

Research Article

A Fractional-Order Model of Biopolyester Containing Naturally Occurring Compounds for Soil Stabilization

Nadka Tzankova Dintcheva , **Marilena Baiamonte**, **Rosalia Teresi**, **Gioacchino Alotta**, **Emanuela Bologna**, and **Massimiliano Zingales**

Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo, Italy

Correspondence should be addressed to Nadka Tzankova Dintcheva; nadka.dintcheva@unipa.it

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Currently, the use of polymers and biopolymers as soil-stabilizer additives for control of the soil degradation, deterioration, and desertification and for improving the arid and semiarid soils has been expanded significantly in the agricultural sector. This research was conducted to determine the effect of naturally occurring compounds, such as quercetin (Q) and sodium montmorillonite (NaMMt) at different weight ratios, in biopolyester, such as polylactic acid (PLA), aiming to formulate ecosustainable materials to control the soil degradation and to protect the environment. As known, the use of sophisticated analytical tools to describe the material rheology and melting properties is nowadays very popular among physicists and material scientists. Certainly, several experimental tests conducted on polymeric- and biopolymeric-based materials, such as rubbers, foams, and hydro/aero gels, show that the relaxation time spectra are a continuous function, and as a consequence, multiple relaxation times are involved in the rheological description of the materials, yielding the need for nonconventional relaxation functions. Indeed, in this work, the considered fractional-order model could be considered a powerful tool to describe and to predict the melting properties of the complex polymer-based systems containing different additives.

1. Introduction

In the last two decades, the biodegradable polymers have widely been investigated to replace synthetic polymers because of environmental problems and decreasing fossil resources. The applications of biodegradable polymers in the agricultural field as covering films, mulching films, packaging, soil subsistence, etc., are a very promising and challenging issue [1]. However, the products formulated using polymers and biodegradable polymers must exert properties, performances, and durability compatible with the specific applications in the agricultural sector. In particular, the maintenance of the performance during their lifetime is a critical topic for successful applications. So, researchers have been focusing on a growing attention to nanocomposite formulation based on polymers and biopolymers containing reinforcement additives and natural stabilizing agents [2, 3].

Furthermore, some polymers, such as polystyrene and polyacrylamide, and biopolymers, such as biopolyester, have been identified and recognized as efficient and valuable soil conditioners because of their ability to stabilize the soil surface structure and pore continuity, preventing the soil erosion and controlling the water infiltration [2, 4, 5]. For example, as known, the arid and semiarid soils are characterized by low erratic rainfall, long periodic droughts, and high water evaporation, and in order to improve the agricultural productivity of these soils, the use of polymers and biopolymers as soil conditioners is absolutely imperative.

Polylactic acid, PLA, is a compostable thermoplastic made from renewable sources and able to degrade into innocuous lactic acid. PLA is used as medical implants and for the encapsulation of many therapeutic agents due to its high hydrophobicity, strong mechanical strength, and slow drug release. Furthermore, PLA can be used as a compostable packaging material, and the maintenance of the

performance during its service lifetime, however, remains a critical point for successful applications [6, 7].

Naturally occurring minerals, such as montmorillonite and bentonite, are very attractive polymer and biopolymer additives because of their ability to improve significantly the gas and water impermeability and to enhance the mechanical performance of the materials [8, 9]. Moreover, the montmorillonite and bentonite nanoparticles are naturally occurring minerals, and their release in the soil can be considered an absolutely eco-friendly issue.

Natural antioxidants receive attention in packaging and in the food industry also because of their presumed safety. Quercetin is an abundant flavonoid suitable in stabilizing polymer against both thermo-oxidation during processing and photo-oxidation during UV exposure. Its protective action is performed by reducing free radical formation, scavenging free radicals and, also, binding transition metal ions [10, 11]. It is of fundamental importance to investigate and to verify the usefulness of flavonoids in the thermo- and photo-oxidation stabilization and also for bio-polymer. The protection of biodegradable polymers provided by the flavonoid compound is similar to that obtained using the synthetic commercial light stabilizer [12, 13].

