Preparation and Properties of Polyether Aliphatic Polymerized Amide as a Vegetable Oil-Based Epoxy Curing Agent

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ABSTRACT: An epoxy curing agent polyether aliphatic polymerized amide (PEAPA) was synthesized using epoxy fatty acid methyl ester and diethylenetriamine. The Fourier transform infrared spectra and 1H NMR analysis indicated successful synthesis of PEAPA. Gel permeation chromatography showed a high degree of polymerization. The obtained PEAPA was used to cure E51 epoxy resin and partially replace rigid 1,3-cyclohexanediamine curing agent. A series of epoxy resins with varying rigidities were prepared. The mechanical and thermal properties of the materials were analyzed. Mechanical property tests showed that the tensile strength and hardness of the materials decreased gradually with increased PEAPA content. However, elongation at breaks of the prepared materials increased with increased PEAPA content. Micromorphological investigation indicated excellent compatibility between PEAPA and the curing system. Furthermore, a dynamic mechanical thermal analysis demonstrated that the glass transition temperature of the epoxy resin decreased with increased PEAPA content. Thermal stability, while still excellent, decreased slightly with the addition of PEAPA. At the primary weight loss stage, initial decomposition temperatures for all resins were above 330 °C.

1. INTRODUCTION

As traditional thermosetting polymers, epoxy resins have many uses, including as adhesives, semiconductor laminates, and insulators for electric devices. The resins have excellent adhesive, mechanical, and electrical properties. In addition, they offer low-cure shrinkage and excellent moisture and chemical resistance.1−3 However, the application of epoxy-cured materials is limited in that they crack easily, are inherently brittle, and exhibit poor elongation upon curing. Therefore, great effort has been made to toughen these materials.4,5

Several chemical or physical means of modification have been advanced to toughen epoxy resins, including particulate, elastomer, and thermoplastic modifications.6,7 Toughening by chemical means could improve the mechanical and thermal properties through the formation of strong covalent bonds, but physical blending depends only on the marginal toughening effect. Thus, many attempts have been made to design epoxies with suitable molecular structures and to synthesize flexible curing agents to toughen epoxy resins.8 For example, a novel aromatic amine bis(4-nonyl-2,5-diamine-penoxyl)alkylate (RAn) was prepared as a curing agent for epoxy resins by a three-step process using nonyl-phenol and dibromoalkylate.9 A novel amine with a flexible polyoxypropylene chain was synthesized with various molecular weights and used to cure the diglycidyl ether of bisphenol A.10 A polyurethane (PU) prepolymer, based on hydroxyl-terminated polyester resin, was synthesized and used to modify epoxy resins of various concentrations.11 Polyesters prepared by direct polycondensation from bisphenol A and aliphatic dicarboxylic acids (adipic, sebacic, and dodecanoic acids) have been used to improve the toughness of the diglycidyl ether of bisphenol A.12 In addition, three types of polyurethane (i.e., polycarbonate-type PU, polyster-type PU, and polycarbonate−polyster-type PU) prepolymers were used to modify epoxy resin.13 Lou synthesized a series of imidazole (MI)-blocked 2,4-toluene
diisocyanate (TDI) with polyethylene glycol (PEG-400) as the soft segment (PEG-MI-b-TDI) for toughening and curing the bisphenol A type epoxy resin (E-44). The E-44 cured by PEG-MI-b-TDI was toughened without sacrificing the tensile shear strength.14

