

A novel high-performance biobased polyamide

Fredrick Nzioka Mutua, Tingting Yang, Yuanbo Gao, and Yong He

Poly(pentamethylene oxamide) exhibits excellent mechanical, thermal, and water absorption properties, and is suitable for the fabrication of plastics, as well as parts in the automobile and electronics industries.

Recently, the demand for natural products to address environmental problems and the depletion of non-renewable resources has increased greatly. As part of this trend, it is thought that sustainable biobased polymers can be produced to compete, or surpass, the use of existing petroleum-based polymers.¹ For instance, 1,5-pentanediamine (also known as cadaverine) is a potential renewable candidate to replace hexamethylenediamine in the production of polyamide (an important polymer in the plastic and textile industries). To date, however, yields of 1,5-pentanediamine have been too low for commercialization,^{2,3} and only recently has industrial-based research produced cadaverine on a mass scale.⁴

Cadaverine can be used to produce a variety of polyoxamides—a class of polyamides that include the shortest possible diacid link (an oxalyl unit) in their parent chain—that have recently gained a substantial amount of attention. These materials are characterized by their high chemical resistance, melting temperature, modulus, and UV light stability, as well as their low water absorption and solubility properties.^{5–7} They include poly(pentamethylene succinamide),³ poly(pentamethylene hexanediamide),^{8,9} poly(pentamethylene decanediamide),^{2,10} and poly(pentamethylene eicosanediamide),¹¹ which are also known as PA54, PA56, PA510, and PA520, respectively. In particular, it has been shown that PA510 has a low water uptake compared with poly(ϵ -caprolactam) and poly(hexamethylene adipamide)² (known as PA6 and PA66, respectively). This means that PA510 has good dimensional stability and mechanical properties, and that it is well-suited for energy-friendly transportation (because of its low density). It has also been demonstrated that PA56 exhibits good thermal properties and a special crystallization behavior.⁹ Despite these attractive engineering properties, polyoxamides have not yet been widely commercialized. Ube Industries Ltd (Japan), however, have recently initiated pilot commercial runs for poly(nonamethylene oxamide)—PA92—which has been intensely studied for many years and has been shown to have good properties.^{6,12}

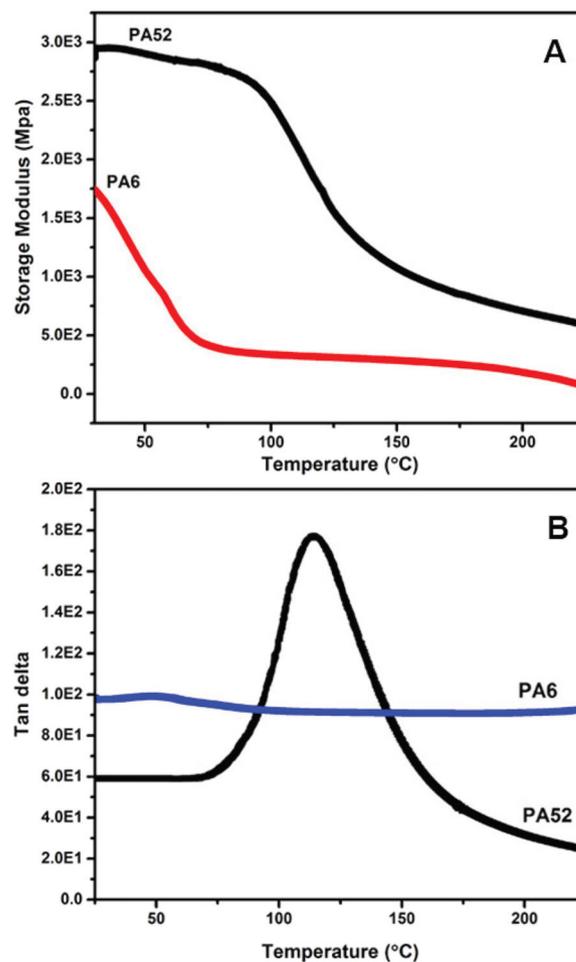


Figure 1. Measured (A) storage modulus and (B) tan delta for the novel biobased polyoxamide poly(pentamethylene oxamide)—PA52—and a commercially available polyamide—poly(ϵ -caprolactam), or PA6—as a function of temperature.

