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Mechanism and kinetics of transesterification in poly(ethylene terephthalate) and poly(ethylene 2,6-naphthalene dicarboxylate) polymer blends

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Abstract

In a previous work [L. Alexandrova, A. Cabrera, M.A. Hernández, M.J. Cruz, M.J.M. Abadie, O. Manero, D. Likhatchev, Polymer 43 (2002) 5397. [1]], a model compounds study on the kinetics of a transesterification reaction in poly(ethylene terphthalate)–poly(ethylene naphthalene 2,6-dicarboxylate), PET–PEN blends, resulting from melt processing, was simulated using model compounds of ethylene dibenzoate (BEB) and ethylene dinaphthoate (NEN). A first-order kinetics was established under pseudo first-order conditions for both reactants, and thus the overall transesterification reaction was second-order reversible. Direct ester–ester exchange was deduced as a prevailing mechanism for the transesterification reaction under the conditions studied.

In this work, the actual PET–PEN system was melt processed by mixing the polymers below the critical reaction temperature in a twin-screw extruder. Thereafter, the reaction was induced by temperature in open glass ampoules. A second order reversible kinetics was measured, in agreement with the kinetics established in the previous model compounds study. The equilibrium constant value corresponds to a forward rate constant which is four times larger than the reverse rate constant. The activation thermodynamic parameters confirmed the direct ester–ester exchange mechanism for the reaction.

Keywords: PET/PEN blends; Transesterification; Kinetics

1. Introduction

Induced compatibility in polyester blends (i.e. PET, PEN) can be achieved by the production of copolymers resulting from intermolecular exchange reactions among the ingredients of the blend. The resulting copolymer initially has a block structure but further transesterification leads to its randomization. The amount of copolymer produced, or transesterification degree, was found to control phase behaviour, optical and mechanical properties of PET/PEN blends, including crystallization degree, solubility, glass transition temperature, and others [2–5].

The kinetics of the transesterification reaction has been given attention by several authors [6–9]. The mechanism of this reaction included direct ester–ester exchange described as a second order reversible reaction. The method of Devaux et al. [6,7] has shown that owing to the presence of random copolymers at equilibrium, the equilibrium constant has a value of one, implying that the rate constants for the forward and reverse reactions are equal. This method has been used widely to model kinetic data of transesterification in polyesters like PEN/PET as a second order reversible reaction with equilibrium constant equal to one [6–11]. The equality of the forward and reverse kinetic rate constants presumes that the reaction of equimolar amounts of the reactants would lead to the equal concentrations of molar fractions of the species when transesterification reaction reaches its equilibrium.

The model compound study on the transesterification of PEN/PET blends using ethylene dibenzoate and ethylene dinaphthoate [1] confirmed that the overall reaction kinetics can be modelled as a second order reversible reaction and the primarily mechanism of transesterification is the direct

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ester–ester exchange. The reaction order was determined with respect to each reagent under pseudo first-order conditions. However, the rate of the forward reaction was four times higher due to the recombination of half the product molecules in the reverse reaction. The kinetics was described using the effective half concentration of the product. This leads to an equilibrium constant of four, implying that the rate constant in the forward reaction is four times that in the reverse reaction.

The apparent disagreement in the value of the rate constants in the case of the PET/PEN blends can be resolved by comparison of equilibrium data which in most cases is not available. In this work, such data is presented for the PEN/PET blends, to confirm whether or not data supports the equality of the rate constants of the transesterification reactions in these polyester blends. Taking as reference the model compounds study, in this work PET and PEN were melt extruded in a twin-screw extruder to provide adequate mixing of the ingredients. The blend was then milled and placed in ampoules. The reaction was induced by temperature and equilibrium data was recorded. Two cases were examined: an equimolar mixture of PEN and PET, and a mixture corresponding to pseudo first order conditions using 10-fold excess of one of the reactants. This provides with the reaction orders respect to each of the reactants to verify the overall order of transesterification in the polymer blend.

