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Ricinoleic acid from vegetable oil

Fatty acid derivatives

Pyrolysis

Sulphur-containing, long-chain diacids

Diamine

Renewable, bio-based, sulphur-containing long-chain polyamide

- Superior impact resistance
- Enhanced ductility and elongation
- Very-low moisture absorption
- Excellent chemical/solvent stability
- Easier processability via lower T_m and suitable rheological profile

■
CHAIN ALIPHATIC SEGMENTS

Y AND LONG-

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ABSTRACT

Thiol-ene ‘click’ chemistry was utilised to prepare dicarboxylic acid monomers containing two sulphur units within the backbone, which subsequently underwent polycondensation to yield a series of renewable, long-chain, fatty-acid derived linear polyamides. The linear sulphur-containing polyamides displayed number-average molecular weights of 8,000-55,000 g·mol⁻¹ and broad polydispersities biased towards higher weight fractions. Glass transition values were slightly above room temperature (31-35 °C), while melting temperatures ranged from 121-170 °C. This novel class of polymers exhibited an impressive property profile, most notably exceptional impact resistance, tear strength, high elasticity, very low water absorption yet high oxygen- and water vapour permeability. The presence of sulphur and the increased aliphatic segment length influenced a wide spectrum of polyamide properties due to the reduced amide linkage (and inter-chain hydrogen bonding) density and less-effective chain packing ability due to the increased atomic radii of the sulphur atoms. The data highlights the technical advantages of these polymers, while also expanding the repertoire and structure-property relationships of both long-chain- and sulphur-containing polyamides, and encouraging further development of polyamide derivatives from renewable sources.

Keywords: polyamide, thiol-ene ‘click’ chemistry, impact resistance

INTRODUCTION

Within the family of technically-relevant and applicable polyamides (PAs), the length of the aliphatic segments are relatively short; usually numbering from 6 to 12 methylene ($-\text{CH}_2-$) groups. Consequently, the physical properties and applicability are determined by the polyamide's functional groups, namely their amide linkages. The strong inter- and intramolecular hydrogen bonds between the amide groups result in a range of favourable properties, including high modulus and strength, high melting- and heat-distortion temperatures and enhanced abrasion resistance. This is especially the case with PA 6 and PA 6,6, which both possess a high methylene:amide ratio per repeat unit, and an even spacing between amide linkages, encouraging a high-as-possible degree of hydrogen bonding. However, this extensive network of hydrogen bonds may present several hindrances; firstly, the increased strength/stiffness associated with these interactions are usually accompanied by brittleness, poor ductility and low impact strength. Likewise, the increased melting temperatures present challenges with processing, requiring elevated temperatures which may promote oxidation/discolouring and limiting potential blend and composite compositions (eg. cellulosic materials which usually begin to degrade at $\sim 200^\circ\text{C}$). Finally, the increased presence of amide groups provides a great affinity for water absorption, leading to reduced strength and dimensional stability, as well as possible degradation during polymerisation (1).

One approach to overcoming these hindrances and limitations is by incorporating longer segments of aliphatic linear chains into the repeating unit. As the length of the aliphatic chains is increased, the influence of hydrogen bonding on polyamide properties begins to diminish; indeed, at very high chain lengths the effect of van der Waal's forces becomes more dominant, as the polyamide approaches properties more akin to polyolefins (especially polyethylene) (2). Thus, long-chain linear polyamides provide an impressive property profile, including high mechanical strength and impact resistance, good solvent resistance, lower melting temperatures and low water absorption (3). Despite these attractive attributes, these polyamides have received somewhat limited attention, due to the lack of viable routes to obtain the di-functional monomers required for polyamide synthesis (other than traditional multi-step synthesis). An alternative option which provides various practical and environmental/sustainable advantages is the utilisation of plant and vegetable-based oils and fats, which contain linear, long-chain hydrocarbon segments (4,5). This generally involves the isolation of fatty acids and esters from

triglycerides via hydrolysis or alcoholysis, which can be subsequently polymerized or functionalised/modified prior to use. For example, ricinoleic acid can be derived from castor oil and subjected to pyrolysis to yield fatty acid derivatives which can serve as monomers for polyamide synthesis. Despite this great potential, the bulk of long-chain polyamides (containing up to 34 carbons per repeating unit) (6-15) reported in literature are synthesised from petroleum-based, non-renewable derivatives. However, research regarding the synthesis of polyamides from renewable sources is steadily growing (16-19). Furthermore, the longest fully- and partially bio-based PAs commercially available have carbon numbers per repeat unit of 16 (PA 6,10), 18 (PA 6,12) or 20 (PA 10,10). Therefore, there exists a need to expand the family of these bio-based long-chain polyamides, while also determining crucial structure-property relationships and subsequent applicability.

Amongst the range of functionalised and modified polyamides prepared, those containing various sulphur derivatives in the backbone chain are amongst the most useful and interesting. The type of physical and chemical properties which can be changed depend on the type of sulphur moiety incorporated, resulting in increased solubility, processability (lower melting temperatures and increased blend miscibility), enhanced ionic conductivity, thermal stability, flexibility and/or chemical stability (20). Aside from using substituents which already contain sulphur within their backbone, such as spirodiamine (21), an effective and versatile method of incorporating sulphur into a polyamide backbone involves taking advantage of fatty acid derivatives with allyl end groups and reacting them with compounds containing thiol moieties; utilising the thiol-ene 'click' reaction. The reaction can be initiated using either UV-light or free radical initiators, proceeding at a high rate to produce a high yield anti-Markovnikov product. Aside from incorporating sulphur into the polymer backbone, the use of thiol-ene chemistry allows great potential for preparing monomers with very long chain (aliphatic segment) lengths. Meier et al (22-24) have utilised thiol-ene reactions to prepare sulphur-functionalised monomers and polyamides, with an emphasis on the monomer synthesis, polymerisation and basic property overview. Similarly, both the aforementioned references, as well as other researchers (25,26) have focused on the synthesis of shorter-chained polyamides, containing a single sulphur atom in the backbone chain. Thus, there is a need to develop a broader structure-property relationship spectrum of these materials, while also investigating the possibilities and limitations of long-chain and multi-sulphur atom containing polyamides. To the best of the

authors' knowledge, this is the first such reporting of very long, linear polyamides with containing multiple sulfide bonds within the backbone.

