

# Dipropylene glycol dibenzoate for improved poly(lactic acid) plasticization

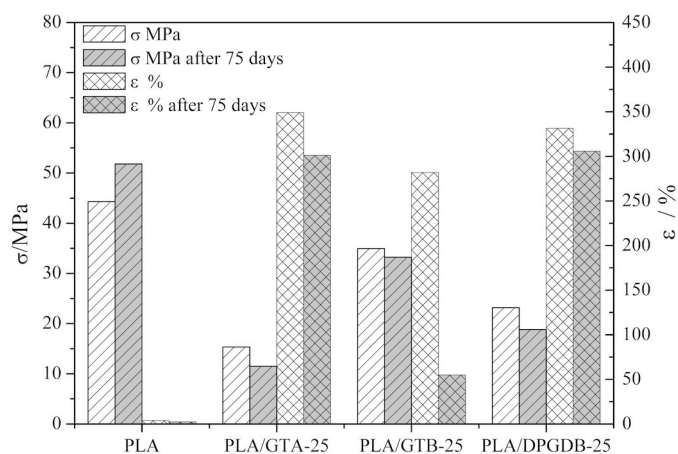
Tong Wan and Yanyan Lin

*The influence of different plasticizer materials on the mechanical properties and storage stability of poly(lactic acid) films is studied.*

Interest in biodegradable materials has increased because of environmental and food-safety concerns.<sup>1</sup> One such material—poly(lactic acid), or PLA—is a biodegradable aliphatic thermoplastic that is synthesized from lactic acid (obtained through the fermentation of sugar, starch, or another biomass).<sup>2</sup> It is thought that PLA could be a replacement for polyolefin in the production of ‘green’ packaging materials,<sup>3,4</sup> but there are several problems that need to be resolved (e.g., its brittle nature).

Plasticization of PLA is the most effective and simple approach for overcoming the brittleness of PLA (i.e., to improve the ductility and flexibility of PLA films).<sup>5,6</sup> However, the high level of migration of the plasticizer material from PLA films means that they have poor storage stability. The use of PLA plasticization is therefore limited in food packaging applications (and for other consumer products). Moreover, there is often poor compatibility between PLA and plasticizers. For food packaging applications, it is desirable for the plasticizers to have a high plasticizing efficiency with PLA (in both the amorphous and crystalline states), to be less volatile than PLA at the processing temperature, and to hardly migrate toward the polymer surface during a long storage period. All these properties are related to the chemical structure and molecular weight of the plasticizers themselves. If the molecular weight of the plasticizer became too high, the miscibility of the material would decrease and thus cause phase separation.<sup>7,8</sup> In addition, a relative increase in the molecular weight of the plasticizer would cause a decrease in the tendency of migration and miscibility could be maintained via the polar interactions.

The aim of our work<sup>9</sup> was therefore to explore the influence of different plasticizers on the plasticizing efficiency, compatibility, mechanical properties, and storage stability of PLA. The plasticizers we examined were glyceryl tribenzoate (GTB), dipropylene glycol dibenzoate (DPGDB), and glyceryl triacetate (GTA). To obtain our samples, we



**Figure 1.** Tensile strength ( $\sigma$ ) and elongation at break ( $\epsilon$ ) of neat poly(lactic acid), PLA, and PLA plasticized with glyceryl tribenzoate (GTB), dipropylene glycol dibenzoate (DPGDB), and glyceryl triacetate (GTA) at 25wt%.

first dried PLA for 12 hours in a vacuum oven at 60°C. We then mixed the PLA granules with the plasticizers, and heated them in the vacuum oven for four hours at 80°C (to ensure the plasticizers were absorbed into the PLA granules). In the subsequent step we plasticized the PLA in a melt compounding process, in which the blends were fed into a twin-screw extruder. We set the temperatures of the extruder for the melting, compression, metering, and die sections to 145, 150, 155, and 160°C, respectively. In addition, we used a screw speed of 30rpm to provide a sufficient shear rate in the melt compounding process. Each of the different plasticizers was included at a concentration of 25wt%, and we thus refer to the final samples as PLA/GTA-25, PLA/DPGDB-25, and PLA/GTB-25.

