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Polymer 46 (2005) 10158–10166

polymer

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Enhancing polyurethane properties via soft segment crystallization

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Received 5 April 2005; received in revised form 25 July 2005; accepted 1 August 2005
Available online 24 August 2005

Abstract

Semi-crystalline polyester diols with relatively high melting points and enthalpies of crystallization are shown to form nearly co-continuous lamellar structures in thermoplastic polyurethanes using polyether soft segments. This high aspect ratio crystalline structure results in materials with exceptional tensile and elastic properties compared to materials made with conventional semi-crystalline soft segments such as polycaprolactone or polybutylene adipate. Additions of semi-crystalline soft segment to foam formulations also result in increased hardness measured by standard foam hardness tests. Halpin–Tsai and percolation model analyses of the results suggest that the crystalline regions exert a global influence on the elastomer structure.

Keywords: Polyurethane; Elastomer; Crystallization

1. Introduction

Phase separated polyurethane structures are copolymers comprised of a rubbery, low T_g soft phase and a high T_g quasi crystalline hard phase. The properties of polyurethane elastomers (TPUs) and foams reflect the balance of their structural influences [1–5]. The phase separated hard segments act as physical crosslinks to inhibit the affine extension of the soft segments and provide a retractive force back to the initial shape [6]. The extensional and low temperature properties of the elastomers are largely a result of the soft segment properties [3,7,8]. Set properties are sometimes a result of the interactions of the hard and soft segments [9–11].

It is possible to modulate the properties of foams and elastomers by varying the chemical constituents that make up the hard and soft phases. We [12,13], along with others [14] have reported on the ability to alter the thermal and elastomeric properties that can be obtained when polyurethane hard phase is a composite of two or more structures. The synthesized elastomers had properties not achievable by elastomers of either hard segment alone. Thus, it is expected that the addition of a second soft segment with substantially different physical properties can also significantly modulate the elastomeric properties.

Recently, we have divulged the property enhancement soft segment crystallization provides [15]. In this article we will provide results from work on soft segment blends in which one of the soft segments is semi-crystalline and capable of providing significant alteration of the elastomeric properties by its contribution of a third phase to the elastomer morphology. In this regard the term soft segment takes on a somewhat different use than the conventional meaning. To be clear, the crystalline diol esters used in this work have glass transitions well below room temperature [16], but also have a crystalline transition which can significantly alter the properties of the resulting elastomer. The crystallizable soft segment diols described in this research are defined by having relatively high melting and recrystallization temperatures and enthalpies, low glass transition temperatures (T_g) (below -20 °C [16]), and their blends with amorphous soft segments result in elastomeric polyurethanes. The higher enthalpy of melting and recrystallization suggests a higher driving force to crystallize assuming the entropy of these transitions is approximately the same for these related materials.

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doi:10.1016/j.polymer.2005.08.006

Semi-crystalline soft segment diols like polybutylene adipate and polycaprolactone are well known and widely used in TPU technology [17–20], but their crystallinity as measured by the enthalpy of melt and melting point are relatively low.

Semi-crystalline polymethylene diol soft segments have been described [21] but their urethanes were non-elastomeric. Recent work has demonstrated that the mixing of soft segments does indeed influence elastomer properties and these influences can be detected using molecular techniques. O'Sickey et al. [22] synthesized polyurethane elastomers mixing polypropylene glycol (PPG) and polytetramethylene glycol (PTMEG) soft segments. Both of these materials are polyethers, but higher molecular weight PTMEG is capable of room temperature and orientational crystallization. The researchers observed that PPG is capable of interfering with the orientational crystallization of PTMEG at relatively high volume fractions. Wen et al. [23] also looked at mixtures of polyethers (polyethylene oxide and polypropylene oxide) and observed enhanced conductivity of doped ions. Queiroz et al. synthesized and analyzed polyurethane elastomers from mixtures of PPG and polybutadiene diol [24] and polydimethylsiloxane diol [25] soft segments. The presence of the non-ether component had implications on gas permeability and hydrogen bond interactions that could be measured spectroscopically. Alternative soft segment rigid phase via inclusion of organo-clay nanocomposites in foam formulations have been made by Cao et al. [26]. The clay increased the compressive strength of the foam, but also increased the foam density.

2. Experimental

Syntheses were performed in the Midland Corporate R&D labs. Bis 4,4′ methylene diphenylisocyanate (MDI), Butane diol (BDO), 2000 dalton polycaprolactone, 2000 dalton polytetramethylene glycol (PTMEG), were obtained from Aldrich Chemicals (Milwaukee, WI). Polybutylene adipate (PBA) was obtained from Crompton Chemical (Fomrez^R 44–56). T-9 and T-12 catalysts, and DC5160 surfactant were obtained from Air Products (Florida). VORANOL^R 3136, a 1000 equivalent weight triol polypropylenoxide triol, and VORONATE^R 80 an 80/20 mix of 2,4 and 2,6 toluyl diisocyanate were obtained from Dow Chemical Co. Pentadecalactone was purchased from Aldrich and distilled prior to use in polymerization. 10-Undecenoic acid was purchased from Aldrich and converted to the methyl-12-hydroxy dodecanoate (MHD) via an esterification and reductive hydroformylation procedure [27].

