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Degradation kinetics and rheology of biodegradable polymers

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Rheological Analysis of Polymers/Special Chapter

Abstract Aliphatic polyesters are readily degradable polymers, hydrolysis being the dominant mechanism of degradation. On one side, this makes them extremely interesting for industrial applications in which degradability is required. On the other side, they present considerable processing problems due to their sensitivity to process and stocking conditions. In this work, the degradation of two aliphatic polyesters was studied in the molten state by analysing the rheological properties with the aim of defining the significance of previous thermal history and of residence time at a given temperature. Rheological measurements were adopted as a mean of analysis for degradation kinetics because rheological properties are strongly dependent on molecular weight. In particular, the change in complex viscosity (at constant frequency) as a function of time at different temperatures was measured. The experimental results show that a significant reduction of viscosity takes place during the isothermal tests for all the materials analyzed. This reduction was ascribed to the hydrolysis reaction. Indeed, a dried sample showed only a marginal viscosity reduction. After this initial decrease, an increase in viscosity (more pronounced at higher temperatures) was found for all the materials and at all the temperatures investigated. This phenomenon was ascribed to the inverse reaction (esterification) taking place in the absence of water. The dried sample showed, in fact, a much faster increase in viscosity with respect to the undried one. The degradation kinetics was modeled considering both forward and reverse reactions. The relative rate of the two reactions depends on the moisture content, and thus the water evaporation from the sample was kept into account in the rate equations.

Keywords Biodegradable polymers · Degradation kinetics · Complex viscosity · Time sweep tests · Hydrolysis · Esterification

Introduction

In the last decades, environmental pollution by synthetic polymers has reached dangerous proportions. As a result, attempts have been made to solve this problem by including degradability into everyday use polymer products. Aliphatic polyesters are biodegradable polymers susceptible to chemical hydrolysis. Their great advantage is degradability by simple hydrolysis of the ester backbone in aqueous environments [1].

Hydrolytic chain scission of ester linkage is also the fastest and the most effective degradation process which polyesters undergo during processing. Therefore, in the case of biodegradable polymers, the presence of weak hydrolysable bonds makes the material sensitive to moisture and heat [2], and thus their properties (especially mechanical and rheological) are extremely sensitive to stocking, processing, and use conditions [3].

It is obviously necessary, in order to exploit optimal material performances, to reach an understanding of material properties as a function of time and thermal history so that the materials can be successfully processed without damaging their characteristics.

The rheological properties of the melt are of great importance to facilitate effective processing. In recent years, many studies investigating the flow behavior of biodegradable polymers were conducted. On one side, in fact, it is of

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crucial importance to understand the rheological behavior of this class of polymers for optimizing processing conditions. On the other side, rheological measurements are a quite powerful mean of investigation for determining degradation kinetics, being viscosity strongly depending on molecular weight distribution. As an example of the use of rheological measurements to understand degradation, the work by Park et al. on PHB melts [4] put into evidence, the chemical changes of the melt caused by thermal degradation through a deviation of complex viscosity from shear viscosity, (not satisfying then the Cox and Merz rule). Palade et al. [5] studied the melt rheological properties of PLA sample and PLA additivated with tris(nonylphenyl)phosphite (TNPP), a stabilizing agent that takes action on hydrolytic and esteric exchange reaction. In this study, time sweep experiments (that is a test in which the viscosity is measured continuously during time) showed that PLA pure samples exhibit a decrease over time in the storage and loss modulus. TNPP additivated samples, on the other hand, showed an increase of G' and G'' during the same times of measure. This demonstrated that the melt stability of the pure polymer preclude long time measurements and unstabilized PLA materials loose molecular weight for long residence time at elevated temperatures. Similarly, the degradation of polyesters like PET and other polymers with high reactive linkages [5, 6] in the molten state has been reported to be dependent on temperature and moisture content. In particular, many authors observed a decrease in the molecular weight of PET sample, during processing from the melt, due to hydrolytic degradation (e.g., [5, 7, 8]), and an increase in molar mass heating polymer in dry state (e.g., [6, 7]).

The fact that rheological measurements are strongly dependent both on polymer structure and on molecular weight makes transient flow experiments a useful approach for determining the degradation kinetics of polymers [8–10]. Daly et al. [11], for instance, have demonstrated how a combined rheology/GPC study can be used to determine the degradation kinetics of a polymer, by measuring the change in complex viscosity (at a particular frequency) as a function of time.

Of course, one of the objective of the study of degradation in the molten state is gathering data to define a suitable modeling of the phenomenon. Modeling polymer degradation needs a kinetic scheme taking into account many processes occurring simultaneously: hydrolysis and condensation, water evaporation from the melt, thermal degradation. Kinetic models reported in the literature for random polymer degradation take into account only some of these processes [8, 11, 12].

