POSS-Substituted Hyperbranched Polyester Blends with Thermoplastic Polyurethanes

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ABSTRACT

Boltorn hyperbranched aliphatic polyesters were functionalised with polyhedral oligomeric silsesquioxane (POSS) and blended with thermoplastic polyurethane (TPU). Functionalisation was confirmed using FTIR. Incorporation of POSS-functonalised Boltorn enhanced thermal stability and mechanical strength. Creep decreased while permanent deformation increased with denrimer concentration. Blends exhibited an increase in storage modulus (E') and glass transition temperature (T_g).

Keywords: functionalisation, thermoplastic polyurethane, hyperbranched polymer, viscoelasticity, POSS

1 INTRODUCTION

An important class of dendritic polymers, hyperbranched polymers have attracted significant attention due to their unique three-dimensional architecture, simple synthesis and useful properties such as high reactivity, high solubility and low viscosity. Aliphatic hyperbranched polyesters based on dimethylpropionic acid have been extensively studied since their introduction in 1993 [1] and commercialisation by Pertorp under the trade name Boltorn [2]. The chemical structure of the Boltorn family of dendrimers contains hydroxyl end groups, allowing for the introduction of functional groups. This versatility has lead to these hyperbranched polymers finding use in various fields, including coating, drug delivery and processing aid applications [2]. Boltorn dendrimers have been blended with other polymers [3], most often used as crosslinking agents in thermoplastic polyurethanes (TPU) [4-6] and tougheners in epoxy resins [7-10]. Although various inorganic groups have been introduced onto the Boltorn structure, including silicate [11] and montmorillonite clay [12], no research has been performed regarding the incorporation of inorganic functionalised Boltorn into polymers and the influence these hybrid organic-inorganic materials have on thermal stability and thermomechanical properties.

The aim was to prepare POSS-functionalised Boltorn-TPU blends, where the treated dendritic polymers will enhance thermal stability and thermomecahnical properties. Objectives included functionalising Boltorn dendrimers with POSS, blending the treated hyperbranched polymers with TPU and evaluating the thermal stability and thermomechanical properties of the blends.

2 MATERIALS AND METHODS

2.1 Materials

Boltorn H20 ($M_W = 2{,}100\ g{\cdot}mol^{-1}$, Figure 1) was obtianed from Perstorp Specialty Chemicals AB, Sweden. TrisilanolheptisobutylPOSS was obtained from Hybrid Plastics, Hattiesburg, USA. Pellethane 2103-85A thermoplastic polyurethane was obtained from Dow Plastics.

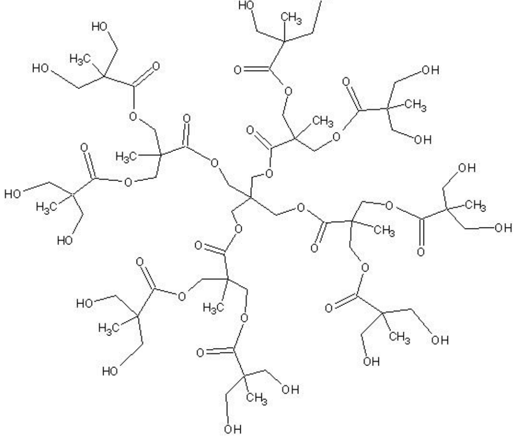

Figure 1 Boltorn H20

2.2 Prepartion of POSS-functionalised Boltorn

TrisilanolheptisobutylPOSS (5.00 g, 6.32 mmol) and 3-aminopropyltriethoxysilane (1.44 g, 6.5 mmol) were dispersed in 40 mL tetrahydrofuran (THF) and stirred at room temperature overnight. The solution was poured into 100 mL methanol and stirred for 10 min, before being suction filtered, washed with methanol and deionised water and dried in a vacuum oven at 75 °C for 12 h.