The use of sophisticated analytical tools to describe material rheology of neat polymer- or complex polymer-based systems is nowadays very popular among physicists and material scientists. Indeed, several experimental tests conducted on materials having different chemical nature, such as rubbers, foams, and hydro/aero gels, show that the relaxation time spectra are a continuous function, and as a consequence, multiple relaxation times are involved in the rheological description of the materials, yielding the need for nonconventional relaxation functions. Among them, the widely used stretched-exponential relations and the power-law relaxation well suited for complex system materials. In the context of linear material hereditariness, the use of power law expression of creep/relaxation to describe experimental data yields a rheological formulation in terms of the current fractional-order operators.

In this study, the authors will use the fractional-order calculus to fit the experimental data obtained for a biodegradable polylactic acid (PLA) containing naturally occurring compounds, such as quercetin (Q) and sodium montmorillonite (NaMMt) nanoparticles, at different ratios, as valuable materials for soil conditioners. The natural polyphenolic compound, i.e., Q, has been added in PLA at different concentrations, e.g., 0.5, 2, and 3 wt.%, considering the currently published experience of the authors in demonstrating the specific concentration dependent anti-/pro-oxidant activity of these molecules if introduced in PLA [14, 15]. Particularly, if these naturally occurring molecules are added at low concentrations, from 0.1 to 0.5 wt.%, they are able to protect the biopolyester against the exposure to UVB irradiation, but if they are added at high concentrations, from 2 to 3 wt.%, they are able to exert a prodegradant effect. Moreover, the naturally occurring silicate, i.e., NaMMt, and the natural phenolic compound, i.e., Q, have been considered in this work because of its beneficial effect as sustainable reinforcement additives for polymers

and biopolymers, and their release in the soil is an absolutely eco-friendly issue.

2. Experimental Part

2.1. Materials. The materials used in this work are as follows:

- (i) Polylactic acid (PLA) 2002D is purchased from NatureWorks LLC. Its main properties are molecular weight, $M_w = 204456$ g/mol; melting point, $T_m = 150^\circ\text{C} - 160^\circ\text{C}$; glass transition temperature, $T_g = 58^\circ\text{C}$; and melting index ($260^\circ\text{C}/2.16$ kg) = 5.0–7.0.
- (ii) Natural sodium montmorillonite is purchased from Cloisite®Na+ (NaMMt) by Southern Clay; Quat. Conc. meq/100 g clay = 92.6 and $d_{001} = 1.17$ nm.
- (iii) 2-(3,4-Dihydroxyphenyl)-3,5,7-trihydroxy-4H-1-benzopyran-4-one hydrate by Sigma-Aldrich; named quercetin (Q); molecular weight = 302,24 (anhydrous basis).

2.2. Processing. The preparation of PLA-based samples was carried out using a Brabender mixer at $T = 170^\circ\text{C}$ and a mixing speed of 50 rpm for 5 minutes. NaMMt and Q have been added at different ratios as follows: 2.5/0.5, 2.5/2, and 2.5/3 (wt./wt.%). The neat PLA matrix and PLA/NaMMt have been subjected to the same processing conditions.

2.3. Characterizations. Rheological tests were performed using a strain-controlled rheometer (mod. ARES G2 from TA Instrument) in parallel-plate geometry (plate diameter of 25 mm). The complex viscosity (η^*) was measured performing time sweep experiments, at $\omega = 1$ rad/s and $T = 170^\circ\text{C}$. The strain amplitude was $\gamma = 2\%$, which preliminary strain sweep experiments proved to be low enough to be in the linear viscoelastic regime.

The X-ray diffraction (XRD) analysis of PLA, PLA/NaMMt, and PLA/NaMMt/Q compound films was performed using an Empyrean Series 2 X-ray diffraction (Panalytical): the spectra of the sample film were recorded in the range 3–30 deg (step size = 0.025; scanning rate = 60 s/step) and Cu-K α radiation at wavelength $\lambda = 0.1542$ nm.