The semi-crystalline soft segments in this work were primarily from the polymerization of MHD and pentadecalactone. Synthesis of MHD polymer (pMHD) involved addition of a diol initiator such as hexane diol to a three necked flask containing MHD with a condenser/N_2 purge, a temperature controlled heating mantle, and heated to 150 °C. Molecular weight targets were reached by varying the monomer to initiator ratios. Upon reaching temperature 0.1% by total weight tin (II) ethyl hexanoate was added to the reaction flask and the flask then heated to 190 °C for 12 h. Evolved methanol condensed in the moisture trap. Reaction was driven to completion by replacement of the N_2 purge with a vacuum at 20 Torr to remove the remaining methanol, and further equilibrated for an additional 12 h at 190 °C. The reaction product was recrystallized from 5% ethyl acetate in hexane and collected by vacuum filtration using a coarse glass filter funnel. The product was further washed with hexane, air dried, ground through a 2 mm sieve to facilitate drying, and then dried under vacuum. Yield was typically 90%. Gel permeation chromatography was done in a THF phase using twin PL gel 5-micron mixed-D columns. Molecular weight was done using a titration and derivitization method [28].

Polypentadecalactone (PPDL) was prepared by a similar procedure except that pentadecalactone was substituted for MHD in the synthesis and no methanol evolves during the reaction.

MDI was kept in a freezer until use to minimize dimer formation, when it was allowed to come to room temperature under dry conditions. All other materials were dried prior to use in a heated vacuum oven with a dry ice moisture trap. Laboratory syntheses were performed in a Haake dispersive mixer (70 cm^3 mixing bowl) with viscosity of reacting ingredients followed by a calibrated torque measurement. Stoichiometry was strictly followed with a 5% equivalence excess of MDI. Correction was made for amounts left in transfer containers during synthesis to assure stoichiometry. MDI was added to the Haake at 110 °C and allowed to melt. The diol was then slowly added with agitation (∼40 rpm) to the MDI along with a small amount of catalyst. The mixer was then heated under nitrogen to 150 °C and allowed to mix while the prepolymer reaction between MDI and diol was allowed to complete. At the end of this period there was no torque measured by the Haake suggesting that chain extension of the urethane polymer had not occurred to any significant extent. The polymer was completed by slowly adding the BDO chain extender to the agitating pre-polymer. Normally, at that point the torque measured by the Haake mixer would jump dramatically as the viscosity of the forming polymer would rapidly climb. The sample was subsequently heated with rapid mixing (∼120 rpm) until the measured torque fell to near zero suggesting that randomization of hard segment length was complete, usually between 180 and 210 °C. Following this, the material was allowed to cool under moderate mixing conditions until the measured torque by the mixer was at least 6 Nm. The value 6 Nm is not absolute since it depends on the quality of the calibration, but merely indicates that the TPU had undergone very substantial recombination and molecular weight re-building [29].

The resulting polymer was subsequently cut into small pieces, dried, compression molded, and then equilibrated at room temperature for at least 48 h. Tensile testing was performed on an Instron tensile testing machine and analyzed using Series 9 or Merlin software supplied by the manufacturer. DMS analyses were done on an Ares II solids analyzer.

Foams (total weight ~700 g) were prepared by first mixing the 20,000 dalton crystalline soft segment with the TDI required to make the foam in a box. The very high molecular weight soft segment added insignificant functionality to the system and was not considered in the subsequent formulation. After adding two drops of T-9 catalyst, the pre-polymer components were mixed at 70 °C with rapid stirring for 2 h in dry conditions under a N_2 blanket. At the end of this procedure the room temperature prepolymer was a low viscosity stable dispersion of crystals that remained in solution and showed no indication of settling. The pre-polymer was used shortly after preparation. The VORANOL 3136 was mixed with four parts water, 1.5 parts DC 5160 surfactant and 0.12 parts T-12 per 100 parts polyol and mixed vigorously with a Cowels high shear mixing blade driven by an air motor. The prepolymer was then added all at once to the polyol mixture with high speed mixing to make 100 index ([NCO]/[OH] = 1) foam, stirred for 10 s, and then dumped into a box to allow it to rise. Control foams were identical except that they did not have any crystalline soft segment in the formulation.

Wide angle X-ray spectra were obtained on a Bruker-AXS D8 difractometer (Co $K_{\alpha 1}$ at 35 kV and 30 mA) with a scintillation detector. Percent crystallinity of pure PPDL and pMHD was calculated from the spectra using Jade Software (MDI Inc. Livermore, CA) iterative least squares fitting routine employing a pseudo-Voigt algorithm (using a linear combination of Gaussian and Cauchy functions) [30]. Convergence was rapid and reproducible to within 2% variance from visually consistent initial fits and baselines. The ratio of the enthalpy of melt of a given sample relative to the pure crystalline soft segment determined from DSC (TA Instruments modulated DSC model 2910) was then used to determine the relative crystallinity of the sample in question. Absolute crystallinity was calculated by normalization to the WAXS determined pure material crystallinity.

