LLNL-JRNL-649713

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February 12, 2014

Polymer Degradation and Stabiltiy

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ABSTRACT

Reported here is the synthesis and thermal characterization of a series of polyhedral oligomeric silsesquioxane (POSS) modified polyurethane elastomers. A novel polyurethane architecture has been synthesized which incorporates a partially opened POSS-diol cage (disilanolisobutyl POSS) directly into the methylene di-isocyanate/poly(tetramethylene) glycol urethane network as a substitute chain extender moiety without the need for an alkyl tether. The effects of the inclusion of a sterically hindered and rigid silsesquioxane cage structure on both the non-oxidative thermal stability and micro-phase segregated morphology of the resultant polyurethane elastomer have been studied extensively over a range of POSS inclusion levels by means of pyrolysis-gas chromatography/mass spectroscopy (Py-

GC/MS) and differential scanning calorimetry (DSC). The results of analytical pyrolysis assays of the polyurethane systems clearly demonstrate that low levels of POSS substitution (<10 wt. %) lead to a significant *increase* in both the onset temperature of thermal de-polymerization and a reduction in the yield of volatile degradation products. A characterization of the products of degradation demonstrate that the POSS modified elastomers show some subtle differences in thermal degradation mechanism, yielding increased levels of propenal and decreased levels of ethane when compared with an unmodified control. POSS inclusion enhances the hard-block crystallinity at low levels and DSC analysis demonstrates that the peak thermal stability of the systems corresponds with a maximum in hard-block crystallinity (at a level of 4-6 wt. % POSS). At higher mass fractions we observe a breakdown in the phase separation of the systems and a decline in hard-block crystallinity, which correlates with an observed decrease in the primary onset degradation temperature. The major mechanistic pathways of degradation (urethane bond depolymerisation followed by secondary radical degradation of the monomers) have been shown to be insensitive to the presence of POSS in the matrix. Rather, it is physical changes in the morphology of the elastomer systems, as a consequence of POSS inclusion that are responsible for the observed improvements in the thermal stability of these materials.

KEYWORDS: polyurethane; POSS; thermal degradation; block copolymers

INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) materials are a class of discrete, 3-dimensional polycyclic compounds with the formula $(RSiO_{1.5})_{2n}$, where ‘n’ is an integer and R can be a range of organic substituents. These unique hybrid organic/inorganic molecules represent a versatile class of 3-dimensional polycyclic compounds which continue to be of interest to a wide range of scientific and technological areas, not least of which is field of advanced polymeric composite and hybrid materials - where they are increasing sought and studied for both structural and functional modification of polymers [1, 2]. And over the last four decades there has been a large volume of research published [3-5] on the modification of a range of polymeric systems by these interesting molecules, so often now referred to as 'nano-fillers'[1, 6, 7] or 'nano-scale' physical property modifiers [8, 9]. One of the most commonly encountered and studied variants [10, 11] is octameric POSS, which has a pseudo-cubic closed cage structure and the general formula ($R_8Si_8O_{12}$). Such cubic POSS molecules have received particular attention in recent years and are often thought of as a discrete, well defined nano-scale form of silica which can be readily modified with a wide range of organic substituents and effectively incorporated into polymeric architectures [1, 12, 13].

One of the major focuses of POSS/polymer research over the last 2 decades has been in the covalent incorporation of POSS moieties into a polymeric architecture either during synthesis or network formation, with the goal of improving the thermal/thermo-oxidative performance of the resultant hybrid system. The core tenant of this approach is that the inclusion of well-defined nano-scale silica (in the form of a functional POSS) as a chain segment, pendant, or crosslinking moiety will impart a range of physical and chemical improvements to the polymeric system that will in turn, make the system more thermally and thermo-oxidatively resilient. Indeed, this conjecture has to some extent been bourne out though investigation and there are many examples in the literature of the benefits of POSS inclusion on the thermal stability of a number of polymeric systems. Xu et al.[14] synthesized poly(acetoxylstyrene-co-isobutylstyryl-POSS)s (PAS-POSS) and poly(vinylpyrrolidone-co-isobutylstyryl-POSS)s (PVP-POSS) copolymers, demonstrating simply that the POSS monomer residues increased the T_g and therefore the thermal stability of the resultant co-polymer. Huang and co-workers demonstrated a similar effect on T_g and thermal stability when a functional POSS was employed as a crosslinker in (POSS)/polyimide (PI) hybrids [15]. This combined nano-reinforcement and stabilizing effect was also demonstrated in glassy epoxy networks by Ni et al.[16].

In more morphologically complex polymer systems such as phase segregated physically crosslinked polyurethane elastomers, POSS reinforcement and modification have also been studied with varying results [17-20]. The effects of covalent POSS inclusion on the thermal properties of segmented PU-

POSS hybrid systems have been reported by Liu [20] who demonstrated that hybrid elastomers had enhanced thermal stability, speculated that the primary mechanism of PU degradation was not significantly altered and that the enhanced stability was due to a condensed-phase action of POSS in the degrading polymer melt. Madbouly et al. [21, 22] presented similar results from TGA studies of POSS-PU hybrids; their results suggested that inclusion of POSS into a PU network does not significantly effect the onset of non-oxidative thermal degradation, but does enhance the high temperature thermal stability leading to higher char yields and a decrease in rate of late-stage, high temperature degradation. Similar degradation behaviour was also reported in the work of Zhang and co-workers [23]; where diol functionalised POSS incorporated into a PU network did not alter the onset of thermal degradation, but increased the final char yield. More recently, Spoljaric et al.[24] reported that the inclusion of dendrimer modified POSS species into a thermoplastic polyurethane which enhanced the thermal stability polyurethane, due to restrictions on chain segmental motions imparted by the functionalized POSS and thermal shielding effects.