On the other hand, recently, considerably attention has been paid to prepare novel polymers from renewable resources to replace petroleum-based products in response to fossil fuel depletion and the need for environmental protection.15 Vegetable oils may offer an ideal alternative to chemical feedstocks. For example, a novel vegetable oil-based polyamine was prepared from grape-seed oil using cysteamine chloride by thiol-ene coupling and used as a curing agent for the bio-based epoxy resin.16 Huang synthesized three C21-based reactive polyamides from tung oil, as displayed in Figure 1a, which were then used as curing agents to prepare toughened epoxies. It was found that the cured materials were superior in tensile and flexural strength to those cured by C36-based polyamides. The flexural modulus of the epoxies cured by C21-based polyamides was also superior to those cured by C36-based polyamides.17 Two rosin-based curing agents containing imide groups were synthesized. For comparison, an imide-diacid derived from trimellitic anhydride was also prepared. The glass transition temperatures, as well as the tensile and dynamic mechanical properties, of the cured epoxy resins were significantly improved over the imide-diacid cured epoxy resin.18 A light colored cardanol-based epoxy curing agent was synthesized with markedly improved toughness and shear strength and also displayed in Figure 1b.19 We also used epoxy fatty acid methyl ester (EFAME) to prepare an epoxy curing agent. EFAME contains multiple active epoxy groups and is derived from vegetable oil. EFAME is a renewable plasticizer, compatibilizer, dispersing agent, surfactant, and softener due to its sustainable production and reasonable costs.20,21 In the past decade, the use of EFAME rapidly developed, according to several research groups. The main objective of this work was to prepare a flexible polyether aliphatic polymerized amide (PEAPA) epoxy curing agent using EFAME. We propose an epoxy ring-opening polymerization and amidation method to prepare PEAPA. EFAME is an environment friendly chemical raw material. Because this epoxy curing agent is prepared using vegetable oil, it offers reduction in environmental pollution and fossil fuel dependence.

2. RESULTS AND DISCUSSION

2.1. Gel Permeation Chromatography Analysis. Figure 2 shows the gel permeation chromatography curves of prepared PEAPA with various degrees of polymerization. Gel permeation chromatography analyses showed that each of the target products was highly polymerized. Polymerization of PEAPA increased with the addition of BF₃·OEt₂. When more than 0.50 wt % (0.67, or 1.00 wt %) BF₃·OEt₂ was added, the number-average molecular weight of the copolymerized system reached very high levels (hundreds of thousands) and the viscosities were high, which could limit the preparation and application of PEAPA. With the addition of less than 0.50 wt % (0.33 wt %) BF₃·OEt₂, polymerization was very low, with a number-average molecular weight (Mn) of only 2307. With the addition of 0.50 wt % BF₃·OEt₂, the molecular weight of the three obvious peaks was 700, 1007, and 1450 respectively, corresponding to the theoretical molecular weights of dimer, trimer, and tetramer in PEAPA. For the overall analysis, the Mn of the 0.50 wt % BF₃·OEt₂ polymerized system was 3599, which is very close to the PEAPA of 10 polymers. Thus, we selected the 0.50 wt % copolymerized system for further study.

2.2. Fourier Transform Infrared Spectroscopy Analysis. Figure 3 shows the infrared spectra of EFAME, PFAME, and PEAPA. The EFAME spectrum shows that the antisymmetric stretching vibration of the epoxy group appeared in 1013.9 and 834.6 cm⁻¹. Furthermore, the EFAME spectrum shows peaks at 1195.5 and 1168.6 cm⁻¹ that are behind the...
overlapped stretching vibrations of the C–O of ester and epoxy groups. In PFAME, the peaks at 3501.5 and 1076.8 cm\(^{-1}\) arise from the stretching vibration of hydroxyl and ether bonds, respectively. This indicates ring opening polymerization. Meanwhile, PFAME with a excellent degree of polymerization can be demonstrated by the emergence of a peak at 3531.8 cm\(^{-1}\).

In PEAPA, the peak at 1646.6 cm\(^{-1}\) is attributed to the C–O of the amide groups. The peak at 1739.5 cm\(^{-1}\) corresponding to the C=O of –COOR–, which exists in the infrared spectrum of PFAME, almost disappears. The amidation between PFAME and diethylenetriamine was confirmed in three ways. First, it was confirmed by the appearance of a C=N–H stretching absorption peak at 1646.6 cm\(^{-1}\). The appearance of a strong, broad characteristic absorption peak of the –N–H stretching vibration at 3289.1 cm\(^{-1}\) was the second confirmation. The third confirmation was from an absorption peak of the C=N–H stretching vibration at 1071.9 cm\(^{-1}\). The weak peak at 3071.1 cm\(^{-1}\) is attributed to the stretching vibration of N–H in the associative state of the cis-antarcticcoexistence secondary amide. The peak at 1550.3 cm\(^{-1}\) is attributed to the bending vibration of N–H on the secondary amide. The peaks at 2921.8 and 2851.7 cm\(^{-1}\) are attributed to the C–H stretching vibration absorption of –CH\(_2\) and –CH\(_3\).