Boltorn H20 (1 mmol) was dispersed in 150 mL of THF and stirred at room temperature for 2 h. Amino-treated isobutylPOSS (1 mmol, Figure 2) was added and the solution was stirred for a further 24 h at room temperature. The solution was cast into glass Petri dishes and the solvent was allowed to evaporate in air overnight. The POSS-functionalised dendritic polymer was washed with acetone and methanol and dried in a vacuum oven at 25 °C for 12 h. The POSS-Boltorn materials were stored in sealed plastic bags kept in a desiccator at 0 % relative humidity.

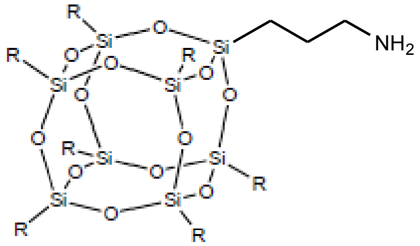

Figure 2 Amino-treated POSS (R = isobutyl)

2.3 TPU-functionalised Boltron blending

TPU was dissolved in a minimal amount of THF at room temperature. POSS-functionalised Boltorn was added to the solution and subjected to ultrasonic disruption (10 min, 25 °C, 20 kHz) to ensure even distribution. The solution was poured into an excess of methanol to precipitate the blend and to restrict filler migration. The sample was isolated using suction filtration and dried in a vacuum oven ar 35 °C for 12 h.

2.4 Blend characterization

A Perkin-Elmer Spectrum 2000 FTIR spectrometer working in diffuse reflectance spectroscopy (DRIFTS) mode was used to characterise the molecular vibration of the functional groups in the POSS and Boltorn. Anhydrous potassium bromide (KBr) was used as dispersing material and all spectra were scanned within the range 400-4000 cm^{-1}, with a total of 20 scans and a resolution of 8 cm^{-1}.

A Perkin-Elmer TGA-7 thermogravimetric analyser with TAC-7/DX thermal analysis controller was used to analyse the thermal stability of the films. Samples of ~10 mg were heated to 850 °C at 20 $°C\cdot min^{-1}$ in an inert environment provided by a 20 $mL\cdot min^{-1}$ nitrogen purge.

An Instron Universal Testing Instrument, Model 4465 was used to perform stress-strain analysis using dumbbell-shaped test bars according to ASTM D638 – 97, specimen type IV. A strain rate of 50 $mm\cdot min^{-1}$ was applied to each sample at ambient temperature. Results presented are the average of five measurements.

A TA Instruments Q800 Dynamic Mechanical Analyser was used to perform creep recovery analysis. Test specimens displaying average dimensions of ~12.80 x 5.50 x 0.80 mm^3 were subjected to an applied stress of 0.5 MPa for 20 min, followed by a recovery period of 80 min with 0.01 MPa applied stress. The applied stress chosen was within the linear viscoelastic region of all polymer films. Tests were conducted at 30 °C and all results presented are the average of triplicate measurements.

Single frequency temperature scans were conducted using a TA Instruments Q800. A static force of 500 mN, modulated force of 100 mN and frequency of 1 Hz were applied. The storage modulus (E'), loss modulus (E"), loss tangent (tan δ) and associated T_g of the films were measured as a function of temperature from -80 to +110 °C at a heating rate of 2 $°C\cdot min^{-1}$.

3 RESULTS AND DISCUSSION

3.1 FTIR Spectroscopy

The infrared spectra of amino-treated POSS and POSS-functionalised Boltorn H20 are presented in Figure 1. The amino-treated POSS displays several bands characteristic of its structure; 1100 cm^{-1} (Si-O-Si stretching), 1462 cm^{-1}, 1400 cm^{-1}, 1366 cm^{-1} and 1328 cm^{-1} (CH_2 and CH_3 bending vibrations and deformation), 2950 cm^{-1} and 2868 cm^{-1} (CH_3, CH_2 and CH vibrational strethcing of isobutyl 'R' groups'). In addition, the lack of a broad peak at ~3300 cm^{-1} indicates the lack of hydroxl (OH) groups and confirms succesful amino-treatment of the POSS.