And in a 2010 study [25] the authors presented a mechanistic study of the thermal degradation of a series of POSS modified nanohybrid polyurethanes in which we demonstrated that a diol functionalized, alkyl tethered POSS could be directly incorporated into the polyurethane hard-block segments as substitute chain extender moiety. This inclusion of POSS into the PU hard-block domains increased the thermal stability of the elastomer, resulting in an increase in degradation onset temperature and a significant reduction in the overall level of volatile degradation products formed. An analysis of the products of degradation indicated that there was an overall reduction in radical chain scission, secondary MDI decomposition and urethane bond depolymerisation reactions. In these systems it was proposed that POSS acted to physically reduce the rate both of reactive species transport and of degradation product diffusion within the PU matrix - effectively stabilising the POSS/PU hybrids towards thermal decomposition. And in a recent study [9], the authors have demonstrated clearly though a combination of DSC, AFM and Solid-state NMR that the inclusion of such a diol-functionalized POSS as a substitute chain extender while increasing the thermal stability, in-fact significantly disrupts the micro-phase segregated morphology of the PU system as a whole - leading to homogenization of the polyol and isocyanate domains, a reduction in crystallinity and an increase in T_g of the bulk network.

The results of such studies appear to indicate that while POSS inclusion can impart beneficial structural and thermal properties to a polymeric system such as a segmented PU elastomer, the interaction of the POSS cages and the existing polymer morphology are complex and not by any means exclusively predictable. Low levels of POSS may for instance, enhance hard-block crystallinity [17] but at higher levels the steric effects of the cage may dominate leading to disruption of phase separation mechanisms [9, 25].

In this study we have utilized an alternative POSS architecture (1,3,5,7,9,11-Octaisobutyltetracyclo[7.3.3.$1^{5,11}$]octasiloxane-endo-3,7-diol - a partially open di-silanol isobutyl POSS cage in order to achieve the incorporation the POSS moiety into a segmented urethane elastomer without an alkyl tether, as was the case with our earlier work [9, 25]. By utilizing a combination of analytical pyrolysis-GC/MS and DSC we have been able to study the effects of POSS on both the micro-phase segregated physical morphology of the PU elastomer and the mechanisms of thermal degradation.

EXPERIMENTAL

Materials. 4,4'-methylenebis(phenylisocyanate) (MDI) and 1,4-butanediol were obtained from Sigma Aldrich Chemical Co. Poly(tetramethylene glycol) (Terathane®) with a number average molecular weight of ~1.4 KDa was obtained from Invista and 1,3,5,7,9,11-Octaisobutyltetracyclo[7.3.3.$1^{5,11}$]octasiloxane-endo-3,7-diol (DSIPOSS) was obtained from Hybrid Plastics Ltd.

Synthesis of POSS-PU Nanohybrid Elastomers. All POSS-PU hybrid elastomer systems were prepared incorporating 0, 2, 4, 6, 8 and 10 weight percent (wt%) DSIPOSS as a substitute chain extender to yield a matrix of six systems. The elastomers were prepared in the following manner: a solution of DSIPOSS and Terathane was prepared by dissolving the functionalized POSS into the polyol by heating to 120°C and then cooling to 60°C. Then, MDI was charged into a 100 ml three-necked round bottomed reactor equipped with a mechanical stirrer and nitrogen inlet, heated to 70°C, and the DSIPOSS /polyol solution added in one portion. The polymerization reaction was performed under a nitrogen atmosphere at 80°C for 2 hours to form a PU prepolymer. The NCO group content was then determined, and the prepolymer was mixed with suitable amount of 1,4-butanediol. The resultant mixture was poured out onto an open mould, cured at 110°C for 2 h and finally post-cured at 80°C for 16 hours to form a solid elastomer. The generalized reaction scheme is shown in **Figure 1** and a formulation summary of the POSS-PU hybrid systems synthesised for this study is given in **Table 1**.