Microscopy samples were taken from foam blocks which had been impregnated with Buehler Epoxicure resin and hardener. Sections from the potted foam, approximately 100 nm in thickness, were then obtained at −100 °C using a Leica AG Ultracut S cryoultramicrotome. The thin-sections collected on a copper support grid were stained for imaging by exposing the sections to RuO_4 vapors for 2 min. The prepared sections were then examined in a JEOL JEM-1230 TEM running at an accelerating voltage of 120 kV. Images were recorded digitally with a Gatan Multiscan CCD camera, Model 794.

3. Results and discussion

The elastomers of the current research differ from the previous studies by incorporating a second reinforcing phase into the elastomer. Effective use of a semi-crystalline second co-soft segment requires several features. First the material must melt and disperse during the processing step so that it can achieve an equilibrium distribution in the final product. Secondly it must phase separate and re-crystallize rapidly upon cooling or the desired crystallization may be inhibited at the higher viscosity of lower temperatures. Lastly it must have a high crystalline fraction and a melt temperature well above the intended use temperature.

Inspection of elastomers in the current work by transmission electron microscopy (Fig. 1(a) and (b)) shows that elastomers containing pMHD and PBA, two room temperature crystalline materials exhibit different morphologies. The pMHD exhibits a lamellar morphology with high aspect ratio crystalline phase. In some areas spherilites and pre-spherilitic sheath structures are observable. At very high concentrations these organized structures became less common and only lamellae are seen as shown for elastomers comprising 40% by weight PPDL of the soft segment (Fig. 1(c)). In contrast, the PBA and polycaprolactone resulted in low aspect ratio crystalline regions. The quantity of contrasting phase in these samples relative to the mass of crystalline component added suggests that the apparently crystalline regions are highly disordered and also contain large amounts of the polyether soft segment. This is easily visualized by observing the very substantial recrystallization hysteresis of the polycaprolactone and PBA phases when incorporated into elastomers (Fig. 2). In contrast, the pMHD material exhibits melting and recrystallization that is almost unaffected by the soft segment or hard segment content in this range. Furthermore, when the hard segment volume fraction of the elastomer is increased; the polycaprolactone and PBA crystallization is inhibited. Fig. 2 shows these concepts in a nested DSC of two different samples. The dashed curve shows the melting and recrystallization behavior of pMHD in an elastomer using a polycaprolactone soft segment. The melting peaks of both soft segments are clearly visible, however; the recrystallization peak is only present for the pMHD (pure 2000 molecular weight polycaprolactone recrystallized around 18 °C). Extended passive aging of the elastomer sample at room temperature was not adequate to reinstate the polycaprolactone crystallization. The solid line shows the melting and recrystallization behavior for a similar elastomer except that the hard segment volume has been increased from 20 to 26%. The melting endotherm of the polycaprolactone is now reduced and the recrystallization is again absent while the pMHD melting and recrystallization are not noticeably affected.

Table 1 provides information related to the driving forces for these crystalline soft segments. The crystalline morphology, the relatively rapid recrystallization