The calorimetric data were evaluated by differential scanning calorimetry (DSC) using a Perkin Elmer DSC7 calorimeter. All experiments were performed under dry N₂ on samples of around 10 mg in 40 μl sealed aluminium pans. Four calorimetric (two heating: 30°C–220°C and two cooling: 220°C–30°C) scans were performed for each sample at the scanning heating/cooling rate of 5°C/min.

The crystallinity degree (X_c) is calculated using the following formula: $X_c (\%) = (\Delta H_m + \Delta H_{cc}/\Delta H^0) \times 100$, where ΔH_m is the heat of melting of the sample, ΔH_{cc} corresponds to the heat of cold crystallization, and ΔH^0 is the heat of fusion for 100% crystalline PLA (93 J/g) [16].

Tensile properties were determined at room temperature and humidity, using an Instron (U.S.A.) dynamometer mod. 3365, according to ASTM test method D882. The specimens

were cut out from films in the machine direction and tested. The modulus was measured at the speed of 1 mm/min. When the deformation was about 10%, the speed was increased up to 100 mm/min until break. The data reported are the average values (with the related error bars) obtained through ten tests per sample.

2.4. Fractional Calculations. Fractional calculus may be considered the extension of the ordinary differential calculus to noninteger powers of derivation orders [17, 18]. In this section, we address some basic notions about this mathematical tool.

The Euler Gamma function $\Gamma(z)$ may be considered as the generalization of the factorial function since z assumes integer values as $\Gamma(z+1) = z!$, and it is defined as the result of the integral as follows:

$$\Gamma(z) = \int_0^{\infty} e^{-x} x^{z-1} dx. \quad (1)$$

The Riemann–Liouville fractional integrals and derivatives with $0 < \beta < 1$ of functions defined over intervals of the real axis, namely, $f(t)$ such that $t \in [a, b] \subset \mathbb{R}$, have the following forms:

$$(\mathbf{I}_a^\beta f)(t) = \frac{1}{\Gamma(\beta)} \int_a^t \frac{f(\tau)}{(t-\tau)^{1-\beta}} d\tau,$$

$$(\mathbf{D}_a^\beta f)(t) = \frac{f(a)}{\Gamma(1-\beta)(t-a)^\beta} + \frac{1}{\Gamma(1-\beta)} \int_a^t \frac{f'(\tau)}{(t-\tau)^\beta} d\tau. \quad (2)$$

Besides the Riemann–Liouville fractional operators defined above, another class of fractional derivative that is often used in the context of fractional viscoelasticity is represented by Caputo fractional derivatives which are defined as

$$({}_c\mathbf{D}_a^\beta f)(t) := \mathbf{I}_a^{m-\beta} (\mathbf{D}_a^m f)(t), \quad m-1 < \beta < m, \quad (3)$$

and whenever $0 < \beta < 1$, it reads as follows:

$$({}_c\mathbf{D}_a^\beta f)(t) = \frac{1}{\Gamma(1-\beta)} \int_a^t \frac{f'(\tau)}{(t-\tau)^\beta} d\tau. \quad (4)$$

A closer analysis of equations (3) and (4) shows that the Caputo fractional derivative coincides with the integral part of the Riemann–Liouville fractional derivative in the bounded domain. Moreover, the definition in equation (4) implies that the function $f(t)$ has to be absolutely integrable of order m (e.g., in (4), the order is $m=1$). Whenever $f(a)=0$, Caputo and Riemann–Liouville fractional derivatives coalesce.

Similar considerations hold true also for Caputo and Riemann–Liouville fractional derivatives defined on the entire real axis. Caputo fractional derivatives may be considered as the interpolation among the well-known, integer-order derivatives, operating over functions $f(\cdot)$ that belong to the class of the Lebesgue integrable functions ($f(\cdot) \in L^1$) as a consequence, and they are very useful in the mathematical description of complex system evolution.