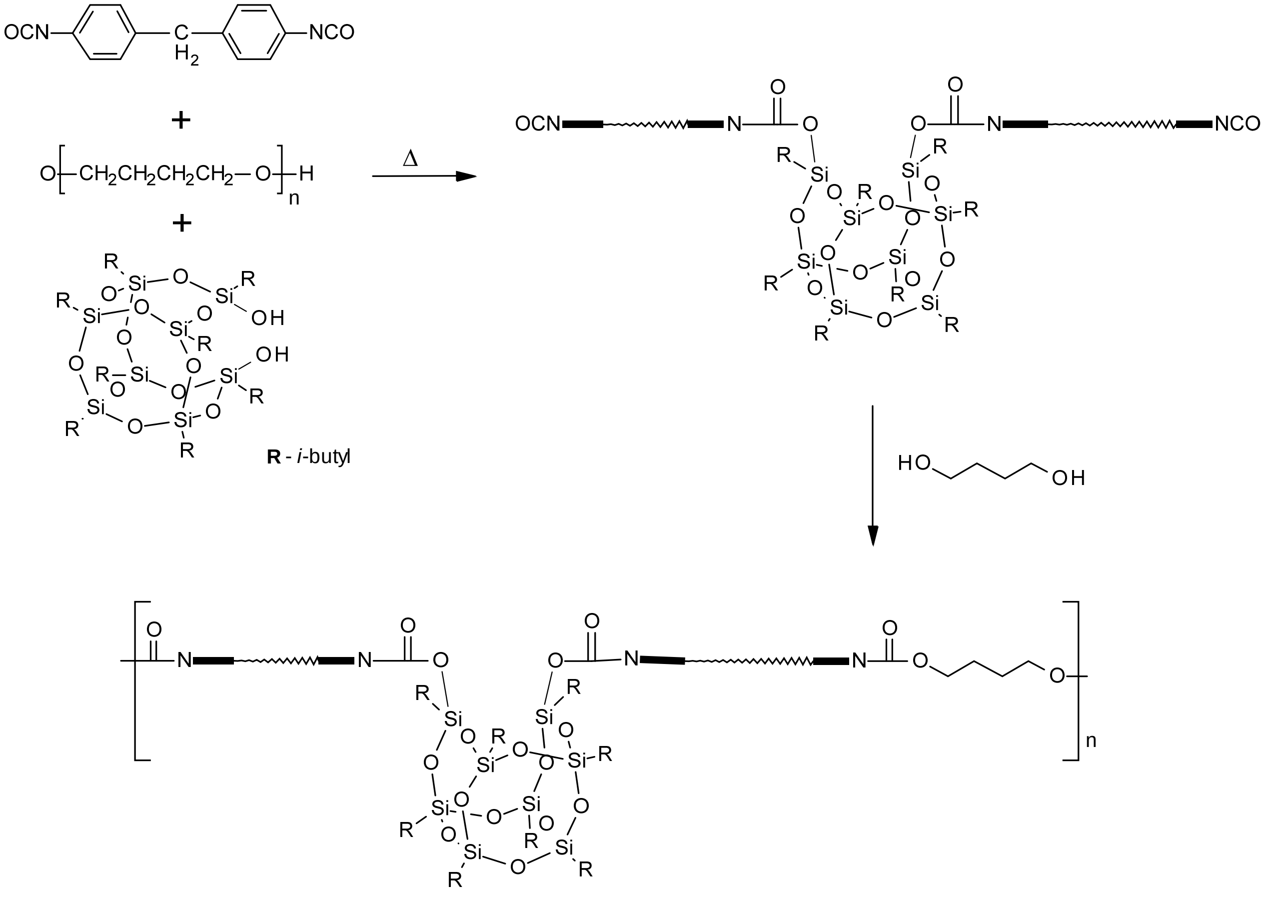

Figure 1. Reaction Scheme

Table 1. Formulation summary of the 0-10% DSIPOSS /PU hybrid elastomers synthesised in this study.

Polyurethane System	Mol. fraction PTMG	Mol. fraction MDI	Mol. fraction BDO	Mol. fraction DSIPOSS	Mol. % POSS as chain extender
Base PU	0.117	0.500	0.383	0.000	0.00
2% POSS	0.120	0.502	0.371	0.007	1.85
4% POSS	0.124	0.498	0.363	0.015	3.97
6% POSS	0.131	0.500	0.345	0.024	6.50
8% POSS	0.135	0.502	0.330	0.033	9.09
10% POSS	0.142	0.504	0.311	0.043	12.15

DSC Analysis. All DSC characterization was carried out using a Perkin-Elmer Diamond DSC operating in non-modulated mode using power-compensation. Six milligram samples of each elastomer were placed in pinholed, sealed hermetic pans. The samples were analysed using a ramping temperature program at 10 °C/min from 60 to 200 °C under a N_2 purge flow. The percentage of crystalline contributions from the MDI-BDO segments for each sample were determined from the area under the crystalline melt peaks, and normalized against the calculated values of crystallization enthalpy ΔH_c for fully crystalline MDI-BDO residues.

Pyrolysis-GC/MS Analysis. All pyrolysis studies were carried out using a CDS Analytical 5150 Pyro-probe coupled to an Agilent 7890 GC with an Agilent 5973N quadrupole MSD for detection of analytes. Samples (~50 μg) of each prepared elastomer system were massed into quartz sample tubes. The sample tubes were loaded into the Pt filament coil of the pyro-probe apparatus for pyrolysis. For the determination of the products of degradation, the sample was held at an initial temperature of 60°C for 0.5 min, and then pyrolysed at a ballistic heating rate from 60 to 1000 °C under a purge flow of helium for a total pyrolysis time of 2.0 min. The pyrolysates were continually transferred from the pyro-probe apparatus to the GC inlet using an inert transfer line (both at 300 °C) with a 20:1 split flow for the total pyrolysis runtime. An Aglient Pora Plot-U (30 m x 0.25 mm i.d. x 0.25 μm i.f.) analytical column under constant flow of 3.0 ml/min with Helium carrier gas was used. The initial GC oven temperature was set at 40°C for 2.0 min and then ramped at 10 °C /min to 300 °C and held for 10 min at the final temperature for a total analysis time of 38.0 min. The MS ion source and quadrupole were 230°C and 150°C, respectively. Total ion chromatograms (TIC) of the pyrolysis products were collected for each run. To obtain overall degradation profiles, a duplicate analysis was performed for each system where sample was held at an initial temperature of 60°C for 0.5 min, and then pyrolysed at a controlled rate of 100°C/min 60 to 1000 °C (with a 2 minute hold at 1000°C) under a purge flow of helium. In this case, the GC column was bypassed and the products of degradation were transferred to the detector without separation, yielding thermograms of total volatiles vs. sample temperature. For both modes of analyses, a total of five replicates were performed for each sample.

RESULTS AND DISCUSSION

Analytical pyrolyis-GC/MS (py-GC/MS) has been ultialsed to both chracterize the non-oxidiatve thermal degradation behaviour of the POSS/PU hybrid systems by monitoring volatile evolution as a fucntion of sample temperature and through the speciation of degradation prodcuts. Given in **Figure 2** are the obtianed Py-GC/MS thermorgams for the degradation of each model POSS/PU system.