In this work, the degradation of biodegradable aliphatic polyesters is studied in the molten state by analyzing the rheological properties with the aim of defining the significance of the previous thermal history and of the residence time at a given temperature. In particular, the degradation kinetics of two aliphatic polyesters are investigated using transient dynamic time sweep rheological tests.

The degradation kinetics modeling is approached taking into account hydrolysis and esterification reactions as well as thermal degradation and water evaporation occurring during the experiments.

Materials and methods

Two aliphatic polyesters having different chemical structure and molecular weight as reported in Figs. 1 and 2 and Table 1 were investigated in this work. The polymer L is a poly(ethylene dodecanedioate), the polymer H is a poly(tetramethylene dodecanedioate). The hydrolytic degradation in the solid state was studied by means infrared spectroscopy in a previous work [13].

Rheometry

The materials, in the form of small pellets having a characteristic dimension of less than 1 mm, were stored at ambient conditions (70% relative humidity, $T = 30$ °C) for at least 7 days.

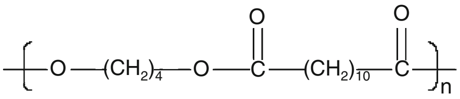
Time sweep experiments were performed with an Ares (Rheometric Inc.) rotational rheometer in a plate–plate configuration ($D = 25$ mm, gap $= 1$ mm) under nitrogen atmosphere. The nitrogen atmosphere was also kept during the heating stage from room temperature to test conditions. A constant strain (5%) and frequency (1 rad s^{-1}) were applied. All dynamic measurements were carried out within the linear response domain and within the Newtonian plateau for both materials. The evolution of viscosity with time was followed at 180, 160, and 140 °C for about 10 h.

A further time sweep test was conducted on the material coded as "H" at the temperature of 180 °C on a dried sample. In this case, the material was kept under vacuum at the temperature of 50 °C for 72 h.

The samples were subjected to dynamic oscillatory tests also during some composite thermal treatments as specified below:

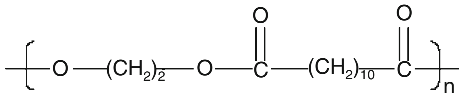
decreasing temperature ramp test (DTRT)

- a time sweep test at $T = 180$ °C;
- a cooling step from 180 to 160 °C, with a rate of about -20 °C $\min^{-1}$;
- a time sweep test at $T = 160°$;



$$\left[O - (CH_2)_4 - O - \overset{O}{\overset{\|}{C}} - (CH_2)_{10} - \overset{O}{\overset{\|}{C}} \right]_n$$

Fig. 1 Chemical structure of polyester H



$$\left[O-(CH_2)_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_{10}-\overset{\overset{\displaystyle O}{\|}}{C} \right]_n$$

Fig. 2 Chemical structure of polyester L

- a cooling step from 160 to 140 °C, with a rate of about −20 °C $\min^{-1}$;
- a time sweep test at $T = 140$ °C.

increasing temperature ramp test (ITRT)

- a time sweep test at $T = 140$ °C;
- a heating step from 140 to 160 °C, with a rate of about 20 °C $\min^{-1}$;
- a time sweep test at $T = 160°$;
- a heating step from 160 to 180 °C, with a rate of about 20 °C $\min^{-1}$;
- a time sweep test at $T = 180$ °C.

This ramp test was carried out only on the material coded as “H”

Thermogravimetry

Thermogravimetric tests were conducted on both materials. The tests were tailored to reproduce the procedure of sample preparation before the start of the rheological tests. In particular, a layer of pellets of about 10 g was placed on the balance in a nitrogen atmosphere and heated while recording the evolution of the mass. A thin thermocouple was placed close to the sample to measure the thermal history. After melting, namely at temperature higher than 100 °C, the bed of powder shaped in an about 1-mm thick plate. The sample was kept at high temperature until no changes in weight with time were detected, and thus the sample was assumed to be completely dry.

Experimental results

Thermogravimetry

From the mass loss monitored during thermogravimetric tests it was possible to measure the initial water content and thus the time evolution of water concentration, C_A. The initial water concentration was found to be about 450 mol m^{-3} for the material L and about 400 mol m^{-3} for the material H. The results of two thermogravimetric tests are reported in Fig. 3. Both temperature and water concentration histories are reported.

