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Biobased chemical recycling: aminolysis of PET using renewable reagents and monomers to synthesize new semi-aromatic polyamides

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Chemical recycling of PET is a method of depolymerizing polymer chains to monomeric components enabling the synthesis of second-generation materials with virgin-like quality. Commercial chemical recycling techniques rely upon high pressure methanolysis to create precursors capable of synthesizing a second-generation PET resin. However, despite the circular approach of methanolysis, a product with a very short lifespan and similar value is created. The approach of the current study is to utilize aminolysis as an ambient pressure technique to create precursors for higher value materials with longer lifespans to address the current crisis in plastic waste. Semi-aromatic polyamides (SAP) are desired in this circumstance because of their high melting point and heat resistance combined with good melt-processability similar to aliphatic polyamides. In this study SAPs were synthesized using precursors recovered from the aminolysis of PET employing biobased diamines and dicarboxylic acids. While aminolysis has been explored in previous studies, this work investigated the use of biobased components from castor oil: decamethylene diamine during recycling and sebacic acid during polymerization. Polymer synthesis resulted in the formation of SAPs similar to polyphthalamides (PPA) with novel structures given the aromatic portion from terephthalic acid (TPA) and aliphatic portion from the diamines and diacids. The synthesized materials exhibited excellent thermal stability with high glass transition temperatures. Novel polymers were created with varying aliphatic chain length to understand fundamental parameters needed to produce a valuable polymer from post-consumer waste.

Sustainability spotlight

The recovery and recycling of plastic waste has many challenges, one of them being the economic incentive to collect and recycle waste. Chemical recycling is a technique that offers the ability to attach more value to waste than mechanical recycling due to the ability to recover pure monomers streams for subsequent generations of polymer synthesis. Aminolysis is a technique of chemical recycling that is able to be performed at ambient pressure and lower temperatures than many other methods due to the enhanced reactivity of amines. In addition, the use of aminolysis allows the synthesis of higher value, and durable materials, used in applications that last years, rather than re-inserting recovered monomers into a cycle of producing one-time-use plastics. The approach of our study utilizes aminolysis as an ambient pressure, low-energy chemical recycling technique to create monomers that are subsequently used to synthesize semi-aromatic polyamides, a polymer class with high heat stability often used in high-performance applications. In addition, we utilize biobased reagents for the chemical recycling and polymer synthesis steps to create fully renewable, and circular, polymers. This work investigated the use of biobased components from castor oil: diaminodecane and sebacic acid that are currently industrially produced from biomass. The use of renewable material aimed to lessen the introduction of non-terrestial carbon while the aminolysis technique was completed in a one step process to minimize energy and resource use. Overall, our work emphasized the importance of UN Sustainable Development Goals (SDG) of affordable and clean energy (SDG 7), responsible consumption and production (SDG 12), and climate action (SDG 13).

1 Introduction

Continuous growth in plastic use has increased the rapid production of polymer resins over the last decade. The demand for plastics is created by their benefits for many applications, such as a wide range of tunable properties and lightweight nature. However, the durability of plastics has become an environmental concern as most polymeric materials do not degrade naturally.[1] About 400 million metric tons of plastic

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were produced globally in the year 2022.[2] Around 6.2% of that was Polyethylene Terephthalate (PET). The PET market size is predicted to grow up to 67.13 billion in 2028 at a CAGR of 9.1%. PET ranks among the top 5 globally produced plastics and is the second most predominantly used plastic in the packaging sector, used in transparent bottles for soda, water, and other consumable liquids.[2,3] PET has gained wider acceptance as a reclaimable and recyclable material, reaching a recycling rate of 18% in 2015.[4] As PET is not readily biodegradable, the development of new recycling techniques is essential to prevent waste from entering the landfill and leaking to natural sources. Mechanical recycling plays a significant role in providing motivation for recovering PET, however, the overall quality of mechanically recycled PET is lowered due to thermal degradation, molecular weight decreases, and contamination of the second-generation material.[5,6]

Chemical recycling is a growing area used to recover purified monomers and chemicals from plastic waste.[7] Chemical recycling of PET has gained broader adoption in academia and industry with techniques such as hydrolysis, glycolysis, and methanolysis, which can successfully break down PET into usable chemical streams.[8] Aminolysis is another less explored avenue of chemical recycling but carries the advantage of using a stronger nucleophile than water, glycols, or methanol, leading to faster reactions under less harsh conditions.[9] Aminolysis of PET can be completed using a wide range of amine components, including alkanolamines, allylamines, multifunctional amines and polyamines, each providing a different functional group on the recycled derivative that can be exploited for various applications.[10] Many groups have successfully depolymerized PET using ethanolamine[11,12] yielding bis(hydroxyethyl) terephthalamide (BHETA), useful for its terminal hydroxyl groups that can lead to the synthesis of poly(ester-amides),[9,13,14] polyurethanes,[15] or other chain extenders and/or crosslinking agents.[16] Using multifunctional amines such as diethylenetriamine (DETA) or triethylenetetramine (TETA) during aminolysis can lead to curing agents for epoxy systems that have demonstrated similar performance to other hardener systems.[17] Products from the aminolysis of PET using diamines have fewer examples of upcycled polymer applications,[18] the products most often being used as asphalt modifiers, or additives in polymer systems,[19,20] despite the work done by Fukushima *et al.* to demonstrate the organocatalytic aminolysis of PET using a wide range of aliphatic and aromatic diamines.[7] The aim of the current study is to demonstrate a pathway to the synthesis of a higher-performing polymer application from the aminolysis of PET. Particularly, we target the polymer class of semi-aromatic polyamides (SAPs) that integrate the high melting points and heat resistance of aromatic polyamides together with the excellent melt processability of aliphatic polyamides facilitating their use on an industrial scale.[21,22] Although the depolymerization of PET with diamines is particularly suited to the synthesis of polyamides, there is a lack of reports demonstrating the ability to synthesize this important polymer class from chemically recycled PET.

SAPs are typically synthesized by reacting derivates of terephthalic acid and/or isophthalic acid with diamines. If the molar concentration of these aromatic diacids reaches 55%, they are categorized as polyphthalamides.[23] The petroleum-based nature of the monomeric components of traditional SAPs require alternative feedstocks to fit with green chemistry principles. One possible alternative is the use of castor oil-based components such as the 10-carbon diacid, sebacic acid, or the 10-carbon diamine, diaminodecane. These components have been used commercially and in academic research to synthesize aliphatic polyamides of various chain lengths.[24] However, to introduce aromatic components into polyamides, biobased routes have mainly utilized the lignocellulosic origin of furan dicarboxylic acid, despite the issues associated with decarboxylation and *n*-methylation during polymer synthesis.[25–27] The current study introduces the novelty of incorporating the aromatic component of terephthalic acid from chemically recycled PET, with the biobased nature of sebacic acid and diaminodecane to produce fully renewable/upcycled SAPs. For the first time, biobased reagents are used to create new polyamides from post-consumer PET. In addition, a series of polymers are produced by alternating the potentially biobased components of hexamethylene diamine and adipic acid with diaminodecane and sebacic acid to probe the structure–property relationships of different polymer formulations. The resulting polymers demonstrate excellent thermal properties characteristic of SAPs and point to a renewable and circular method for synthesizing a high-performing polymer class.