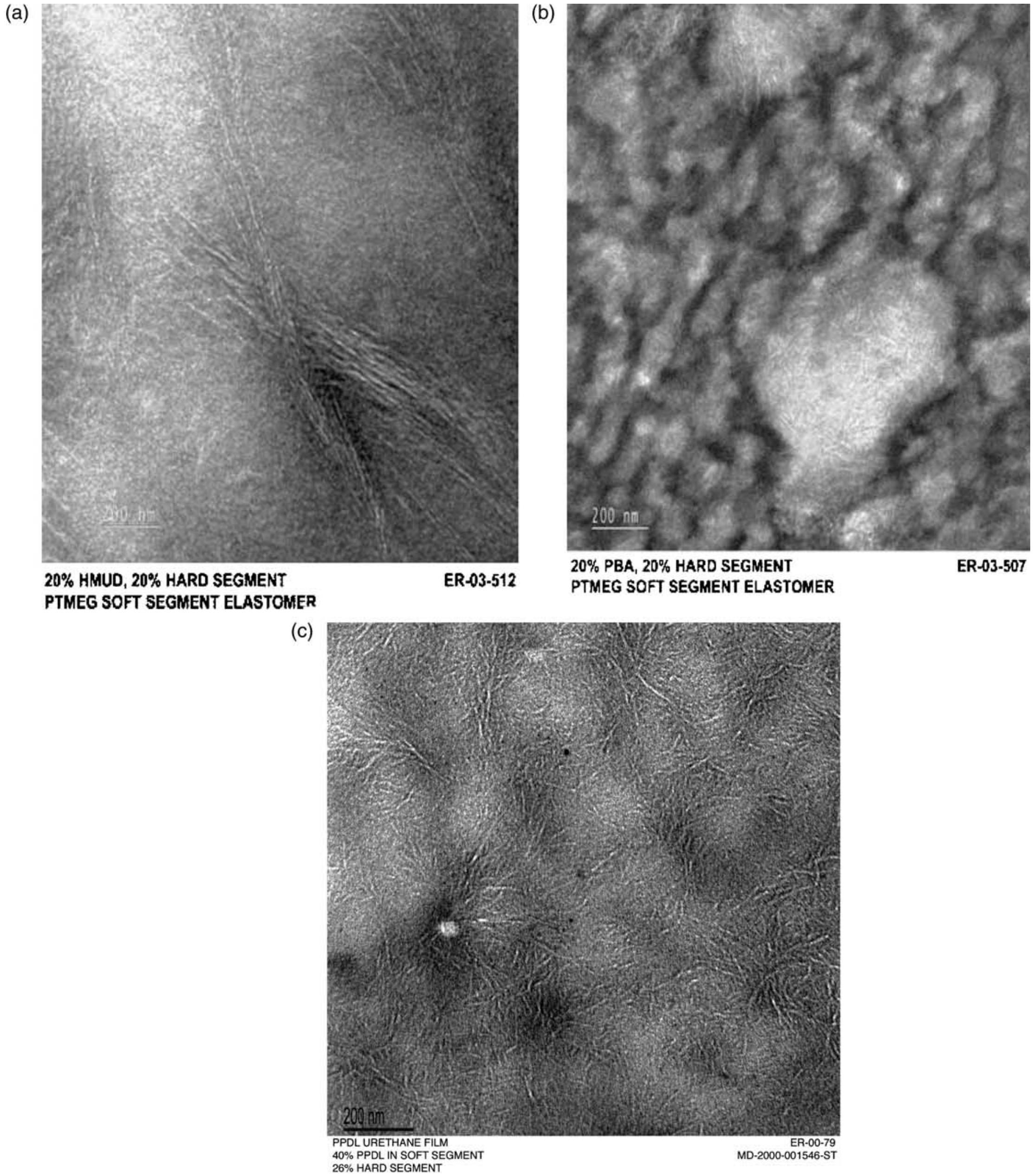

Fig. 1. TEM of polyurethane elastomers (a) and (b) are both 20% hard segment volume with 20% of the soft segment being 2800 molecular weight pMHD or 2000 molecular weight polybutylene adipate, respectively. (c) Is a polyurethane elastomer with 26% hard segment and 40% of the soft segment is 2400 molecular weight PPDL. The balance of the soft segment (not PBA or pMHD) is 2000 molecular weight PTMEG.

kinetics, and trend towards higher melting points and enthalpies of melting, point to the implication that these highly aliphatic polyesters have much in common with polyethylene. Wide angle X-ray scattering (Fig. 3) confirms this hypothesis and previous observations that high hard segment volume can destructively influence co-polymer phase structure [31].

WAXS powder scan of neat PPDL (Fig. 3(a)) shows peak reflections corresponding to the (110) and (200) lattice planes similar to an orthorhombic poly(ethylene) crystal

Table 1
Thermal properties of the semi-crystalline soft segments used in this work and high density polyethylene

	PE (linear)	PPDL	pMHD	Polycaprolactone	Polybutylene adipate
Melting point (°C)	133	91	83	50–55	57
Enthalpy of melt (J/g)	270–295	182	170	90–100	85

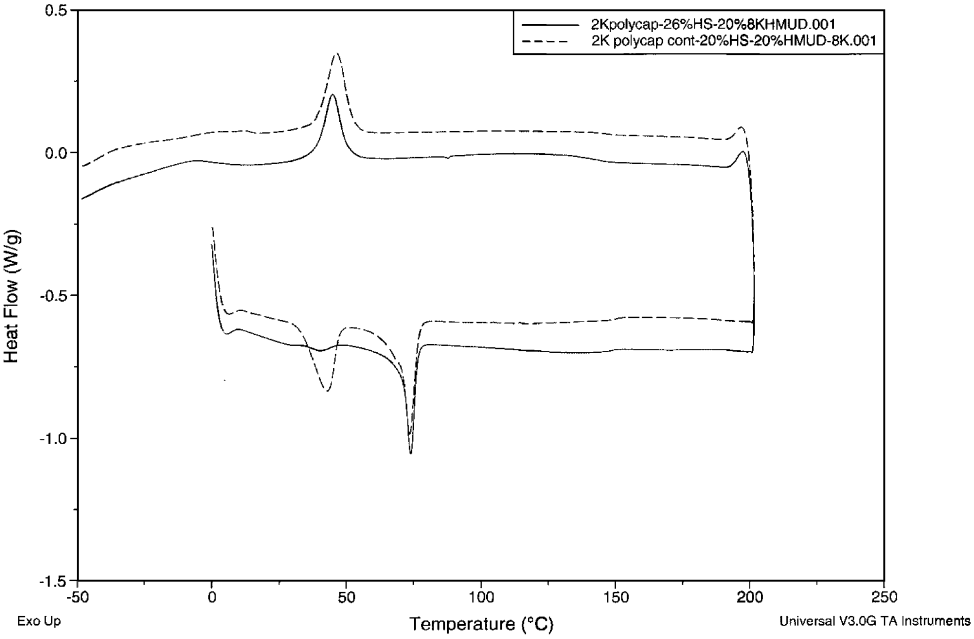

Fig. 2. DSC of polyurethane elastomers of blended soft segments. The dashed trace is from an elastomer that is 20% hard segment and the soft segment blend is 80% polycaprolactone (2000 molecular weight) and 20% pMHD (8000 molecular weight). The solid trace is from the same soft segment blend but with 26% hard segment. The polycaprolactone recrystallization exhibits hysteresis and its crystallization is inhibited by soft segment interference.