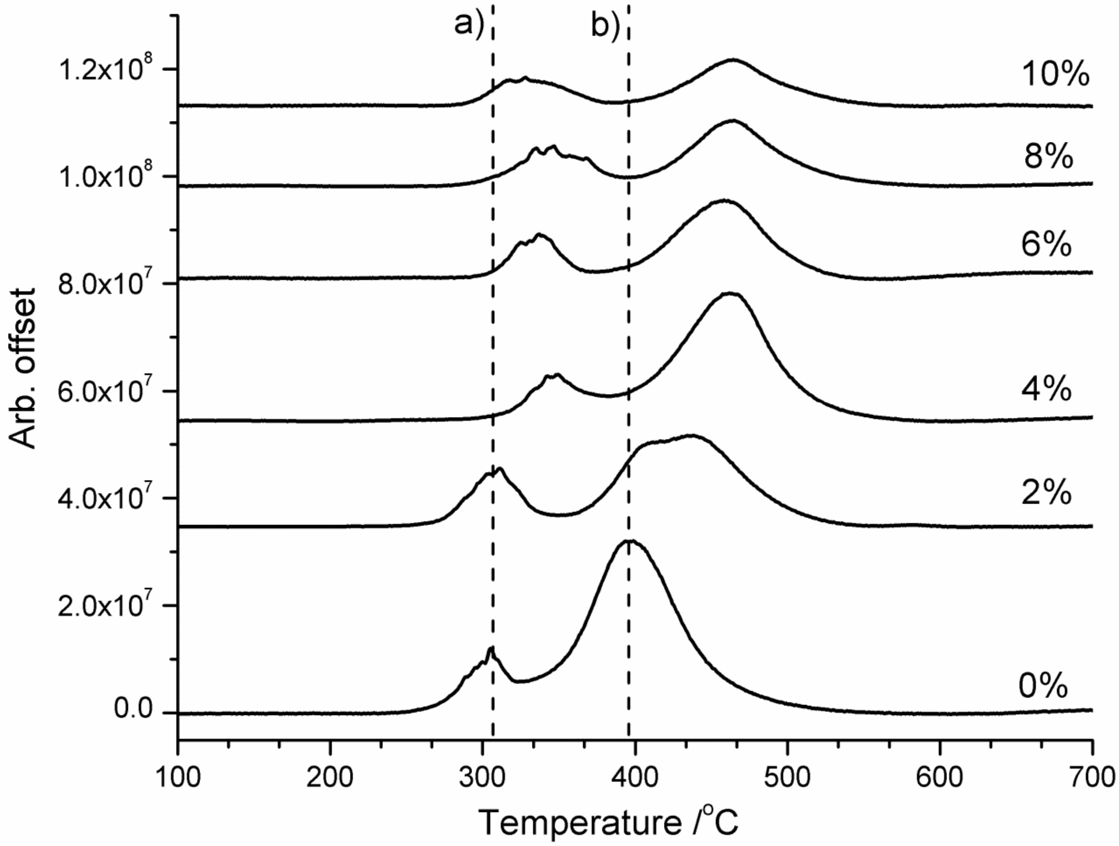

Figure 2. Py-GC/MS thermograms for the non-oxidative thermal degradation of the 0-10% DSIPOSS /PU hybrid elastomers. Note that in the unmodified elastomer a primary de-polymerization event (a) with an onset of ~250°C that is followed by a second high temperature process (b) – attributed to the degradation of the monomer units. It is evident from these data that the inclusion of DSIPOSS both shifts (a) & (b) to higher temperatures and decreases the overall yield of volatile degradation products.

The results of pyrolytic analyses shown in **Figure 2** clearly show that the unmodified (0%) PU elastomer degrades in a two stage process consisting of (a); a primary urethane bond de-polymerization event that occurs between 250-300°C, followed by (b); a series secondary degradation reactions of the now free polyol, MDI and BDO 'monomers', consisting of various radical and elimination processes that occur temperatures above 350°C to form a range of volatile small molecule degradation products. Such degradation behaviour is consistent with the mechanism(s) reported for polyol-MDI thermoplastic PU elastomers in the literature [26, 27]. What is also immediately apparent froth these data in **Figure 2** is that as the levels of POSS are increased, the onset, peak temperatures of processes (a) and (b) increase and the total levels of evolved volatile matter observed to decrease significantly with respect to the unmodified (0%) PU system. Values for these processes are summarized in **Table 2** and the individual trends are presented in **Figures 3-5**.

Table 2. Onset, peak degradation temperatures and relative volatiles evolution levels for the 0-10% DSIPOSS /PU hybrid elastomer systems.

Mass fraction POSS	**% Volatiles relative to base**	**Onset temp. /°C**	**1st Peak max. /°C**	**2nd Peak max. /°C**
0 (base)	100.0	268±3	305±3	397±3
0.02	69.0 ±3.5	274±3	312±3	434±3
0.04	77.6 ±3.9	313±3	348±3	461±3
0.06	48.1 ±2.4	307±3	336±3	459±3
0.08	43.8 ±2.2	304±3	347±3	437±3
0.1	28.6 ±1.6	290±3	326±3	462±3

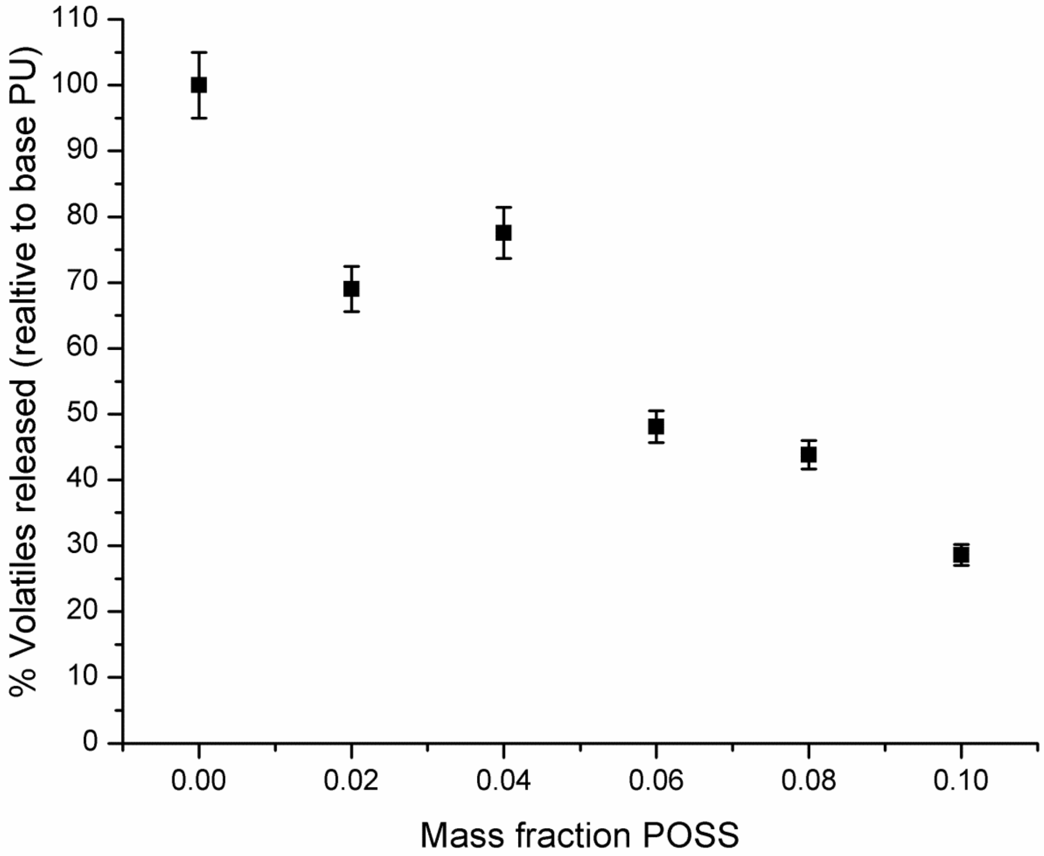

Figure 3. % Volatiles evolved on degradation, relative to the base PU elastomer for the 0-10% DSIPOSS /PU hybrid elastomer systems. Note that significant reductions in volatiles evolution accompany increasing mass fractions of POSS inclusion within the PU system indeed, at 10 wt. % DSIB POSS, volatiles evolution is reduced ~70% compared with the unmodified PU.