Herein, the preparation of AABB-type, renewable linear polyamides containing two sulphur atoms in the backbone chain is presented. Thiol-ene 'click' chemistry was utilised to prepare sulphur-functionalised monomers with increased aliphatic segment length, for the subsequent polymerisation of long chain sulphur-functionalised linear polyamides. The influence of sulphur and repeating unit length on molecular weight, crystallinity, thermal, mechanical, barrier and water absorption properties of the synthesised polyamides is presented, with structure-property relationships being identified and highlighted.

EXPERIMENTAL

Raw materials

1,2-ethanedithiol (EDT), 2,2-dimethoxy-2-phenylacetophenone (DMPA), 10-undecenoic acid (UDA), hexafluoroisopropanol (HFIP), 1,6-hexanedithiol (HD), and acetonitrile were purchased from Aldrich. 1,10-decanedithiol (DDT) and dodecamethylenediamine (DMDA) were purchased from TCI Europe NV. Ethanol was purchased from Altia. All other solvents were purchased from Aldrich. All reagents were used as received.

Preparation of sulphur-containing dicarboxylic acids via thiol-ene 'click' chemistry

A dithiol and 10-undecenoic acid (molar ratio 1:2) were charged into a pre-dried bottle. In a separate beaker, 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator (1 %·mol relative to the alkenoic acid) was dissolved in minimum amount of acetonitrile and added to the alkenoic acid/aminothiol mixture. The whole mixture was covered with aluminum foil to prevent light irradiation. The mixture was stirred with a vortex mixer for 1 h, then poured into petri dishes. The reaction mixture was irradiated with a 15 W lamp ($\lambda = 254$ nm) for 40 min. A white solid appeared, indicating the completion of the reaction. The sulphur-containing, dicarboxylic acid product was purified by dissolving (at 75 °C) and recrystallization from ethanol. Finally, the product was dried in a vacuum oven overnight at 40 °C. A schematic of the reaction is summarized in Scheme 1, while the composition, yield and structure of the sulphur-containing dicarboxylic acids are displayed in Table 1.

Scheme 1 Preparation of sulphur-containing, dicarboxylic acid monomer (AABB-type monomer)

Table 1 Composition, yield and structure of sulphur-containing dicarboxylic acids

S-containing dicarboxylic acid	Dithiol utilised	Yield (%)	Chemical structure
12,15-dithiahexacosanedioic acid	1,2-ethanedithiol	56	
12,17-dithiatriacontanedioic acid	1,6-hexanedithiol	74	
12,22-dithiatetratetracontanedioic acid	1,10-decanedithiol	78	

Synthesis of sulphur-containing, long-chain, aliphatic polyamides

Polyamides were synthesised via a two-step method; firstly, a crystalline, solid nylon salt was prepared from sulphur-containing dicarboxylic acid and diamine; the respective diamine and dicarboxylic acids utilised, as well as polyamide nomenclature are summarized in Table 2. This was done to ensure a precise 1:1 molar ratio of both components, which subsequently encourages polymer chain growth (i.e. high molecular weight) and prevents premature termination of the polycondensation reaction. Secondly, the nylon salt was feed into the reaction vessel and subjected to melt polycondensation at elevated temperature and high vacuum. **NOTE:** The nomenclature utilised for the S-containing polyamides follows the convention of listing the total number of carbons within the diamine and diacid constituents, respectively. This was done to keep the abbreviations as short and simple as possible. However, we kindly remind the reader to consider the structure of the functionalised diacid and location of the sulphur atoms along the backbone chain (refer Table 1) when considering the overall structure of the polyamides.

Table 2 Nomenclature, composition and reaction conditions of synthesised sulphur-containing polyamides

S-containing polyamide	Monomers/constituent materials		Reaction temperature (°C)
	<i>Diamine</i>	<i>S-containing dicarboxylic acid</i>	
S-PA 6,24	Hexamethylenediamine	12,15-dithiahexacosanedioic acid	210

S-PA 6,28	Hexamethylenediamine	12,17-dithiatriconanedioic acid	180
S-PA 6,32	Hexamethylenediamine	12,22-dithiatetratriacontanedioic acid	180
S-PA 12,28	Dodecamethylenediamine	12,17-dithiatriconanedioic acid	180
S-PA 12,32	Dodecamethylenediamine	12,22-dithiatetratriacontanedioic acid	170

Nylon salt preparation

In general, fatty acids are insoluble in water, thus nylon salts were prepared in ethanol solution. The nylon salt preparation procedure was applied to all polyamides synthesized in this project. Dicarboxylic acids were dissolved in absolute ethanol at approximately 75 °C to obtain 10 %·wt clear transparent solutions. Then, 5 %·mol excess of hexamethylenediamine dissolved in ethanol solution was added under vortex stirring to the dicarboxylic acid solution. The nylon salt precipitated as soon as it was formed. After the addition was complete, the reaction mixture was continuously stirred for 1 h at 75 °C, following by an additional stirring period of 1 h at 0 °C (achieved with an ice bath). The resulting product was vacuum filtered, and the precipitate was washed with ethanol. The product was dried in a vacuum oven overnight at 40 °C. Table 3 summarizes the yield of the nylon salts.