[32]. The neat PPDL polymer is estimated to be about 50% crystalline based on the relative scattering of the crystalline and amorphous phases [30]. The introduction of PPDL into the PU matrix does little to disrupt the PE crystal structure in the case of 20% loading of hard segment (Fig. 3(b)), however; at 40% hard segment loading, the peak reflections are broader indicating a disruption in crystallinity due to the hard segments (Fig. 3(c)). Such behavior has been previously reported for high molecular weight polycaprolactone and ascribed to hard segment interactions with the ester linkages [31]. Normalized to weight incorporation, the fractional efficiency of recrystallization of PPDL varies from about 0.5 to about 0.15 based on the neat material enthalpy of melting normalized to that of the pure crystalline soft segment enthalpy of melting and its total crystallinity derived from X-ray scattering. Very similar behavior is observed for pMHD.

That crystalline soft segment components can have dramatic affects on elastomer tensile properties is shown in Fig. 4. This graph shows the affect of incremental increases of 2400 molecular weight PPDL on the dynamic mechanical spectroscopy on polyurethane elastomers. The provided differential scanning calorimetry of pure 2400 molecular weight PPDL shows the functional dependence of elastomer modulus on crystalline content with the properties of the elastomers converging on the control elastomer (0% crystalline soft segment) above the crystalline melting point. The scanning calorimetry shows that for this low molecular weight PPDL there is a broad distribution of crystalline melting points due to the inability of the low molecular weight component to undergo chain folding [33], or that the distribution of fold lengths might be very broad compared to higher molecular weight PPDL. This affect is mitigated for higher molecular weights of the crystalline

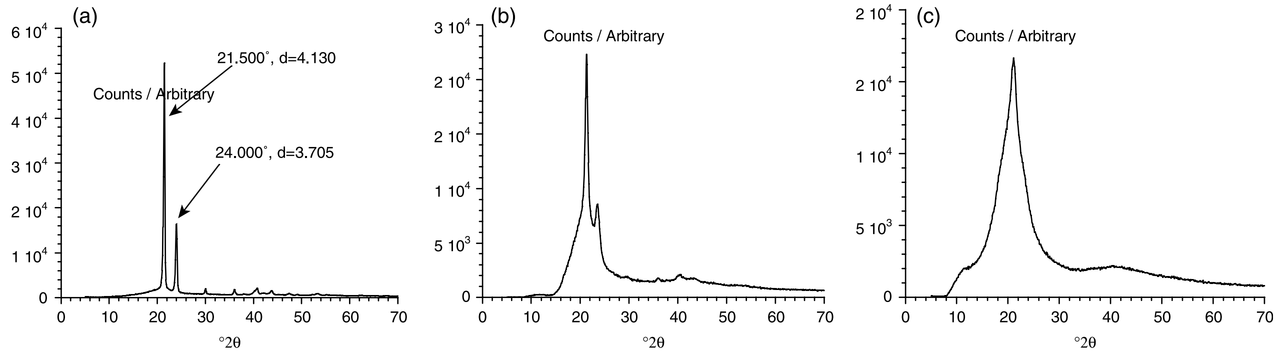

Fig. 3. WAXS patterns for (a) 2400 molecular weight PPDL and polyurethane elastomers from a blend of 20% PPDL in PTMEG at (b) 20%, (c) 40% hard segment. The crystalline structure becomes increasingly disturbed by the hard segment phase.