2. Experimental section

2.1. Materials

Poly(ethylene terephthalate) with intrinsic viscosity of 0.79 dl/g was supplied by Celanese and poly(ethylene naphthalene 2,6-dicarboxylate) with intrinsic viscosity of 0.51 dl/g was supplied by Eastman Chemical. They were used without previous treatment.

2.2. Procedure

Kinetic measurements were performed under isothermal heating at 300 and 320 °C of an equimolar mixture of PET and PEN, without adding catalyst. However, it is known that in industry samples there is residual catalyst left in the polymerization reaction, which may have an effect upon the kinetics and activation enthalpy. This aspect is given attention later. The reaction order regarding each reactant was determined using physical blends of the same polymers in a 10:1 ratio, with excess of either PET or PEN at 300 °C.

The PET and PEN polymers were previously dried in a Cole–Palmer vacuum oven at 120 °C with −45 mm Hg pressure during 10 h. Blending of the polymers was carried out in a Haake Rheocord 90 TW-100 twin-screw conical counter-rotating extruder of 331 mm length, with temperature profile of 230, 240 and 250 °C and screw speed of 30 RPM. Although the melting temperatures of PET and PEN are 239.5 and 258.4 °C, respectively, thermomechanical work and viscous dissipation rise the blend temperature above the melting points with the temperature profile considered. The resulting mixture was milled and placed in open glass ampoules, 2 g each. Sets of eight samples were immersed into a thermostated silicon oil bath at 300 and 320 °C during defined time intervals. Thereafter, samples were cooled to room temperature. Solids obtained were dissolved in a 70/30 vol. $CDCl_3$ and CF_3COOD solvent mixture for ^1H NMR analyses. NMR spectra were obtained in a Brucker Advance 400 spectrometer.

3. Results and discussion

The transesterification reaction in PET/PEN blend can be represented by the general equation:

$$\mathrm{TET} + \mathrm{NEN} \underset{k'}{\overset{k}{\rightleftharpoons}} 2\mathrm{TEN} \tag{1}$$

where TET, NEN and TEN represent terephthalate–ethylene glycol–terephthalate, naphthalene–ethylene glycol–naphthalene and terephthalate–ethylene glycol–naphthalene units, respectively.

The transesterification kinetics was followed by measuring the integral intensities of the aliphatic proton signals for TET, NEN and TEN. Fig. 1 shows the bands corresponding to aliphatic protons at different stages of the transesterification reaction. No additional spectral changes were observed during the process, which may correspond to degradation products such as hydroxyl, carboxyl, or any other functional groups. This allows to conclude that transesterification was the sole reaction taking place under the working conditions.

The transesterification reactions at two temperatures approach equilibrium around 120–150 min at 300 °C and 80–100 min at 320 °C (Fig. 2(A) and (B)). Concentrations of TET, TEN and NEN at equilibrium reached almost equal ratio between reactants and reaction products of roughly 0.27:0.5:0.25, respectively. The equilibrium constant for the reaction (Eq. (1)) can be expressed as:

$$K = \frac{k}{k'} = \frac{[\mathrm{TEN_e}]^2}{[\mathrm{TET_e}][\mathrm{NEN_e}]} \tag{2}$$

where $[\mathrm{TET_e}]$ and $[\mathrm{NEN_e}]$ are concentrations of the reactants and $[\mathrm{TEN_e}]$ the reaction product at equilibrium. The asymptotic curves in Fig. 2(A) and (B) render the following values of the equilibrium concentrations: $[\mathrm{TEN_e}]=0.5$, $[\mathrm{TET_e}]=0.25$–0.27, $[\mathrm{NEN_e}]=0.25$.