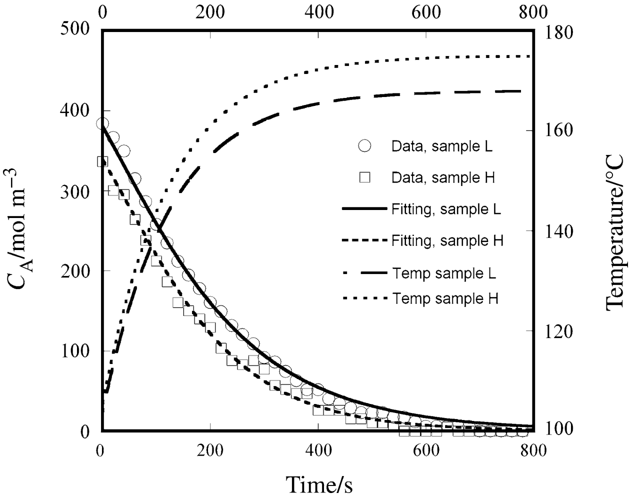


Fig. 3 Results of thermogravimetric tests for samples H and L. The *fitting lines* represent the results of Eqs. 1 and 3 with the parameters reported in Table 2

Rheometry

In Figs. 4 and 5, the effect of residence time at each temperature (140, 160, and 180 °C) was analyzed for materials coded as H and L, respectively. For all temperatures and both materials, complex viscosity decreases with time until a minimum is reached. This minimum occurs at shorter times the higher the temperature is. The initial decrease is quite significant: at 180 °C, the viscosity values reduce to about 90 and 70% of the initial value for the material coded as H and L, respectively. The viscosity decrease is normally attributed to a reduction of the molecular weight of the sample, due to hydrolytic degradation [8].

At longer times, a rise in viscosity is observed at all investigated temperatures and it is more pronounced the higher the temperature is. Again, the increase is much more

Table 1 Properties of the polyesters adopted in this work [13]

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	M_z/g mol^{-1}	M_w/M_n	M_z/M_w	T_m^a/°C	T_g^b/°C	X_c^c	ρ^d/kg m^{-3}
H	20,000	45,000	90,000	2.3	2.0	66	−23	60	1,110
L	21,000	64,000	162,000	3.1	2.5	65	−20	58	1,120

[a] Peak value of DSC thermogram at 10 °C $\min^{-1}$

[b] From DSC thermogram at 10 °C $\min^{-1}$

[c] From X-ray diffraction of compression molded films

[d] Measured in density gradient columns at 25 °C

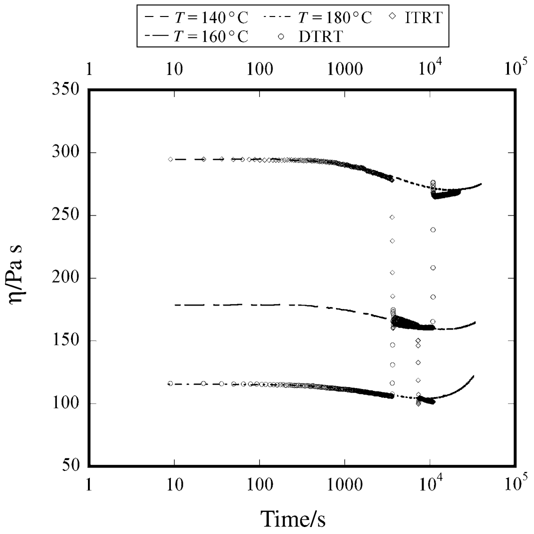


Fig. 4 Effect of residence time on viscosity at each temperature (140, 160, and 180 °C) and ramp tests for sample H

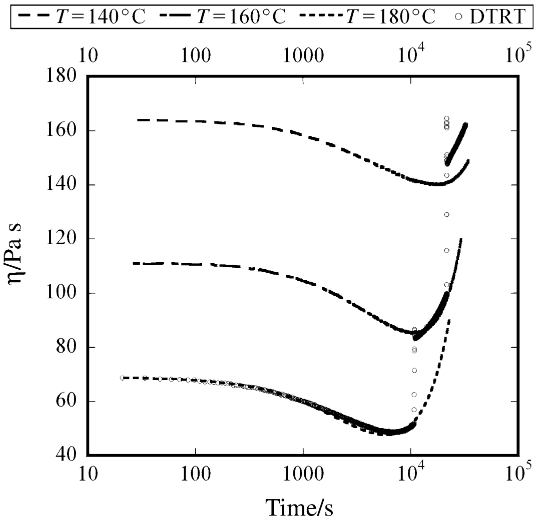


Fig. 5 Effect of residence time on viscosity at each temperature (140, 160, and 180 °C) and ramp test for sample L

noticeable for the material coded as L. This phenomenon can be ascribed to the inverse reaction (esterification).