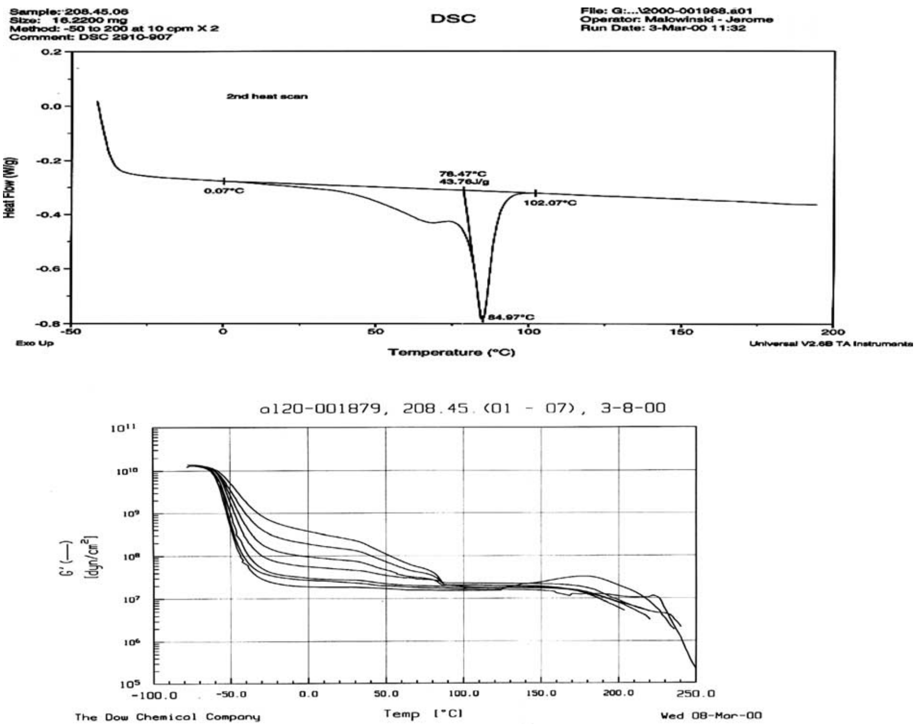

Fig. 4. Composite image of DSC of 2400 molecular weight PPDL and dynamic mechanical spectra of polyurethane elastomer (20% hard segment) with progressively increasing quantities of PPDL (from 0 to 40% of the soft segment blended with 2000 dalton PTMEG). The spectra show that the modulus of the elastomers is very sensitive to the crystalline content.

component (Fig. 2) and provides a flatter modulus temperature response prior to melting.

The conventional hard segment provides rigidity to the TPU elastomer via its rigid co-continuous structure. The addition of a supplementary rigid structure through the semi crystalline soft segment amplifies this affect. Fig. 5 shows that incorporation of the crystalline component into the soft segment phase produces significant modulus increases using pMHD or PBA, but the affect is significantly greater for the pMHD. We ascribe this difference to the morphological differences demonstrated in Fig. 1.

The mechanism of crystalline reinforcement can be analyzed by comparison of the modulus vs. crystalline volume fraction data to several model equations. Particularly applicable could be comparison to a modified Halpin–Tsai equation [34] and percolation model [35] which can distinguish behavior based on isolated or interacting filler effects, respectively.

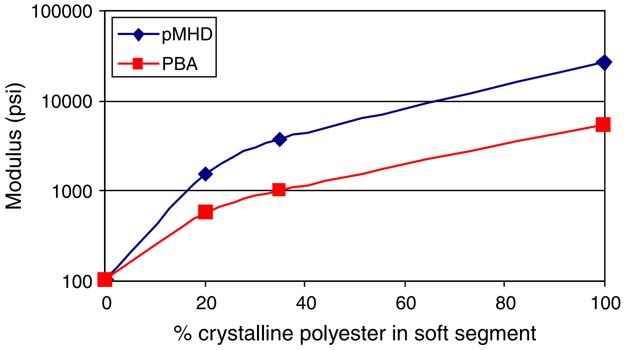

Fig. 5. Tensile modulus of polyurethane elastomers with blends of 2800 molecular weight pMHD and PTMEG and 2000 molecular weight PBA and 2000 molecular weight PTMEG. The lines between the points are added to aid the eye.

For materials where discrete hard fibers of a given aspect ratio reinforce a continuous soft matrix, the Halpin–Tsai equation can be cast into a form describing the elastic behavior of the lamellar fiber reinforced matrix where E is the modulus of the indicated phase, ϕ is the hard filler volume fraction and A is the filler's aspect ratio:

$$E_{\text{composite}} = E_{\text{matrix}} \frac{\{E_{\text{filler}} + 2A[\phi E_{\text{filler}} + (1-\phi)E_{\text{matrix}}]\}}{\{(2A+\phi)E_{\text{matrix}} + (1-\phi)E_{\text{filler}}\}} \tag{1}$$

If we assume the semi-crystalline soft segment phase recrystallizes 50% (consistent with elastomer DSC data) from it's pure material potential (50% crystalline from WAXS data) we anticipate the modulus reinforcements for different geometry and orientation cases and different volume fractions relative to experiment found in Table 2.

In comparing the normalized experimental modulus enhancement to the Halpin–Tsai results we can conclude (1) that both the amorphous PBA and pMHD significantly raise the modulus of the matrix, (2) that there is a long range interaction in theses elastomers that raises the reinforcing effect far above that of randomly oriented reinforcements. Even though the images of Fig. 1 do not suggest a global

Table 2
Experimental and calculated reinforcement factors for crystalline soft segment modified TPUs

Volume fraction	pMHD	PBA	RO rods	RO disks	RO spheres	PO rods or disks
0	1	1				
.05	14.6	5.4	1.25	1.91	1.14	6.3
.0875	35.6	9.5	1.37	2.03	1.25	10.7
.25	254	51.9	2.04	2.64	1.85	34.7

For the experimental results the volume fraction of crystallites is approximated to be 25% of the weight added amount consistent with WAX and thermal analyses. The calculated results assume a Halpin–Tsai model for random orientation (RO) of filler [36] and for perfect ordering (PO) or alignment of the fillers using Eq. (1). For these calculations $A=50$ the matrix modulus is 1 and the filler modulus, assumed to be rigid, was adjusted high enough such that the results were not sensitive to its value. The actual matrix modulus is 105 psi (Fig. 5).

preferential orientation (there may be local orientation), the experimental results are roughly equivalent to the Halpin–Tsai calculations assuming high modulus, highly oriented, high aspect ratio reinforcing filler. The fact that the crystalline structures do not possess the morphological requirements to be correctly fit to the Halpin–Tsai model strongly suggest that the assumption of a disconnected reinforcing filler structure is not relevant to these elastomers.