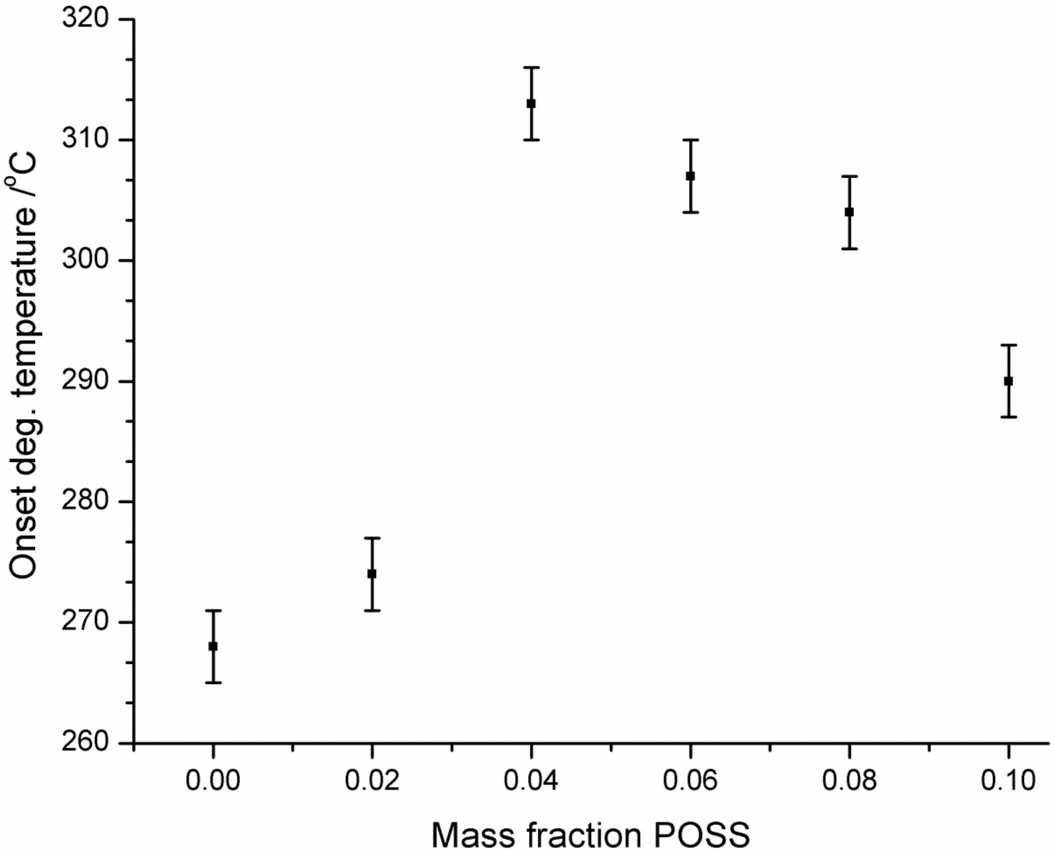

Figure 4. Onset degradation temperature for primary thermal depolymerisation as a function of mass fraction POSS for the 0-10% DSIPOSS /PU hybrid elastomer systems. Note that the onset degradation temperature increases to a maximum at 4-6wt. % POSS and then begins to decline thereafter.

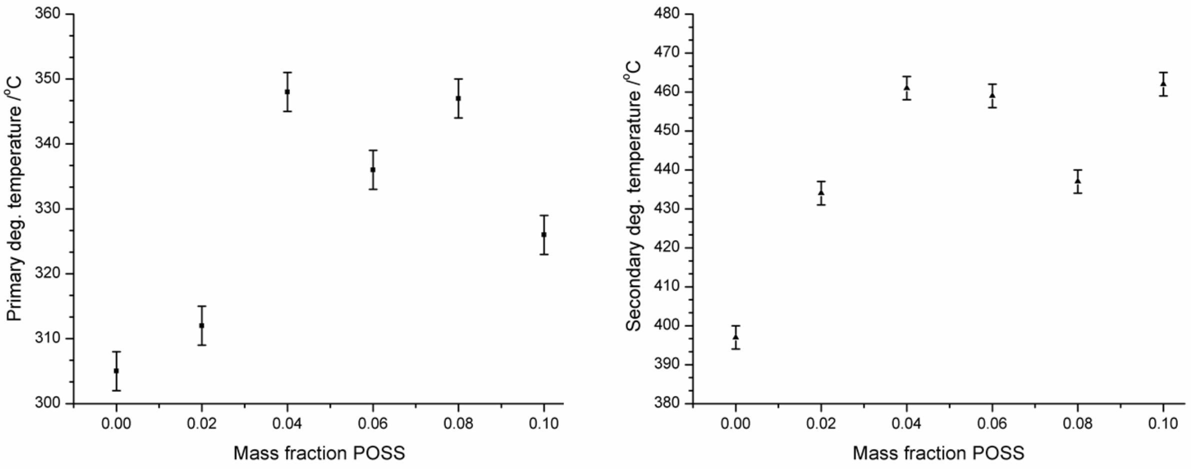

Figure 5. Peak degradation temperatures for both primary thermal depolymerisation and secondary monomer degradation as a function of mass fraction POSS for the 0-10% DSIPOSS /PU hybrid

elastomer systems. Note that for both processes, a maximum increase in peak degradation temperature is reached at 4-6 wt. % POSS and that in both cases; the improvements in thermal stability are quite pronounced.