2 Experimental section

2.1 Materials

All reagents and solvents were used as received without any purification. 1,6-Diaminohexane (HMD, 99.0%), 1,10-Diaminodecane (DMD, >98.0%), 1,5,7-Triazabicyclo [4.4.0] dec-5-ene (TBD, >98.0%), sebacic acid (>98.0%), and Bromocresol Green were purchased from Tokyo Chemical Industry. The dimer diamine, under trade name Priamine 1074, was kindly provided by Cargill. *n*-Methylpyrrolidinone (NMP), Dimethyl sulfoxide-d_6 (DMSO, 99.95%), sulfuric acid (95–98%), hydrochloric acid (HCL, 1 N) and acetone were purchased from VWR Chemicals. Triphenyl phosphite (TPP, 99%) was purchased from Thermo Fisher. Adipic acid (AA, 99%) was purchased from Acros Organics. Toluene (≥99.3%) was purchased Sigma-Aldrich. 1,1,1,3,3,3-Hexafluoro-2-propanol was supplied by Oakwood Chemicals.

2.2 Aminolysis of post-consumer PET to produce terephthalamide precursors

Aminolysis reactions of PET were performed using two types of diamines: HMD and DMD with varying carbon chain lengths. First, the post-consumer PET bottles (transparent, purified water containing) were washed with acetone, dried and cut into 2 × 2 mm flakes. To optimize the reaction conditions of the aminolysis process and achieve maximum yield and reduced reaction time, varying reaction temperatures and run times were tested (Table S1). According to the optimal conditions, about 5 g of PET flakes were added into 500 ml, 2 neck round bottom flask containing excess diamine (50 g) to act as solvent and reagent during aminolysis. TBD was used as catalyst in 0.1 mole concentration compared to the molar amount of the repeating unit of PET. For DMD, NMP was used as the solvent since the melted reagent was unable to fully dissolve PET at the reaction conditions. Reactions were performed at 110 °C with HMD and 180 °C with DMD for 2 h under a nitrogen atmosphere. At the conclusion of the reaction the product was isolated by recovering the excess reagent in a suitable solvent and precipitating the terephthalamide precursor. The product of the reaction with HMD (termed HMDTA) was washed with water three times and a final rinse was done with acetone followed by filtration. The product of the DMD reaction (termed DMDTA) was washed with hot toluene three times and final rinse with acetone followed by filtration. Both samples were dried at 70 °C for 8 h in a vacuum oven. The percent yield of precursors was calculated by finding the theoretical yield of the terephthalamide using the molecular weight of the repeating unit of PET and the molecular weight of the diamine.

2.3 Synthesis of SAPs

Four novel SAPs were synthesized *via* solution polycondensation of HMDTA and DMDTA, together with sebacic or adipic acid. A predetermined amount (5 g, 0.01053 mol DMDTA and 0.013812 mol HMDTA) of terephthalamide precursor was mixed with an equivalent amount of diacid (molar ratio of diamine : diacid of 1 : 1) was applied in a two necked, round bottom flask with (10%) TBD as catalyst and TPP as an antioxidant. In all the reactions NMP was used as the solvent to create a homogeneous reaction mixture. The mixture was heated under vacuum for 12 h at 180 °C. A condenser was used during the polymerization to prevent solvent from evaporating. At last, upon completion of polymerization, the mixtures were cooled to ambient temperature to precipitate the polymers. The resulting SAPs were purified by washing them with water and acetone, then dried in a vacuum oven for 8 h. The SAPs were named according to the number of carbon atoms in the diamines and diacids. Following solution polymerization, resulted polymers were subjected to post polymerization in a vacuum oven at 200 °C for 4 h to further improve the molecular weights of the SAPs.

2.4 Synthesis of copolyamide

A novel type of copolyamide was synthesized using a prepolymer composed of a dimer diamine to investigate improving the flexibility of the polymer. Initially a prepolymer was synthesized by reacting a predetermined amount of dimer diamine and adipic acid with a molar ratio of diamine : diacid of 1 : 2 in a two necked round bottom flask with 10% TBD and TPP at 170 °C for 2 hours under nitrogen. Then HMDTA precursor was introduced into the reaction flask with molar ratio of diamine : diacid of 1 : 1 and reacted for 5 hours at 180 °C under nitrogen to synthesis the copolymer. NMP was used as a solvent in the second part of the reaction (HMDTA addition). Upon completion, the mixture was cooled to room temperature and the resulting copolyamide was then purified by washing with water and acetone. Finally, the polymer was oven dried under vacuum for 8 h.

2.5 Characterization of precursors, SAPs and the copolyamide

^{13}C NMR spectra of HMDTA and DMDTA were obtained on a Bruker Avance instrument at 300 MHz using DMSO-d_6 with 10% H_2SO_4. Infrared spectra of both precursors and SAPs were collected by a Thermo Scientific NICOLET iS10 spectrometer from 500–4000 cm^{-1} using 32 scans with a 4 cm^{-1} spectral resolution.

DSC analysis was performed on a TA DSC250 instrument. All runs were carried out under nitrogen atmosphere, with constant flow rate of 50 ml min^{-1}. Samples were initially heated to 300–350 °C at 10 °C min^{-1}. heating rate depending on the sample type. Cooling was completed down to −50 °C at 10 °C min^{-1}. The second heating cycle was then performed with the same conditions as the first heating ramp.

Thermogravimetric analysis of about 4–8 mg of precursors and polymers was performed under nitrogen purge at 10 °C min^{-1} to 700 °C with an initial 10 minutes isothermal hold as pre-purge on a AutoTGA 2950 V5.4A Thermogravimetric Analyzer.

The amine values of precursors were determined through titration with a standardized solution of 0.1 M HCL using bromocresol green as the indicator. About 0.23 g of precursors were dissolved in 20 ml of NMP to prepare the samples for the titration. The endpoint was determined when the dark blue solution turned into a green color. The average value of three titrations was taken for accuracy.

Gel permeation chromatography (GPC) was performed using TOSOH EcoSEC Elite HLC-8420 GPC instrument to obtain molecular weight. HFIP was used as the mobile phase with sample and reference flow rates of 0.35 ml min^{-1} and 0.175 ml min^{-1}, respectively. About 0.05 mg of material was solubilized in 10 ml HPIF to prepare the samples for analysis. 80 μL of prepared sample was injected into the column.

Intrinsic viscosity (η) of SAPs were analyzed in an Ubbelohde viscosimeter at 25 °C in concentrated sulfuric acid using polymer solutions of 0.05 g ml^{-1}. The intrinsic viscosity values were calculated according to the following equation:[28]

$$[\eta] = \frac{1}{c}\sqrt{2\left(\frac{t-t_0}{t_0} - \ln\frac{t}{t_0}\right)}$$

where (c) is the polymer concentration in dL g^{-1} and t and t_o are the flow times of the polymer solution and reference solvent, respectively.

Samples for dynamic mechanical analysis (DMA) and tensile testing were made using a laboratory vacuum compressed molding machine (MeltPrep, Gras, Austria). About 0.5 g of sample was placed in the mold between Teflon sheets, sealed and placed on the heating plate and pressed under vacuum for 12–15 minutes. The melting temperatures of SAP samples varied between 240–285 °C according to the type. The resulting sample bars had dimensions of 39 × 9 × 1 mm (L × W × thickness).

DMA analysis was carried out on a DMA Q800 V21.3 operated in tension mode. 12 × 7 × 1 mm specimens were cut from bars made *via* compression molding. The samples were mounted on the holder with a preload force of 1.5 N. A temperature sweep was analyzed from −50 °C to 150 °C at a frequency of 5 Hz and 0.3% max strain to obtain data, storage modulus (E'), loss modulus (E'') and tan delta.

