken for the constant HS weight content of 30%. In this case the respective spacings are 8.8 nm, 11.2 nm, 13.6 nm and 16.5 nm as the SS molecular weight is increased from 2K to 12K – see Table 3.

In summary the SAXS results, which are very systematic, nicely reflect what one might well expect from these materials if microphase separation occurs. Certainly these data are highly supportive of the DMA results in general - in fact, the broader interference peaks noted for the 2K SS materials is basically in line

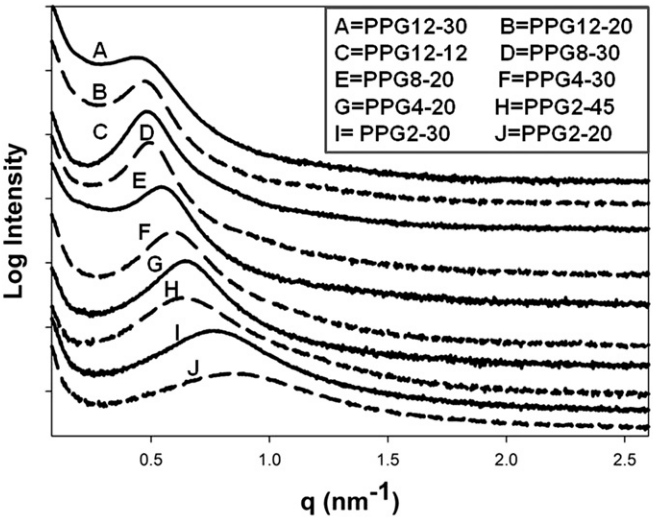

Fig. 4. SAXS profiles of PPG based polyurethaneurea copolymers.

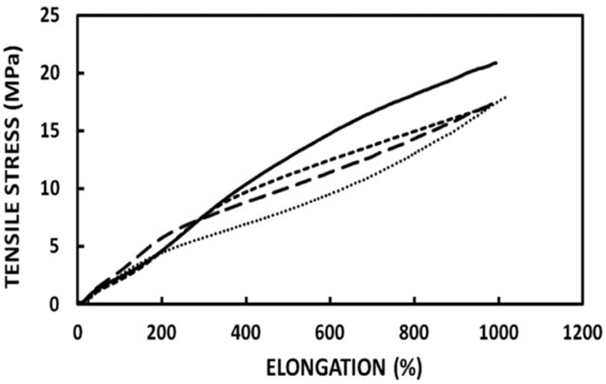

Fig. 5. Representative stress-strain curves for PPG based polyurethaneurea copolymers PPG-2-30 (●●●●●●), PPG-4-30 (———) and PPG-8-30 (-----), PPG-12-30 (——).

Table 4
Stress-strain properties of the urethaneurea PPG segmented copolymers.

Sample code	PPG $<M_n>$ (g/mol)	Modulus (MPa)	Tensile Str (MPa)	Elongation (%)
PPG-2-20	2030	1.40	5.00	>2000
PPG-2-30	2030	6.00	17.8	1010
PPG-2-45	2030	70.0	26.7	480
PPG-4-20	4040	1.80	4.50	710
PPG-4-30	4040	3.10	17.4	1000
PPG-8-18	7960	1.20	8.40	1550
PPG-8-20	7960	2.65	7.40	1170
PPG-8-30	7960	4.50	17.0	980
PPG-12-12	11,800	0.80	4.60	1470
PPG-12-20	11,800	2.20	8.10	1200
PPG-12-30	11,800	4.10	20.9	990
PTMO-2-20	2040	3.10	25.20	1070
PTMO-2-30	2040	14.50	43.80	750

with the earlier broader DMA Tg transition for the 2K material given in Fig. 3 (all DMA data for all samples was not shown for brevity).

3.4. Stress-strain behavior of polymers

Representative stress-strain curves for PPG based polyurethaneureas with 30% by weight hard segment content are reproduced in Fig. 5. They all show typical soft elastomeric behavior with relatively low modulus, reasonably high tensile strength (>15 MPa) and fairly good elongation at break values of about 1000%. PPG-8-30 and PPG-12-30 seem to display a very slight strain hardening, which may be due to much longer urethaneurea hard segments in these copolymers when compared with those of PPG-2-30 and PPG-4-30, as shown on Table 2.