The results of temperature ramp tests are also reported in Figs. 4 and 5. The TRT tests (both in increasing and in decreasing temperature modes) almost perfectly superpose to the standard isothermal tests during the first temperature step, ensuring a high reproducibility of the tests. Regarding the DTRT, the time derivatives of the viscosity curve at 160 and 140 °C are larger than those relative to the corresponding isothermal tests at the same time, indicating that the phenomena occurring at these two temperatures are somehow anticipated because of the permanence at higher temperatures.

The opposite happens for the ITRT: the time derivatives of the viscosity curve at 160 and 180 °C are smaller (negative, and larger in absolute values) than those relative to the corresponding isothermal tests at the same time. Coherently with the DTRT results, it seems that the phenomena occurring at these two temperatures are somehow delayed because of the permanence at lower temperatures.

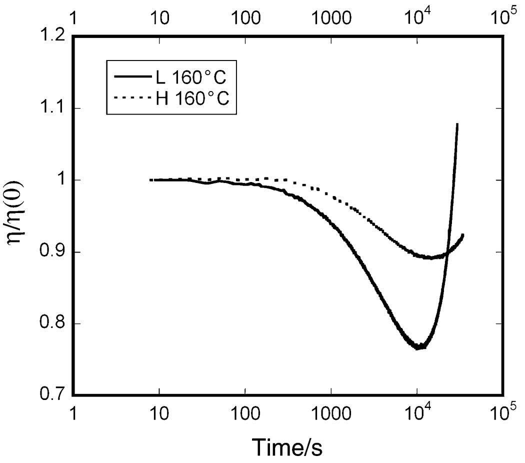


Fig. 6 Comparison between the time evolution of normalized viscosity for the L and H samples at 160 °C

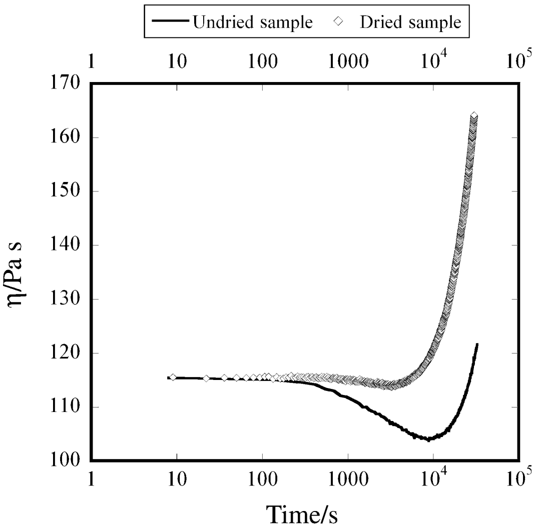


Fig. 7 Comparison between the time evolution of viscosity between the dried and the undried H sample at 180 °C

In Fig. 6, a direct comparison is reported between the time evolution of the viscosities for the L and H samples at the same temperature ($T = 160$ °C). The values reported are normalized respect to the values of viscosity measured at very short times. The curve obtained analyzing the material L shows a more pronounced decrease with respect to the one obtained analyzing the H sample. At longer times, a rise in viscosity is observed for both samples but the viscosity rise of the sample L is much steeper with respect to the one of the H sample. Similar trends are found at all the temperatures investigated in this work.

The comparison between the time evolution of viscosity between the dried and the undried H sample at 180 °C is reported in Fig. 7. The initial viscosity is the same for both the samples. The dried sample, however, shows just a very weak decrease in viscosity before a dramatic increase which takes place much earlier than what occurs for the undried sample. This confirms the fact that the water content is extremely relevant in determining the rate of the reactions occurring inside the sample.

Analysis

Thermogravimetry

The time evolution of water concentration inside the sample during thermogravimetric tests was modeled assuming a lumped parameter analysis. In particular, considering that the external concentration of water was negligible (due to the presence of nitrogen), it was assumed that

$$\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}t} = -K_\mathrm{E} C_\mathrm{A} \tag{1}$$

where C_A is the water concentration inside the sample and K_E is a coefficient whose expression is

$$K_\mathrm{E} = \frac{K_\mathrm{c} K}{L_\mathrm{c}} \tag{2}$$

in which K_c is the external mass transfer coefficient, K is the equilibrium partition coefficient, and L_c is a characteristic length (namely the volume/surface ratio).

The *evaporation* coefficient K_E was assumed to change with temperature according to the following Arrhenius type dependence:

$$K_\mathrm{E} = \alpha_\mathrm{E} \exp\left(-\frac{\beta_\mathrm{E}}{T}\right) \tag{3}$$

The parameters α_E and β_E were found by a best fitting analysis on the thermogravimetric data reported in Fig. 3. The results of the fitting procedure are reported in Fig. 3, and the values of the coefficient are reported in Table 2.