Mechanical properties including tensile stress, tensile strain, and Young's modulus of SAPs were investigated using a universal testing frame from Instron (34SC-1) and a 500N load cell, with 12 mm min^{-1} crosshead speed and gauge length between 15–19.05 mm. Final values for tensile strength, strain and Young's modulus were taken by averaging results of three samples of each polymer.

3 Results and discussion

3.1 Aminolysis of PET and structural characterization of recovered terephthalamide precursors

Two terephthalamide precursors (Fig. 1), 1,10-Diaminodecane terephthalamide (DMDTA) and 1,6-Diaminohexane terephthalamide (HMDTA) were created through aminolysis of post-consumer PET using DMD and HMD, respectively. HMDTA was synthesized following the methods in previous reports.[7,18] A novel terephthalamide; DMDTA was created using DMD, a biobased diamine derived from castor oil, which was not reported in previous aminolysis reports. Contrary to HMDTA synthesis, the melted diamine during DMDTA synthesis was not sufficient to act as a solvent. Therefore, NMP was used as solvent to complete the aminolysis of PET when DMD was used as reagent. A series of preliminary aminolysis experiments with DMD at different temperatures and times (Table S1), revealed that 180 °C had the most consistent yield of DMDTA at a reaction time of 2 hours. A higher temperature (180 °C *vs.* 110 °C) was needed during DMDTA synthesis to counteract the lower reactivity of DMD *vs.* HMD. The yield of the recycled product (∼72–75%) was similar to earlier reports of HMD[7] but lower than other reports using shorter diamines such as ethylenediamine (see Table S5).

The purity of the recycled product was very important to monitor given that the polycondensation reaction in the subsequent step required precise ratios of end groups to reach

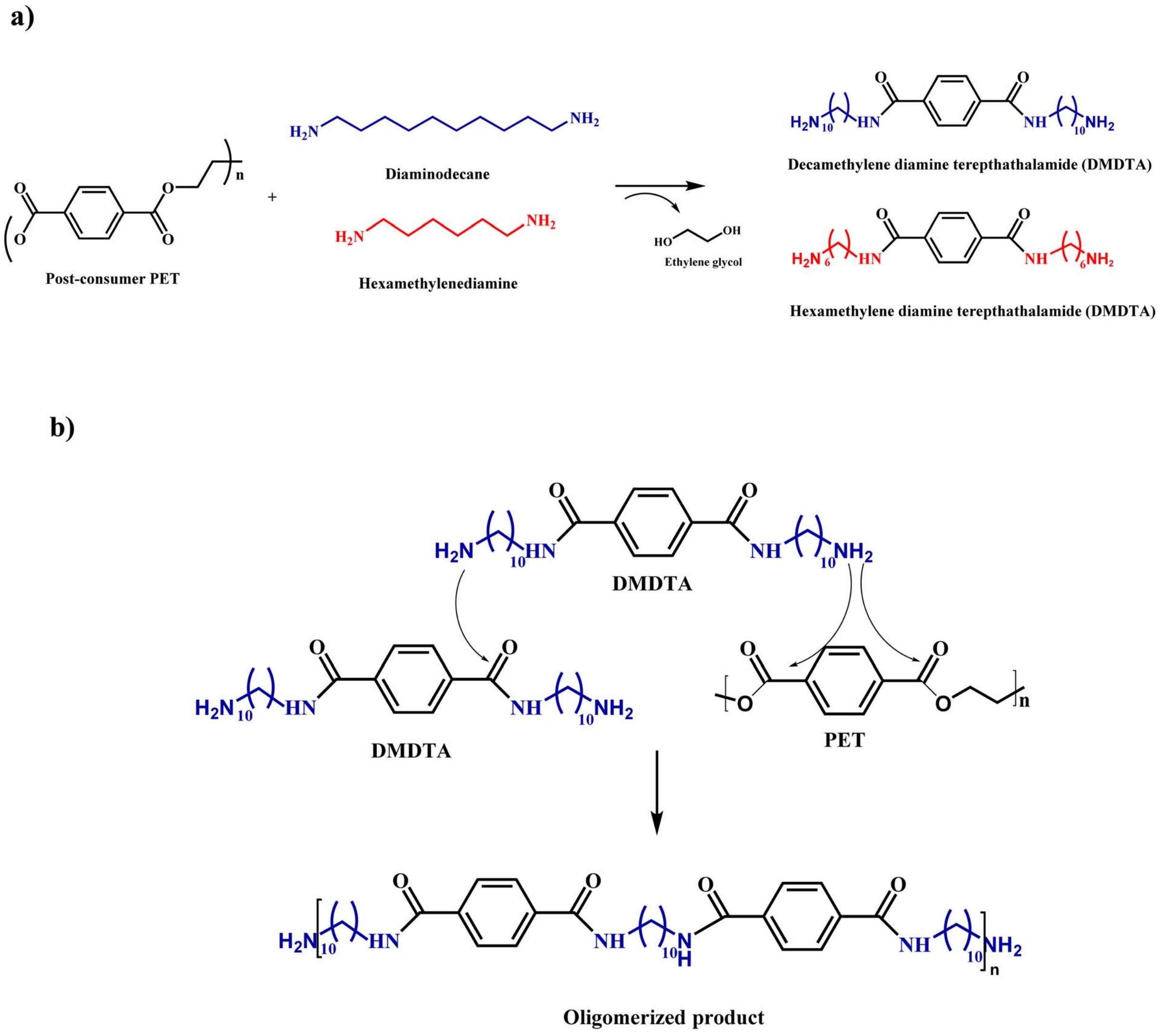

Fig. 1 (a) Aminolysis reaction scheme of PET into terephthalamides, (b) side reactions associated with oligomerization during aminolysis.

Table 1 Reaction data and properties of terephthalamide precursors

Terephthalamide precursor	Yield (%)	T_m (°C)	Amine value (theoretical) (mmol g^{-1})	Amine value (measured) (mmol g^{-1})	MW (theoretical) (Da)	MW (GPC) (Da)
DMDTA	72 ± 0.20	177	4.2	4.05 ± 0.22	474	465
HMDTA	75 ± 3.82	178	5.5	5.33 ± 0.02	362	306

high degrees of polymerization. Amine groups from previously depolymerized DMDTA could react with other DMDTA molecules or again with PET to produced oligomerized products (Fig. 1). The excess diamine reagents used in aminolysis reactions was aimed at minimizing these pathways, and several analytical techniques were used to assess the purity of the recycled product.

First, an amine titration was used to compare the measured and theoretical amine value for each recycled product. The amine value of both DMDTA and HMDTA compared well to the theoretical value, varying by an average of about 3% in both cases (Table 1). Significant oligomerization would decrease this value by decreasing the concentration of amine end groups on the recycled product. Although the molecular weight of the recycled precursors was at the limit of the calibration curve for GPC, the spectrum (Fig. S2) for DMDTA showed no peaks associated with higher molecular weight products while the spectrum for HMDTA did show a small signal at longer retention times. The contribution of this higher molecular weight signal with HMDTA was not significant enough to alter the average molecular weight (M_w), reflecting its small concentration in the recycled product (Table 1).