Table 4 gives the results of stress-strain tests for all copolymers synthesized. As expected, when copolymers based on the same PPG soft segment are compared, their initial modulus and tensile strength values increase substantially with an increase in their hard segment contents. These results clearly indicate that ultimate tensile strengths of the copolymers depend much strongly on the hard segment length and content as compared to the PPG soft segment molecular weight. For comparison, tensile properties of PTMO-2K based polyurethaneureas are also provided on Table 4. PTMO based segmented copolymers display strong strain hardening behavior and as a result possess very high tensile strengths when compared with those of homologous PPG based systems as shown in Table 4.

To understand the influence of constant urethaneurea hard segment molecular weight (1680 ± 10 g/mol) on tensile strength of the copolymers two different plots were prepared using the data provided in Table 4. In the first plot, given in Fig. 6a, the tensile strengths were plotted as a function of PPG molecular weight in the copolymer. In the second graph, given in Fig. 6b, tensile strength was plotted as a function of the hard segment content of the four copolymers.

As can be seen from Fig. 6a there is a steady decrease in the tensile strength as the molecular weight of PPG in the copolymer increases at constant hard segment length or molecular weight. This is expected since as the molecular weight of PPG in the copolymer increases the constant molecular weight hard segment content (in weight percent) decreases, as shown on Table 2. On the other hand, as shown in Fig. 6b, when tensile strength is plotted as a function of hard segment content, the tensile strength of the copolymers with constant hard segment molecular weight but with decreasing PPG soft segment molecular weight, increase linearly.

3.5. Hysteresis behaviors of copolymers

In our earlier studies with polydimethylsiloxane-urea copolymers we observed the important effect of the soft segment molecular weight on the hysteresis behaviors, where as the PDMS molecular weight in the copolymers increased, a dramatic reduction in the hysteresis was observed [19]. To understand if such a relationship between the hysteresis behavior of PPG based polyurethaneureas and the PPG soft segment molecular weight also existed, we investigated the hysteresis behaviors of the PPG based polyurethaneureas containing 20% by weight hard segment. As stated earlier in this report, the 10 cycle hysteresis behaviors of the copolymers were studied by stretching the samples to 300% elongation with a rate of 100% elongation per minute and then reversing the crosshead direction at the same rate. Experimental hysteresis curves for PPG-2-20, PPG-4-20, PPG-8-20 and PPG-12-20 are provided in Fig. 7.

Hysteresis curves provided on the first column (in Fig. 7) are for the first five cycles (Cycle 1–5) and on the other column for the next five cycles (Cycle 6–10). As expected, the first cycle results in the highest hysteresis for all copolymers due to the substantial deformation applied, resulting in dramatic changes in the initial morphology. After the second cycle hysteresis decreases gradually in all subsequent cycles until the final, tenth cycle. Detailed analysis of hysteresis behavior for all copolymers after each cycle is provided on Table 5.

As can be seen from Fig. 7 and Table 5, a very interesting observation is a decrease in the percent hysteresis of the copolymers with an increase in the PPG molecular weight. For example, PPG-2-20 displays a first cycle hysteresis of 34.2%, while PPG-4-20 and PPG-8-20 display slightly lower first cycle hysteresis values of 33.5% and 27.3% respectively. As for the PPG-12-20, first cycle hysteresis is only 22.6%, much lower than the others. Very similar behaviors are observed in the subsequent hysteresis cycles. This behavior and trend in hysteresis as a function of the PPG molecular

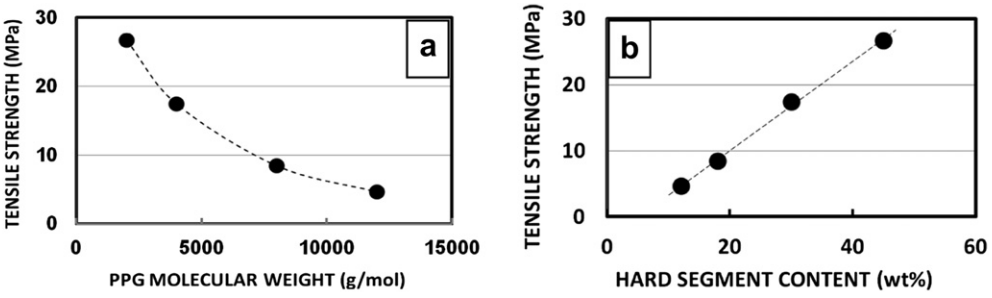

Fig. 6. Tensile strengths of copolymers with constant urethaneurea hard segment molecular weight of 1680 ± 10 g/mol, plotted as a function of; (a) PPG molecular weight, and (b) hard segment content.