Modeling viscosity changes

The zero-shear rate viscosity of a polymer can be related to the molecular mass of the polymer by the following equation

Table 2 Parameters found for the temperature evolution of the evaporation coefficient K_E

	Material H	Material L
$\alpha_\mathrm{E}/\mathrm{s}^{-1}$	1.2×10^{-2}	3.4×10^{-3}
$\beta_\mathrm{E}/\mathrm{K}$	1,947	1,501

$$\eta = cz^\mathrm{a} (M_n)^\mathrm{a} \tag{4}$$

in which z is the polydispersity ($M_\mathrm{w}/M_\mathrm{n}$), a is an exponent whose value is generally accepted to be 3.4 (this value will be kept in the following) and c is a parameter depending on temperature. A discussion on the origin of Eq. 4 and on the meaning of its parameters can be found in [14]. In this work, it will be assumed that the polydispersity does not change during degradation.

The carboxylic end-groups concentration, C_C, and the ester concentration, C_E, can be related to the molecular mass as follows [15]:

$$C_\mathrm{c} = \frac{\rho}{M_n} \tag{5}$$

$$C_\mathrm{E} = \frac{\rho}{M_n}(2DP - 1). \tag{6}$$

In these equations, ρ is the density of the polymer sample and DP is the average degree of polymerization, defined as the ratio M_n/M (M is the molecular mass of the repeating unit). Equation 6 takes into account the number of ester linkages in the monomer unit in the case of the polyesters studied in this work.

The reaction taking place inside the samples can be written as

$$\mathrm{H_2O} + \mathrm{ester} \underset{R_\mathrm{r}}{\overset{R_\mathrm{f}}{\rightleftarrows}} -\mathrm{COOH} + -\mathrm{OH}. \tag{7}$$

The forward reaction is the hydrolysis, whose rate can be expressed as $R_\mathrm{f} C_\mathrm{E} C_\mathrm{A}$ and the reverse reaction is the esterification. The simplest possible expression for esterification rate is $R_\mathrm{r} C_\mathrm{C}^2$ [7].

The rate of change of ester concentration can be thus written as

$$\frac{\mathrm{d}}{\mathrm{d}t} C_\mathrm{E} = -R_\mathrm{f} C_\mathrm{E} C_\mathrm{A} + R_\mathrm{r} C_\mathrm{c}^2 - R_\mathrm{t} C_\mathrm{E}, \tag{8}$$

in which the last term keeps into account the thermal breakdown reaction (thermal degradation) which can be assumed to be a first-order reaction [8].

Similarly, the rate of change of water concentration can be written as

$$\frac{\mathrm{d}}{\mathrm{d}t} C_\mathrm{A} = -R_\mathrm{f} C_\mathrm{E} C_\mathrm{A} + R_\mathrm{r} C_\mathrm{c}^2 - K'_\mathrm{E} C_\mathrm{A} \tag{9}$$

in which the last term keeps into account the water loss through the sample surface. Concerning this term, similarly to the analysis of thermogravimetric tests, a lumped parameter analysis is assumed and the water concentration in the atmosphere surrounding the sample was considered negligible due to the presence of the purge gas.

All the reaction constants appearing in Eqs. 8 and 9 were assumed to depend on temperature according to the Arrhenius equation:

$$R_i = \alpha_i \exp\left(-\frac{\beta_i}{T}\right) \tag{10}$$

where the subscript i identifies the reaction (f for forward, r for reverse ad t for thermal reaction, respectively).

The *evaporation* coefficient K_E' was assumed to be equal to the analogous coefficient measured by thermogravimetry, multiplied by a factor which keeps into account the different geometrical configuration and the different characteristic length

$$K_E' = \delta K_E. \tag{11}$$

At each temperature, starting from the initial values of C_A, C_E, and C_C, the evolution of the concentrations can be found by simultaneously solving Eqs. 5, 8, and 9. The values of molecular weight at each time can be found by Eq. 6 and finally the time evolution of viscosity can be calculated by Eq. 4. According to the model depicted above, the water evaporation from the sample is the cause of the occurrence of a minimum in viscosity (that is in molecular weight). It is in fact easy to understand that without a loss of water from the sample, the viscosity described by the model would follow a monotonic evolution until a plateau is reached.

Model parameters and description of viscosity changes

In order to describe viscosity evolution by the model described above, a series of parameters must be identified. In the following, the choices made to define each of them are described.

The parameter c in Eq. 4 for each material and at each temperature was found by substituting the experimental value of viscosity and molecular weight at the time at which rheological test starts (*initial time*).

The initial values of C_E and C_C were found by Eqs. 5 and 6, starting from the knowledge of molecular weight distribution.

