Data Article

Mechanical, thermal, morphological, and rheological characteristics of high performance 3D-printing lignin-based composites for additive manufacturing applications

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A B S TR A C T

The article presents different mechanical, thermal and rheological data corresponding to the morphological formation within various renewable lignin-based composites containing acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene rubber (NBR41, 41 mol% nitrile content), and carbon fibers (CFs). The data of 3D-printing properties and morphology of 3D-printed layers of selected lignin-based composites are revealed. This data is related to our recent research article entitled "A general method to improve 3D-printability and inter-layer adhesion in lignin-based composites" (Nguyen et al., 2018 [1]).

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S p e c i f i c a t i o n s Table

| Subject area          | Polymer Physics                   |
|-----------------------|-----------------------------------|
| More specific subject area | Composite and additive manufacturing |
| Type of data          | Table, image, graph, and movie    |
| How data was acquired | Mechanical analysis (RSA-3 and DMA-Q800, TA instruments), thermal characterization (TGA-Q500 and DSC-Q2000, TA instruments), Fourier |

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transform infrared spectroscopy analysis (PerkinElmer Frontier), optical analysis (Olympus BX50F4), scanning electron microscopy measurements (Hitachi S-4800), rheological measurements (DHR-3, TA instruments), and printing process (LulzBot TAZ printer).

Data format
Analyzed

Experimental factors
The prepared samples were characterized without pretreatment

Experimental features
The lignin based-composites were prepared by melt-mixing without the presence of any solvent. Selected high-loading renewable lignin based-composites were used to prepare the 3D-printing filaments and test their 3D-printing characteristics

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

Data accessibility
Data in this article

Value of the data
- The data presented in this article provide some background for lignin valorization via composite and additive manufacturing.
- The relationship of thermal relaxation data within the glassy region and the data of lignin phase separation within the composites can be applied for various polymer-based composite systems.
- The measured rheological data and morphological data of the 3D-printed layers suggest a good method to improve the materials’ 3D-printability and the 3D-printing interlayer adhesion, respectively.

1. Data

First, the mechanical performance data are presented to reveal the effects of lignin and CFs on the synthesized composites. Table 1 and Fig. 1 show the measured Young’s modulus, tensile at break, strain at break, and tensile energy to break of the studied materials.

Second, the thermal characteristics of pristine ABS, lignin, NBR41, and the synthesized composites are shown. The normalized heat flow and heat capacity data are presented in Fig. 2 and 3, and Tables 2 and 3. The measured glass transition temperatures correlated to the data calculated by using the Couchman rule are revealed in Fig. 4 and Table 4.

Next, the measured morphology data are presented to correlate with the thermal and rheological relaxation data. The scanning electron microscopy data are shown in Figs. 5–7. Fig. 8 presents the