3. Results and Discussion

It is shown that power law relaxation, in the functional class of

$$G(t) = \sum_{j=1}^N c_{\beta_j} t^{-\beta_j}, \quad (5)$$

yields an accurate representation of the experimental data for several kinds of mixtures analysed. Introducing the Boltzmann superposition principle for time-varying deformation law $\varepsilon(t)$, the rheological model yields:

$$\sigma(t) = \sum_{j=1}^N c_{\beta_j} \left({}_c\mathbf{D}_0^{\beta_j} \varepsilon \right) (t). \quad (6)$$

For the considered semicrystalline polymer, the maximum number $N=2$ yields the inverse relation of equation (6) as

$$\varepsilon(t) = \int_0^t E_{\alpha,\beta}(t-\tau) \sigma(\tau) d\tau, \quad (7)$$

where $E_{\alpha,\beta}(t)$ is the two parameters Mittag-Leffler function defined as

$$E_{\alpha,\beta}(t) = \sum_{k=0}^{\infty} \frac{t^k}{\Gamma(\alpha k + \beta)}, \quad (8)$$

where the parameters β_i and c_{β_i} have been estimated via the least-squared method for different concentrations of natural-based silicates as sodium montmorillonite (NaMMt).

However, the rheological analysis on PLA-based samples containing NaMMt and Q at different ratios has been carried out, and the fitting between the experimental data obtained and theoretical calculated data has been established.

The complex viscosity of the material, obtained by experimental data, is defined as

$$\eta(\omega) = [G'(\omega)^2 + G''(\omega)^2]^{1/2}, \quad (9)$$

where the complex storage $G''(\omega)$ and loss $G'(\omega)$ moduli are defined as the real and imaginary parts of the Fourier transform of eq. (5) as

$$G'(\omega) = \sum_{j=1}^N \frac{c_{\beta_j} \omega^{\beta_j+1} \sin(\beta_j \pi/2)}{\Gamma(1-\beta_j)}, \quad (10)$$

$$G''(\omega) = \sum_{j=1}^N \frac{c_{\beta_j} \omega^{\beta_j+1} \cos(\beta_j \pi/2)}{\Gamma(1-\beta_j)}.$$

In Figure 1, the trends of the complex viscosity for neat PLA and PLA/NaMMt containing different amounts of Q as a function of time have been plotted. It can be observed that the adding of 2.5 wt.% NaMMt in PLA leads to a slight increase in the complex viscosity values at the early stage of the rheological analysis, while, at long experimental times, the adding of NaMMt nanoparticles leads to a slight decrease in the complex viscosity values probably because

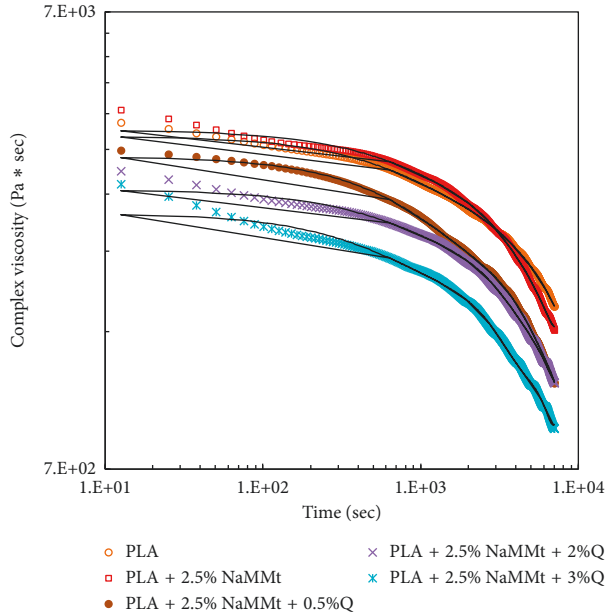


FIGURE 1: Complex viscosity data (symbols) and theoretical fittings (continuous lines) of neat PLA and PLA/NaMMt containing different amounts of Q.

of these flexible nanoplatelets that are able to align themselves along the flow direction, as proposed in literature [19]. Besides, the addition of naturally occurring molecules, as quercetin, in PLA/NaMMt nanocomposite leads to decrease in the complex viscosity values. This last issue could be understood considering that these low molecular weight molecules if added at high concentrations are able to exert pronounced plasticizing action, which leads to a significant decrease in the complex viscosity values.

