Improvement of Interlayer Adhesion and Heat Resistance of Biodegradable Ternary Blend Composites 3D Printing

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Supplementary Data

Figure S1. (a) Complex viscosity as a function of shear rate of neat polymers and PLA/PBAT/PB/nano talc composites at 210 °C; (b) Power regression of power law index for shear thinning behavior of neat polymers.

The power-law model for determining the shear thinning behavior [27, 36, 42].

\[ \eta = K\dot{\gamma}^{n-1} \]  

(S1)

Where \( \eta \) is the shear viscosity at shear rate of 0.2 s\(^{-1}\), K is the consistency index, \( \dot{\gamma} \) is the shear rate, and \( n \) is the power-law index.
Table S1. Determination of flow behavior of neat polymers and PLA/PBAT/PBS/nano talc composites.

| Polymer   | $\eta$ at $\dot{\gamma}$ 0.01 s$^{-1}$ (Pa·s) | $\eta$ at $\dot{\gamma}$ 0.2 s$^{-1}$ (Pa·s) | $K$ | $n$ |
|-----------|---------------------------------------------|---------------------------------------------|-----|-----|
| PLA       | 340                                         | 339                                         | 274 | 0.98|
| PBAT      | 1412                                        | 847                                         | 536 | 0.85|
| PBS       | 4482                                        | 1143                                        | 535 | 0.55|
| 70/30/0/10| 4032                                        | 1753                                        | 953 | 0.65|
| 70/0/30/10| 7075                                        | 2069                                        | 983 | 0.49|
| 70/10/20/10| 3758                                       | 1648                                        | 873 | 0.64|

$^1$ Analyzes by power regression.

The estimation of blend composition in the vicinity of phase inversion [36, 42].

$$\frac{\eta_1}{\eta_2} = \frac{\varphi_1}{\varphi_2}$$

Where $\eta_1$ is the viscosity of polymer 1, $\eta_2$ is the viscosity of polymer 2, $\varphi_1$ is the volume fraction of polymer 1, and $\varphi_2$ is the volume fraction of polymer 2. If the ratio of $\frac{\eta_1}{\eta_2} > \frac{\varphi_1}{\varphi_2}$, then polymer 2 will be the continuous phase [35].

Table S2. The ratio of viscosities and the volume fractions of polymers for predicting phase inversion in binary polymer blends.

| Binary Blends       | Matrix | Dispersed phase | Phase inversion |
|---------------------|--------|-----------------|-----------------|
| PLA/PBAT (70/30)    | $\frac{\eta_1}{\eta_2} > \frac{\varphi_1}{\varphi_2}$ | PLA             | PBAT > 71.5 %   |
| PLA/PBS (70/30)     | $\frac{\eta_1}{\eta_2} > \frac{\varphi_1}{\varphi_2}$ | PLA             | PBS > 77.5 %    |
| PBAT/PBS (70/30)    | $\frac{\eta_1}{\eta_2} > \frac{\varphi_1}{\varphi_2}$ | PBAT            | PBS > 57.5 %    |
| PBS/PBAT (70/30)    | $\frac{\eta_1}{\eta_2} > \frac{\varphi_1}{\varphi_2}$ | PBS             | PBS > 42.5 %    |

Remark: Shear viscosity of $\eta_1$ and $\eta_2$ at shear rate 0.2 s$^{-1}$ [23-24, 36].

The Harkin’s spreading equation can be used to predict the type of wetting phenomenon in ternary blends [20, 23-24, 37-41].

$$\lambda_{ABC} \text{ or } \lambda_{BC} = \gamma_{AC} - \gamma_{AB} - \gamma_{BC}$$

$$\lambda_{ACB} \text{ or } \lambda_{CB} = \gamma_{AB} - \gamma_{AC} - \gamma_{BC}$$

$$\lambda_{BAC} \text{ or } \lambda_{AB} = \gamma_{BC} - \gamma_{AB} - \gamma_{AC}$$
Where $\lambda$ is the spreading coefficient, $\gamma$ is the interfacial tensions for the polymer pairs and sub-indices refer to each phase in the mixture. A is PLA, B is PBAT and C is PBS.

Surface tension and interfacial tension from the harmonic mean equation for calculation of interfacial tension [23].

$$\gamma = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p}$$  \hspace{1cm} (S6)

Where $\gamma$ is surface tension, $\gamma^d$ is the dispersive contribution of surface tension, and $\gamma^p$ is the polar contribution of surface tension.

**Table S3.** Surface tensions of PLA, PBAT and PBS and interfacial tensions of polymer blends [23].

| Polymer (Phase) | $\gamma$  | $\gamma^d$ | $\gamma^p$ | $\gamma$ of polymer blends | Interfacial tension (mN/m) |
|----------------|-----------|------------|------------|----------------------------|----------------------------|
| PLA (A)        | 38.8 ± 0.2| 30.3 ± 0.2 | 8.5        | $\gamma_{PLA/PBAT}$        | 0.08 ± 0.01                |
| PBAT (B)       | 41.4 ± 0.3| 32.3 ± 0.2 | 9.1 ± 0.1  | $\gamma_{PLA/PBS}$         | 0.33 ± 0.03                |
| PBS (C)        | 43.6 ± 0.4| 33.1 ± 0.3 | 10.5 ± 0.1 | $\gamma_{PBAT/PBS}$        | 0.11                       |

1. $\gamma$, $\gamma^d$ and $\gamma^p$ from the reference [23].

**Table S4.** The Harkin’s spreading coefficient of ternary blend PLA/PBS/PBAT.

| Spreading coefficient (mN/m) | $\lambda$ |
|------------------------------|-----------|
| $\lambda_{PLA/PBAT/PBS}$     | 0.14 ± 0.02|
| $\lambda_{PLA/PBS/PBAT}$     | -0.36 ± 0.02|
| $\lambda_{PBAT/PLA/PBS}$     | -0.31 ± 0.03|