From Eq. (2), values of the equilibrium constant lie in the range 3.8–4.0, which means that

$$k = 4k' \tag{3}$$

Since the equilibrium constant is fairly independent of temperature indicates that there is no change in enthalpy in the transesterification reaction Eq. (1). The release of

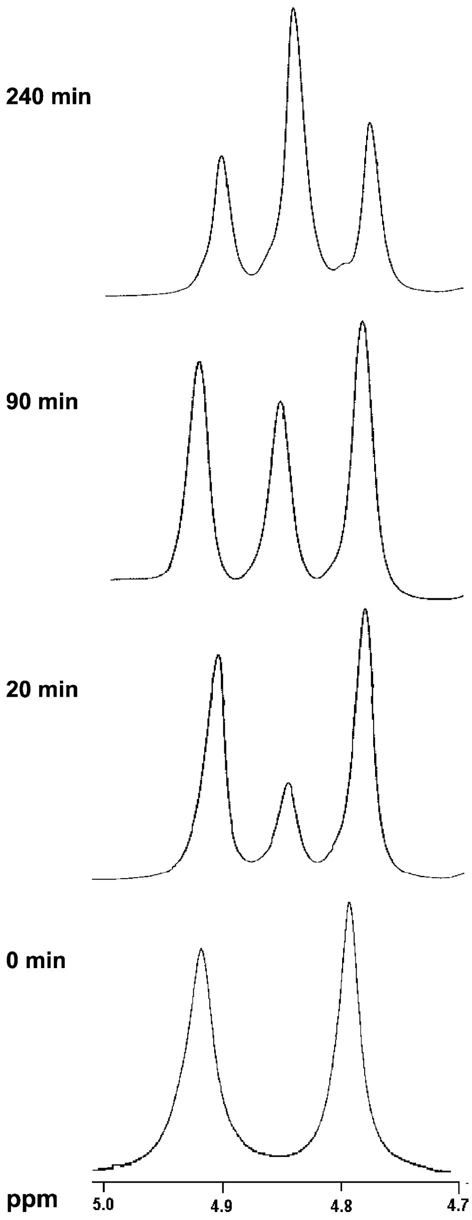

Fig. 1. Proton NMR spectra of the TET/NEN blend at different stages of the transesterification reaction.

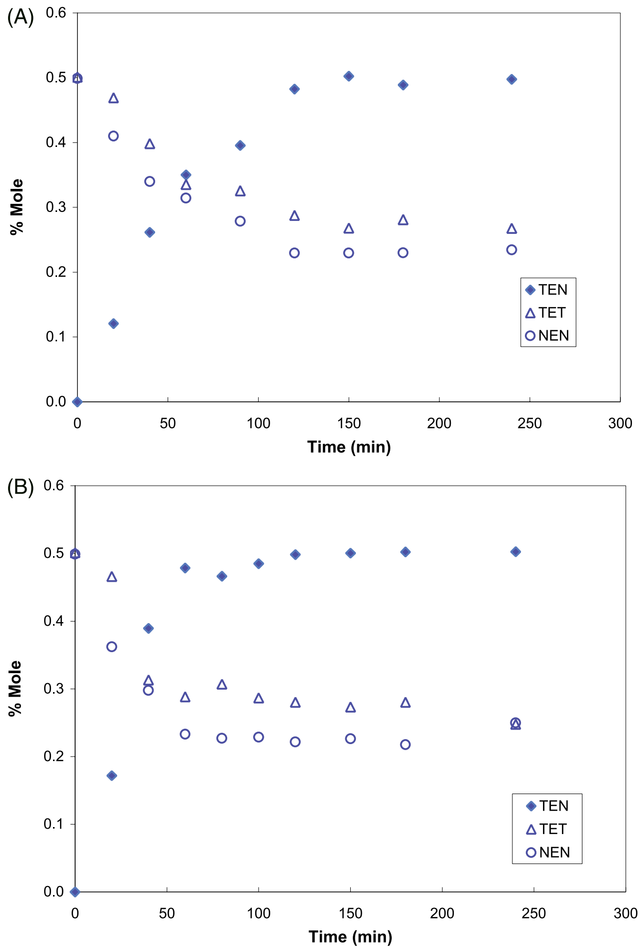

Fig. 2. Kinetics of reagents consumption and products formation. (A) At 300 °C, (B) at 320 °C.

entropy (ΔS_0) in the reaction can be calculated from the following well known thermodynamic relations:

$$\Delta G_0 = -RT \ln K = \Delta H_0 - T\Delta S_0 \tag{4}$$

where G_0 is the free energy. Table 1 shows the values of the equilibrium constants and the entropy release involved in the reaction. This slight change in entropy drives the reaction and reflects the composition of products with more disordered mixed sequences of TEN. These results are in agreement with those of the model compounds study [1].