| Table 1 | The measured tensile data of different investigated samples. Note that all samples were molded for the mechanical tests. |
|---------|----------------------------------------------------------------------------------------------------------------|
|          | Young’s modulus (GPa) | Tensile at break (MPa) | Strain at break (%) | Tensile energy to break ($ \times 10^5$ J/m$^3$) |
| Pristine ABS | 1.91 ± 0.32 | 54.09 ± 3.82 | 8.3 ± 1.74 | 39.05 ± 8.28 |
| ABS-Lignin-64 | 1.82 ± 0.08 | 20.5 ± 3.34 | 1.21 ± 0.17 | 1.43 ± 0.44 |
| ABS-NBR41-73 | 0.88 ± 0.09 | 26.13 ± 1.29 | 151.79 ± 18.81 | 364 ± 35.35 |
| ABS-NBR41-91 | 1.91 ± 0.15 | 41.92 ± 0.74 | 45.12 ± 13.33 | 185.8 ± 54.59 |
| ABS-NBR41-Lignin-514 | 1.41 ± 0.14 | 39.79 ± 3.54 | 3.48 ± 0.15 | 7.92 ± 0.37 |
| ABS-NBR41-Lignin-613 | 1.19 ± 0.05 | 31.16 ± 0.72 | 7.19 ± 0.88 | 18.2 ± 2.72 |
| ABS-NBR41-Lignin-712 | 1.36 ± 0.14 | 35.59 ± 0.98 | 10.52 ± 1.23 | 34.06 ± 5.71 |
| ABS-NBR41-Lignin-CF1/8_4141 | 2.44 ± 0.09 | 50.76 ± 1.39 | 2.84 ± 0.17 | 8.73 ± 0.9 |
| ABS-NBR41-Lignin-CF1/8_5131 | 2.64 ± 0.14 | 64.68 ± 2.54 | 3.85 ± 0.24 | 16.33 ± 2.13 |
| ABS-NBR41-Lignin-CF1/8_6121 | 2.31 ± 0.15 | 53.7 ± 3.68 | 3.89 ± 0.12 | 13.93 ± 0.63 |
Fig. 1. (a) Young's modulus and (b) tensile strength at break of ABS and ABS-NBR41 blends. (c) Tensile strength at break and (d) Strain at break of ABS-Lignin-64 and different ABS-NBR41-Lignin composites. (e) Tensile energy at break (the area under the stress-strain curve) and (f) Tensile strength at break of ABS-NBR41-Lignin-514 and different composites containing 10 wt% CFs and 10 wt% NBR41.
Fig. 2. (a) The normalized heat flow as a function of temperature of pristine ABS, NBR41, lignin and their composites. (b) and (c) The corresponding zoomed in data at low and high temperature ranges for clear observation. Note that the same color codes were used.
Fig. 3. (a) The normalized heat capacity as a function of temperature of pristine ABS, NBR41, lignin and their composites. (b) and (c) The corresponding zoomed in data at low and high temperature ranges for clear observation. Note that the same color codes were used.
frequency dependent loss modulus and phase angle data. Figs. 9–11 and Table 5 exhibit the thermal stability of the synthesized composites.

Finally, the rheological data and 3D-printing characteristics are shown. Examples of selected 3D-printing filaments made from lignin-based composites are presented in Fig. 12. The measured rheology data are shown in Figs. 13 and 14, and Table 6. The 3D-printability of the studied materials is shown in Figs. 15 and 16 and Movies 1–4 (see Supporting Information).

Supplementary material related to this article can be found online at doi:10.1016/j.dib.2018.05.130.

Table 2
The average $T_g$ ($^\circ$C) of different investigated samples measured by DSC. The standard deviation was computed from three individual measurements.

| Sample                      | $T_g$ ($^\circ$C) ± Standard Deviation |
|-----------------------------|----------------------------------------|
| ABS                         | 104.1 ± 0.2                            |
| ABS-NBR41–73                | 85.7 ± 1.6/ -6.4 ± 1                   |
| ABS-NBR41-Lignin-514        | 90.5 ± 1.3                             |
| ABS-NBR41-Lignin-CF-4141    | 90.1 ± 0.9                             |
| ABS-NBR41–91                | -12.8 ± 3.1                            |
| Lignin                      | 86.2 ± 1.2                             |
| ABS-NBR41-Lignin-613        | 93.1 ± 0.7                             |
| ABS-NBR41-Lignin-CF-5131    | 90.9 ± 0.3                             |
| ABS-NBR41–73 Lignin         | 92.0 ± 0.9                             |
| ABS-NBR41-Lignin-613        | 95.8 ± 0.6                             |
| ABS-NBR41-Lignin-712        | 94.6 ± 0.7                             |
| ABS-NBR41-Lignin-CF-6121    | 92.3 ± 0.7                             |

Table 3
The measured average changes in heat capacity ($J/g ^\circ$C) of different investigated samples. The standard deviation was computed from three individual measurements.