The spectrum of POSS-functionalised Boltorn H20 displayed several bands indicating the presence of the amino-treated POSS. The characteristic Si-O-Si band is clearly visible at 1100 cm^{-1}, as well as the various bands corresponding to the alkyl groups on the isobutyl 'R' compatibilising molecules. The most evident of are the bands at 2950 cm^{-1} and 2868 cm^{-1}. The large band at 3388 cm^{-1} corresponds to the OH end groups on the Boltorn dendrimer. This suggests that interaction bewteen the hyperbranched denrmier and POSS has occurred at some, though not all, hydroxyl groups. The benefit in retaining several OH groups is that they provide an affinity between the Boltorn dendrimer and polar groups within linear TPU.

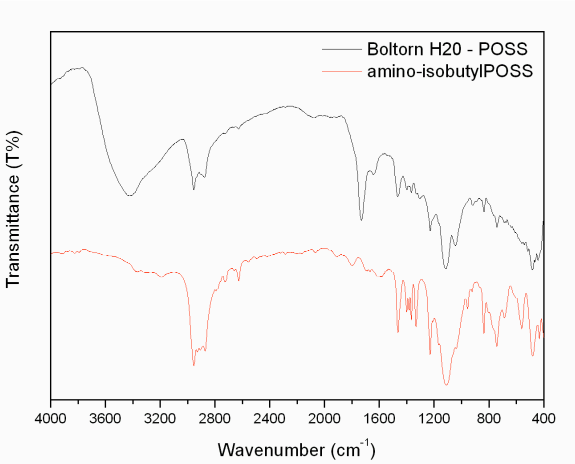

Figure 3 FTIR spectra of amino-treated POSS and POSS-functionalised Boltorn H20

3.2 Thermal stability

The mass loss curves of TPU and the blends are displayed in Figure 4. Blends exhibited an increase in degradation temperature with increaseing functionalised Boltorn concentration. Dendritic polyesters have been shown to exhibit superior thermal stability properties than their linear counterparts, due to their chemical structure [13]. Maji et al [14] observed an increase in thermal stability of TPU prepared with Boltorn crosslinks. In addition, the inorganic structure of POSS leads to the molecule exhibitng a high intrinstic thermal stability. Polymer segments near POSS molecules may degrade more slowly due to the POSS providing the "most torturous path" for degradation. Another proposed mechanism is that POSS restrict polymer chain motions, due to polymer-filler interactions or by the large inertia exhibited by segments of polymer containing POSS [15, 16]. The results indicate that Boltorn and POSS provide a synergetic effect in increasing the thermal stability of TPU.

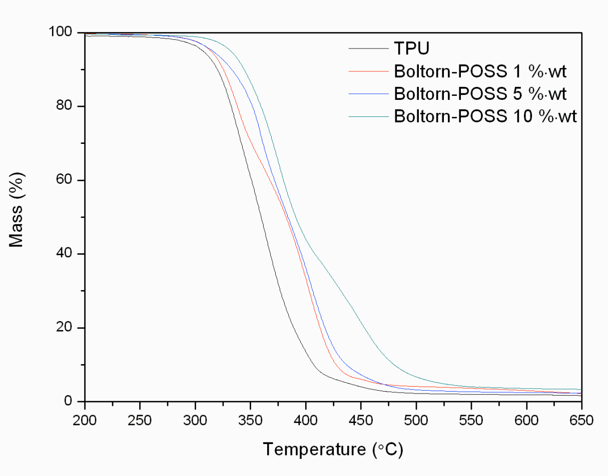

Figure 4 Mass loss curves of TPU and blends

3.3 Stress-strain

The stress-strain curves of TPU and the blends are presented in Figure 5. Pure TPU displayed a tensile modulus (E) of 11.32 MPa and yield strength of 17.13 MPa. Increasing Boltorn-POSS content had a positive effect on E and yield strength, reaching maximum values at 10 %·wt. In linear-dendriitic polymer blends, enhancement of mechanical properties will occur if the dendrimer possess a rigid structure due to the presence of aromatics or if it is cryslatlline [17, 18]. The presence of rigid POSS restricts motions of pollyurethane chains and allows applied stress to be absorbed from the polymer. In addition, Boltorn dendrimers can interact with linear TPU via the unreacted hydroxyl groups, acting as physical crosslinks [14]. Elongation at break decreased with increasing blend concentraiton, due to the increase in rigidity imparted by POSS.