To confirm the conversion of PET into terephthalamide precursors ^{13}C NMR spectroscopy was completed. Fig. 2 verified the anticipated chemical structure of DMDTA by displaying the expected shift of methylene peaks in the aliphatic backbone of the diamine portion as well as the aromatic and carbonyl signals stemming from incorporation of terephthalic acid from PET. The structure of HMDTA (Fig. S1) was confirmed by referring to previous reports.[18] The spectra of both HMDTA and DMDTA did not show any occurrence of side reactions during the aminolysis reaction such as *N*-methylation and decarboxylation which would appear at 37.88–46.66 ppm and 110–150 ppm, respectively.[29,30] In addition, the presence of one carbonyl peak at 166 ppm excludes the possibility of insufficiently depolymerized PET incorporated into the recycled precursor's structure.

FTIR data shown in Fig. 3 was used for further verification of the structures of precursors. The conversion of the ester group in PET to the amide group of terephthalamide can be observed in the shift of carbonyl stretching bands (C═O) from ~1720 cm^{-1} (ester) to ~1620 cm^{-1} (amide). The band attributed to –NH$_2$ of the primary amine group was observed between 3312–3319 cm^{-1} along with a sharp peak at around 1539 cm^{-1} representing the C–N stretch of the amide bond. Methylene signals of the precursors were denoted by two peaks displayed between 2848–2921 cm^{-1} and aromatic groups were exhibited by two peaks between 1472–1497 cm^{-1} representing the carbon backbone of the precursors. The OH stretching and C–O signals corresponded to PET chemical structure detected at

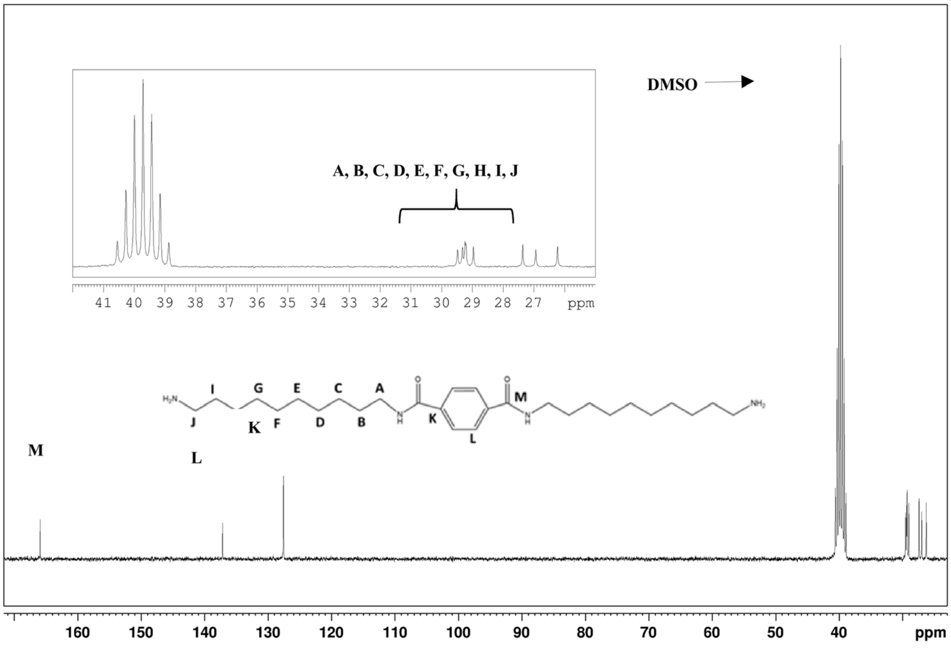

Fig. 2 ^{13}C NMR spectra of DMDTA.

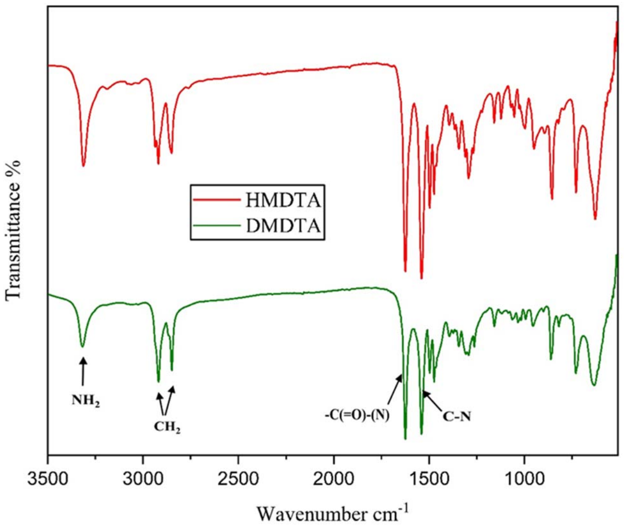

Fig. 3 FTIR spectrum of recovered terephthalamides.

~3500 cm^{-1}, and ~1100 cm^{-1} were not observed, suggesting full conversion of the PET into terephthalamide precursors.

DSC traces (Fig. 4A and B) of DMDTA and HMDTA demonstrate the depolymerization of PET through the shift in melting endotherm typically observed between 225–240 °C for PET to terephthalamide precursors with melting points between 177–178 °C. Another high temperature endotherm is observed in both spectra above 200 °C possibly due to oligomerization. It is likely that the oligomerized material is the result of polycondensation of the aminolysis reaction rather than unreacted PET. The small endotherms present between 70–100 °C of both precursors (Fig. 4A and B) is elucidated by TGA results (Fig. 4C) where a small weight loss is observed in this region, referring to water or CO_2 molecules bound to the amine-terminated compounds. TGA curves of both monomers followed a typical two-step degradation mechanism referring to the dissociation of amide bonds and volatilization of aliphatic components, then the breakdown of more thermally stable aromatic groups

Analysis of the recycled precursors showed an efficient reaction of about 70–80% yield with minimal side products. Due to the absence of foreign species in ^{13}C-NMR, we can conclude that the small difference between theoretical and actual amine values most likely derives from small fractions of oligomerized products produced through transamidation reactions during aminolysis. The recovered precursors were then subjected to solution polymerization to develop four analogs of SAPs (Fig. 5).

3.2 Synthesis and structural characterization of semi-aromatic polyamides

The synthesis of four novel SAPs, described in Table 2, was performed using solution polycondensation. The main idea behind using different diamines and carboxylic acids in the synthetic sequence was to create polymers with varying recycled, and biobased carbon contents, while probing the structure–property relationships of varying aliphatic chain length.