Table 3 Nylon salt yields

Nylon salt	Yield (%)
S-PA 6,24	96
S-PA 6,28	96
S-PA 6,32	98
S-PA 12,28	98
S-PA 12,32	94

Melt polycondensation

Polymerization was conducted for 24 h utilizing a 1 L stainless-steel reactor, with the reaction temperatures being summarized in Table 2. The reactor consists of a 1 L stainless-steel vessel, surrounded by a heating element that encompasses the sides of the vessel. A lid which includes a mechanical stirrer column, and inlets for vacuum and nitrogen was fastened to the top of the reaction vessel/heating element ‘base’ during the polycondensation reaction. The vessel was charged with nylon salt at room temperature, after which the temperature was increased (under

nitrogen purge) to the reaction temperatures described in Table 2. Upon reaching the desired temperature, the nitrogen purge was stopped, the valves of the reactor were closed, and these conditions maintained for 2 h. Nitrogen purge was subsequently reapplied for 1 h to remove any water polycondensate. Finally vacuum of less than 0.07 mbar was applied and the reaction proceeded for a total of 24 h. To harvest, the polyamides were soaked immediately into liquid nitrogen to cool and prevent any possible thermal degradation.

Preparation of test specimens

Films and Charpy impact test specimens for subsequent use were prepared via heated press (Fontijne TP 400). Samples were placed between steel plates with poly(tetrafluoroethylene) sheet liners, heated to 280 °C, 150 kPa of pressure applied, held for 10 min and cooled to ambient.

Characterization

¹H Nuclear magnetic resonance (NMR)

¹H NMR spectra were recorded with a Bruker AVANCE-III 400 MHz spectrometer operating at 400.13 MHz for ¹H. The spinning speed of samples was 8000 Hz, contact time 2 ms and delay between pulses 5 s. Samples were dissolved in chloroform-d₁ (deuteration at no less than 99.8 %) with 10 % v/v trifluoroacetic anhydride added, in 5 mm NMR tubes, at room temperature.

Size exclusion chromatography

SEC analyses were performed at room temperature with a Waters 717plus Autosampler, Waters 515 HPLC pump, and a Waters 2414 refractive index (RI) detector. A set of two columns in series (HFIP-803 and HFIP-804 ‘Shodex’ columns, Showa Denko Europe GmbH.) was utilised. Hexafluoroisopropanol (HFIP) with 5 mM sodium trifluoroacetate (CF₃COONa) was used as eluent at 0.5 mL·min⁻¹, and calibration was performed against PMMA standards. All samples were prepared at 1 mg·mL⁻¹ concentrations using the eluent solvent.

X-ray powder diffraction

The crystallinity of the synthesised polyamides were calculated from XRD analysis data obtained with a PANalytical X’pert Pro/Pw 3040/60, with Cu K α radiation (λ = 0.154 nm). Data was collected in the 2 Θ range from 2 to 70 ° with a scanning speed of 3 °·min⁻¹. All analyses were carried out at room temperature. Radiation conditions were 45 kV and 40 mA.

Density measurements

The density calculations were based on Archimedes' principle. The specimens were weighed in both air and water (23 °C), with Equation 1 being used to determine the volume of the specimen:

$$V = \frac{m_1 - m_2}{\rho_{H_2O}} \quad (1)$$

where V is the volume of the specimen (cm^3), m_1 and m_2 are the mass of the specimen (g) in air and water, respectively, and ρ_{H_2O} is the density of water ($1 \text{ g} \cdot \text{cm}^3$). The mass of the object in air was then divided by this calculated volume to yield the density. Specimens were analysed in triplicate.

Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) analyses were conducted with a TA Q2000 Modulated Temperature DSC in order to observe the melting, crystallization and fusion processes. Nitrogen was used as the purge gas. Approximately 5 mg of sample were sealed in T-zero aluminum pans. The heating-cooling was programmed from 25-250 °C at a heating rate of $20 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, with the samples being subjected to two heating-cooling cycles. The transition temperatures were measured the second heating/cooling cycle. All the measured temperatures were recorded at the peak values or middle-set values.

Dynamic mechanical analysis

The glass transition temperatures were measured by dynamic mechanical analysis (DMA). The samples (approximate dimensions $\sim 10.0 \times 5.3 \times 0.2 \text{ mm}^3$, prepared using a press-cutting mold) were heated from room temperature to 250 °C at $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, while subjected to a 1 Hz frequency within 1 % strain. The glass transition temperatures were determined from the peak of tan delta curve which is the ratio of the loss modulus and the storage modulus. Samples were analyzed in duplicate.

Tensile analysis

Tensile analysis was conducted using an Instron 4204 Universal Tensile Tester with a 100 N static load cell. The film specimens were prepared in a rectangle shape, $20.0 \times 5.3 \text{ mm}^2$ by press-cutting mold. The thickness varied from ~ 0.1 - 0.3 mm . The measurements were strain-control with an increasing strain-rate of $10 \text{ mm} \cdot \text{min}^{-1}$. Films were allowed to equilibrate at in a

humidity-controlled atmosphere 50 % relative humidity and 23 °C for at least 88 h prior to testing. Each measurement was repeated at least 5 times. The Young's modulus, yield stress, yield strain and, where possible, tensile strength and elongation at break were determined. Results presented are the average of five reproducible repeats.