We can evaluate the storage stability of our samples according to the stability of their mechanical properties during a storage period. We thus measured the tensile strength ( $\sigma$ ) and elongation at break ( $\epsilon$ ) of

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the samples (see Figure 1). We find that the neat PLA sample exhibits brittle fracture, with very low  $\varepsilon$  (2.6%) and high  $\sigma$  (49.8MPa). These results are in agreement with those that have previously been reported.<sup>10</sup> Our results also clearly indicate that plasticization gives rise to a substantial increase in  $\varepsilon$  and decrease in  $\sigma$ . Of the plasticized samples, PLA/GTA-25 exhibits the highest  $\varepsilon$  and lowest  $\sigma$  (345% and 16MPa, respectively), whereas PLA/GTB-25 has the lowest  $\varepsilon$  (270%) and the highest  $\sigma$  (39MPa). After storage for 75 days, we find that the  $\varepsilon$  of the PLA/GTB-25 sample has significantly decreased, but the mechanical properties of the PLA/DPGDB-25 sample have remained stable.

To further explore the effect of the storage period on the crystallization stability of our plasticized samples, we measured their crystalline patterns (x-ray diffraction patterns) after one, 30, and 75 days of storage (see Figure 2). Before making these measurements, we used liquid nitrogen to quench the plasticized PLA from the melt state to the solid state. The x-ray diffraction patterns we obtained illustrate that only the amorphous state can be observed after one day. This result confirms that freshly plasticized PLA is in an amorphous state after the

quenching process. After 75 days of storage at room temperature, the PLA/GTA-25 sample exhibits characteristic diffraction peaks (at 16.5 and 18.9°) that correspond to the typical  $\alpha$ -crystalline phase of PLA (i.e., described by a pseudo-orthorhombic or orthorhombic unit cell). Our measurements indicate, however, that the PLA/DPGDB-25 and PLA/GTB-25 samples are still in the amorphous stage after 75 days of storage (because of their slow crystallization rates). These two samples therefore did not experience phase separation or plasticizer exudation, and thus exhibit better storage stability than the PLA/GTA-25 sample.

In summary, we have studied the effect of different plasticizers on the mechanical properties and storage stability of PLA. Our results indicate that the mechanical properties of PLA that is plasticized with dipropylene glycol dibenzoate (at 25wt%) remains stable after 75 days of storage. In addition, our x-ray diffraction measurements show that this sample did not suffer from phase separation or plasticizer exudation during this time period. DPGDB is therefore a promising option for plasticizing of PLA for flexible packaging materials. In the future we plan to further develop our research on plasticizing of PLA into the areas of disposable packaging materials and 3D printing (by fused deposition modeling).

## Author Information

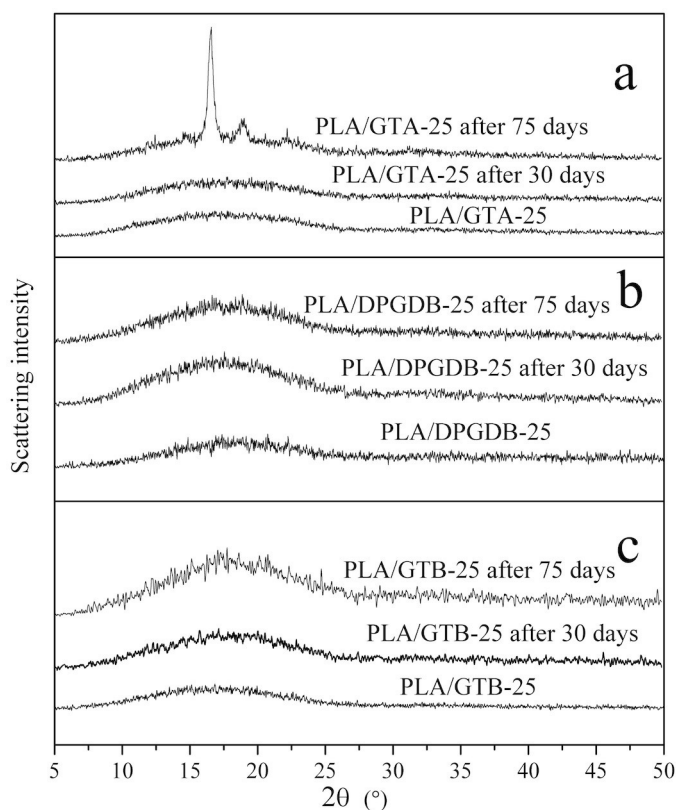
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**Figure 2.** X-ray diffraction patterns of the (a) PLA/GTA-25, (b) PLA/DPGDB-25, and (c) PLA/GTB-25 samples after storage periods of one, 30, and 75 days.  $2\theta$ : Measured angle of diffraction.

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