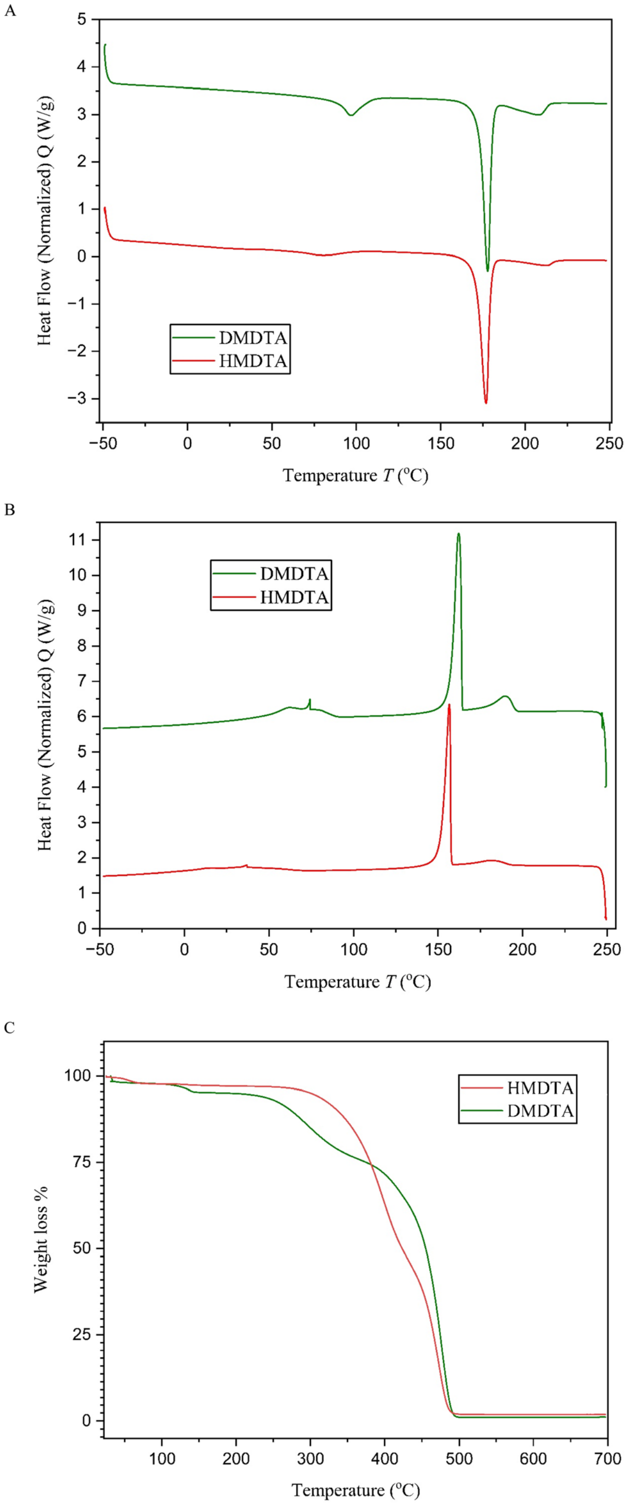

Fig. 4 Thermal analysis of HMDTA and DMDTA. (A) First heating cycle of DSC (B) First cooling cycle of DSC, (C) TGA.

The recycled carbon content in these four polymers varied between 21.1–30.8%, referring to the aromatic carbons of TPA recovered from PET (Table 2). The biobased content varied between 0–78.9%, referring to the use of DMD and sebacic acid, manufactured from castor oil. PA 10.10.T contained the highest

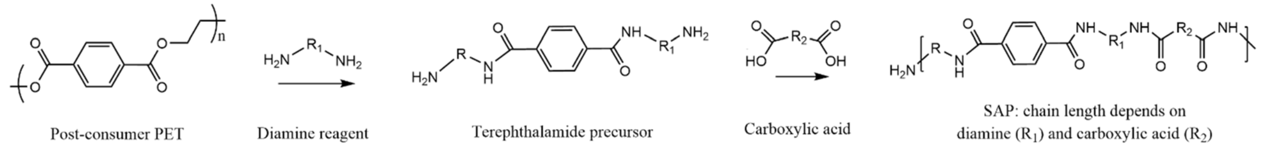

Fig. 5 General reaction scheme for polymerization of recycled terephthalamides and dicarboxylic acids to SAPs.

Table 2 Chemical makeup, aliphatic carbon chain length and recycled carbon content of synthesized SAPs

HMDTA (R_1 = C6)	Adipic acid (R_2 = C6)	Sebacic acid (R_2 = C10)
Polymer name	PA 6.6.T	PA 6.10.T
Aliphatic carbon chain length	18	22
Recycled carbon	30.8%	26.7%
Bio based carbon	0%	33.3%
DMDTA (R_1= C10)		
Polymer name	PA 10.6.T	PA 10.10.T
Aliphatic carbon chain length	26	30
Recycled carbon	23.5%	21.1%
Bio based carbon	58.8%	78.9%

biobased carbon content as it was synthesized from both DMD and sebacic acid. Radiocarbon analysis of PA 10.10.T (ASTM D6866) reported a value of 81% modern carbon, close to the theoretical amount of 78.9%. While there are biobased routes to produce HMD and adipic acid from sugars and lignocellulose-based feedstocks, we placed them outside the biobased reagent category as they are not commercially produced using those methods.

The successful synthesis of the four polymers was confirmed by FTIR spectroscopy (Fig. 6). The amide groups at ~1620 cm^{-1} are complimented by the primary amine groups at 3299–3307 cm^{-1}. The sharp peek observed at ~1539 cm^{-1} represented the C–N stretch of the amide bonds. Aromatic groups were observed between 1465–1470 cm^{-1}. Methylene signals coming from both diacids, and diamines were denoted by two peaks at ~2854 and 2934 cm^{-1}. The absence of a dominant stretching of carboxylic carbonyl groups at 1715 cm^{-1} or OH stretching at ~3500 cm^{-1} suggested the complete polymerization of terephthalamide precursors with carboxylic acids.

Solid state ^{13}C NMR spectroscopy was completed for further verification of the structures of SAPs (Fig. 7). The recorded spectrum confirmed the successful polymerization of SAPs with the appearance of peaks at 174 and 168 ppm for the two types of amide bonds present in the polymer structure (Fig. 7, "N" and "O"). Aromatic carbons were observed between 130–137 ppm. The methylene carbons of both diamine and diacids chains were assigned between 14 to 53 ppm. None of the spectra of SAPs exhibited occurrence of side reactions during polymerization such as *N*-methylation or decarboxylation. Peaks observed at around 60, 110 and beyond 190 ppm correspond to spinning side bands. Spinning side bands are duplicate peaks that result from modulation of magnetic field at the spinning frequency.[31] The intensity of the spinning side band is proportional to the intensity of main band. Overall, the NMR spectra of all four SAPs were very similar to each other, shown in Fig. S2.

Thermal properties of the four SAPs were investigated using DSC depicted in Fig. 8 and organized in Table 3. All four polymers exhibited relatively high T_m ranged between 218–281 °C. A general trend was observed where SAPs synthesized using

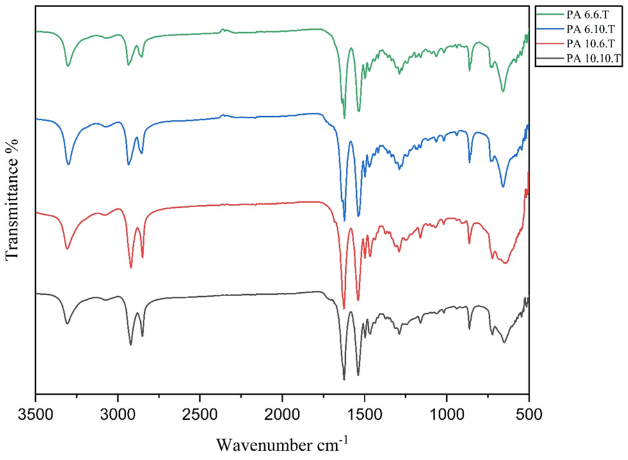

Fig. 6 FTIR spectrum of SAPs.