| Sample                      | Heat Capacity Change ($J/g ^\circ$C) ± Standard Deviation |
|-----------------------------|------------------------------------------------------------|
| ABS                         | 0.281 ± 0.009                                             |
| ABS-NBR41–73                | 0.205 ± 0.028/ 0.128 ± 0.016                              |
| ABS-NBR41-Lignin-514        | 0.201 ± 0.028                                             |
| ABS-NBR41-Lignin-CF-4141    | 0.175 ± 0.016                                             |
| ABS-NBR41–91                | 0.548 ± 0.016                                             |
| Lignin                      | 0.490 ± 0.031                                             |
| ABS-NBR41-Lignin-613        | 0.211 ± 0.008                                             |
| ABS-NBR41-Lignin-CF-5131    | 0.279 ± 0.020                                             |
| ABS-NBR41–73 Lignin         | 0.548 ± 0.016                                             |
| ABS-NBR41-Lignin-613        | 0.490 ± 0.031                                             |
| ABS-NBR41-Lignin-712        | 0.211 ± 0.008                                             |
| ABS-NBR41-Lignin-CF-6121    | 0.279 ± 0.020                                             |
| ABS-NBR41–91 Lignin         | 0.286 ± 0.022                                             |
| ABS-NBR41-Lignin-613        | 0.205 ± 0.020                                             |
| ABS-NBR41-Lignin-712        | 0.246 ± 0.037                                             |
| ABS-NBR41-Lignin-CF-6121    | 0.218 ± 0.029                                             |

Fig. 4. The measured DSC glass transition temperatures ($T_g$) of the investigated samples in comparison to $T_g$ computed by using the Couchman rule.

Figures 9–11 and Table 5 exhibit the thermal stability of the synthesized composites.
2. Experimental design, materials and methods

The experimental design, materials, sample preparation, and characterization methods used in this data article were reported recently [1,2]. Pristine ABS and various composites, namely ABS-NBR41-91 (containing 10 wt.% NBR41), ABS-NBR41-73 (30 wt% NBR41), ABS-Lignin-64 (40 wt% lignin), ABS-NBR41-Lignin-514 (10 wt% NBR41 and 40 wt% lignin), ABS-NBR41-Lignin-613 (10 wt% NBR41 and 30 wt% lignin), ABS-NBR41-Lignin-712 (10 wt% NBR41 and 20 wt% lignin), ABS-NBR41-Lignin-CF-4141 (10 wt% NBR41, 40 wt% lignin, and 10 wt% CFs), ABS-NBR41-Lignin-CF-5131 (10 wt% NBR41, 30 wt% lignin, and 10 wt% CFs), and ABS-NBR41-Lignin-CF-6121 (10 wt% NBR41, 20 wt% lignin, and 10 wt% CFs), were characterized.

Table 4

| T<sub>g</sub> (°C) of investigated samples computed by the Couchman rule [3]. |
|-----------------------------------------------------------|
| ABS-Lignin-64 | ABS-NBR-91 | ABS-NBR-73 | ABS-NBR41-Lignin-514 | ABS-NBR41-Lignin-613 |
| 94.4          | 79.9       | 45.5       | 76.4                  | 77.1                  |
| ABS-NBR41-Lignin-712 | ABS-NBR41-Lignin-CF-4141 | ABS-NBR41-Lignin-CF-5131 | ABS-NBR41-Lignin-CF-6121 |
| 78            | 74.3       | 75         | 75.8                  |                       |

Fig. 5. SEM micrographs of the fractured surface of different samples after performing tensile tests: (a) ABS. (b) ABS-NBR-91. (c) ABS-NBR-73.
In this article, we used the Couchman method [3] to determine the dependence of glass transition temperature on the components within the composites. The molar entropy ($S$) of the composite can be determined by the molar entropy of independent components (Eq. (1)) [3].

$$S = \sum_{i=1}^{4} X_i S_i + \Delta S_m$$

where $X_i$ and $S_i$ is the mole fraction and molar entropy of component $i$, respectively; $\Delta S_m$ is the excess entropy of mixing.

Using the thermodynamic theory, the entropy of component $i$ at an interested temperature is computed by (Eq. (2)).

$$S_i = S_0^i + \int_{T_{gi}}^{T} C_{pi} \, d\ln T$$

where $T_{gi}$ and $C_{pi}$ is the glass transition temperature and heat capacity of the pristine component, respectively, in which $S_0^i$ is the corresponding entropy.