The reaction orders regarding each one of the reactants were determined to verify the overall order of transesterification reaction, established in the model compound study. The reaction was carried out at 300 °C under pseudo first order conditions, using a 10-fold excess of either PET or PEN. Kinetics was followed by the limiting reactant disappearance, as well as the formation of the product TEN. Kinetic data obtained were treated in terms of first order kinetics, according to the following equation:

Table 1
Equilibrium and rate constants. Thermodynamic and activation parameters

T (°C)	K	ΔH° (kcal/mol) ΔS° (cal/kmol)	$k\times10^2$ (min^{-1})	E_a (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol) $\Delta S^{\neq}$ (cal/kmol)
300	3.8161	$\Delta H^\circ\approx0$	2.29	18.23	$\Delta H^{\neq}=17.07$
320	4	$\Delta S^\circ\approx2.7$	3.93		$\Delta S^{\neq}=-45.61$

$$\ln\frac{[\mathrm{NEN}]_0}{[\mathrm{NEN}]} = kt \tag{5}$$

The linearity of the concentrations ratio versus time shown in Fig. 3 for the PET/PEN blend with 10:1 mole ratio indicates that transesterification reaction in PET/PEN system is first order regarding one of the reagents. Same result is obtained in the case where PEN is in excess. Thus it should be concluded that the overall order of the reaction (Eq. (1)) is second order. The value obtained for the rate constant is $1.29\times10^{-2}\,\mathrm{min}^{-1}$.

As was pointed out in the model compounds study, in the case of the PEN/PET blend, effective collisions of the reactants lead to the formation of two mixed sequences TEN (or NET), respectively. However, the reverse reaction is only half as effective, because 50% of the collisions TEN+TEN would result in the recombination of the parts of these molecules without formation of the initial reactants [9]. Thus, kinetics of the transesterification reaction (Eq. (1)) should be described using only half concentration of TEN, which would be effective in the reverse reaction. The rate equation can then be written as follows:

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{TET}] = \frac{1}{2}\frac{\mathrm{d}[\mathrm{TEN}]}{\mathrm{d}t}$$
$$= k[\mathrm{TET}][\mathrm{NEN}] - k'[\mathrm{TEN}]^2 \tag{6}$$

where [TET], [NEN] and [TEN] are concentrations of TET, NEN and TEN at time t.

In terms of the molar fractions a, b and c for TET, NEN and TEN, respectively, and x for $c/2$ (or $2x$ for c), their current values at time t can be expressed according to

$$a = a_0 - x \tag{7}$$

$$b = b_0 - x$$

$$c = 2x$$

where a_0, b_0 are the molar fractions of the reactants at time $t=0$. Eq. (6) becomes:

$$-\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t} = kab - k'c^2 \tag{8}$$

or

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a_0 - x)(b_0 - x) - k'(2x)^2 \tag{9}$$

Since $k=4k'$ (Eq. (3)) and knowing that $a_0+b_0=1$, Eq. (9) becomes:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a_0b_0 - x) \tag{10}$$

at equilibrium we have:

$$x_e = a_0b_0 \tag{11}$$

At time $t=0$, the molar fractions of the reactants are equal ($a_0=b_0=0.5$). Then, Eq. (11) shows that $x_e=0.25$, and therefore, from Eq. (7):