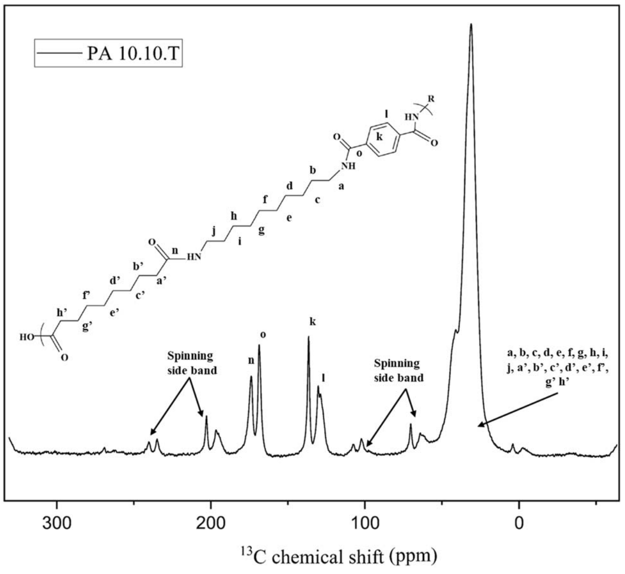

Fig. 7 ^{13}C soild state NMR spectrum of PA 10.10.T.

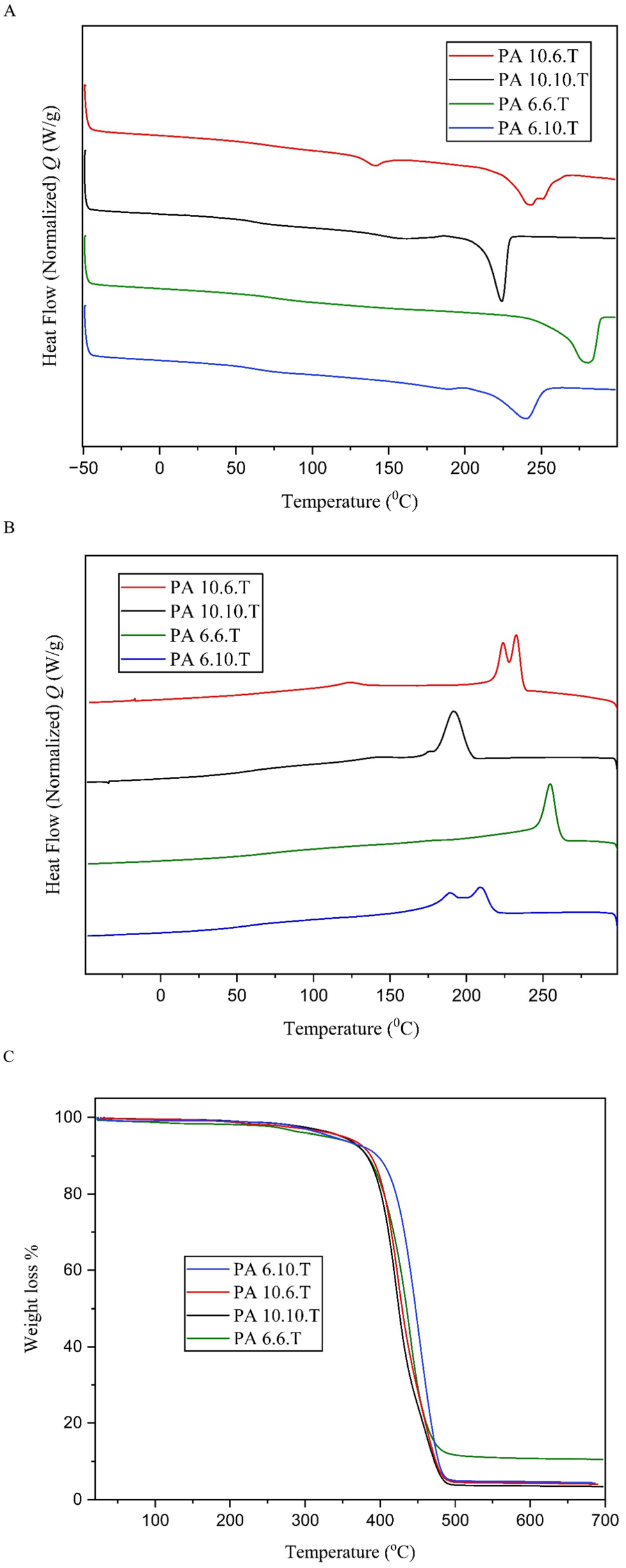

Fig. 8 Thermal analysis of SAPs, (A) DSC first heating cycle, (B) DSC first cooling cycle, (C) TGA.

shorter aliphatic chain monomers such as HMDTA and adipic acid resulted in higher T_m values compared to the ones with longer aliphatic chain monomers; DMDTA and sebacic acid.

Table 3 Thermal properties of synthesized SAPs

Polyamide	T_m (°C)	T_g (°C)	$T_{d5\%}$ (°C)	E' (MPa) at 25 °C
10.10.T	218	60	349	2466
10.6.T	242	81	352	1490
6.10.T	241	80	337	2644
6.6.T	281	109	329	3508

Higher concentrations of methylene groups on the polymer chains increase the distance between amide groups where stronger hydrogen bonding and dipole–dipole interactions can occur.[32] Longer aliphatic chains would also decrease the frequency of π–π interactions resulting from the aromatic portion of the polymer, further increasing the flexibility and molecular movement of polymer chains.[33] An increase in length of aliphatic chains from 18 to 30 methylene units gradually decrease the T_m of SAPs from 281 to 218 °C. The T_g values were obtained using the peak of the Tan Delta curve from DMA. T_g values also followed the same trend observed for melting point where shorter aliphatic chain lengths resulted in higher T_g (*i.e.* PA 6.6.T at 109 °C) and longer aliphatic chain lengths in the polymer resulted in lower T_g (*i.e.* PA 10.10.T at 60 °C). A remarkable similarity in T_g was observed in the SAPs with similar aliphatic chain length, PA 6.10.T (22 aliphatic carbon length) and PA 10.6.T (26 aliphatic carbon length). These two polymers observed a T_g between 80–81 °C demonstrating the correlation between aliphatic content and thermal properties.

TGA thermograms (Fig. 4) followed the typical two-step mechanism of degradation referring to the dissociation of amide bonds and volatilization of aliphatic components, then the breakdown of aromatic groups as anticipated by the chemical structures. Each polymer exhibited excellent thermal stability with $T_{d5\%}$ ranging from 329 to 352 °C (Table 3).

The polymers synthesized here show similar characteristics to other SAP reported in the literature, showing some improvements in different areas. A study[34] found that polymers composed of aliphatic chain lengths of 10 (also from diaminodecane) and higher aromatic carbon contents of 8, 12, 14 (from terephthalic acid, 4,4′-dicarboxydiphenyl ether, 4,4′-biphenyldicarboxylic acid and 4,4′-dicarboxydiphenyl sulphone) had $T_{5\%}$ of 445 °C and melting points between 305-343 °C. Other reports[21] (Table S3) show lower T_g, melting points, and $T_{5\%}$, often when the precursors were composed of aromatic diamines such as 4,4′-oxydianiline and 4,4′-diaminodiphenylmethane. Commercial examples of SAPs have very similar thermal properties to the polymers synthesized here. Table S4 displays SAPs of varying aliphatic chain lengths with T_g from 90–125 °C and T_m from 226–325 °C. Shorter aliphatic chain lengths, as observed in PA 4T[28] (Table S4), have higher T_g and T_m (160 and 345 °C respectively) as would be expected by the higher aromatic content of the polymers.