In this work,⁴ we report the preparation of a novel biobased polyoxamide: poly(pentamethylene oxamide) or PA52. We initially synthesized the PA52 from dibutyl oxalate and 1,5-pentanediamine with the use of a conventional two-step solution (i.e., pre-condensation in

Continued on next page

Table 1. Summary of the properties of PA52, compared with those of three commercially available polyamides, i.e., PA46,^{14,15} PA6, and PA66¹⁴).⁴ PA46: Poly(tetramethylene adipamide). PA66: Poly(hexamethylene adipamide).

Property	Polyamides			
	PA52	PA46	PA6	PA66
Melting temperature (°)	302	295	220	258
Heat of fusion (Jg ⁻¹)	90.7	91.0	57.0	50.0
Crystallization enthalpy (Jg ⁻¹)	85.6	–	40.0	49.0
Glass transition temperature (°)	125	80	54	60
Decomposition temperature (°)	449	350	448	458
Water absorption (wt%)	3.2	12.4	10.0	9.0

solution and post-condensation in the solid state) polymerization technique. In addition, we performed several measurements to characterize PA52. Compared with commercially available polyamides—PA6, PA66, and PA46, poly(tetramethylene adipamide)—we find that PA52 has a high melting temperature, low water absorption, and excellent crystallization characteristics (see Table 1). PA52 is thus well suited for high-temperature applications in the thermoplastic industry.

Our use of solvents in the preparation of PA52, however, can have a negative environmental impact—particularly in industrial situations—and is thus undesirable. To address this challenge, we have therefore also developed a spray polymerization technique¹³ for the rapid synthesis of polyoxamides (e.g., PA52) at room temperature, without the need for solvents and under the atomizing action of nitrogen gas. Although we find that the PA52 synthesized via either of our approaches has very similar properties, the conventional solution polymerization technique provides higher polymer yields than our spray polymerization method. We expect, however, that with scale up, we will be able to produce greater polymer yields with our spray polymerization approach.

To further explore the properties of our polymerized PA52, we performed dynamic mechanical measurements on compression-molded film samples (30 × 10mm in size) of PA52, as well as of commercially available PA6 (for comparison). For these tests we used a Q800 DMA (TA Instruments) in tensile mode and performed the measurements at a frequency of 1Hz and a heating rate of 5°C/min (over a temperature range of 30–250°C and 25–215°C for the PA52 and PA6, respectively).

From the results of these tests (see Figure 1) we find that the storage modulus of PA52 is significantly higher than that of PA6 at temperatures below 130°C. We attribute this to the high density of hydrogen bonds in the biobased polymer (i.e., PA52), which gives rise to a better stability at high temperatures than PA6. In addition, the glass transition temperature we obtain for PA52 (125°C) is about 75°C higher than that of PA6 (about 50°C). These findings confirm the excellent crystallizability and mechanical properties of the copolymer (PA52) at high temperatures compared with those of PA6.

In summary, we have used both a conventional two-step solution polymerization technique and a new spray polymerization method to synthesize a novel biobased polyoxamide, PA52. We find that this material exhibits a high melting temperature, good mechanical properties, low water absorption, and excellent crystallization characteristics. PA52 is thus suitable for the production of high-performance parts in the automobile and electronics industries. We attribute the useful properties to the high density of double hydrogen bonds within the polyoxamide, which provide excellent dimensional stability. As efforts to increase the efficiency of generating 1,5-pentanediamine from renewable resources continue to accelerate, PA52 has great potential to compete with and replace fossil-fuel-based polyamides (e.g., PA6 and PA66) in the near future. We are now continuing our work with further investigations that are focused on the morphology, crystallization behavior, and kinetics of PA52. We are also studying potential applications of the material, e.g., as a resin for fiber-reinforced thermoplastic composites.