Tear strength

Tear strength analysis was conducted with the same device and conditions utilised during tensile testing, with the exception of specimen dimensions. Trouser tear specimens (average dimensions 20.0 x 12 x 0.2 mm³) with a vertical incision running length-wise from the middle of the sample were utilised.

Charpy (V-notch) impact analysis

Impact analysis was conducted using a Zwick pendulum impact tester, utilising an impact energy of 1 J. Specimens with average dimensions ~80 x 10 x 5 mm³ were prepared utilising heated press treatment, after which a 45 ° v-notch with 2 mm depth was cut. The results presented are the average of five reproducible repeats.

Water absorption

The water absorption was measured by soaking a known-mass of polyamide in distilled-water for 10 days. After this, the samples were taken out and excess water from the surface of the samples was dried gently with tissue paper. The water absorption percentages were calculated by the ratios of dry and their wet samples. Three specimens were measured for each sample.

Water vapour transmission rates

Water vapour transmission rates (WVTR) of the films were determined gravimetrically using a modified ASTM E-96B (wet cup) procedure. Samples with a test area of 30 cm² were mounted on a circular aluminum dish (68-3000 Vapometer EZ-Cups), which contained deionized water. Dishes were stored at 23 °C and 50 % RH and weighed periodically until a constant rate of weight reduction was attained. Water vapour permeability was determined by normalizing the transmission rates to the thickness of the films.

Oxygen transmission rates

Oxygen transmission rates (OTR) of selected polyamides films were determined according to standard ASTM D3985 using an Oxygen Permeation Analyser Models 8001 (Systech

Instruments Ltd, UK). The test area of the sample was 50 cm². The measurements were carried out at 23 °C and 50 or 90 % RH, using 100 % oxygen as a test gas. Oxygen permeability was determined by normalizing the transmission rates to the thickness of the films.

Solubility and solvent resistance

The synthesized polyamides were immersed in ethanol, acetone, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), chloroform (CHCl₃), formic acid, toluene, methanesulfonic acid, *m*-cesol, hexafluoropropanol, dichloroacetic acid, sulfuric acid and co-solvents such as formic acid/dichloromethane (CH₂Cl₂) (50:50 %·v/v) and CHCl₃/Trifluoroacetic anhydride (TFFA) (10:1 %·v/v) at room temperature for at least 7 days to determine polymer solubility.

RESULTS AND DISCUSSION

Chemical structure

The ¹H NMR spectra of the synthesized S-containing PAs are presented in Figure 1, displaying characteristic peaks associated with typical polyamide structures (10,12). Protons adjacent to –NH and –CO groups were assigned to the peaks at 3.7 and 2.8 ppm, respectively, while peaks at 1.6 and 1.3 ppm correlated to protons along the aliphatic chain. A new peak at 2.5 ppm was observed for the specimens, which was assigned to protons adjacent to sulphur atoms (22,25).

Figure 1 ^1H NMR spectra of S-containing PAs: i) S-PA 6,24, ii) S-PA 6,28, iii) S-PA 6,32, iv) S-PA 12,28, v) S-PA 12,32. Note: the 'x' in the general polyamide structure is not present for S-PA 6,24. For all other polyamides 'x' corresponds to $-\text{CH}_2-$ units which can be assigned chemical shifts designated 'b'

Molecular weight distribution

The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) of the S-containing PAs were obtained via SEC and are summarized in Table 4. The synthesised polyamides displayed M_n values in the range of 8,000-55,000 $\text{g}\cdot\text{mol}^{-1}$, with a majority being in the range of 42,000-55,000 $\text{g}\cdot\text{mol}^{-1}$ (S-PA 6,32, S-PA 12,28 and S-PA 12,32, respectively). These values are generally larger than those displayed by commercial PAs (usually $\sim 10,000$ -30,000 $\text{g}\cdot\text{mol}^{-1}$), and can be attributed to a number of factors, including:

- **Increased reaction times:** S-containing polyamides were synthesised utilising reaction times of 24 h, which is considerably longer than times utilised for commercial polycondensation of PA (~ 3 -10 h). This highlights the relationship between reaction time and the degree of polycondensation, while also providing a degree of control if a specific molecular weight is desired.

- **Effective condensate (water) removal:** The application of vacuum and sufficient mechanical stirring during polycondensation allows for the rapid and effective removal of water, while also preventing any ‘dead-zones’ within the molten polycondensate. This in turn encourages chain growth and reduces the likelihood of premature reaction termination, or moisture-induced chain scission (degradation).
- **Nylon salt stoichiometry:** Finally, filtration utilised during nylon salt preparation encourages the formation of a monomer with a precise 1:1 stoichiometric ratio. Aside from preventing the introduction of potential contaminants into the reaction vessel, this factor also prevents premature reaction termination and interruption of chain growth.

Upon comparing the M_w and PDI values, it is evident that significant fractions of very-high molecular weight S-containing PA are present in the specimens. This is especially the case with S-PA 6,32 and S-PA 12,28. This behaviour may be a consequence of the aforementioned factors which similarly encouraged high M_n values, confirming that the reaction conditions and presence of a homogenous polyamide melt encouraged chain growth with little possibility of chain degradation or premature reaction termination. However, specimen S-PA 6,32 displayed a M_n value of $8,000 \text{ g}\cdot\text{mol}^{-1}$, considerably lower than the remaining polyamides. One hypothesis may be for this phenomenon may be due to the nylon salt T_m of S-PA 6,32 (and subsequent reaction temperature) being 20-30 °C higher than the remaining specimens. The increased reaction temperature may be more-difficult to maintain, resulting in a polymer melt with increased viscosity. This may serve as a barrier to effective water (condensate) removal during polymerization, leading to premature termination of the reaction and subsequent lower (number average) molecular weight.