From **Figure 3** It is observed that as the mass fraction of POSS is increased in the PU system, there is a corresponding decrease in the levels of volatile products of degradation - which follows a linear relationship as a function of mass fraction DSIPOSS . At 10 wt.% POSS there are ~70% less volatile material evolved from the degradation of the POSS/PU elastomer when compared with the unmodified (0%) system. This marked decrease in volatile species evolution can be linked to physical modification of the PU melt-phase by POSS[22] and may also be an indicator that the condensed-phase degradation chemistry is being driven towards higher levels of intractable macromolecular residue versus volatile small molecule degradation products[25]. Interestingly (and in contrast to the linear trend in the volatile evolution data), the data given in **Figures 4-5** appear to indicate that while the onset and peak maxima temperatures for both primary de-polymerization and secondary monomer degradation increase significantly as a function of POSS inclusion level (~40°C increase in onset degradation temperature in the 4% POSS/PU hybrid compared with the unmodified PU) in general, the improvements in degradation temperatures reach a maximum at a loading between 4-5 wt. POSS. Indeed, as the POSS levels are increased above 4%, the onset degradation temperature for primary de-polymerization is observed to decrease (**Figure 4**). These data therefore would seem to suggest that while POSS has a relatively simple effect on total volatiles evolution and inhibits or otherwise retards the release of volatile species as a linear function of mass fraction POSS in the matrix, the onset and peak degradation data indicate that there is some regime change that occurs above 4% POSS. Previous studies have clearly demonstrated that POSS [9] and other cage structures, such as Carboranes [28] tend to disrupt the crystalline order of MDI-BDO segments at loadings above 5wt. % through steric interactions. Such disruption of the crystalline phase-segregated morphology is likely to contribute to a reversal in the thermal stability trends, therefore in order to explore the potential link between the morphology and thermal stability of the hybrid systems DSC was employed to quantify the hard-block crystalline content of the POSS/PU hybrid systems. Given in **Figure 6,** with values summarized in **Table 3** are the results of DSC analysis of the POSS/PU hybrid systems

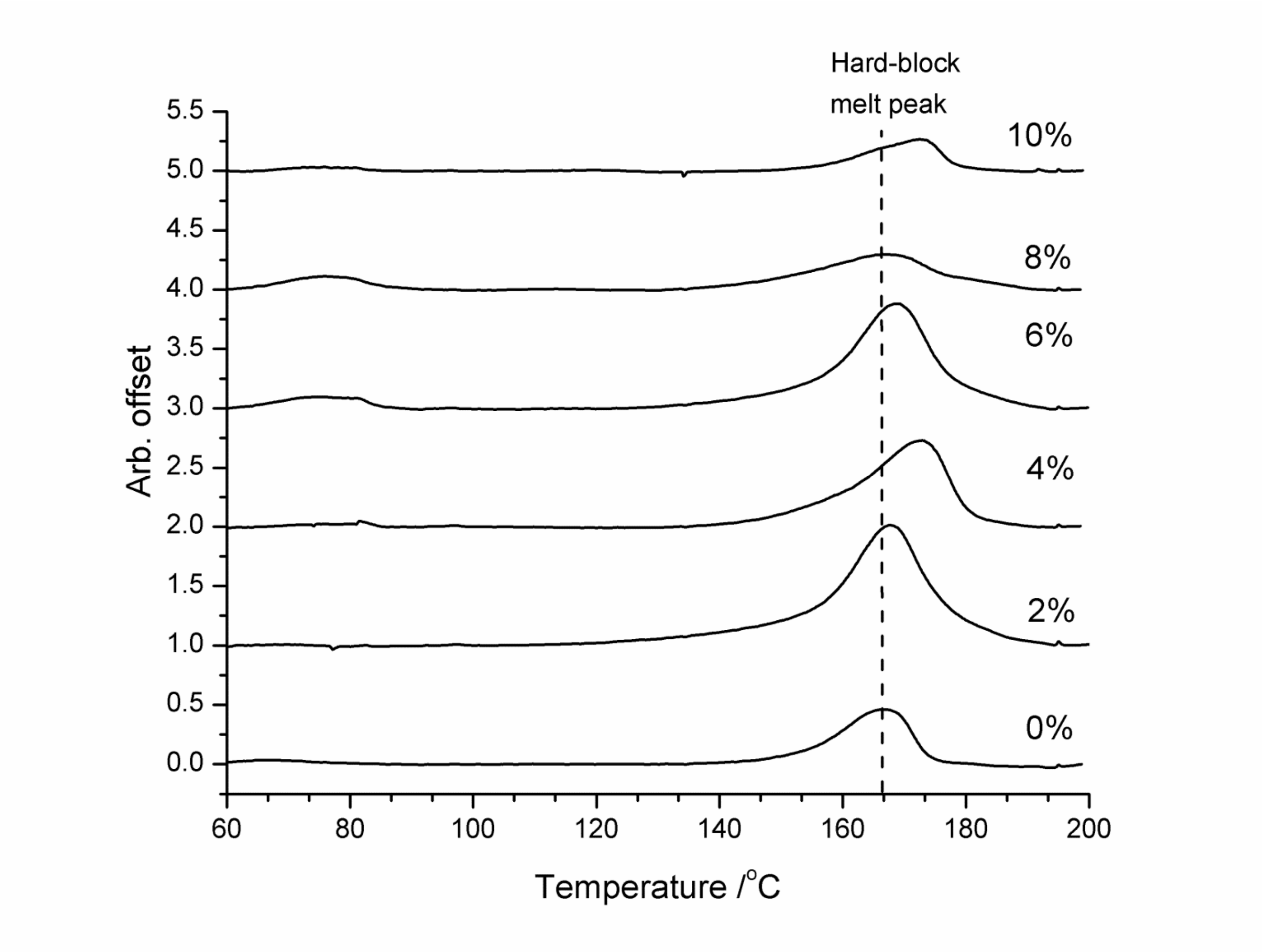

Figure 6. DSC Characterization of the crystalline hard-block morphology of the 0-10% DSIPOSS /PU hybrid elastomer systems. Note that the melting peak initially increases at low DSIB POSS levels only to decline as the levels of POSS in the system are increased.