The initial water concentration at each temperature is obviously unknown. It was estimated by solving Eq. 1 with the parameters found by thermogravimetric tests and the thermal history measured during the heating stage. It took about 10 min to reach the test temperature, after which the upper plate was lowered, the gap adjusted and the test started. The values found for the initial water content at each temperature are reported in Table 3.

Seven parameters remain to be identified, namely the two constants of Arrhenius equation describing each of the three reaction constants (Eq. 10) and the parameter δ appearing in Eq. 11. As a first step, the thermal degradation was neglected and thus five parameters remained unknown.

A best fitting procedure was performed to identify the five parameters for each of the two materials by minimization of the quadratic error between the evolution of viscosity with time at each temperature and the model predictions. The parameter δ was constrained to be the same for both the materials. Only the time sweep tests at constant temperatures for the undried materials were used to tune the model parameters. The values of parameters identified are listed in Table 4 and the obtained description of viscosity changes at each temperature is reported in Fig. 8 for the material coded as “H” and in Fig. 9 for the material coded as “L”. The whole set of data is satisfactorily described. The model description of viscosity evolution is reported in Figs. 8 and 9 for a time longer than experimental measurements, to give an idea of the future evolution of the viscosity. It should however be pointed out that the hypothesis of constant polydispersity could be not verified for large conversions. This could

Table 3 Estimated values for the initial water content at each temperature

T/°C	H C_{A0}/mol m^{-3}	L C_{A0}/mol m^{-3}
140	89	101
160	67	82
180	49	66

Table 4 Values of parameters identified in this work

	H	L
α_f/m^{3}mol^{-1} s^{-1}	0.095	134.2
β_f/K	7997.6	10732.0
α_r/m^{3}mol^{-1} s^{-1}	3.45	8525.6
β_r/K	8134.2	10694.5
δ	0.02	

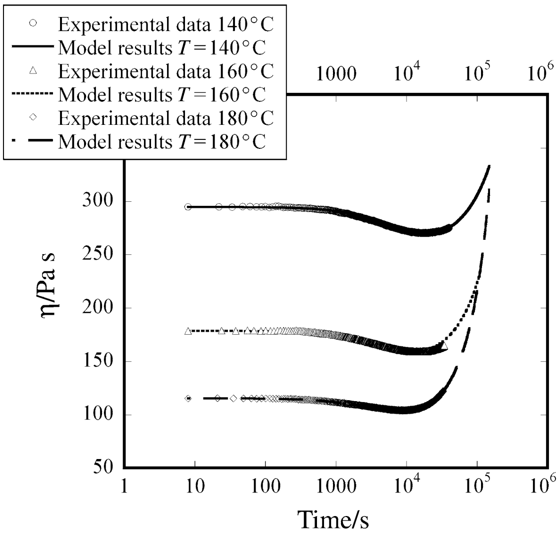


Fig. 8 Comparison between experimental data and model results of viscosity change for sample H

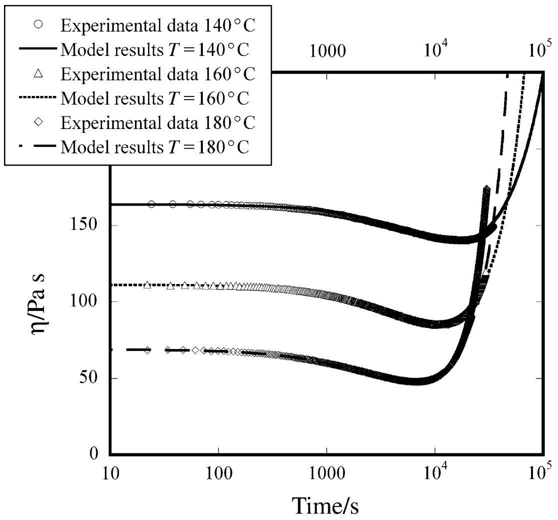


Fig. 9 Comparison between experimental data and model results of viscosity change for sample L

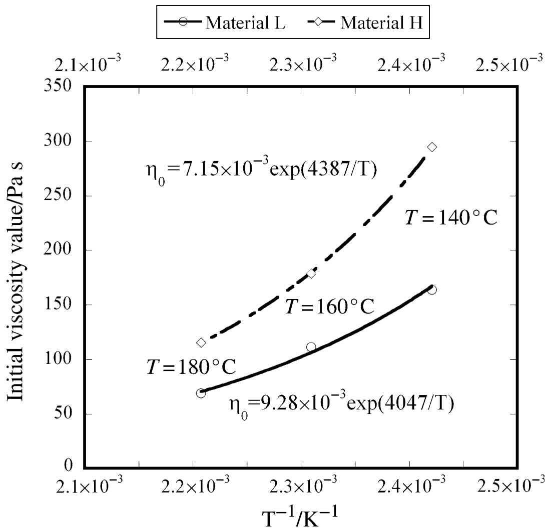


Fig. 10 Initial values of viscosity for samples H and L

be the reason why the test at 180 °C for the sample coded as L is not perfect described at very long times, namely when the changes in molecular weight are larger than about 10%.