If the ratio of hard phase to soft phase modulus is much greater than one so the soft phase contribution can be neglected, and if crystalline domain continuity sets up at a threshold of $\phi = p_c$ and percolates as randomly placed objects, simple models based on percolation theory can apply.

$$E_{\text{composite}} \sim E_{(\text{crystalline phase})}(\phi - p_c)^{\beta} \quad (2)$$

Fig. 6 shows the modulus data of Fig. 5 with the best fit line to Eq. (2). The exponent value was 1.7 for pMHD and 1.9 for PBA, which are in the range of values found when this model is appropriately applied. Also, the data fitting was obtained with a p_c of zero, characteristic of highly anisotropic reinforcing particles such as observed in Fig. 1 [37]. The results of these model analyses indicates that the crystalline domains exhibit long range effects within the elastomer bulk and that the affects should be observable at relatively low crystalline volume fractions due to the highly anisotropic nature of the particle morphology.

The crystalline elastomer morphology created by pMHD and PPDL also affects the tear properties of elastomers. Fig. 7 shows that high aspect ratio lamellae significantly enhance the tear strength of these materials. These data show that the overall toughness of the material is influenced by the semi-crystalline soft segment phase since tear properties reflect the entirety of the stress strain curve [38]. The data also reveals a significant affect of pMHD molecular weight on elastomer tear strength. The improved tear strength performance of higher molecular weight pMHD probably reflects its improved ability to chain fold upon itself in the re-crystallization process and the higher rate of crystallization this entails during the cooling of the material from the melt [39].

Foam properties are also affected by the presence of crystalline structures with the soft segment phase. The situation is slightly different from the application of crystalline structures to thermoplastic elastomers. Polyurethane foams have high hard segment volumes, usually more than 33%. High hard segment volumes exert inhibiting affects on recrystallization following melting as seen in Fig. 3. Secondly, the polyurea hard segments which form during the foaming do not melt while the crystalline component is melted (foam temperatures of the size

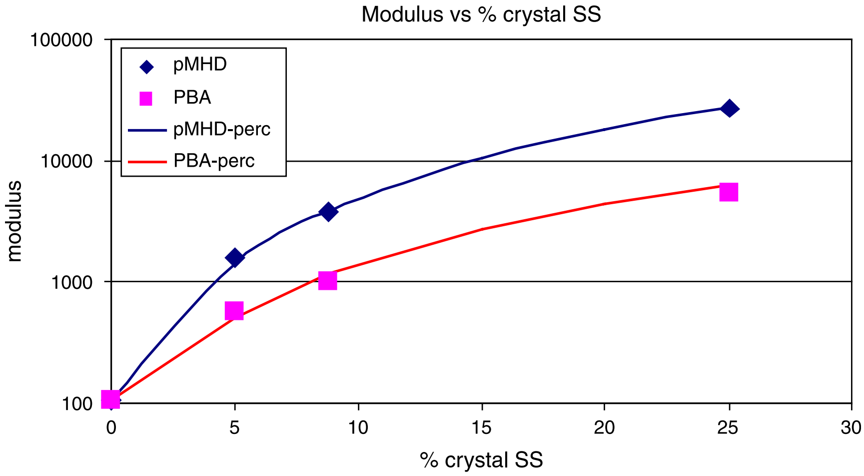

Fig. 6. Elastomer modulus data of Fig. 5 with the best fit lines using Eq. (2) and β values of 1.7 for pMHD and 1.9 for PBA and a $p_c=0$ for each case. The non-crystalline soft segment is in all cases 2000 molecular weight PTMEG.

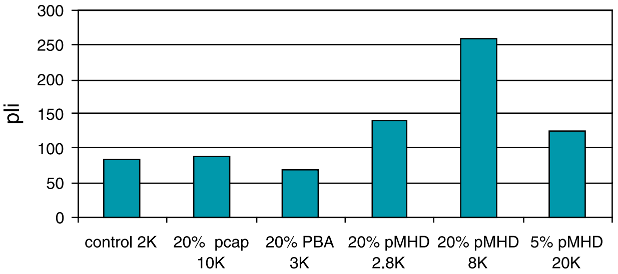

Fig. 7. Measured tear strengths using a trouser tear configuration of polyurethane elastomers with and without crystalline soft segment inclusion. The 2000 control sample is made with 2000 molecular weight PTMEG. All the others represent addition of crystalline soft segment of the indicated molecular weight. Addition of high molecular weight crystalline soft segment pMHD results in very high tear strengths. High molecular weight polycaprolactone is not a significant modification to the control elastomer tear properties.