Table 3. Summary of data derived from DSC thermograms giving the enthalpy of crystallization, calculated percentage crystallinity and crystalline melting temperature for the hard-block segments of the 0-10% DSIPOSS /PU hybrid elastomer systems.

Mass Fraction POSS	**ΔH_c /Jg^{-1}**	**% Hard-block Crystallinity**	**Hard-block T_m /°C**
0	48.0	32.0 ± 0.5	167 ± 3
0.02	84.8	56.5 ± 0.5	168 ± 3
0.04	82.9	55.3 ± 0.5	173 ± 3
0.06	104.6	69.7 ± 0.5	169 ± 3

0.08	46.1	30.8 ± 0.5	166 ± 3
0.1	23.6	15.7 ± 0.5	173 ± 3

From these DSC data presented in **Figure 6** and **Table 3**, it can be observed that while the crystalline melt temperature of the MDI-BDO segments does not change as a function of POSS loading, the, the hard-block crystallinity of the PU systems increases significantly as a function of POSS loading from 0-6 wt.%, then at higher loadings, the crystallinity declines to a ~50% the value of the unmodified PUS system. These data demonstrate that the direct inclusion of the DSIPOSS as a chain extender in the between MDI segments in the PUS systems actually *enhances* the existing crystalline hard-block domain (to a point). And above a loading of 6 wt. % the effects of DSIB POSS become disruptive leading to a loss of crystallinity which is paralleled by the decline in thermal stability. It is likely that at low inclusion levels, the POSS acts to reduce segmental mobility and may also act as an nucleation site for crystallization – therefore promoting the growth of a crystalline hard-block domain. However beyond 12 % mol. fraction of POSS as a chain extender substitute, the steric bulk of the cages becomes significant and disrupt the h-bonded & Π-Π stacked crystalline order of extended MDI-BDO-MDI chain segments required for effective crystalization [9].

So far, the overall degradation properties of the POSS/PU hybrids in relation to their physical crystalline morphology have been discussed. In the following section, the effects of POSS inclusion on the mechanistic pathways of thermal degradation will be examined. Given in **Figure 7** are the composite total ion chromatogram (TIC) plots of the speciated products of degradation of all six POSS/PU hybrid systems, as determined by Py-GC/MS. In **Table 4** the degradation products are identified along with their relative abundances in the analysed degradation product streams.

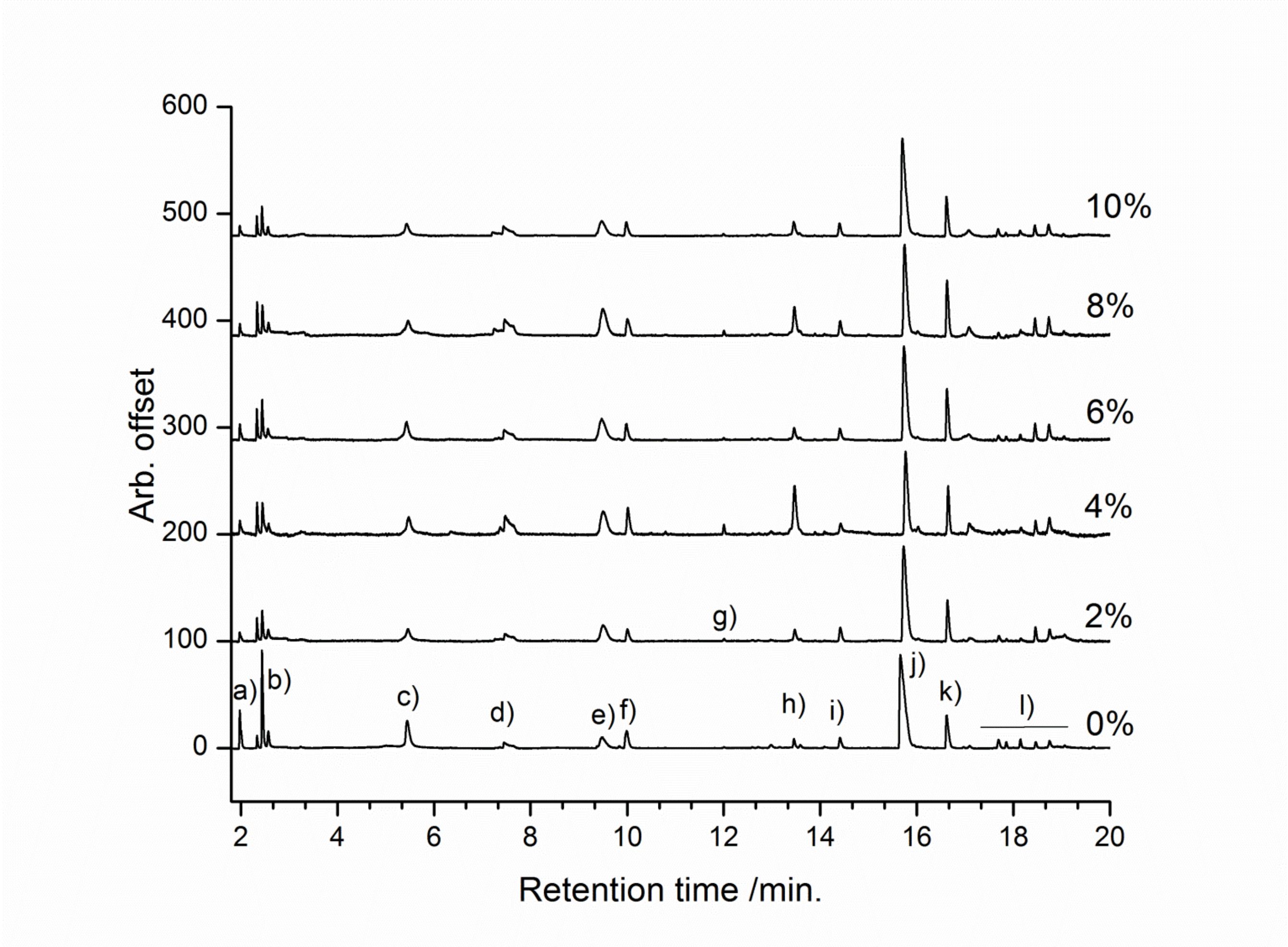

Figure 7. Composite TIC plots showing the speciation of degradation products from the 0-10% DSIPOSS /PU hybrid elastomer systems. Peaks corresponding to degradation products are labelled (a-k) and are assigned in **Table 3**. Note that while there are some minor notable differences, the degradation product profiles remain similar between systems.