Validation of the model: description of ramp tests

In order to check the predictive capabilities of the model depicted above, the ramp tests carried out on both materials were simulated by adopting the values of the parameters found previously. The experimental thermal history was considered for the simulation.

Since in the case of TRT it is necessary to describe the viscosity change with temperature, the parameter c in Eq. 4 was assumed to depend on the temperature, according to an Arrhenius equation whose constants were found by best fitting the initial values of viscosity, as shown in Fig. 10.

The initial water content (at 180 °C for DTRT and at 140 °C for ITRT) was taken from Table 3. Experimental data collected during ramp tests and simulation results are reported in Fig. 11 (sample H—DTRT and ITRT) and 12 (sample L—DTRT).

The description of viscosity changes is satisfactory for both materials. In particular, for the material coded as H, the viscosity is correctly described at all temperatures. As far as the material coded as L is concerned, the viscosity at 140 °C is slightly overestimated. This is due to the fact that the initial values of viscosity for this material are not perfectly described by an Arrhenius equation, as it can be noticed from Fig. 10. In spite of this, the slopes of the curve are well reproduced at all temperatures, confirming the validity of the model. It is worth mentioning that there was no need to include the thermal degradation term inside the model.

The values found for the forward and reverse kinetic constants are reported in Fig. 13 for both the materials. It can be noticed that the material coded as L presents higher values of both kinetic constants; in particular, the hydrolysis was about three times faster for the material L than for the material H. It is worth mentioning that a characterization of degradation rate carried out on both materials in the solid state showed the same ratio found in this work.

Validation of the model: description of time sweep test for dried sample

An attempt was made to describe the time evolution of viscosity for the dried sample at 180 °C by changing the value initial water content, only. Indeed, it was expected that the effect of the drying step was just to lower the water content of the sample with respect of the undried one.

The attempt was quite frustrating, as reported in Fig. 14, it was not possible to obtain a satisfactory description of the test, since the predicted increase of viscosity is slower than what shown by experimental data. Indeed, even trying to change all the model parameters, it was not possible to obtain a set of values which allowed a satisfactory description of the time evolution of the viscosity for dried and undried sample at 180 °C assuming that the only difference between the two samples was the initial water content only. It was therefore assumed that between the undried and dried samples there could be a further difference than just the initial water content. Indeed, as reported in Fig. 14, the time sweep test of undried sample could be perfectly simulated by keeping the same parameters reported in Table 4 and changing only the exponent *a* describing the effect of molecular weight on viscosity in

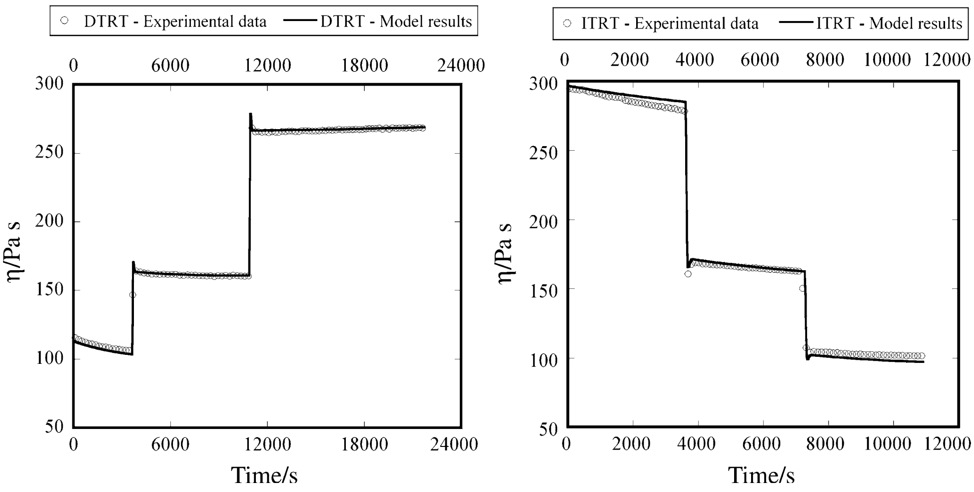


Fig. 11 Experimental data collected during ramp tests and simulation results for sample H (DTRT and ITRT)

Eq. 4 from 3.4 (value assumed for all the other tests) to 6 (for the dried sample only). The initial water content which allowed the description reported in Fig. 14 was 15 mol m^{-3}. Obviously, this would mean that the drying step (72 h under vacuum at 50 °C) influences not only the initial water content of the sample, but induces some further change inside the sample. Similar findings were reported in the literature with reference to Nylons [6]: the molecular weight exponent of the melt viscosity was found in that work to be increased to about 5 only for previously dried samples. This phenomenon deserves a further investigation since our data do not allow to draw any deeper conclusion about the reason of such difference in behavior.