3.4 Creep-recovery

Creep-recovery curves of TPU and the blends are shown in Figure 6. Creep deformation decreased with increasing Boltorn content, which was attributed to two factors. Firstly, the Boltorn dendrimers interwave throughout the TPU matrix, restricting molecular motions and rearrangements under applied stress. Secondly, the presence of rigid filler, such as POSS, provides additional stiffness, further reducing creep deformation. Permanent deformation increased with Boltorn concentration. Higher loadings of Boltorn (and POSS), restrict the relaxation of TPU chains, causing irreversible chain slippage and unraveling. These observations strongly suggest that POSS-functionalised Boltorn restricts the flow of TPU.

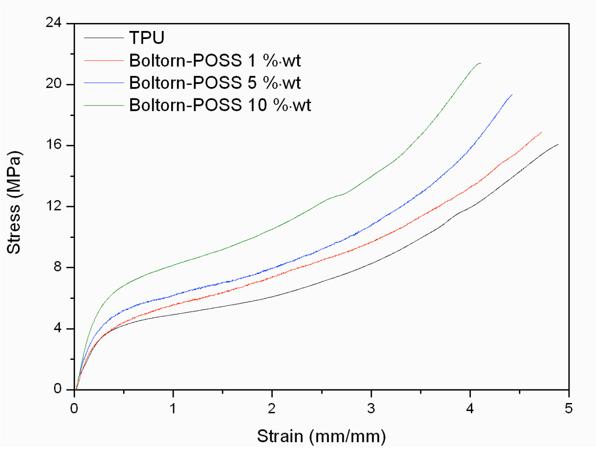

Figure 5 Stress-strain curves of TPU and blends

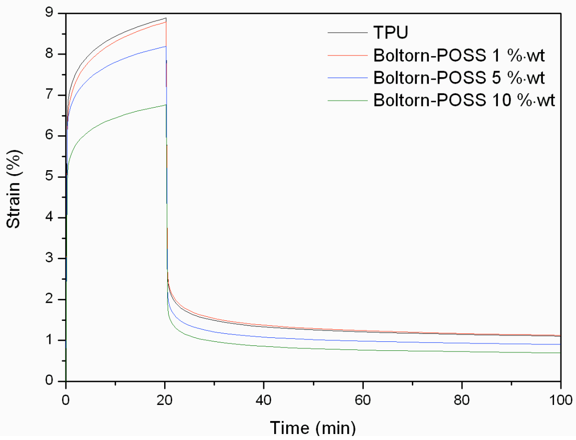

Figure 6 Creep-recovery curves of TPU and blends

3.5 Modulated force – thermomechanometry

The storage moduli (E') of pure TPU and the TPU-Boltorn-POSS blends are shown in Figure 7a. Increasing the POSS-functionalised Boltorn concentration increased E' values, due to the higher strength the blends posses.

Pure TPU displayed a T_g of -47 °C, as displayed in Figure 7b. Addition of functionalised Boltorn caused the T_g to increase, reaching maximum values at loadings of 10 %·wt. This is attributed to the Boltorn dendrimers and POSS functional groups restricting molecular motions of TPU chains, causing the blends to lose flexibility. Blends experienced glass-rubber transition across a larger temperature range, as indicated by broader loss (E") modulus peaks. Peak broadening indicates an increase in the segmental relaxation times of the matrix. Peak breadth was observed to increase with Boltorn concentration, reaching maximum values at loadings of 10 %·wt.