The fitting parameters obtained for $N=1$ expansion in equation (10) is reported in Table 1.

It is interesting to highlight that the fitting of the experimental data, based on the Caputo fractional derivative model for semicrystalline polymers, and the experimentally obtained results are very good, especially at long experimental times. The slight deviation between experimental data obtained and theoretical trends at early stage of the experiment could be understood by taking into account two different issues: (i) the description of the behaviour for complex polymer-based systems is very hard matter because of some morphological evolution of these systems and (ii) the interactions between the constituents, e.g., NaMMt and Q, can change because of alignment and/or orientation of the nanofillers can occur during the experiment.

Moreover, the morphology of the investigated systems has been evaluated through XRD and DSC analysis. The neat PLA and PLA/NaMMt samples containing different amounts of Q show similar XRD spectra (Figure 2). The main diffraction peak at around 15° slightly decreases due to the presence of Q molecules highlighting a reduction of the polymer crystalline structure. The diffraction peak at around

TABLE 1: Fitting parameters for the power laws expansion in equation (10).

Sample	N	β	C_β
PLA	1	0.1985	7373,54
PLA + 2.5% NaMMt	1	0.1762	6545,61
PLA + 2.5% NaMMt + 0.5%Q	1	0.2229	6666,19
PLA + 2.5% NaMMt + 2%Q	1	0.1852	5164,57
PLA + 2.5% NaMMt + 3%Q	1	0.2052	4710,70

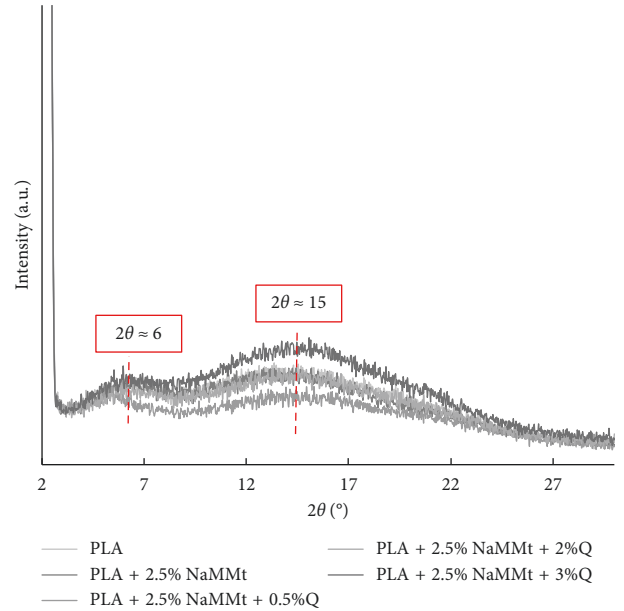


FIGURE 2: XRD spectra of neat PLA and PLA/NaMMt containing different amounts of Q.

6° can be attributed to intrinsic PLA crystalline structure and to the presence of NaMMt nanoparticles; due to the signal overlapping, the estimation of nanofiller morphology in the PLA almost amorphous samples is a very hard matter.

The obtained results of the DSC analysis are shown in Table 2. In particular, the glass transition (T_g) and melting (T_m) temperatures, fusion (ΔH_m) and cold crystallization (ΔH_{cc}) enthalpies, and calculated crystallinity degree (X_c) of the samples are reported. As expected, the crystallinity degree of PLA slightly increases due to the addition of NaMMt nanoparticles and decreases due to the presence of the large amount of Q molecules.