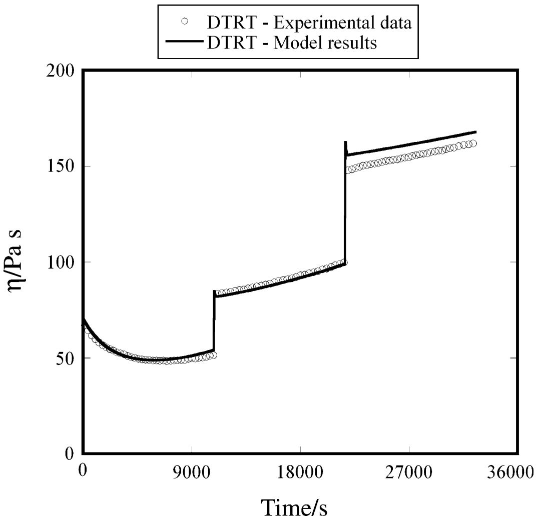


Fig. 12 Experimental data collected during ramp tests and simulation results for sample L (DTRT)

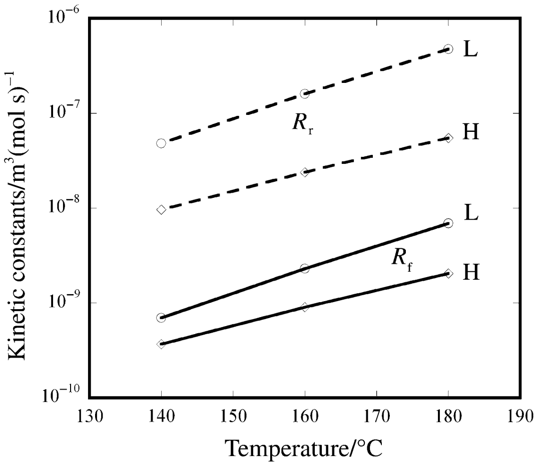


Fig. 13 Values found for the forward and reverse kinetic constants for both materials

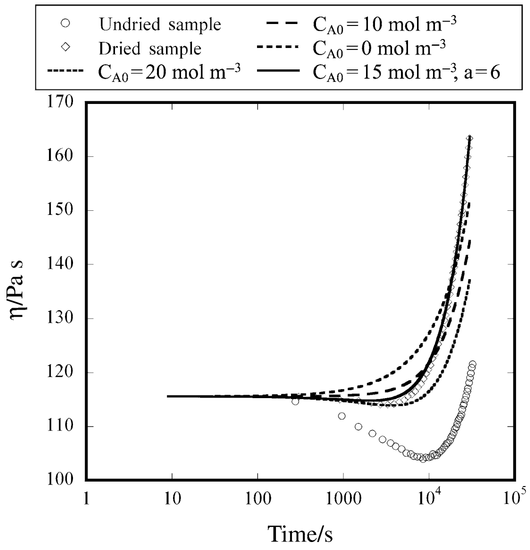


Fig. 14 Comparison between experimental data and model results of viscosity change for dried sample H at 180 °C

Conclusions

In this work, the degradation of two aliphatic polyesters was studied in the molten state by analysing the viscosity evolution during transient dynamic time sweep rheological tests.

The experimental results show that a significant reduction of viscosity takes place during the tests for both the materials analyzed. This reduction was ascribed to the hydrolysis reaction. After this initial decrease, an increase in viscosity (more pronounced at higher temperatures) was found for all the materials and at all the temperatures investigated. This phenomenon was ascribed to the inverse reaction (esterification) taking place in absence of water. A dried sample showed only a marginal initial decrease of viscosity and a subsequent sudden increase.

The degradation kinetics was modeled taking into account both direct and inverse reactions (hydrolysis and esterification). The relative rate of the two reactions depends on the moisture content. The water evaporation from the sample was kept into account in the rate equations.

The suggested model satisfactorily describes the viscosity change as a function of time for all the materials and thermal histories investigated. Only the dried sample could not be described by keeping the same model parameters and considering only the different initial water content. It was necessary to change also the exponent describing the dependence of viscosity on molecular weight to a much larger value for the dried sample.

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