Gel permeation chromatography was used to estimate the molecular weight of the polymers (Table 4). Solution polymerization resulted in polymers with weight average molecular weight (Mw) between 4350–34 600 Da and number average

Table 4 Molecular weight data of synthesized SAPs

	Solution polymerization				Post polymerization		
Polyamide	Mw (Da)	Mn (Da)	PDI	Intrinsic viscosity (dL g^{-1})	Mw (Da)	Mn (Da)	PDI
10.10.T	9800	3500	2.8	0.20	19 800	2500	7.8
10.6.T	34 600	15 000	2.3	0.29	62 000	4700	13.1
6.10.T	4400	2200	2.0	0.13	15 400	3100	5.0
6.6.T	25 600	7444	3.4	0.26	48 600	3500	14.0

molecular weight between 2200–15 000 Da. The shape of the GPC traces (Fig. S3) demonstrated a long tail at short residence times, indicating the possibility of agglomeration or cross-linking of polymer structures. The molecular weight was calculated without this tail, by cutting off the integral of the peak at the inflection point of the trailing line to avoid excessive inflation of Mw. The highest Mw and Mn values were demonstrated by PA 10.6.T and PA 6.6.T where adipic acid was used for polymerization. The disparity between adipic and sebacic acid may refer to the higher reactivity of adipic acid during polymerization. However, the biobased terephthalamide precursor, DMDTA, produced higher molecular weight polymers than the shorter chained HMDTA. Polydispersity index of SAPs from solution polymerization ranged from 2.0 to 3.4, typical for similar studies (Fig. S3). The Mw was able to increase through post polymerization carried out at 200 °C for 4 hours under vacuum. However, the PDI of polymers following by post polymerization drastically increased (4.98–13.98) demonstrating boarder molecular weight distribution due to chain scission. The higher Mw values after post polymerization reflect some combination reactions to higher molecular weight species, despite the decrease in Mn. Synthesis using sebacoyl chloride, as substitute for sebacic acid, was also completed in an attempt to increase molecular weight. However, rather similar results were obtained with Mw values ranging between 13 000–18 000 Da (Table S2). Molecular weight results obtained through GPC were compared to intrinsic viscosity measured by solution viscometry shown in Table 4. Intrinsic viscosity values of SAPs range between 0.13 and 0.29 dL g^{-1} and corresponded directly, in terms of lowest to highest intrinsic viscosity, to molecular weight from GPC. While the molecular weights of the synthesized polymers here are quite modest, several studies record similar ranges of molecular weights for novel SAPs.[35–37] Future work will be completed to understand how to increase the molecular weight of polymer using alternate synthetic methods.

Thermomechanical analysis of SAPs was carried out using DMA to measure the viscoelastic properties of the novel polymers. DMA traces illustrated in Fig. 9 exhibited anticipated plateaus for storage modulus (E') and tan delta (E''/E') below T_g and rapid decrease of E' above T_g. T_g was determined at the maximum of tan delta and ranged between 59–109 °C. The storage modulus at 25 °C, representing ambient conditions, varied between 1489 and 3508 MPa and generally followed a decreasing trend based on aliphatic chain length, however some anomalies were observed. While PA 6.6.T demonstrated the highest modulus at ambient temperature typical of shorter aliphatic chain lengths, PA 10.10.T with the highest aliphatic content demonstrated a modulus similar to PA 6.10.T. The symmetrical structural associated with alternating aliphatic and aromatic segments of PA 10.10.T (*versus* the mismatched aliphatic chain lengths of PA 6.10.T) could allow for better hydrogen bonding and π–π interactions of the amide groups

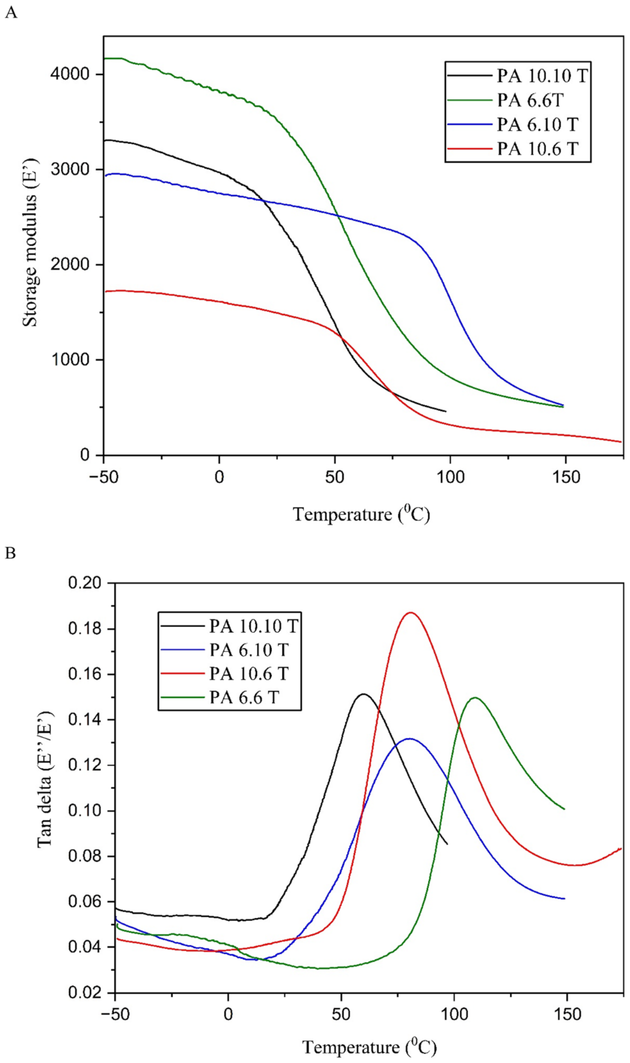

Fig. 9 DMA analysis of SAPs, (A) storage modulus (E'), (B) tan delta (E''/E') as function of temperature.

Table 5 Mechanical properties of compression molded SAP bars

SAP	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
PA 10.10.T	26.75 ± 3.0	5.3 ± 2.6	912.2 ± 277.5
PA 10.6.T	6.5 ± 3.0	3.9 ± 1.4	261.9 ± 196.9
PA 6.10.T	20.84 ± 8.6	5.8 ± 2.5	482.3 ± 203.5
PA 6.6.T	19.6 ± 13.1	10.1 ± 6.3	1086.9 ± 753.5

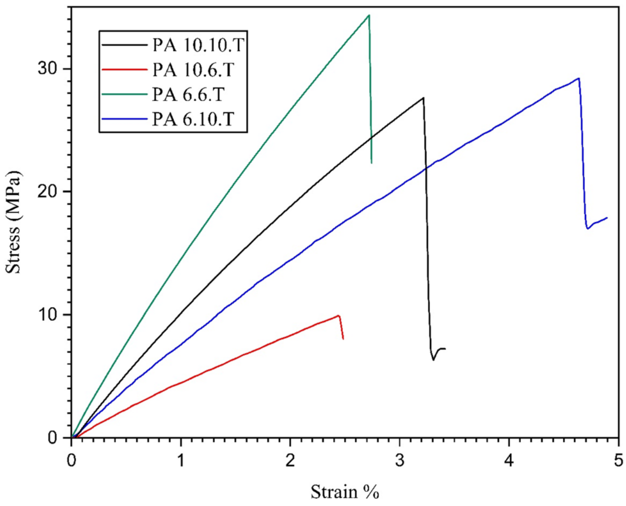

Fig. 10 Stress–strain curve of synthesized SAPs.