Table 4 Molecular weight, crystallinity, density and thermal data of commercial and synthesised polyamides

Polyamide	$M_n \text{ (g}\cdot\text{mol}^{-1})$	$M_w \text{ (g}\cdot\text{mol}^{-1})$	PDI	$\chi_c \text{ (%)}$	$\rho \text{ (kg}\cdot\text{m}^{-3})$	$T_g \text{ (}^\circ\text{C)}$	$T_c \text{ (}^\circ\text{C)}$	$T_m \text{ (}^\circ\text{C)}$
S-PA 6,24	8,000	34,000	4.17	15	1.06	34	153	170
S-PA 6,28	18,000	75,000	4.11	14	1.04	31	117	160, 154, 125
S-PA 6,32	42,000	270,000	6.39	18	1.02	32	117	154, 141, 126
S-PA 12,28	55,000	298,000	5.45	16	1.02	35	113	147, 125
S-PA 12,32	48,000	189,000	3.90	14	1.01	31	107	142, 121

Crystallinity

Table 4 summarizes the percentage crystallinities (χ_c) of the S-containing polyamides, determined utilising XRD. The synthesised polyamides displayed crystallinities values within a narrow range, from 14-18 %, with no apparent influence of repeat unit length being evident. Crystallization within polyamides is generally facilitated and encouraged through hydrogen-bonding amongst amide linkages; this is especially evident in shorter polyamides with a symmetrical amide linkage distribution along the backbone (ie PA 6 and PA 6,6), however this is also the case in long-chain aliphatic polyamides (27). The incorporation of long aliphatic segments into the backbone chain reduces the overall density of amide linkages within the polyamide, thereby reducing the number of units able to participate in inter-chain hydrogen bonding. Furthermore, the increased molecular weight values exhibited by the S-PA specimens may impart additionally stiffness into the polyamide chains, as well as increasing the likelihood of chain entanglements. Subsequently, this reduced chain flexibility can hinder effective packing of polyamide chains and prevent van der Waals interactions amongst methylene units from contributing towards crystalline domain formation. Finally, the presence of sulphur atoms within the may backbone may also impart an influence on polymer chain packing due to sulphur's increased atomic radius (88 pm) compared with carbon (67 pm), nitrogen (56 pm) or oxygen (48 pm). Therefore, the combination of long aliphatic chain segments and sulphur atoms within the backbone may serve to limit the extent of crystalline domain formation. Although the presence or absence of crystalline domains will exert an influence on material properties, the relatively narrow range of crystallinities suggests that the degree of crystallinity is not as dominant an influence on material properties.

The XRD patterns of the S-containing PAs are presented in Figure 2. All polyamides exhibited spectra with similar features. A small, broad peak was visible within the range $2\theta = \sim 7-10^\circ$ (001 or 002), which correlates to the length of the chemical repeat unit, while the peak at $2\theta = \sim 38^\circ$ stems from the amorphous component of the polyamides (15). Two distinct peaks were not visible for the (001) and (002) indices, however specimens S-PA 6,24, 6,28 and 6,32 displayed a more-prominent (002) peak, while S-PA 12,28 and 12,32 showed only a single broad peak attributed to (001). This can be attributed to the effects of destructive interference, with the (001) peak becoming weaker as the distance between carbonyl groups becomes more equal (28). A prominent peak (100) at $2\theta = \sim 20^\circ$ is visible, correlating to the inter-chain distance of the α -

crystalline phase, while a shoulder peak appears at $2\theta = \sim 21^\circ$ which may suggest the presence of β -pseudo-hexagonal crystal structure. Similarly, a smaller peak is located at $2\theta = \sim 23^\circ$ ($010/110$), and is attributed to the inter-sheet distance of the γ -crystalline phase (29). The peak (100) location shifted towards slightly lower 2θ values as the repeating unit chain length increased, while the ($010/110$) peak remained constant. This indicates that the inter-chain distance increases with repeat unit length, while the inter-sheet distance remains relatively similar. It is apparent for all polyamides that the α -crystalline phase dominates the structure, with the ratio of (100):($010/110$) peak intensities being similar for all specimens. Pagacz et al. (15) compared the WAXD profiles of various long-chain AABB-type polyamides, observing that reducing the methylene:amide linkage ratio may increase (100) peak intensity relative to the ($010/110$) peak. However, the polyamides utilised within the aforementioned study (PA 4,10 to PA 10,12) possess significantly shorter repeat unit lengths than the sulphur-containing polyamides. Therefore, it is likely that the S-PAs chain lengths are sufficiently long, such that subtle changes in repeat unit length may not produce a drastic change in crystalline morphology.

Figure 2 XRD spectra of sulphur-containing polyamides

Density

As summarized in Table 4, the S-containing polyamides displayed a reduction in density (ρ) with increasing chain length; S-PA 12,32 displaying the lowest ρ value of 1.01. This may be attributed to the reduced weight ratio of amide linkages per repeat unit, as the length of the repeating units increases. In addition to encouraging crystalline domain growth, hydrogen bonding amongst amide linkages can also encourage closer packing of polyamide chains (30). Reducing the extent of this interaction would lead to a ‘looser’ configuration of chains, with an increased proportion of unoccupied ‘free’ volume and subsequently reduced density. This less-densely packed structure is also encouraged by the increased likelihood of chain entanglement with increasing repeating unit length, as well as the incorporation of larger sulphur atoms into the backbone chain.