2.3. \(^1\)H NMR Analysis. The molecular structures of EFAME, PFAME, and PEAPA were detected with \(^1\)H NMR analysis. Figure 4 shows the \(^1\)H NMR spectra of EFAME, PFAME, and PEAPA.

![Figure 4. \(^1\)H NMR spectra of EFAME, PFAME, and PEAPA.](image)

PFAME, and PEAPA. There are many lapped peaks in the \(^1\)H NMR spectra of EFAME, PFAME, and PEAPA because of the complexity of the raw material and finished product. In the \(^1\)H NMR spectrum of EFAME, the peaks of methine protons on the epoxy groups appear at 3.10–2.90 ppm. The main characteristic peaks at about 1.55 ppm correspond to the methylene protons adjacent to two epoxy groups, whereas the characteristic peaks at about 1.72 ppm are attributed to the methylene protons adjacent to two epoxy groups.

The PFAME spectra show characteristic peaks at 3.68–3.65 ppm corresponding to the methine protons on the generated ether bonds of the –CH–O–CH– group. The complexity of this peak indicates a number of protons adjacent to oxygen atoms. The overlapped peaks at about 1.60 ppm correspond to the methylene protons adjacent to the newly formed ether bonds and the methylene protons adjacent to carbonyl groups in mesoposition. In addition, the peaks of the methylene and methine protons corresponding to the epoxy groups have disappeared, which confirmed the ring-opening polymerization of the epoxy groups.

The PEAPA \(^1\)H NMR curves had characteristic peaks at 2.85–3.15 ppm corresponding to methylene and methine protons adjacent to –NH or –NH\(_2\) groups. The newly formed characteristic peaks at 1.49 ppm are related to the protons on NH and –NH\(_2\) groups, and the intensity of the overlapped peaks at 3.68–3.65 ppm clearly decreased due to the disappearance of –CH\(_3\) groups. The results of \(^1\)H NMR analysis show that PEAPA was synthesized successfully.

2.4. Tensile Properties. Figure 5 shows typical tensile stress–strain curves of the prepared epoxy-cured materials.

![Figure 5. Tensile stress–strain curves of the various epoxy-cured systems.](image)

These stress–strain curves indicate flexible tensile behavior with no yield stress point, indicating that the prepared epoxy materials are all flexible. The tensile strength and hardness of the epoxy materials generally decreased with increased PEAPA. However, the elongation at break increased with increased PEAPA content, indicating that epoxy materials containing PEAPA had good flexibility. The tensile strength and elongation at break of the epoxy materials are determined by the chemical structures and state of cross-linking curing systems, which also change with the amount of curing agent used.\(^{22}\) The PEAPA molecule contains multiple ether bonds and a flexible chain alkyl group, which enables the mixed curing agents to have outstanding curing capabilities and improves the flexibility of the cured system (Table 1).

The tensile tests showed that the mechanical properties are dominated by the polyether chains from PEAPA. More PEAPA in the system means greater flexibility. When the PEAPA curing ability is above 70%, chemical structure is the main factor.

| formula for the mixed curing system | tensile strength (MPa) | elongation at break (%) | hardness (HD) |
|-----------------------------------|------------------------|-------------------------|--------------|
| PEAPA50/CHDA50                    | 51.79                  | 1.58                    | 78           |
| PEAPA70/CHDA30                    | 37.54                  | 5.00                    | 77           |
| PEAPA90/CHDA10                    | 16.59                  | 9.98                    | 76           |
| PEAPA100                          | 15.54                  | 13.20                   | 73           |

Table 1. Tensile Properties and Hardness Data of Various Epoxy-Cured Systems
influencing the materials’ breaking elongation and their tensile strength; therefore, the PEAPA70/CHDA30 cured system had high tensile strength (37.54 MPa) with low elongation at a break of 5.00%. With 100% PEAPA, the elongation at break reached 13.20% but the tensile strength was only 15.54 MPa, likely because the curing and epoxy material system exists in many ether bonds and long aliphatic chains, which endows the materials with very high flexibility.