This work was supported by the Fundamental Research Fund for the Central Universities (2232015A3-06, 2232015A3-01), the State Key Laboratory for Modification of Chemical Fibers and Polymer Materials at Donghua University, and the Shanghai Natural Science Foundation (15ZR1400100).

Author Information

Fredrick Nzioka Mutua, Tingting Yang, Yuanbo Gao, and Yong He
Donghua University Center for Civil Aviation Composites
and
State Key Laboratory for Modification of Chemical Fibers and Polymer Materials
Donghua University
Shanghai, China

Continued on next page

References

1. G. Lligadas, J. C. Ronda, M. Galià, and V. Cádiz, *Renewable polymeric materials from vegetable oils: a perspective*, **Mater. Today** **16**, pp. 337–343, 2013.
2. S. Kind, S. Neubauer, J. Becker, M. Yamamoto, M. Völkert, G. von Abendroth, O. Zelder, and C. Wittmann, *From zero to hero—production of bio-based nylon from renewable resources using engineered *Corynebacterium glutamicum**, **Metabol. Eng.** **25**, pp. 113–123, 2014.
3. S. Kind and C. Wittmann, *Bio-based production of the platform chemical 1,5-diaminopentane*, **Appl. Microbiol. Biotechnol.** **91**, pp. 1287–1296, 2011.
4. F. N. Mutua, C. Cheng, Y. Dong, C. Zheng, B. Zhu, and Y. He, *Synthesis and properties of bio-based poly(pentamethylene oxamide)*, **Polym. Eng. Sci.**, 2017. doi:10.1002/pen.24596
5. T. Nakagawa, S. Maeda, K. Nozaki, and T. Yamamoto, *Crystal structure of an aliphatic polyoxamide containing methyl side-groups: poly(2-methyl-1,8-octamethyleneoxamide)*, **Polymer** **55**, pp. 2254–2261, 2014.
6. T. Nakagawa, K. Nozaki, S. Maeda, and T. Yamamoto, *Polymorphism of poly(nonamethyleneoxamide) crystal*, **Polymer** **57**, pp. 99–104, 2015.
7. S. W. Shalaby, E. M. Pearce, R. J. Fredericks, and E. A. Turi, *Structure and thermal stability of aliphatic polyoxamides*, **J. Polym. Sci. Part B Polym. Phys.** **11**, pp. 1–14, 1973.
8. J. Puiggali, L. Franco, C. Alemán, and J. A. Subirana, *Crystal structures of nylon 5,6. A model with two hydrogen bond directions for nylons derived from odd diamines*, **Macromolecules** **31**, pp. 8540–8548, 1998.
9. L. Morales-Gómez, D. Soto, L. Franco, and J. Puiggali, *Brill transition and melt crystallization of nylon 56: an odd–even polyamide with two hydrogen-bonding directions*, **Polymer** **51**, pp. 5788–5798, 2010.
10. P. Villaseñor, L. Franco, J. Subirana, and J. Puiggali, *On the crystal structure of odd–even nylons: polymorphism of nylon 5, 10*, **J. Polym. Sci. Part B Polym. Phys.** **37**, pp. 2383–2395, 1999.
11. X. Cui and D. Yan, *Synthesis and characterization of novel odd–even nylons based on eicosanedioic acid*, **J. Appl. Polym. Sci.** **93**, pp. 2066–2071, 2004.
12. L. Franco, J. A. Subirana, and J. Puiggali, *Structure and morphology of odd polyoxamides [nylon 9, 2]. A new example of hydrogen-bonding interactions in two different directions*, **Macromolecules** **31**, pp. 3912–3924, 1998.
13. C. Cheng, F. N. Mutua, Y. Dong, B. Zhu, and Y. He, *Bio-based poly(pentamethylene oxamide) synthesized by spray/solid-state polycondensation*, **Polym. Bull.**, 2017. doi:10.1007/s00289-017-2023-1
14. G. Wypych, **Handbook of Polymers**, Elsevier, 2016.
15. D. Glasscock, W. Atolino, G. Kozielski, and M. Martens, *High performance polyamides fulfill demanding requirements for automotive thermal management components*, **DuPont Eng. Polym.**, 2008.