Thermal properties

The glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures of the sulphur-containing polyamides are summarized in Table 4, while the DSC spectra are presented in Figure 3. With the exception of S-PA 6,24, specimens displayed two or three distinct melting endotherms; this behaviour has been previously documented in various sulphur-containing polymers (24,31,32), and is attributed to the presence of various crystalline structures and/or the melting and recrystallization processes which occur during the calorimetry experiment. Furthermore, polyamides are known to exhibit polymorphic transitions behaviour upon heating, resulting in the formation of lamellae with varying thickness (15,33).

A reduction in T_c and T_m was observed as chain length increased. In contrast, increasing either the diamine or functionalised diacid length reduced T_g , however no clear correlation between T_g and total repeating unit length was apparent. These phenomena in thermal behaviour may be attributed to a number of factors:

- Backbone chain flexibility is expected to increase with repeating unit length. Thus, the activation energy for segmental rotation is reduced (lower T_g), while also increasing the entropy change upon melting (lower T_m).
- Although the increased molecular weights exhibited by the S-PAs would lead to an overall stiffer polymer, with a greater number of tie molecules between crystalline domains or high likelihood of chain entanglement (as evidenced by the similar

- crystallinity values and reduced T_c values), a significant degree of ‘free’ volume is entrapped within the polymer simultaneously, in which the more-flexible local chain segments can undergo segmental motion. Given that there was no evident reduction in T_g as the total repeat unit length increased and similar T_g values for S-PA 6,28, 6,32 and 12,32, there may be competing mechanisms which influence T_g behaviour. The high molecular weight and bias towards higher weight segments may also contribute towards the ‘spike’ in T_g exhibited by specimen S-PA 12,28.
- The ratio of methylene:amide linkages also increases with increasing unit length. This reduces the weight ratio of amide linkages per repeat unit which could potentially partake in hydrogen bonding; these hydrogen bond sites restrict chain motion and increase the energy required for glass-rubber transition (T_g) and melting (T_m) (30).

Figure 3 DSC endotherms of sulphur-containing polyamides, a) cooling showing crystallization peaks, b) heating showing melting peaks

Upon comparing the S-containing polyamide T_g values with commercial polyamide grades or similar chain-length equivalents which lack sulphur atom(s) within the backbone chain, a drastic reduction in T_g is displayed by the S-PA specimens. There are two possible reasons which contribute towards this behaviour. Firstly, the incorporation of sulphur into the polymer backbone increases the ratio of carbon:amide linkages per repeating unit. This reduces the number of potential hydrogen bonding sites for each repeat unit, which can restrict segmental chain motion during the glass-rubber transition. Secondly, introduction of larger-radius sulphur atoms into the main polymer chain may prevent effective packing or interactions between chain segments, resulting in increased ‘free volume’ (unoccupied space between polymer chains) and greater room for rotation about bonds. This leads to more-flexible polymer chains which require less energy for segmental motion (lower T_g).

Tensile properties and tear strength

Figure 4 shows the stress-strain curves of the sulphur-containing polyamides, while the tensile data is summarized in Table S1 of the Supplementary Data. The profile of the stress-strain curves

was similar for all specimens, with the polyamides undergoing yielding following the linear-viscoelastic region. A degree of strain hardening was visible prior to specimen failure.

Figure 4 Stress-strain curves of sulphur-containing polyamides

The polyamide specimens displayed a distinct reduction in Young's modulus with increasing repeat unit length, reducing from 540 (S-PA 6,24) to 300 MPa (S-PA 12,32). Similarly, a reduction in work-to-break (toughness) with increasing aliphatic segment length was observed, while yield stress, tensile strength and elongation at break remained similar. One consequence of increasing the length of the repeating unit (more specifically, incorporating additional aliphatic groups) is that the prevalence of amide linkages within these repeating units is diminished. The subsequent decrease in the degree of inter-amide hydrogen bonding leads to these long-chain polyamides displaying reduced moduli, strength and toughness values, and increased elongation and ductility. Furthermore, chain flexibility is increased with aliphatic segment length, which may also impart a similar influence on tensile behaviour. The influence of repeating unit length and amide:methylene group ratio was most apparent for Young's modulus and toughness, which strongly suggests that these properties are more-directly dependent on the aforementioned variables.

In addition to the influence of repeating unit length and amide:methylene group ratio, the presence of sulphur atoms within the backbone chain is another key consideration. As mentioned previously, the increased atomic radius of sulphur relative to other atoms which comprise the polyamide may prevent effective packing of polymer chains, leading to reduced overall crystallinity values. Furthermore, these hindrances can result in a greater degree of 'free' (unoccupied) volume within the polymer, while also restricting the total potential of inter-amide linkage H-bonding. Therefore, stiffness and strength values were diminished. However, this also serves to promote the dissipation of load through various chain motions as opposed to specimen failure. As a result, these motions encourage increased elongation and ductility, while also contributing towards polyamide toughness.

Furthermore, the influence of molecular weight and polydispersity is an important consideration in tensile behaviour, and may account for the 'spike' in Young's modulus and work-to-break values of S-PA 12,28, the specimen which displayed the largest molecular weight. This can be attributed to two key phenomena. Firstly, the increased likelihood of chain entanglement that accompanies higher molecular weight enables polymer chains to better withstand- and dissipate applied load. Secondly, high molecular weight polymers experience a much slower time scale of motion than shorter equivalents. Furthermore, both the time scale of motion and chain entanglements are intensified as the molecular weight bias towards higher weight fractions increases. The tensile data highlights that although the effects of repeating unit length and amide:methylene group ratio are most apparent, the influence of molecular weight distribution and presence of sulphur cannot be overlooked, and contribute in part towards the overall tensile profile of the polyamides.