employed in these experiments typically reach 120 °C or higher), so there is less chain freedom for re-crystallization of the soft segment. This tends to minimize the recrystallization efficiency relative to the elastomers. Lastly, foam formation is a more complicated process than elastomer synthesis, with catalysis and surfactancy issues that must be adjusted for large departures of hydrophilic balance in the formulation. Thus, large formulation changes make it more difficult to make control specimens that are only different in the soft segment micro-structure as opposed to some macro change such as cell openness or strut thickness. For this reason we have limited the addition of crystalline component to 5 vol% of the soft segment volume. With such a small addition it is highly unlikely that co-continuous crystalline structures can be formed and TEM analysis only sees discontinuous crystalline structures (Fig. 8); however, other foam structural features such as cell openness, and foaming parameters such as cream time, blow off time, gel time are nearly unaffected.

Mechanical analysis (Fig. 9) shows that even at this low loading the mechanical properties are altered. While the crystalline soft segment foam shows increased load bearing, there is also a slight increase in hysteresis when normalized to the overall stress. It is possible the crystalline or amorphous polyester phase retards larger scale relative movements of the hard and soft phases on the time scale of the hysteresis measurement [40,41].

4. Conclusion

Polyurethanes comprising conventional hard segments and soft segment blends of amorphous and semi-crystalline diols have been synthesized. Semi-crystalline polyester diols with long polymethylene runs exhibit lamellar morphologies with WAXS patterns that are nearly identical to polyethylene. The crystals act as reinforcement additional to the polyurethane hard phase, and at sufficient concentrations demonstrates increased modulus and toughness. The reinforcement of the elastomer does not closely follow a Halpin–Tsai model but does follow a percolation model suggesting that the crystals have a continuous rather than discrete affect on the elastomer properties. Flexible foam load bearing is also increased at small additions, but the phase interactions are observed to increase energy loss mechanisms.

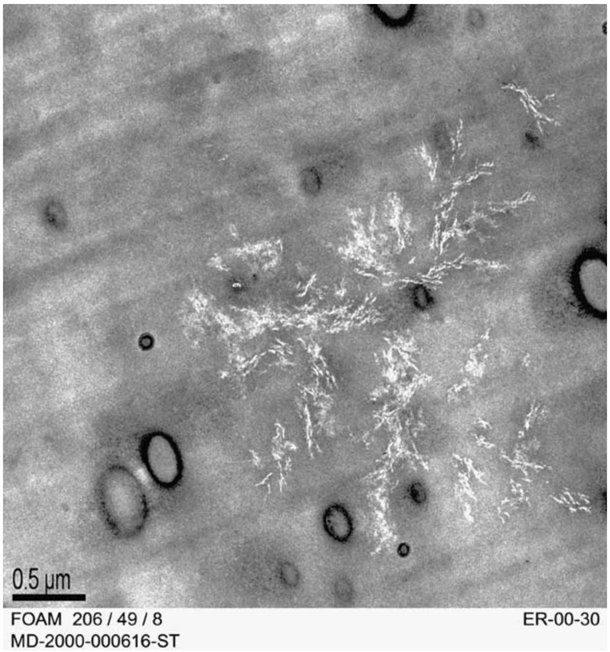

Fig. 8. TEM of a foam strut with a crystalline 20,000 molecular weight pMHD soft segment. Low volume additions and poor recrystallization efficiency results in foams with isolated crystalline structures.

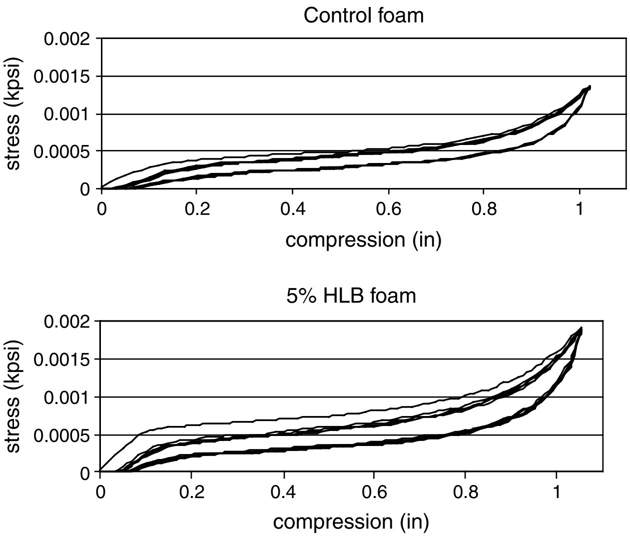

Fig. 9. Hysteresis loops for flexible polyurethane control foams (a) and for the identical formulation but with the addition of 5% (of the soft segment) by weight of a 20,000 molecular weight pMHD semi-crystalline soft-segment. No change was made in the foam formulation with the pMHD since the stoichiometric correction for such a large molecular weight was below significance.

Acknowledgements

It is a pleasure to acknowledge the contributions of Drs Francois Casati, Robert Cieslinski, Jozef Bicerano and Mr William VanBergen to this work. We would like to thank Professor Tony Ryan (Univ. of Sheffield) for the WAXS spectra.

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