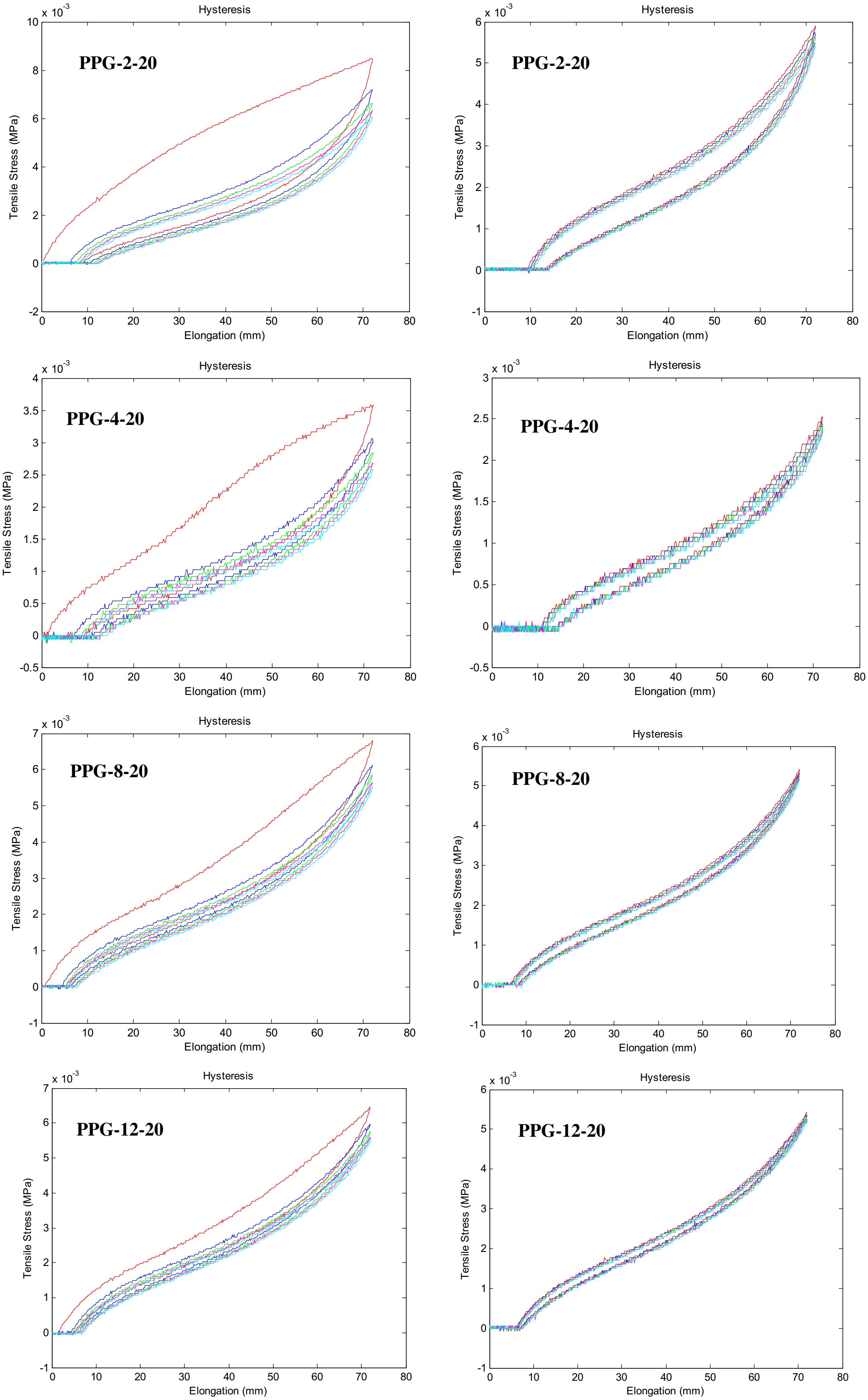

Fig. 7. 300 Percent, 10 cycle hysteresis curves for PPG based polyurethanureas.