The tear strength values are summarized in Table S1 of the Supplementary Data. Sulphur-containing polyamides displayed a remarkable increase in tear strength, exhibiting values in the range of 25-50 kN·m. Tear resistance behaviour is dominated by various factors, including branching, crystallinity, molecular weight and molecular weight distribution. As was discussed with regards to the tensile behaviour, increased molecular weight- and distribution, two main phenomena occur; namely 1) increased likelihood of chain entanglement and 2) a slower time-scale of motion. This enables the polyamide chains to better resist deformation under increased loads. Furthermore, the increased ductility and elongation at break displayed by the synthesised

polyamides contributes towards the increased resistance to tear by allowing dissipation of applied load through chain slippage and other motions, rather than breakage. This is encouraged by the reduced weight of amide linkages per repeat unit, which leads to a net reduction in the likelihood of interchain hydrogen bonding. Sulphur-containing polyamides further highlight this phenomenon due to their increased repeating unit length and the presence of sulphur within the backbone chain. The larger atomic radii of the sulphur atoms prevents effective packing of polyamide chains, which prevents the already-limited occurrence of inter-chain H-bonding. This reduction in packing efficiency also serves to increase the amount of potential 'free volume'/unoccupied space within the polyamides, thus allowing a greater volume for chain sliding and other motions during periods of applied load.

Impact resistance

The Charpy (V-notch) impact test was utilised to evaluate the impact strength of S-containing polyamides. Furthermore, the impact strength of various commercial polyamides, have been characterised and published previously (34). The S-containing polyamides did not fail/break following impact, with the trend continuing as the same test specimen was subsequently struck with hammers of increasing potential energy (ranging from 0.5 to 5 J). Although the notch increased with hammer size, the specimen remained in one piece. This behaviour is displayed Figure S1 of the Supplementary Data, and is in contrast to the behaviour previously documented with conventional polyamides. Amongst the various factors which may contribute to this superior behaviour, the influence of molecular weight and weight distributions skewed towards higher weight fractions on impact resistance has been reported previously (35), and is in correlation with the tensile data. Furthermore, this exceptional behaviour can be attributed to the enhanced flexibility and ductility sulphur provides within polymer backbones, allowing for greater absorption of energy. The increased repeating unit lengths and fewer amide linkages facilitate this flexibility, encouraging energy dissipation via various chain motions. Similar properties have also been documented with polysulfones (36).

Water absorption

The percentage water absorption of several commercial- and sulphur-containing polyamides are displayed in Figure 5, while the values are summarized in Table S2 of the Supplementary Data.

Figure 5 Water absorption as a function of repeating unit length; a) commercial PAs and S-PAs, b) detailed evolution of water absorption with chain length of S-PAs

Polyamides are renowned for their ability to absorb water via hydrogen bonding with amide groups; this is exemplified by the relatively high absorption values of PA 6 (9.50 %) and PA 6,6 (8.53 %). The degree of moisture absorption can vary based on composition, and can significantly influence material properties and present challenges in utilisation and storage. Most notably, water molecules can plasticize polyamide chains. Increasing the length of the repeating unit led to a reduction in water absorption, as the number of non-polar aliphatic groups increases. Similarly, water absorption is diminished as the ratio of amide:methylene groups per repeat unit is reduced. Thus, PA 11 and PA 12 exhibited the lowest water absorption values, of 1.94 and 1.67 %, respectively. As indicated in Figure 3, sulphur-containing polyamides displayed exceptionally low water absorption values, reaching a minimum of 0.04 %·wt for specimen S-PA 12,32. Furthermore, the absorption percentage reduced with increasing chain length. This behaviour can be attributed to a number of phenomena. Firstly, the increased presence of aliphatic segments (and subsequent reduction in amide linkage density) increases the overall hydrophobicity of the polymer, resulting in fewer sites which can participate in hydrogen bonding with water molecules. Secondly, increased molecular weights and weight distribution biased towards higher mass fractions may promote the formation of chain entanglements, which may serve as physical barriers to water penetration and absorption. Finally, the presence of sulphur may also reduce the total hydrophilicity of the polyamide, since the sulfide linkages are more hydrophobic than amides (37).

Barrier properties

Table 5 summarizes the oxygen transmission rates (OTR) and water vapour transmission rates (WVTR) of selected sulphur-containing polyamides and reference polymers. Upon comparison with the barrier properties of various commercial polymers, the S-PA specimens display noticeably higher permeation values, especially when compared to that of EVOH and PET, as well as both commercial PAs (PA 6 and PA 11). One exception to this behaviour was the WVTR value of PA 6, which was the highest for all test specimens. This may be attributed to the high water affinity and increased water absorption rate (refer Figure 4) exhibited by this polyamide. However, despite exhibiting extremely low water absorption values, S-containing PAs displayed high OTR rates and WVTR approaching that of commercial PA 6. One factor may be the increased molecular weight and presence of high weight fractions. This is due to the reduced packing efficiency which occurs as molecular weight (and chain stiffness) increases. The

resulting increase in ‘free volume’ within the polyamides may lead to increased permeability. Additionally, the presence of sulphur atoms within the polyamide backbone may also contribute towards these increased transmission rates. As mentioned previously, the atomic radius of sulphur is larger than other atoms present within the polyamide. This may serve to further prevent effective chain packing, leading to additional unoccupied space between chain segments and increased permeation rates.

