Data Article

Data of thermally active lignin-linkages and shape memory of lignin-rubber composites

Ngoc A. Nguyen*, Kelly M. Meek, Christopher C. Bowland, Amit K. Naskar*

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

A B S T R A C T

This data article presents the utilization of thermally dynamic covalent bonds of lignin linkages such as β-O-4', Co-O of β-5' phenylcoumaran, and β-β resins to modify the thermomechanical properties of high loading lignin-nitrile rubber composites. These thermally active lignin linkages can be triggered at 180 °C to generate free-radicals for crosslinking reactions. The evolution of crosslinking density was measured in-situ using dynamic mechanical analysis and rheological characterization. The shape programmability and shape recovery of these composites were determined by both ex-situ and in-situ methods. The thermally modified composites exhibited excellent shape memory properties. The data in this article are related to our recent research article entitled “Responsive lignin for shape memory applications” (Nguyen et al., 2018).

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* Corresponding authors.
E-mail addresses: nguyenna@ornl.gov (N.A. Nguyen), naskarak@ornl.gov (A.K. Naskar).
How data were acquired
Thermal characterization (TGA-Q500, TA instruments), in-situ thermal activation and dynamic mechanical analysis (DMA-Q800, TA instruments), in-situ thermal shear activation and rheological measurements (DHR-3, TA instruments), shape programmability and shape recovery (Hot-plate and dynamic mechanical analyzer DMA-Q800, TA instruments)

Data format
Analyzed

Experimental factors
The studied samples were thermally annealed or thermally sheared at 180 °C to modify their structural and mechanical characteristics. These changes were characterized and correlated to their shape memory properties.

Experimental features
50 wt% softwood and 50 wt% hardwood lignin in nitrile rubber composites were prepared by melt-mixing without the presence of any solvent. Thermally active lignin linkages such as β-O-4 and available active sites of lignin structural units were employed to control the crosslinking density. Tunable glass transition temperature and applicable stress of the interested composites were achievable for shape memory and potential automobile applications.

Data source location
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Data accessibility
Data in this article

Related research article
N.A. Nguyen, K.M. Meek, C.C. Bowland, A.K. Naskar, Responsive lignin for shape memory applications, Polymer 160 (2018) 210–222 [1]

Value of the data
- Heat treatment can be utilized to activate the thermal dynamic covalent bonds of lignin linkages.
- Crosslinking reactions and molecular rearrangement induced by lignin free-radicals generated at 180 °C can be determined by in-situ dynamic mechanical and rheological analyses.
- Structural and crosslinking evolution during a thermal annealing process and thermal dynamic shear results in significant improvement of the materials’ thermomechanical characteristics.
- Long thermal treatment of the lignin-nitrile rubber composites make the materials more rigid causing difficulties for melt processing. The investigated data shown in this study suggest a good route to process any lignin-based materials by controlling the temperature and time window appropriately. Post-thermal treatment can be used to further reinforce the materials.
- Thermally activated lignin-nitrile rubber composites still maintain good (even better) shape recovery and much higher applicable stress in comparison to the before heat-treated samples.
- The thermal activation of lignin dynamic covalent bonds can be applied for various lignin-thermoplastic composites as well.

1. Data

The measured data shown in this report exhibit different thermomechanical and shape memory characteristics of 50 wt.% hardwood (HW) and 50 wt.% softwood (SW) lignin–nitrile rubber composites after a thermal annealing process and thermal dynamic shear at 180 °C.

First, the thermal degradation of SW and HW lignin at 180 °C in air for 5 h is presented in Fig. 1. Second, in-situ thermal annealing and dynamic mechanical analysis of 50 wt% SW and 50 wt% HW composites are presented in Fig. 2. The data in Fig. 3 are the thermal degradation of 50 wt% SW and 50 wt% HW composites during an isothermal process at 180 °C. The thermal dynamic glass transition temperatures of the corresponding composites determined by the peak of tan (δ) are presented in Fig. 4. The following graphs in Fig. 5 are the measured different rheological properties of the
investigated composites before and after thermal dynamic shear at 180 °C for 24 h. Next, the shape programmability and shape recovery characteristics of 50 wt% HW and 50 wt% SW composites at different temperatures are shown in Fig. 6. The measured stress and modulus data of the two composites before and after thermal annealing are presented in Fig. 7. The corresponding stress/strain curves of these samples are presented in Fig. 8. Finally, examples of different shape recovery and shape fixity of 50 wt% HW and 50 wt% SW composites after programming at two selected temperatures, 50 °C and 100 °C, are shown in the Supporting Movies S1–S5.

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.dib.2018.12.046.

2. Experimental design, materials and methods

Softwood (SW) and hardwood (HW) lignin were combined with an acrylonitrile-butadiene rubber, NBR41 (41 mol% nitrile) to prepare excellent shape memory composites. The experimental design, materials and methods were performed following our recent reports [1,2].

2.1. Lignin composite preparation

Lignin was melt-mixed with NBR41 (1:1 weight ratio) with a mixing rate of 90 rpm at 180 °C for 60 min. The corresponding blends are named as 50 wt% HW and 50 wt% SW composites. The material was collected and stored at room temperature before compression molding at 190 °C for 20 min. The molded films with a thickness of ca. 2 mm were used for thermal, dynamic mechanical, and rheological analyses, as well as shape memory characterization.