Table 5
10 Cycle, 300% hysteresis behaviors of PPG based polyurethaneureas.

polymer Code	Hysteresis after cycles (%)									
	1	2	3	4	5	6	7	8	9	10
PPG-2-20	34.2	23.0	21.6	21.3	20.5	20.0	19.8	19.5	19.2	18.9
PPG-4-20	33.5	22.6	21.1	19.3	18.3	18.6	18.0	17.7	17.0	16.5
PPG-8-20	27.3	14.8	12.7	12.3	12.0	11.8	11.4	11.0	11.0	10.8
PPG-12-20	22.6	11.5	9.7	8.8	8.8	8.5	8.4	8.3	8.2	8.0

Table 6
Comparison of the 300% hysteresis behaviors of PPG and PTMO based polyurethaneureas.

polymer Code	Hysteresis after cycles (%)									
	1	2	3	4	5	6	7	8	9	10
PPG-2-20	34.2	23.0	21.6	21.3	20.5	20.0	19.8	19.5	19.2	18.9
PPG-2-30	55.5	30.5	28.4	27.6	26.8	26.6	25.9	25.7	25.4	25.3
PTMO-2-20	47.7	33.4	30.0	28.1	27.5	25.9	25.2	25.0	24.4	24.3

weight is very similar to our results reported on PDMS based segmented polyurea copolymers [19].

When the *first cycle* hysteresis values are plotted against PPG molecular weight, as shown in Fig. 8, a near linear relationship is observe in that hysteresis decreases as the soft segment molecular weight increases. As we have discussed earlier, these results are very similar to the hysteresis behaviors of polydimethylsiloxane-urea copolymers [19]. Since a higher first cycle hysteresis tends to imply a greater level of structural disruption with strain, our data suggest that there is less structural alteration with the initial cycle as both the soft and hard segment molecular weight increases which we believe results from a sharper microphase separation of the soft and hard segments. This is certainly expected due to the enhanced segment lengths which help increase the incompatibility of these two segment types and also lead to a decrease in the entropy of mixing of the hard and soft segments.

In order to understand the effect of hard segment content on the multi-cycle hysteresis behavior, a 10 cycle hysteresis experiment on PPG-2-30 was also carried out under similar experimental conditions. The results are provided on Table 6. As can be seen from this Table, an increase in the hard segment content of the copolymer results in a substantial increase in the percent hysteresis in all cycles as might be expected due to the development of greater hard segment continuity which will undergo disruption with deformation – other factors being viewed as constant. The hysteresis behavior of a more conventional polyurethaneurea PTMO-2-20, which is based on PTMO-2K, had a hard segment content of 20% by weight and identical urea hard segment structure as in PPG-2-20. It is interesting to note from Table 6 that first cycle hysteresis of PTMO-2-20 is 47.7%, much higher than that of PPG-2-20, which has a 34.2% hysteresis. This may be due to the difference in the molecular weight distribution of PTMO-2K oligomer (broad MWD) compared to PPG-2K oligomer (narrow MWD), which may lead to poorer microphase separation in PTMO-2-20. Another possibility is the strain induced crystallization of the PTMO soft segments leading to major reorganization in the initial morphology of the material after the first cycle. This may be an interesting topic, which needs to be investigated and reported separately.

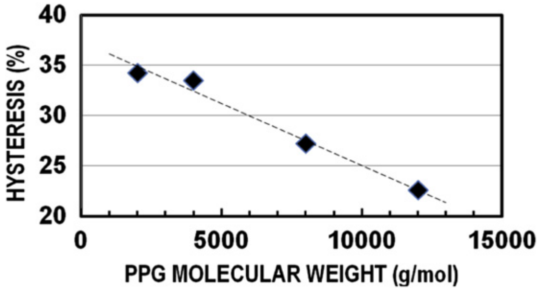

Fig. 8. Effect of PPG molecular weight on the first cycle hysteresis behaviors of polyurethaneureas with constant (20% by weight) hard segment content.

3.6. *Creep behavior of copolymers*

Two important performance related properties of thermoplastic elastomers are compression set and creep. Creep is defined as the time dependent change in dimensions of polymers upon application of an instant constant stress. Creep behavior of polymers depends on many factors such as; magnitude of the initial stress applied, loading time, temperature, chemical structure of the polymer, topology and morphology. At sufficiently high initial stress or long loading time the polymer may extend until it ruptures. Creep resistance of a polymer also generally decreases with increasing temperature.