The tan delta curves (Figure 7c) showed an increase in peak location (and T_g) with filler content, corresponding to trends observed in loss moduli curves. Maximum T_g values were obtained at Boltorn loadings of 10 %wt. Increasing Boltorn content reduced tan delta peak heights, indicating a reduction in dampening ability due to restricted chain motions [3]. The observation of a single T_g peak in both the E' and tan delta curves indicates adequate miscibility of the Boltorn within TPU, with little-to-no phase separation.

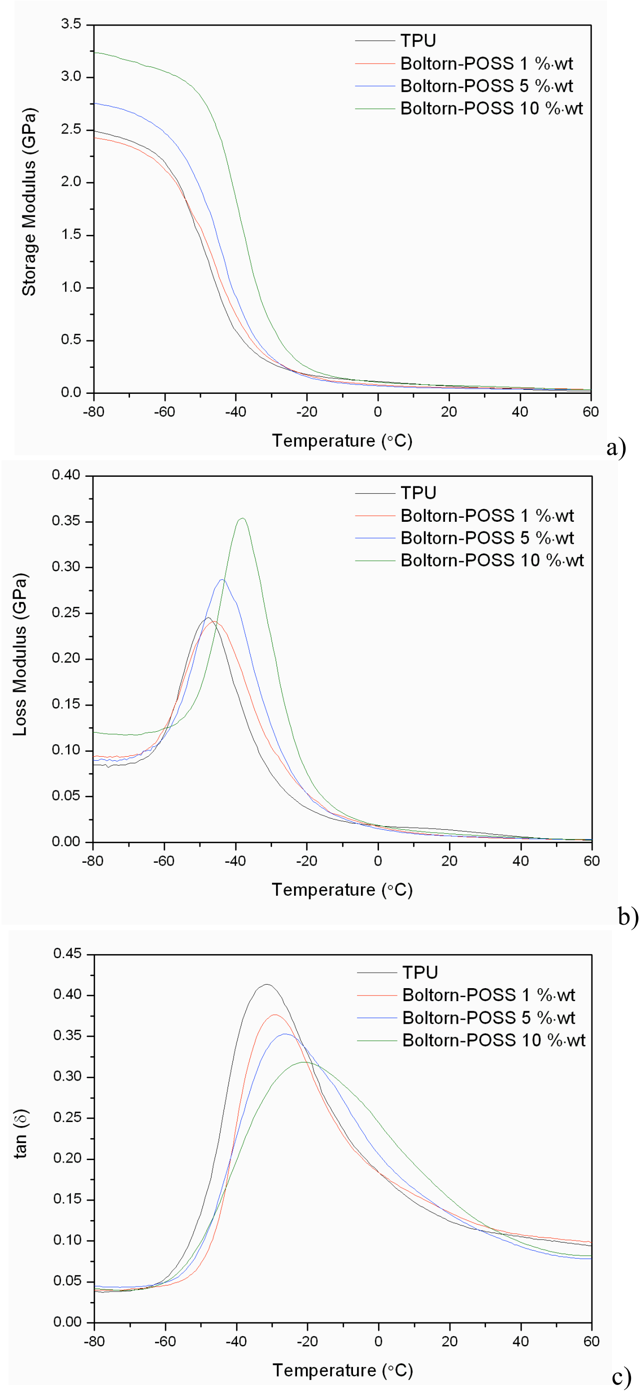

Figure 7 mf-TM curves of TPU and blends; a) storage, b) loss, c) tan(δ)

4 CONCLUSION

Boltorn dendritic polyester was functionalised with POSS and blended with linear TPU. Functionalisation was confirmed using FTIR. Blends displayed an increase in thermal stability. The incorporation of POSS-functionalised Boltorn had a positive effect on tensile modulus and strength while decreasing creep deformation. Storage modulus and T_g increased with Boltorn content. Boltorn dendrimer and isobutylPOSS both contributed to the enahcned mechanical and thermal properties of the blends.

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