Table 4. Peak assignments for the identified products of degradation from the 0-10% DSIPOSS /PU hybrid elastomer systems. (a-l) correspond to the peak labels on **Figure 7**. Trace products not labelled on **Figure 7** are also listed along with non-eluting species that were detected during the pyrolysis degradation analyses.

Peak (group) identifier	Retention time/min	Assignment	Abundance	Comment
a	2.33-2.57	Methane & CO	minor	constant
b	2.43	CO_2, Ethene & Ethane	rel. minor	ethene reduced in hybrids
c	5.45	Propene	minor	constant
d	7.46	Allene & water	minor	constant

e	9.49	Butane	rel. minor	increased in hybrids
f	9.99	Methylenecyclopropane	trace	constant
g	12.00	Butyl amine	minor	present in hybrids only
h	13.45	Propenal	minor	increased in hybrids
i	14.41	Dihydrofuran	minor	constant
j	15.66	THF	major	constant
k	16.62	Butanal	rel. major	increased in hybrids
l	17.70-19.00	Benzene, 1-butanol, branched diols	minor	Benzene and butanol reduced in hybrids
N/A	3.27	Acetaldehyde	trace	constant
N/A	9.40	Methanol	trace	constant
N/A	9.83	Butene	trace	constant
N/A	12.59	Ethanol	trace	constant
N/A	~17-20	Butane diol	major	constant, direct detect
N/A	N/A	MDI	major	constant, direct detect
N/A	N/A	Oligomeric polyols	major	constant, direct detect

From the degradation product speciation data presented in **Figure 7** and **Table 4** it is apparent that the distribution of products of degradation remains broadly similar across all of the POSS/PU hybrid systems and with respect to the unmodified PU elastomer: In all cases, large quantities both free polyol, MDI and BDO were observed in abundance along with a range of volatile organics, which and can be traced as the products of the secondary degradation of these monomers. It should also be noted that in no cases was free DSIPOSS observed as degradation product. These data strongly suggest therefore that the POSS modifier, while significantly changing the physical morphology of the PU system, does not chemically alter the major degradation pathways. While this is true, it is also apparent from these data however, that there are small but significant differences in the speciation of the small molecule, secondary degradation products as a function of POSS inclusion level. The products (a-l) with the exception of (g) and the inclusion of acetaldehyde, methanol, butane and ethanol can all be considered to be secondary thermal degradation products of MDI, BDO and PTMG and the reader is directed to both the excellent works by Grassie [26, 27] and the authors own recent study [25] for the specific mechanisms of their formation. For the purposes of this discussion we will therefore only focus on those products that have changed as a result of POSS inclusion.

There is a significant decrease in the levels of ethene and an increase in the levels of propenal and butanal - all scission products of PTMG. A small yet significant decrease in the levels of benzene (a degradation product of MDI) is also observed in the POSS modified systems and reduction in the yield of 1-butanol (a degradation product of BDO) were also observed. Finally, a butyl amine was detected as a minor product which was only observed in the POSS hybrid systems and is thought to be are-arrangement product of the butyl ‘R” groups of the DSIPOSS. While it is difficult to prescribe fully accurate mechanisms to the formation of these minor products in the absence of further experimental evidence, some conclusions may nonetheless still be drawn from these observations. The increase in yield of aldehydes (propenal and butanal) and the reduction in ethene yields suggest a subtle, yet real shift in the manner in which the PTMG degrades. This product shift may simply be a consequence of the elevated temperatures at which the more crystalline POSS modified PU systems degrade and indeed the peak level of propenal is observed at a 4 wt. % loading of POSS, which appears to be where an optimum lies for thermal stability and crystallinity. The reductions in the levels of benzene and 1-butanol also point towards small but real shifts in the hard-block monomer degradation mechanisms which correspond with POSS loading levels. In general, it appears that these small shifts in the distribution of secondary products are a consequence of the increased degradation temperatures brought on by the altered phase morphology rather than being themselves indicators of an active chemical role of the POSS within the degrading matrix.

In summary, the inclusion of DSIPOSS in the PU matrix leads to a significant reduction in volatile evolution of small molecule products on degradation and a simple mass balance therefore implies that the yields of condensed phase intractable products are consequently increased at the expense of the volatile species. No free POSS is observed in the gas or liquid phase therefore it must be assumed that it remains in the residual intractable fraction. It has been established that peak thermal stability corresponds with a maximum enhancement in crystalline content, therefore it can be surmised that all of these effects observed are at their root, a consequence of the physical effects of POSS on the phase segregated morphology of the PU matrix.

CONCLUSIONS

From the data presented in this study, it can be concluded that the incorporation of di-silanol isobutyl POSS into the hard-block segment of a PTMG-BDO-MDI thermoplastic elastomer structure has a significant and predominantly physical effect on the resultant morphology of the now ‘hybrid’ system, which in turn has a number of significant consequences for both the thermal stability, gas and condensed phase thermal degradation chemistry of these materials. Significant improvements in non-oxidative thermal stability correlate with a maximum in hard-block crystalline content which is thought to be due to the nucleating effects of the POSS cage. As with previous studies on both POSS/PU [9] and Carborane/PU hybrid materials [29], a ‘breakdown’ in the phase segregated morphology of the hybrid systems is observed at POSS inclusion level *typically* above 5 wt.% and ascribed to the steric penalties of the POSS cages becoming significant at these higher loading levels. Importantly, this study has also demonstrated that the inclusion of a POSS cage structure without the need for an alkyl tether yields more significant and predicable enhancements in physical structure and thermal properties than that observed in earlier POSS/PU architectures.

ACKNOWLEDGEMENTS

Portions of this work were performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. This work has also been partially supported by the National Science Centre in Poland under contract No. DEC-2011/02/A/ST8/00409~~.~~

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