Combining (Eq. (1)) and (Eq. (2)):

$$S = X_1 \left( S_1^0 + \int_{T_{g1}}^{T} C_{p1} \, d\ln T \right) + X_2 \left( S_2^0 + \int_{T_{g2}}^{T} C_{p2} \, d\ln T \right) + X_3 \left( S_3^0 + \int_{T_{g3}}^{T} C_{p3} \, d\ln T \right) + X_4 \left( S_4^0 + \int_{T_{g4}}^{T} C_{p4} \, d\ln T \right) + \Delta S_m$$

Fig. 6. SEM micrographs of the fractured surface of different samples after performing tensile tests: (a) ABS-Lignin-64. (b) ABS-NBR-Lignin-613. (c) ABS-NBR-Lignin-712.
The entropy $S$ at the glassy state ($g$) and liquid state ($l$) are identical. Therefore, (Eq. (3)) is expressed by the following relationship:

$$X_g^1 S^0 + \int_{T_g^1}^{T_g} C_g^0 \frac{d\ln T}{T} + X_g^2 S^0 + \int_{T_g^2}^{T_g} C_g^0 \frac{d\ln T}{T} + X_g^3 S^0 + \int_{T_g^3}^{T_g} C_g^0 \frac{d\ln T}{T} + X_g^4 S^0 + \int_{T_g^4}^{T_g} C_g^0 \frac{d\ln T}{T} + \Delta S_m^g = 0.$$  

where $T_g$ is the glass transition temperature of the composite.

The composition of component $i$ in the liquid and glassy state is unchanged. Therefore, $X_l^i = X_g^i$ and $S_l^0 = S_g^0$.

(Eq. (4)) can be simplified to (Eq. (5)).

$$X_1 \left\{ \int_{T_g^1}^{T_g} (C_{p1} - C_{p1}) \frac{d\ln T}{T} \right\} + X_2 \left\{ \int_{T_g^2}^{T_g} (C_{p2} - C_{p2}) \frac{d\ln T}{T} \right\} + X_3 \left\{ \int_{T_g^3}^{T_g} (C_{p3} - C_{p3}) \frac{d\ln T}{T} \right\} + X_4 \left\{ \int_{T_g^4}^{T_g} (C_{p4} - C_{p4}) \frac{d\ln T}{T} \right\} + \Delta S_m^l - \Delta S_m^l = 0.$$  

Fig. 7. SEM micrographs of the fractured surface of different samples after performing tensile tests: (a) ABS-NBR41-Lignin-CF-4141. (b) ABS-NBR41-Lignin-CF-5131. (c) ABS-NBR41-Lignin-CF-6121. The red circles indicate the percolation of CFs.
Fig. 8. (a) The loss modulus and (b) the phase angle as a function of angular frequency of three studied 3D-printing materials obtained from the master curve construction at $T_{ref} = 230^\circ$C.

Fig. 9. The measured FTIR data of the investigated samples. The inset shows the presence of hydrogen bonds.
**Fig. 10.** (a) Thermogravimetric analysis (TGA) of the investigated samples. (b) The corresponding zoomed in data at 5% weight loss ($T_5$). (c) The derivative of weight loss as a function of temperature. The dashed circle shows the first maximum peak of weight loss ($T_{m1}$).

**Fig. 11.** The measured temperature corresponding to 5% weight loss ($T_5$) and first maximum weight loss ($T_{m1}$) obtained from TGA scans.
The excess entropy of mixing for ideal mixtures can be negligible so (Eq. (5)) is reduced to (Eq. (6)) [3]

\[ X_1 Z T g_1 \Delta C_{p1} \frac{d \ln T}{T} + X_2 Z T g_2 \Delta C_{p2} \frac{d \ln T}{T} + X_3 Z T g_3 \Delta C_{p3} \frac{d \ln T}{T} + X_4 Z T g_4 \Delta C_{p4} \frac{d \ln T}{T} = 0. \]  