$$a_e = 0.25 \tag{12}$$

$$b_e = 0.25$$

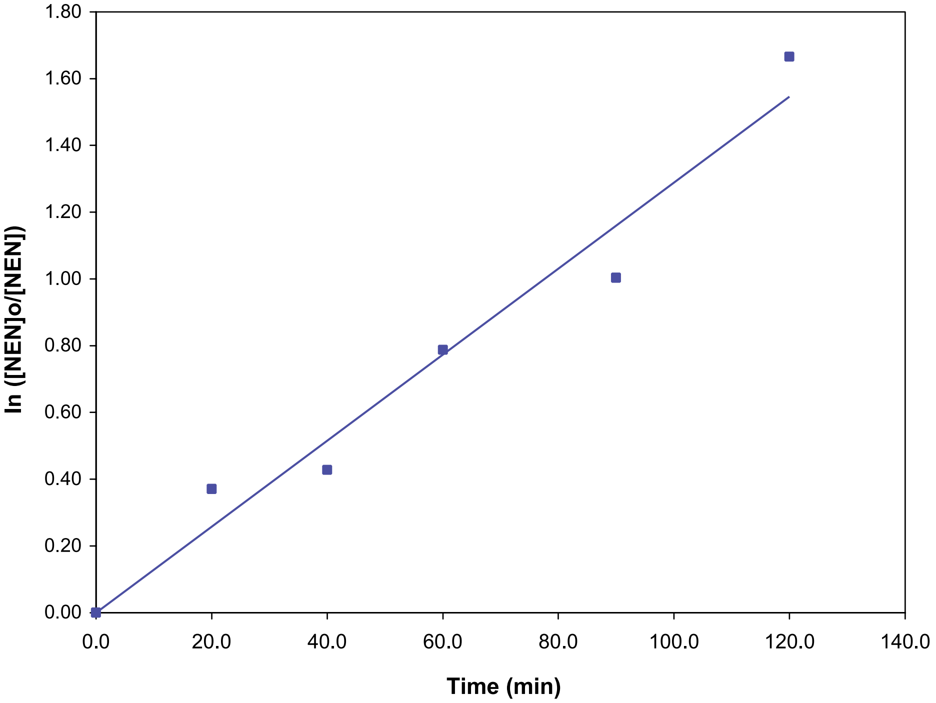

Fig. 3. Transesterification kinetics for the PET/PEN blend 10:1 mol.

$c_e = 0.5$

These equilibrium concentrations are in agreement with the kinetic data shown in Fig. 2(A) and (B). Integration of Eq. (9) gives:

$$\ln\left(\frac{b_0}{b_0 - x/a_0}\right) = kt \tag{13}$$

or the equivalent form used in the model compounds study:

$$\frac{1}{2a_0}\ln\frac{a_0}{a_0 - 2x} = kt \tag{14}$$

Eqs. (13) and (14) are equal, provided that $a_0 = b_0 = 0.5$.

Eq. (13) (or (14)) is used to process the kinetic data for the transesterification reaction carried out at the two temperatures. The linearity of the corresponding plot (Fig. 4) confirms that transesterification process is second order. The rate constants for each temperature were determined from the kinetic plots. Fig. 4 shows the kinetic curves of the transesterification reaction for PET/PEN blend 1:1 M. It should be noted that the scatter of experimental points is normally higher for the polymers than it was observed in the model compounds study.

The temperature dependence of the rate constants provided the activation energy according to the Arrhenius equation:

$$\ln k = \ln A - \frac{Ea}{RT} \tag{15}$$

Furthermore, the activation enthalpy and entropy ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) can be calculated according to the following relations:

$$\Delta G^{\neq} = RT(\ln k_B/h - \ln k/T) = \Delta H^{\neq} - T\Delta S^{\neq} \tag{16}$$

$$\Delta H^{\neq} = E_a - RT \tag{17}$$

where k_B and h are the Boltzmann and Planck constants, respectively.

Results of this analysis are listed in Table 1. The kinetic constants show values higher than those of Ref. [1], although in the latter the range of temperature is 220–250 °C, while in this work is 300–320 °C. Therefore, comparison of the rate constants with those of the model compound study is not straightforward because the transesterification reaction in polymers occurs at higher temperatures, in partly due to the additional steric hindrance in the polymers. However, comparison with data from blends prepared by melt extrusion [10,11] shows values that are between one to two times those reported in Table 1, which is logical if one considers the difference in the reaction procedures. In this case, previous intensive mixing in a twin-screw extruder followed by temperature-induced reaction outside the extruder is different to reaction induced in situ with simultaneous mixing in the extruder.