and aromatic components, respectively. This hypothesis is supported by the tensile testing results (below, Table 5) where PA 10.10.T observed a higher Young's modulus than PA 6.10.T. In fact, the Young's modulus of polymers with matching alternating aliphatic segments (PA 6.6.T and PA 10.10.T) were about twice that of PA 6.10.T and PA 10.6.T where alternating aliphatic segments were not matched in chain length. Another potential anomaly can be seen in DMA when comparing the storage modulus of PA 6.10.T and PA 10.6.T at 25 °C. Whereas the melting point and T_g of both polymers are very consistent, PA 10.6.T shows a much lower E' (Table 3). This could be explained by the longer aliphatic chain length of PA 10.6.T (Table 2). Although difficult to understand simply from the naming convention, PA 10.6.T is composed of 26 aliphatic carbon atoms between aromatic units compared to PA 6.10.T at 22 aliphatic carbon atoms between aromatic units (*c.f.* Fig. 1 and 6). An explanation based on molecular structure seems to hold its ground given that the molecular weight of PA 10.6.T is the highest of all polymers (Table 4), despite its low modulus value. Overall, the storage modulus of polymers, as well as the Young's modulus during mechanical testing, follow a ranking based on aliphatic chain length with the exception of PA 10.10T described above.

Generally, semi aromatic polyamides exhibit considerably high mechanical performance such as tensile strength values above 75 MPa as shown in available literature (Table S3). The maximum tensile strength of the SAPs created in this study only reached 26.75 MPa (Table 5). The low values for elongation at break could contribute to premature breakage of the polymer samples due to their brittleness (Fig. 10). The brittle nature of the SAPs during mechanical testing could result from testing the polymers below their brittle to ductile transition temperature.[37] Although the crystallinity was not measured directly, DSC traces demonstrate well defined melting and crystallization phase transitions. The highly crystalline nature of the polymers could also contribute to low elongation values. Similar SAPs have also demonstrated brittle behavior, for example, PA 10T was reported to have an elongation at break of 4.9% by Xia *et al.*[38] and a similar brittleness was observed by Djukic *et al.*[39] in PA 6I/6T (I = isophthalic acid) when the terephthalic acid-based copolymer ratio was increased. Increasing terephthalic acid increases the crystallinity of the polymer due to its symmetrical nature allowing better crystal packing.

The long tail in the GPC spectrums (Fig. S4 a–d) mentioned above, could also reflect the presence of crosslinking in the polymer matrices, decreasing the flexibility and elongation at break during mechanical testing. No clear trend exists for mechanical properties and molecular weight results: the highest molecular weight sample (PA 10.6.T) recorded the lowest tensile strength while similar values were found between other polymers. Polymers with uneven number of carbon chains (PA 10.6.T and PA 6.10.T) required the addition of a filler (hydrotalcite) to create uniform samples for tensile testing, due to their low melt viscosity. However, as discussed above, the modulus calculated from mechanical testing does follow a predictable trend based on aliphatic chain length. The tensile properties displayed here must be taken as a preliminary assessment, where future work will aim to create SAPs with similar properties to commercial materials and address the brittle nature of polymers.

Table 6 Properties of copolyamide synthesized with dimer diamine, adipic acid, and HMDTA

SAP	Mw (Da)	Mn (Da)	PDI	T_m (°C)	$T_{5\%}$ (°C)	Tensile strength (MPa)	Strain at break (%)
PA 6.6DD	14 100	6000	2.3	264	388	16.9 ± 2.4	16.9 ± 1.3

As an attempt to further modify the SAPs, we synthesized a copolyamide incorporating a biobased dimer diamine with HMDTA monomer and adipic acid (PA 6.6DD) to decrease the crystallinity and add flexible, aliphatic components to the chemical structure of the polymer. The biobased diamine is a commercially produced cycloaliphatic diamine containing linear aliphatic chains with polyethylene-like side segments. This monomer is generally used in polyurea, epoxy foams, and polyurethane foams to promote flexibility and reduce the density of materials.[40] The synthetic procedure included synthesizing a prepolymer composed of the dimer diamine and adipic acid, then adding HMDTA from recycled PET to complete polymerization. Results from these synthetic attempts, Table 6, demonstrate similar molecular weight, melting point, and degradation ($T_{5\%}$) temperature to the previously discussed SAPs. However, a significant increase in elongation at break was observed in the fatty acid-based SAPs reflecting the successful incorporation of flexible aliphatic chains. While the flexibility was increased in this sample, its value (16.9%) is still rather low compared to other SAPs (Table S4), requiring further modification to compete with commercial materials. Future work will continue to explore ways to improve the mechanical properties of the biobased and chemically recycled SAPs to demonstrate a commensurate material with typical commercial resins.

3.3 Sustainability of SAPs

The chemical recycling and synthesis of SAP's utilized industrially available diamines and dicarboxylic acids to demonstrate a feasible process for transforming waste-PET into a valuable material. Adipic acid and hexamethylene diamine have long been used for the synthesis of commercial polyamides such as PA 6,6; sebacic acid and diaminodecane from castor oil now have commercial applications in biobased polyamides such as PA 11, PA 6,10, and PA 10,10. The technique of aminolysis also has the advantages of using ambient pressures and moderate temperatures, often reporting lowering environmental impacts than other chemical recycling techniques such as hydrolysis or glycolysis.[41] Even so, because the production of diamines is often more energy intensive than other precursors, polyamides (and even biobased polyamides) often have higher environmental impacts than other commodity polymers. For example, one company has estimated the primary energy demand of their PA 10,10 product as 239 MJ,[42] about twice that of PET[43] and about 3-times that of HDPE.[43] While this comparison is not quite fair given that PET and HDPE are lower performing resins typically used in shorter lifespan products, the need to reduce the impacts of polyamide production can be seen. While a full lifecycle analysis is needed for the materials displayed in this report, the motivation for using the lower energy technique of aminolysis stems from the desire to lower the environmental impact of producing a high-performance polymer such as a SAP. The high T_g and degradation temperatures of these materials make them suitable for durable applications, transforming one-time-use waste into materials that could potentially be used for decades. This scenario minimizes the accumulation of plastic waste both on the side of one-time-use packaging and in the second-generation material that would be stored in a new product with an extended lifespan.

4 Conclusion

The present work demonstrated a sustainable route to develop novel biobased semi-aromatic polyamides from post-consumer PET, biobased diamines, and diacids. Diaminodecane, a previously unreported biobased diamine for aminolysis, was demonstrated to be an efficient route to chemical recycling enabling the synthesis of new SAPs with entirely circular content: either biobased or recycled. Overall, the SAPs exhibited high T_g, and T_m values while preserving excellent thermal stability, similar to other SAPs available commercially and in the literature. The limited molecular weight and possible crosslinking of the SAPs were identified as the most probable cause of inferior mechanical properties compared to incumbent materials. One attempt to modify the brittleness of the structures was completed using a dimer diamine. The modified structure exhibited improvement in elongation at break, but still demonstrated lower values expected for SAPs. Future work will include alternate synthetic techniques to increase molecular weight as well as a lifecycle analysis to determine the environmental performance of the SAPs demonstrated in this report.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this study will be made available upon request. Supplementary information: additional characterization and comparison to other polymers in the literature. See DOI: **https://doi.org/10.1039/d5su00547g**.

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