2.5. Morphological Properties. Figure 6 depicts the scanning electron microscope (SEM) images of the tensile fracture surface of the epoxy materials. The relatively smooth fracture shows that the curing agents formed a perfect cross-linked structure with the E51 epoxy resin after cross-linking polymerization and formed the continuous phase of materials, which indicated the excellent compatibility of the mixed curing systems. There were significant differences in the tensile fracture surfaces of the samples. The fracture surface of the PEAPA50/CHDA50-cured system had irregular broken cracks and abundant scaly fragments. The rough fracture surface might be attributed to more ring structures in the material. Under external force, the stress extended in multiple directions until it broke due to its greater strength and rigidity. As a result, the fracture surface presented an irregular scaly crack and was not in a plane state. With the reduction of the rigid structure in the PEAPA70/CHDA30 cured system, the fracture surface of the material showed a less scaly structure than the PEAPA50/CHDA50-cured system. As shown in Figure 6c, the fracture surface of the PEAPA90/CHDA10 cured system showed a gully state, which is attributed to the flexible fatty chain structure. With the more flexible chain structure, the free motion of the chain segments increased. Under external tension, the free segments were arranged in an orderly way along the direction of tension. When the external tension increased, the material started to break and showed the fracture characteristics of an elastomer. Figure 6d shows an orderly strip structure on the fracture surface. The samples were arranged in a regular manner along the direction of tension at the beginning of the stretching process because of its excellent toughness. Eventually, the sample began to tear in the direction of the stress and attained a relatively regular strip fracture-surface structure.

2.6. Dynamic Mechanical Analysis (DMA). The dynamic mechanical behaviors of the samples were studied. Figure 7, the dynamic mechanical analysis curves, including loss factors (tan δ) and storage modulus (′E), are studied. In our study, the cross-linking density (νe) was determined by DMA analysis with rubber theory as follows:

\[ E' = 3\nu_e RT \]

where \( E' \) is the storage modulus of the rubber state (MPa), \( \nu_e \) is the cross-linking density (mol m\(^{-3}\)), \( R \) is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \( T \) is the temperature in Kelvin (K).

To ensure that each sample is in a rubber state, \( T_g + 30 \) K was removed as the temperature used in the calculation. The cross-linking density of each sample is shown in Table 2.

As shown in Figure 7b, the \( E' \) of the PEAPA50/CHDA50-cured system was much higher than that of other cured systems. This may be because the PEAPA50/CHDA50-cured system possesses a much higher cross-linking degree than that of the other cured systems, which is in accordance with the data of \( \nu_e \) in Table 2. All \( E' \) curves showed the same tendency: \( E' \) decreases sharply in two stages from –45 to 15 °C and from 40 to 60 °C. At low temperature, the materials were in a glassy state, in which case, all of the molecular segmental motions were frozen, and thus \( E' \) remained above 2000 MPa. With increasing temperature, the frozen segmental structure began to relax. All tan δ curves showed a single peak, indicating the excellent compatibility of the mixed curing systems. The
The intensity of the tan $\delta$ peaks increased with the PEAPA content, indicating that more flexible long-chain structures improved the chain-sliding ability of the cured system, and thus the tan $\delta$ curves showed broad peaks. With the increase of the PEAPA content, the energy needed to relax the molecular chains of each cured component was less, resulting in a temperature decline corresponding to the tan $\delta$ peak ($T_g$). Therefore, materials with the highest PEAPA (100% curing ability) content had the lowest $T_g$ ($62.67^\circ C$). In addition, the $T_g$ of the PEAPA50/CHDA50-cured system ($85.16^\circ C$) was much higher than that of the other cured systems. As shown in Table 2, the PEAPA50/CHDA50-cured system possesses much higher $\nu_e$, resulting in a significant improvement of $T_g$.

### 2.7. Thermal Stability Analysis (TGA)

The TGA curves of the cured epoxy materials in nitrogen ($N_2$) are shown in Figure 8. The cured samples had similar thermal TGA curves; all curves displayed one-stage degradation behavior in $N_2$. The obvious weight loss in a range from 330 to 450 $^\circ C$ was attributed to the decomposition of amidogens and carbon–carbon bonds and the decreased cross-linking density of the cured epoxy resin. In addition, as shown in Table 3, the initial decomposition temperature decreased slightly with increased PEAPA. This was attributed to the improved thermal stability resulting from the reduction in the number of ring structures in the system. In general, the char yield of the epoxy-cured materials decreased with increased PEAPA. This was attributed to the increased methyl and methylene in PEAPA and the lower number of ring structures with the reduction of 1,3-cyclohexanediame (CHDA) in the whole system. At the main weight loss stage of heating, initial decomposition temperatures were all above 330 $^\circ C$, indicating that all PEAPA-modified epoxy materials had excellent thermal stability.

