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*Cynaracardunculus* Biomass Recovery: an Eco-Sustainable, Non-Edible Resource of Vegetable Oil for the Production of Poly(lactic acid) Bioplasticizers

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FTIR

In Figure S1a,b, FTIR comparison of CO and ECO spectra in the high frequency (a) and finger print (b) regions, are reported. In particular, in Fig.S1a, the presence of a shoulder at 3009 cm\(^{-1}\) in CO oil, related to the stretching vibration of double bond \(=\text{CH}\), disappeared in ECO oil spectrum, confirming that the epoxidation occurred at the expense of all unsaturated group conversion. In Figure S1b, besides the peak at 1250 cm\(^{-1}\) related to both C-O-C stretching from oxirane group (in ECO) and C-O stretching of ester group in both oils, oil, is possible to observe small intensity vibrations around 785, 826 and 842 cm\(^{-1}\), specifically attributed to the C-O-C stretching of oxirane groups (in ECO)\(^{1,2}\).

Figure S1a,b. FTIR spectra of neat (CO) and epoxidized cardoon oil (ECO)

In Figure S2, PLA, PLA_ECO and PLA_CO spectra are reported. The main absorption regions of PLA and PLA/oil based systems are attributed to the vibrations of \(–\CH\) stretching between 3100–2800 cm\(^{-1}\), \(\text{C}=\text{O}\) stretching in the range of 1760–1745 cm\(^{-1}\), \(–\CH\) bending at 1500–1400 cm\(^{-1}\) and \(–\text{C–O}\) stretching in the interval between 1100–1000 cm\(^{-1}\) (Figure S2)\(^{3,4}\).

Unfortunately, most of the vibration frequencies of the above functional groups were reciprocally overlapped, so the corresponding spectra comparison were not enlightening. Anyway, from a spectra
subtraction, it was possible to collect information related to PLA-oil interactions (see Figure 2a,b in the full text).

Figure S2. FTIR spectra of PLA, PLA_CO, PLA_ECO films.

In Figure S3, the fingerprint region of PLA, PLA_ECO and their spectral subtraction is reported. From the analysis of spectra, it is worthy to note the presence of the oxirane C-O-C vibrational frequency, at 820, 842, 855 cm⁻¹. This outcome suggested that, although the strong physical interaction occurring between the polar groups of PLA and ECO, no chemical reaction, involving the oxirane ring opening, occurred after the extrusion and compression moulding processes.

Figure S3. PLA, PLA_ECO and their spectral subtraction of the fingerprint region.
During the second heating run, PLA based systems evidenced two cold crystallization phenomena (red circle in Figure. S4), whose parameters are detailed in Table S1.

Cold crystallization phenomena, observable after the glass transition temperature, are very common mostly in the case of the polyesters, as widely reported in literature\(^5\). So far, three major mechanisms have been used to explain this phenomenon, as widely reported in literature\(^6\)-\(^8\).

In the specific case of PLA based systems, the cold crystallization believed to be aroused from the melting-recrystallization-remelting model, in which PLA unstable crystallites formed during the cooling process (see Figure. 4 in the full text), melted and then recrystallized in unsteady crystalline patterns, thermally susceptible to further melting process. Hence, the crystallization exotherms\((T_{cc1}\) and \(T_{cc2}\)) found in the DSC traces (FigureS4) corresponded to the recrystallization of the unstable melt crystallites, whereas the main endothermic peak were referred to the melting of highly thermally stable crystallites formed during the cooling step\(^9\). In all the films investigated, the first cold crystallization phenomenon was induced by the increasing of macromolecular mobility, since it occurred upon the glass transition of PLA. Anyway, while neat PLA film evidenced the melting of the metastable crystals formed, the plasticized films did not show any clear melting phenomena. This outcome could be due to the very closeness of the two consecutive processes, not discernible in presence of oil plasticizers, since the fast developed chain mobility. The second cold crystallization occurred very close to the main melting process of the more stable crystal lamellae fraction.

### Table S1. Thermal properties of PLA, PLA_CCO and PLA_ECO films measured by DSC.

| Samples | \(T_{c\text{melt}}\) | \(\Delta H_{c\text{melt}}\) | \(T_g\) | \(T_{cc1}\) | \(T_{cc2}\) | \(\Delta H_{cc1}\) | \(\Delta H_{cc2}\) | \(\Delta H_m\) | \(T_m\) |
|---------|-----------------|-----------------|--------|-----------|-----------|----------------|----------------|----------------|-------|
| PLA     | 97.4            | 33.5            | 62.2   | 93.4      | 160        | 3              | 3.4            | 44.0           | 174   |
| PLA_CCO | 98.1            | 30.4            | 59.8   | 93.6      | 158        | 4.1            | 4.4            | 47.7           | 174   |
Figure S4. DSC second heating run. Red circles: first and second cold crystallization process

TGA

From the analysis of thermograms, it is worthy to highlight that both oils evidenced the highest thermal stability; in particular, as expected, the presence of epoxidized rings, increasing the molecular complexity of the corresponding oil, delayed its thermal decomposition; indeed ECO degradation onset was shifted to higher temperature with respect to CO oil\textsuperscript{10}. It is interesting to note that PLA was thermally stabilized by both oils, as shown by both thermograms and Table 2. Actually, the physical interaction occurring between PLA chains and oils induced a structural reassembling of the polymer creating a protective physical barrier, able both to hinder the permeability of volatile degradation products out from the blend, and to promote a drastic delay of blend thermal degradation. Moreover, only a single degradation pattern could be evidenced by TGA and DTG curves (Figures S5a,b) of PLA-oils based films, evidencing a fine oil dispersion among macromolecular chains. Nevertheless, it is outstanding to observe that PLA_CO blend showed higher thermal stability compared to PLA_ECO system (see Table 2). This outcome was somewhat expected, since the enhanced plasticization effect of epoxidized oil on polymeric matrix, as previously proved by DSC data and
morphological analysis, and following detailed by mechanical properties. Indeed, the epoxidized oil interspersed between the polymeric chains, increasing the free volume of the system. As a consequence, the polymer was more prone to thermal degradation\textsuperscript{11,12}.

From the analysis of DTG thermogram, reported in Figure S5, it is worthy to highlight that both oils evidenced the highest thermal stability; in particular, as expected, the presence of epoxidized rings, increasing the molecular complexity of the corresponding oil, delayed its thermal decomposition; indeed ECO degradation onset was shifted to higher temperature with respect to CO oil. It is interesting to note that PLA was thermally stabilized by both oils, as widely detailed in the full text. Moreover, only a single degradation pattern could be evidenced by DTG curves of PLA-oils based films, evidencing a fine oil dispersion among macromolecular chains.

\textbf{Figure S5a,b.} TGA (a) and DTG (b) thermograms of CO and ECO oils, PLA, PLA\_CO and PLA\_ECO films

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