2.2. Thermal stability analysis

All studied materials, including SW and HW lignin, as well as 50 wt% SW and 50 wt% HW composites, were kept isothermally at 180 °C for 5 h to determine their corresponding weight loss. These measurements were performed to demonstrate that there is no significant weight loss of the materials during the thermal annealing process at 180 °C for 5 h. The sample was kept isothermally at 105 °C for 20 min to remove the moisture before ramping (10 °C/min) to 180 °C for thermal annealing. A thermogravimetric analyzer (Q500, TA instruments) equipped with air and nitrogen flow was used for the measurements.
Fig. 2. (a) and (b) The zoomed-in dynamic mechanical storage modulus as a function of temperature at low and high temperature zones of the 50 wt% SW and the 50 wt% HW composites at different annealing time, respectively. (c) The corresponding measured dynamic mechanical storage modulus at 25 °C.

Fig. 3. Weight loss versus time of the 50 wt% SW and 50 wt% HW composites during an isothermal process at 180 °C in (a) air and (b) nitrogen.
Fig. 4. Tan (δ) as a function of temperature obtained from the dynamic mechanical analysis of the 50 wt% HW and the 50 wt% SW composites at different annealing times.

Fig. 5. (a) The dynamic shear storage modulus as a function of oscillation strain of the 50 wt% SW and the 50 wt% HW composites before and after in-situ shear for 24 h at 180 °C. (b) The corresponding phase angle. (c) Phase angle as a function of angular frequency of the 50 wt% SW and the 50 wt% HW composites before and after shear at 180 °C for 24 h. All measurements were performed at 180 °C.
Fig. 6. Examples of shape recovery: (a) The 5 h thermally annealed 50 wt% HW composite after stretching at 50 °C and fixing at ambient temperature. The sample demonstrates a quick recovery after placing on a hot-plate at 50 °C for 90 s. (b) The 5 h thermally annealed 50 wt% SW composite after programming at 100 °C and fixing at ambient temperature. The sample demonstrates a quick recovery after putting on a hot-plate at 100 °C for 60 s.

Fig. 7. (a) and (b) Recoverable stress; (c) and (d) Recoverable modulus of the 50 wt% HW and 50 wt% SW composites after 4 cycles of programming of the pristine (0 h) and (5 h) annealed samples. (See the Experimental section for more detail.)
2.3. In-situ thermal dynamic analysis

A dynamic mechanical analyzer (DMA-Q800, TA instruments) was used to investigate the thermomechanical properties of 50 wt% SW and 50 wt% HW composites. Temperature ramp from 25 °C to 150 °C at a ramp rate of 3 °C/min, a preload of 0.001 N, and a small strain amplitude (0.1–0.2%) was performed to determine the dynamic mechanical properties of these materials before and after in-situ thermal annealing at 180 °C for 1–5 h. After the first temperature ramp test, the sample was in-situ thermally annealed at 180 °C then kept isothermally at 25 °C for 5 min before repeating the temperature ramp test.

2.4. In-situ thermal dynamic shear analysis

A discovery hybrid rheometer (DHR-3, TA instruments) was employed to in-situ measure the crosslinking evolution of the 50 wt% SW and 50 wt% HW composites during the dynamic shear at 180 °C. Dynamic time sweeps at 180 °C with an oscillatory frequency of 10 rad/s and 0.1% strain were performed. The frequency sweeps and strain sweeps at 180 °C of the before and after shear samples were performed as well. A setup of 8 mm diameter parallel plates with ca. 0.4 mm sample gap was used for all rheological measurements.

2.5. Shape memory analysis

The shape memory characteristics of selected samples were studied by both ex-situ and in-situ methods.

For the ex-situ characterization, the materials were programmed on a hot-plate at two interested temperatures, 50 °C and 100 °C, then fixed at ambient temperature. The programmed shapes were recovered by placing on the hot-plate again.

For the in-situ characterization, the materials were initially stretched to 50% strain at a strain rate of 10%/min at 50 °C in a uniaxial tensile mode. The temperature was cooled to 0 °C at a ramp rate of 50 °C/min for fixing the programmed shape. The applied force was removed before heating the sample with a ramp rate of 10 °C/min to 50 °C and kept isothermally for 30 min. The shape recovery was measured. This shape memory characterization was repeated 4 times.
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Transparency document. Supporting information

Transparency document associated with this article can be found in the online version at https://doi.org/10.1016/j.dib.2018.12.046.

References

[1] N.A. Nguyen, K.M. Meek, C.C. Bowland, A.K. Naskar, Responsive lignin for shape memory applications, Polymer 160 (2018) 210–222.

[2] N.A. Nguyen, K.M. Meek, C.C. Bowland, S.H. Barnes, A.K. Naskar, An acrylonitrile–butadiene–lignin renewable skin with programmable and switchable electrical conductivity for stress/strain-sensing applications, Macromolecules 51 (2018) 115–127.