### 3. CONCLUSIONS

FTIR and $^1$H NMR analyses demonstrate that a new type of PEAPA epoxy curing agent was synthesized successfully. Gel permeation chromatography (GPC) analysis showed that the target product had a high degree of polymerization. The even dispersion of PEAPA on the tensile fracture surface showed good compatibility between PEAPA and the curing system. The weight ratios of PEAPA in the curing system significantly affected the mechanical properties of the produced epoxy materials. The dynamic mechanical analysis showed a result similar to the micromorphologic investigation, and the changing tendency of $T_g$ shows perfect compatibility of the mixed curing systems. TGA indicated excellent thermal stability in the PEAPA-modified epoxy curing systems. In our study, the prepared PEAPA curing agent contained long flexible chain segments that can be bonded to the dense cross-linking

![Figure 7](image-url) Dynamic mechanical analysis traces of epoxy materials with various curing systems. (a) $E'$ curves of epoxy resins with different curing systems; (b) tan $\delta$ curves of epoxy resins with different curing systems.

![Figure 8](image-url) TGA curves of various weight ratios of PEAPA/CHDA.

**Table 2. $\nu_e$ of the Cured Sample**

| sample                | $T_g + 30$ (K) | $E'$ at $T_g + 30$ (MPa) | $\nu_e$ (mol m$^{-3}$) |
|-----------------------|---------------|--------------------------|------------------------|
| PEAPA50/CHDA50       | 388.31        | 15.30365                 | 1580                   |
| PEAPA70/CHDA30       | 366.70        | 3.03796                  | 332                    |
| PEAPA90/CHDA10       | 366.11        | 5.48874                  | 601                    |
| PEAPA100             | 365.82        | 7.68763                  | 842                    |

**Table 3. TGA Data for the Epoxy Materials in Various Curing Systems**

| sample                | $T_i$ ($^\circ C$) | char yield (%) |
|-----------------------|--------------------|----------------|
| PEAPA50/CHDA50       | 342.5              | 6.12           |
| PEAPA70/CHDA30       | 341.2              | 5.50           |
| PEAPA90/CHDA10       | 339.3              | 6.11           |
| PEAPA100             | 337.3              | 4.93           |
network of the epoxy resin and thus the toughness of the epoxy system was significantly improved.

4. EXPERIMENTAL SECTION

4.1. Materials. EFAME (epoxy value, 0.34, derived from genetically modified soybean oil) was purchased from Taixing Yuanda Chemical Industry Co., Ltd., China and used as received. E51 epoxy resin (epoxy value, 0.51) and 1,3-cyclohexanediamine (CHDA) were purchased from Wuxi resins Co., Ltd., China and used as received. 1,4-Dioxane (stabilized 99.5%), tetrahydrofuran (THF, 99.9%), and BF$_3$·OEt$_2$ (stabilized, 98.0%) were purchased from Shanghai Chemical Reagent Co., Ltd., China and used as received. Diethylenetriamine (stabilized 99.0%) was purchased from Shanghai Saen Chemical Technology Co., Ltd., China and used as received.

4.2. Preparation. 4.2.1. Preparation of Polymerized Fatty Acid Methyl Ester (PFAME). Ring-opening polymerization of EFAME was carried out in a 1 L four-necked round-bottom flask equipped with a mechanical stirrer, a condenser, and a thermometer. First, 150.0 g of EFAME and 225.0 g of 1,4-dioxane were added to the reactor. The mixture was then heated to 45 °C in a water bath. With the temperature controlled at 70−80 °C in the water bath, 0.50, 0.75, 1.00, or 1.50 g of BF$_3$·OEt$_2$, were slowly charged into the mixture. The weight ratios of BF$_3$·OEt$_2$ to EFAME were 0.33, 0.50, 0.67, and 1.00 wt %, respectively. The reacting system was adjusted and controlled at 45 °C. After the reaction of 2 h, 2 mL of ethanol−H$_2$O (1:1) was added to the reaction to deactivate the catalyst. Finally, a highly viscous liquid of PFAME (yield: 97.53%) was obtained by removing the solvent dioxane and the residual H$_2$O with vacuum distillation.