To understand the effect of polymer composition and the molecular weight of the PPG soft segments on creep behavior of copolymers, constant engineering stress creep experiments were performed. The magnitude of the constant initial stress applied to all samples was equal (1.50 MPa) in order to make a reliable comparison. The change in the length of the specimens was monitored for up to 10 days or until failure. Percent elongation versus time plots obtained in creep experiments for copolymers containing 30% by weight hard segment, but based on PPG oligomers with different molecular weights, are provided on Fig. 9.

Upon application of the constant engineering stress of 1.50 MPa, all samples show an extension around 60–70% after 10 s. Interestingly, all samples except PPG-2-30 display almost no change until 10,000 s or 3 h. Then they only show a slight creep for up to 1,000,000 s or 12 days, reaching to about 120–130% elongation. On the other hand PPG-2-30 behaves quite differently and shows considerable creep much earlier, reaching to 140% and 250% elongation after 10,000 and 100,000 s. After this point the rate of creep further increases and reaches to 600% after 600,000 s. Since all samples display very similar stress-strain curves as shown in Fig. 5 and fairly similar tensile strength and elongation at break values as was provided in Table 4, such a difference in the creep behavior is

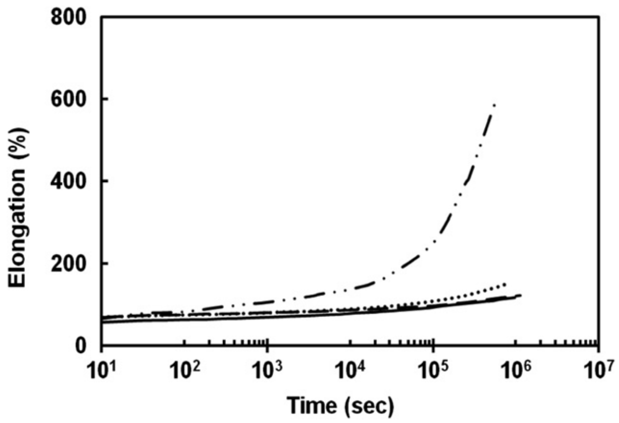

Fig. 9. Constant initial stress (1.50 MPa) creep behavior of PPG based polyurethaneureas with 30% by weight hard segment content. PPG-2-30 (— •• — •• —); PPG-4-30 (——); PPG-8-30 (••••••); PPG 12-30 (— — —).

interesting. Since all samples have 30% by weight hard segment contents, we believe two parameters may be playing critical roles in determining the creep behavior of these homologous copolymers, which are the PPG soft segment length and the urethaneurea hard segment length, or their combination.

4. Conclusions

PPG based segmented polyurethaneureas with soft segment molecular weights from 2000 to 12,000 g/mole and hard segment contents of 12–45% by weight were synthesized and characterized. The main focus of the study was to understand the effect of soft segment molecular weight and hard segment content on the morphology and tensile properties of PPG based polyurethaneureas.

The reader will recall from earlier discussion above that when copolymers with similar hard segment contents are compared, their modulus-temperature curves indicated better microphase separation for copolymers prepared by using longer PPG soft segments. As the PPG soft segment length increased, the rubbery plateau of the copolymer also became longer and more temperature insensitive, which may be an indication of the contribution of soft segment entanglement as would be expected - recall Fig. 2. The SAXS results reported earlier also supported this same conclusion.

Tensile strengths of copolymers increased linearly with increasing hard segment content, which is in agreement with our earlier studies [19]. Interestingly, copolymers with similar hard segment contents displayed slightly higher tensile strengths, with increasing soft segment molecular weight possibly due to a higher soft segment entanglement density. 300%, 10 cycle hysteresis studies on copolymers with constant hard segment content of 20% by weight showed a dramatic reduction in hysteresis with increasing PPG soft segment molecular weight. Similarly, constant initial stress creep measurements on copolymers with similar hard segment contents of 30% by weight showed dramatically increased creep resistance with increasing PPG soft segment molecular weight. Again, we postulate that this latter behavior may also be due in part to a higher soft segment entanglement density.

All of these results indicate the critical contribution of soft segment molecular weight and soft segment entanglements on the morphology and tensile properties, especially the hysteresis and creep behavior of PPG based polyurethaneureas, are similar to those of PDMS based polyurethaneureas reported earlier [19].

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