The activation enthalpy value of 17 kcal/mol is about half that reported in the model compounds study [1] and in Ref. [11], and it is closer to that reported by Stewart et al. [3] of 27.5 kcal/mol. Although this value was obtained from the data at two temperatures, and errors in the regression curve may be big, however it is noteworthy that this value is very similar to that obtained with model compounds in the

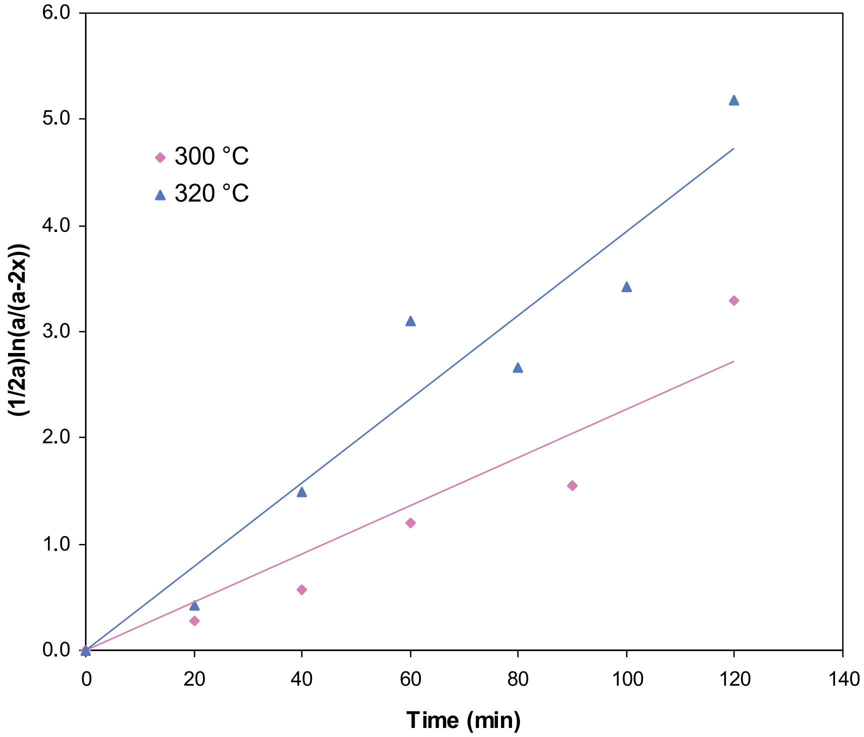

Fig. 4. Transesterification kinetics for the PET/PEN blend 1:1 mol.

presence of a catalyst (around 20 kcal/mol). The possibility of catalyst traces in the industry samples employed here may account for the similarity with the low value obtained for the model compounds in the presence of catalyst. Anyway, this value of the activation enthalpy is not much smaller than that reported by other authors [6], and reflects the fact that the reaction has been facilitated by the previous intensive mixing in the extruder. This result also suggests that the direct ester–ester exchange, in which the bond breaking is the dominant step in the transition state. As was pointed out in Ref. [1], the acyl-oxygen fission mechanism is very likely for the cleavage of the ester C–O bonds.

The value of the activation enthalpy obtained here leads to a quite negative value of the activation entropy (−45.6 cal/K mol) as is readily expected for a true second order reaction. Furthermore, this large negative value is again consistent with the assumed ester–ester interchange reaction [6,12].

4. Conclusions

The temperature-induced transesterification reaction between PET and PEN, previously melt-blended in a twin-screw extruder below the critical reaction temperature, confirms the results found in a previous simulation study with model compounds. In fact, heating the blend above 300 °C direct ester–ester exchange mechanism produces the TEN sequences with reversible second order kinetics. Conversion of the reactants TET and NEN and their concentrations at equilibrium lead to a value of four for the equilibrium constant, implying that the forward rate constant is four times the reverse rate constant. The correct kinetics was described using the effective half concentration of the product assuming the recombination of half of TEN molecules. The reaction order was confirmed using pseudo first order conditions, which leads to an overall second order reversible kinetics. The activation parameters, i.e. the enthalpy and entropy of activation, confirmed the ester–ester exchange mechanism of the reaction.

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