4.2.2. Preparation of Polyether Aliphatic Polymerized Amide (PEAPA). PEAPA was prepared by amidation using the prepared PFAME as raw material. First, 150.0 g of the selected PFAME sample with a suitable degree of polymerization was added to a 500 mL four-necked round-bottom flask equipped with a mechanical stirrer, a condenser, and a thermometer. The mixture was then heated to 45 °C in a water bath. With the temperature controlled at 70−80 °C in the water bath, 0.50, 0.75, 1.00, or 1.50 g of BF$_3$·OEt$_2$, were slowly charged into the mixture. The weight ratios of BF$_3$·OEt$_2$ to PFAME were 0.33, 0.50, 0.67, and 1.00 wt %, respectively. The reacting system was adjusted and controlled at 45 °C. After the reaction of 2 h, 2 mL of ethanol−H$_2$O (1:1) was added to the reaction to deactivate the catalyst. Finally, a highly viscous liquid of PFAME (yield: 97.53%) was obtained by removing the solvent dioxane and the residual H$_2$O with vacuum distillation.

4.2.3. Preparation of Epoxy Materials. A series of epoxy materials were prepared using CHDA and PEAPA as mixed curing agents. First, PEAPA, CHDA, and E51 epoxy resin were mixed evenly in different weight ratios. Next, cured epoxy products were produced by casting the above mixture into a special mold (standard of sample preparation: GB/T 2567-2008, tensile area size of spline: 50 mm × 10 mm × 4 mm, normal pitch: 50 mm), followed by curing at 60 °C for 3 h. After removal from the mold, epoxy splines were obtained. Details of the mixed system are in Table 4.

4.3. Characterizations. 4.3.1. Gel Permeation Chromatography Analysis. Gel permeation chromatography (GPC) analyses were carried out in Viscotek model TDA 302. The sample was solubilized in THF and subsequently filtered using a ChromaXtra filter (type PVDF e 45/25 with 0.45 μm pore size).

4.3.2. Fourier Transform Infrared Spectroscopy Analysis. FTIR analyses were performed using an IS10 spectrometer (Nicolet) and an attenuated total reflectance method. Samples were studied in the form of powder or films on a diamond window. Each sample was scanned from 4000 to 400 cm$^{-1}$.

4.3.3. $^1$H NMR Analysis. $^1$H NMR (300 MHz) spectra were recorded on a Bruker ARX300 spectrometer. The solvent is chloroform-$d$ (CDCl$_3$).

4.3.4. Tensile Properties Tests. Pour the epoxy resin E51 and the mixed curing agent into the mold for the specific tensile figure 9. Typical route of PEAPA synthesis.


test. Tensile properties were studied according to GB/T 2567-2008. The tensile samples were tested by a CMT4303 universal test machine (SANS, China). The tensile test speed was 10 mm min⁻¹. The test region of the samples was 4.00 ± 0.10 mm thick, 10 ± 0.10 mm wide, and 50 ± 0.50 mm long. Both the tensile strength and elongation at break were measured. Five sample pieces were prepared for each group and tested at 25 °C.

4.3.5. Scanning Electron Microscopy Analysis. The exposed tensile fracture surface of the cured material was coated with a thin layer of gold using a high-vacuum gold sputter at low voltage. The micrographs were observed using 200x and 500x magnifications with an S-3400N scanning electron microscope (SEM; Hitachi, Japan) under conventional secondary electron imaging conditions at an accelerating voltage of 20 kV.

4.3.6. Dynamic Mechanical Analysis. The storage modulus (E') and loss factor (tan δ) were measured by a Q800 dynamic mechanical thermal analyzer in tensile test mode. All samples had a dimension of 40 mm × 5 mm × 1 mm and were tested from −70 to 120 °C at a heating rate of 3 °C min⁻¹ and a frequency of 1 Hz.

4.3.7. Thermal Stability Analysis. Thermogravimetric analysis (TGA) was performed using a 409PC thermogravimetric analyzer (Netzsch, Germany). Each sample was tested from 25 to 800 °C at a heating rate of 15 °C min⁻¹ under a nitrogen atmosphere.

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**Notes**
The authors declare no competing financial interest.

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