Table 5 OTR and WVTR data of selected reference polymers and sulphur-containing polyamides

Polymer	OTR (23 °C, 50 % RH) $\text{cm}^3 \times \mu\text{m}/(\text{m}^2 \times 24\text{h} \times$ kPa)	OTR (23 °C, 90 % RH) $\text{cm}^3 \times \mu\text{m}/(\text{m}^2 \times 24\text{h} \times$ kPa)	WVTR (23 °C, 50 % RH) $\text{g} \times \mu\text{m}/(\text{m}^2 \times 24\text{h} \times$ kPa)
<i>Reference polymers</i>			
LDPE	2180	1480	41
HDPE	240	240	6
PP	550	550	21
EVOH	0.09	0.81	225
PET	15	17	79
<i>Commercial PAs</i>			
PA 6	8 ± 4	18 ± 7	738 ± 5
PA 11	65 ± 5	71 ± 6	133 ± 4
<i>S-PA specimens</i>			
S-PA 6,24	678 ± 103	750 ± 95	510 ± 49

S-PA 6,28	338 ± 10	380 ± 20	405 ± 35
S-PA 6,32	686 ± 37	790 ± 14	650 ± 23

Dissolution and chemical stability

The stability of the S-PA specimens following immersion in a range of solvents is summarized in Table 6. Sulphur-containing polyamides exhibited good stability following exposure to common, mild laboratory solvents and co-solvent systems, which is indicative of most polyamides. Strong acids are known for their ability to dissolve polyamides, and as such methanesulfonic- and dichloroacetic acid dissolved all specimens. However, formic acid failed to dissolve any S-PA specimens, while S-PA 6,32, 12,28 and 12,32 were stable within sulphuric acid. This enhanced stability against solvents and acids may stem from a number of factors. Firstly, the increased molecular weight and distribution may result in a more-entangled structure. This increases the difficulty for solvent penetration and swelling of the polymer. Furthermore, the relatively long segments of aliphatic chain per repeating unit reduce the total amide linkage density. This is particularly crucial for dissolution mechanisms which rely on ionization (in the case of formic acid) (38,39) or hydrolysis (as for sulphuric acid) (38,40) of amide linkages; the fewer of these linkages results in a less-pronounced effect from acids. Finally, the relative inert nature of sulfur-based linkages within polymer backbones is well-documented (37,41-43).

Table 6 Chemical stability of sulphur-containing polyamides

Solvents	S-PA 6,24	S-PA 6,28	S-PA 6,32	S-PA 12,28	S-PA 12,32
THF	-	-	-	-	-
DMF	-	-	-	-	-
CHCl ₃	-	-	-	-	-
NMP	-	-	-	-	-
Formic Acid	-	-	-	-	-
DMSO	-	-	-	-	-
CHCl ₃ /TFFA	-	-	-	-	-
Methanesulfonic Acid	+	+	+	+	+

Formic Acid/DCM	-	-	-	-	-
H ₂ SO ₄	+	+	+	-	-
Dichloroacetic acid	+	+	+	+	+
HFIP	+	+	+	+	+

+: dissolvable, -: not dissolvable

CONCLUSIONS

A series of novel sulphur-containing polyamides were synthesised utilising polycondensation. Sulphur was incorporated into the polyamide backbone via thiol-ene ‘click’ modification of the dicarboxylic acid monomer. The sulphur-modified polyamides displayed high number-average molecular weights approaching 55,000 g·mol⁻¹, with broad polydispersities biased towards higher M_n values. Additionally, the synthesised polyamides exhibited reduced glass-, crystallization- and melting temperatures than conventional commercial polyamide grades, exceptionally higher impact- and chemical resistance, increased elongation and ductility. Furthermore, remarkably low water absorption yet high oxygen- and water vapour permeation were exhibited by the specimens.

The overall property profile of the polyamides and correlations between polymer structure and behaviour were influenced by three primary factors. Firstly, the incorporation of sulphur into the polyamide backbone chain hinders effective packing of polyamide chains, while also restricting the extent of interchain hydrogen bonding. This resulted in reduced strength and moduli values, crystallinity, melting temperatures and high permeability. At the same time, this led to increased elongation and ductility which further influence impact resistance, while the relative stability and inertness of the sulphide linkages led to superior chemical/solvent resistance. Secondly, the increased repeating unit length (and reduced ratio of amide:methylene linkages) imparts chain flexibility and hydrophobicity into the polyamides, while also reducing the overall density of amide linkages able to participate in hydrogen bonding. Thirdly, the increased molecular weight and polydispersity biased towards larger weight fractions encourages formation of chain entanglements, while also increasing chain stiffness that may restrict effective chain packing and increase ‘free volume’ within the polymer. It is hypothesised that material properties are influenced by more than one of the aforementioned factors, with a synergetic effect (in which one of the factors may dominate) being a plausible scenario.

The sulphur-functionalised polyamides display an interesting and specific combination of material properties, distinguishing them from conventional polyamides and many other polymer classes. This provides great potential for utilisation in a range of applications, particularly where high impact- and chemical resistance, low water absorption and high permeability is desired. Furthermore, by characterizing and understanding the key structure-property correlations within these polyamides, strategies for property modification and manipulation can be further exploited towards specific targets or property ranges. Finally, the possibility to prepare such materials from renewably sourced monomers encourages additional development of such polymers, to compliment or outright replace petroleum-derived counterparts.

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RENEWABLE POLYAMIDES VIA THIOL-ENE ‘CLICK’ CHEMISTRY AND LONG-CHAIN ALIPHATIC SEGMENTS

- Renewable sulphur-containing polyamides were synthesized via ‘click’ chemistry
- Polyamides displayed exceptional impact- and tear resistance, low water absorption
- Polyamides also displayed high oxygen- and water permeability
- Properties influenced by the presence of sulphur and long repeating-unit length