Finally, to evaluate the possibility to use the PLA-based materials for soil stabilization, the mechanical tensile properties, i.e., elastic modulus (E), tensile strength (TS), and elongation at break (EB), of all instigated samples have been carried out and the obtained results are reported in Table 3. It can be observed that the addition of the NaMMt nanoparticles leads to the increase of the system rigidity and, in particular, the E and TS increase due to the presence of nanofillers, and this reinforcing effect has not been penalized by the presence of Q molecules in the solid state. The last issue highlights the possibility to consider these materials as

TABLE 2: Thermal properties of neat PLA and PLA/NaMMt containing different amounts of Q evaluated during second heating scan.

Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_{cc} (J/g)	X_c (%)
PLA	58.3	150.2	17.4	8.1	10
PLA + 2.5% NaMMt	58.7	146.8	21.8	5.8	17.5
PLA + 2.5% NaMMt + 0.5%Q	58.0	147.2	19.2	5.5	14.3
PLA + 2.5% NaMMt + 2%Q	57.0	151.0	24.5	14.4	5.6
PLA + 2.5% NaMMt + 3%Q	57.3	147.3	15.0	8.8	4.5

TABLE 3: Main mechanical properties: elastic modulus (E), tensile strength (TS), and elongation at break (EB), of neat PLA and PLA/NaMMt containing different amounts of Q.

Sample	E (MPa)	TS (MPa)	EB (%)
PLA	1555 ± 50	47.0 ± 2.5	9.1 ± 1.5
PLA + 2.5% NaMMt	1845 ± 58	51.2 ± 3.5	9.5 ± 2.0
PLA + 2.5% NaMMt + 0.5%Q	1848 ± 55	43.8 ± 2.1	15.0 ± 2.5
PLA + 2.5% NaMMt + 2%Q	1832 ± 51	42.8 ± 2.2	14.1 ± 2.5
PLA + 2.5% NaMMt + 3%Q	1808 ± 52	40.8 ± 2.5	13.0 ± 2.5

good candidates for soil stabilizations, considering also their naturally occurring nature.

4. Conclusions

In this work, the effect of naturally occurring compounds, such as NaMMt and Q, in PLA has been investigated through experimental and theoretical analysis, considering these materials as suitable candidates for soil stabilization in the agricultural sector. In particular, the rheological behaviour of the investigated systems has been estimated through the evaluation of the complex viscosity trends as a function of time. Besides, the fitting between experimental data obtained and theoretical calculated data has been accurately investigated and analysed. It can be concluded that the theoretical model is able to predict exactly the rheological behaviour of the investigated complex biopolymer-based systems at long experimental time, while, at short experimental time, the interactions between the system components are pronounced, and for these reasons, some deviations have been observed.

To evaluate the system morphology and solid-state properties of all investigated samples, accurate XRD and DSC analyses and mechanical tensile tests have been carried out.

Finally, all obtained results suggest the possibility to consider these materials as suitable candidates for soil stabilization.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

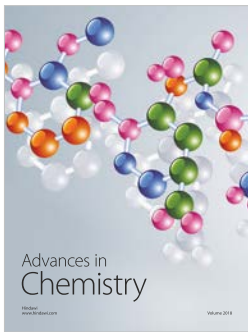
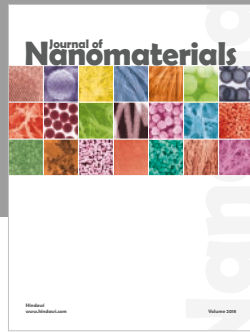
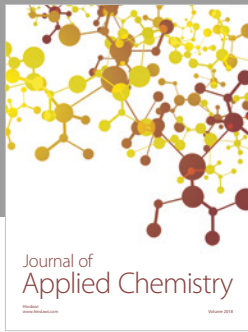
Conflicts of Interest

The authors declare that they have no conflicts of interest.

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