Therefore,

\[ X_1 \Delta C_{p1} \ln \left( \frac{T_g}{T_{g1}} \right) + X_2 \Delta C_{p2} \ln \left( \frac{T_g}{T_{g2}} \right) + X_3 \Delta C_{p3} \ln \left( \frac{T_g}{T_{g3}} \right) + X_4 \Delta C_{p4} \ln \left( \frac{T_g}{T_{g4}} \right) = 0. \]  

In this study, the heat capacity was measured per unit mass [3]. If call the \( M_i \) is the mass fraction of component \( i \). The (Eq. (7)) becomes:

\[ \ln T_g = \frac{M_1 \Delta C_{p1} \ln T_{g1} + M_2 \Delta C_{p2} \ln T_{g2} + M_3 \Delta C_{p3} \ln T_{g3} + M_4 \Delta C_{p4} \ln T_{g4}}{M_1 \Delta C_{p1} + M_2 \Delta C_{p2} + M_3 \Delta C_{p3} + M_4 \Delta C_{p4}}. \]

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Table 5
The measured temperature corresponding to 5% weight loss (\( T_5 \)) and first maximum weight loss (\( T_{m1} \)) obtained from TGA scans.

| Sample                | \( T_5 \) (°C) | \( T_{m1} \) (°C) |
|-----------------------|----------------|------------------|
| ABS                   | 335.6          | 408.6            |
| Lignin                | 251.6          | 270.4            |
| NBR41                 | 383.2          | 370.9            |
| ABS-Lignin-64         | 304.5          | 332.7            |
| ABS-NBR41-73          | 345.7          | 371.1            |
| ABS-NBR41-91          | 349.6          | 416.1            |
| ABS-NBR41-Lignin-514  | 314.2          | 330.1            |
| ABS-NBR41-Lignin-613  | 323.4          | 340.8            |
| ABS-NBR41-Lignin-712  | 323.7          | 346.3            |
| ABS-NBR41-Lignin-CF1/8_4141 | 311.4 | 326.9            |
| ABS-NBR41-Lignin-CF1/8_5131 | 317.8 | 334.3            |
| ABS-NBR41-Lignin-CF1/8_6121 | 328.6 | 345.1            |

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Fig. 12. 3D-printing filaments made from three investigated samples: (a) ABS, (b) ABS-NBR41-Lignin-514, (c) ABS-NBR41-Lignin-CF-4141.
Fig. 13. (a) Complex viscosity as a function of angular frequency of three studied 3D-printing materials obtained from the master curve construction at $T_{\text{ref}} = 230^\circ$C. (b) The shear stress as a function of shear rate at $T_{\text{ref}} = 230^\circ$C obtained from the Cox-Merz flow curves.

Fig. 14. The shift factor as a function of temperature data obtained from the master curve construction at $T_{\text{ref}} = 230^\circ$C.
Table 6
The measured shift factor obtained from the master curve construction at $T_{ref} = 230^\circ\text{C}$.

| Temperature (°C) | ABS | AB-NB41-AC-514 | AB-NB41-AC-CF-4141 |
|-----------------|-----|----------------|-------------------|
| 170             | 91.4| 61.0           | 117.7             |
| 190             | 13.1| 13.5           | 21.5              |
| 210             | 3.1 | 3.8            | 4.2               |
| 230             | 1.0 | 1.0            | 1.0               |

Fig. 15. (a) An example of a 3D-printing process using the ABS-NBR41-Lignin-CF-4141 composite. (b) An example of 3D-printed samples: ABS, ABS-NBR41-Lignin-514, and ABS-NBR41-Lignin-CF-4141 (from left to right). (c) An example of a 3D-printed ABS-NBR41-Lignin-514 sample used for the tear test. The dashed circle indicates a pre-crack of the sample before doing the tear test. (d) A close view of a 3D-printed ABS-NBR41-Lignin-514 sample used for the tear test showing individual printed layers.

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Fig. 16. The side-view optical images (left) and the corresponding side-view SEM images (middle and right) of: (a) ABS. (b) ABS-NBR41-Lignin-514. (c) ABS-NBR41-Lignin-CF-4141.

Supplementary data associated with this article can be found in the online version at https://doi.org/10.1016/j.dib.2018.05.130.

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