



Hydrolysis kinetics of condensation polymers under humidity aging conditions

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ABSTRACT

The hydrolytic stability of polycarbonate (PC), poly(ethylene terephthalate) (PET), and resorcinol polyarylate (RPA) films was studied at 65–95 °C and 23–95% relative humidity (RH) by measuring the time to embrittlement as measured by a bending test on films. The data show that the hydrolysis of these polymers is second order in RH with overall kinetics $1/t_{\text{fail}} = A \exp(-E_a/RT) [\text{RH}]^2$ where t_{fail} is the embrittlement time in days, R is the gas constant, T is the temperature in kelvins, and RH is the fractional relative humidity. The activation energy, E_a , in kJ/mol and $\ln(A)$, respectively, for the polymers were PC: 92, 24.9; PET: 129, 39.3; RPA: 102, 30.0.

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1. Introduction

Condensation polymers such as polyesters and polycarbonates can undergo reaction with water to cause main chain scission resulting in loss of molecular weight and eventual embrittlement. Polyamides generally are much more stable toward hydrolysis. Predicting the lifetime of the polyesters and polycarbonates under warm, moist conditions requires knowing the rate of property loss at some defined temperature and humidity, the activation energy (E_a), and the rate dependence on relative humidity.¹ Although there is an extensive literature for polymer hydrolysis, data on the kinetic parameters are not really sufficient for good lifetime predictions. In particular, the data pertaining to the effect of humidity on the hydrolysis rate are sparse and present some difficulties.

We have investigated the effects of temperature and humidity on the embrittlement times of BPA polycarbonate (PC) and two polyesters: poly(ethylene terephthalate) (PET) and resorcinol polyarylate (RPA). Structures are shown in Scheme 1.

1.1. Hydrolysis kinetics

The reaction of water with a polymer can be considered as Eqn. (1) in which P represents a polymer chain and P' represents a

polymer chain fragment [1]. More properly, P represents a repeat unit of the polymer and P' represents the products of the reaction with water. The rate of this reaction depends on the concentration of P, the concentration of water, the temperature, and the concentration of any catalysts. Acids, bases, and metals can act as catalysts, and some small concentration invariably is present as a result of impurities in the monomer, residual polymerization catalysts, and degradation products of additives. Since the reaction takes place in a solid polymer, we have to take what we get in terms of these catalytic impurities, and it is not surprising if hydrolysis rates for nominally the same polymer differ over time as processes and formulations change. For example, we know that PC is very sensitive to decomposition products of the phosphite stabilizer added to inhibit discoloration during processing.



The rate of hydrolysis at a given temperature is expressed by Eqn. (2) where the brackets show the concentration of P and water and k is a rate constant. Only 1–2% of the P units need be hydrolyzed to embrittle a polymer, so [P] can be considered constant. It, as well as other constants such as the presence of catalytic species can be consolidated into a revised rate constant k' as shown in Eqn. (3).

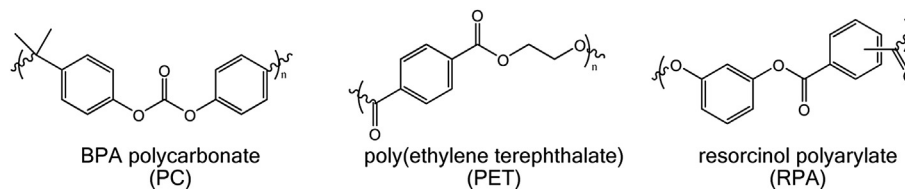
$$-\frac{d[\text{P}]}{dt} = k[\text{P}][\text{H}_2\text{O}] \quad (2)$$

$$-\frac{d[\text{P}]}{dt} = k'[\text{H}_2\text{O}] \quad (3)$$

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¹ RH without other designation refers to the fractional relative humidity: $\text{RH} = p_{\text{H}_2\text{O}}/p_{\text{sat}}$, and all equations will use fractional humidity. In the text, humidity will often be given as %RH since it is a more familiar way of speaking of it.



Scheme 1. Structures of the polymers in this study.

The rate constant k is a function of temperature. The temperature dependence of a reaction is approximated by the Arrhenius Law, commonly given as Eqn. (4) where k is the rate constant, A is a factor gathering various constants as well as entropy considerations, E_a is the activation energy commonly expressed as calories/mol or joules/mol, R is the gas constant ($1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$ or $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature in kelvins. Thus, Eqn. (3) becomes Eqn. (5).

$$k = A \exp(-E_a/RT) \quad (4)$$

$$-\frac{d[P]}{dt} = A' \exp\left(\frac{-E_a}{RT}\right) [\text{H}_2\text{O}] \quad (5)$$

The concentration of water in a polymer at a given temperature is equal to the saturation solubility times the relative humidity: $[\text{H}_2\text{O}] = S \times \text{RH}$. Water sorption has been found to be nearly linear for PET at 45°C [2] and linear for PC at 100°C [3]. The solubility usually is proportional to an Arrhenius-like expression where E_a is replaced by the enthalpy of solvation (or heat of sorption) H_s allowing Eqn. (5) to be expressed as Eqn. (6). Experimentally, if one does a series of experiments at various temperatures and humidities, the energy terms are combined into an effective activation energy E_a^{eff} as shown in Eqn. (7).

$$-\frac{d[P]}{dt} = A' \exp\left(\frac{-E_a}{RT}\right) \times \text{RH} \exp\left(\frac{-H_s}{RT}\right) \quad (6)$$

$$-\frac{d[P]}{dt} = A' \exp\left(\frac{-E_a^{\text{eff}}}{RT}\right) \times \text{RH} \quad (7)$$

It is important to note that the key parameter is relative humidity at the sample temperature, not the vapor pressure of water. This is because the water solubility in the solid is defined at 100% relative humidity at some temperature, not at 1 atm of water vapor pressure since that is not achievable below 100°C . The question of

what RH to use is not trivial. Consider an article subjected to outdoor exposure. During the day, an object can be hot, making the rate constant part of Eqn. (7) large. The ambient humidity may be high, leading one to think that hydrolysis might be fast, but the relative humidity will be low in the hot air at the boundary layer near the hot surface. For example, if the air temperature is 30°C and the ambient humidity is 80%, a black article might be 65°C making the relative humidity at the boundary layer only 14%. RH conversions can be made using the Magnus formula, explanations of which are easily found on the World Wide Web [4]. Although Eqn. (7) indicates that the rate should be a linear function of RH, the literature shows that often it is not. This is more fully discussed below.

1.2. PC hydrolysis

There are surprisingly few papers on the kinetics of polycarbonate hydrolysis containing data useful for lifetime prediction. The most complete work is in a pair of papers by Zinbo and Golovoy [3,5] summarized in Fig. 1 and Fig. 2. The authors found that the solubility of water in PC was directly proportional to relative humidity. The degradation was determined as the fractional loss in the weight average molecular weight (M_w). The E_a found in this work is 18.5 kcal/mol (77 kJ/mol), which is essentially the same as the $18 \pm 2 \text{ kcal/mol}$ ($75 \pm 8 \text{ kJ/mol}$) determined by Pryde et al. [6], and 20.7 kcal/mol (87 kJ/mol) calculated from data by Gardner and Martin [7]. Since factors such as phenolic endgroup concentration [8], acidic stabilizer residues, and other impurities [9] are known to act as hydrolysis catalysts and lower the E_a , it was not clear that recent, presumably cleaner, PC would have the same E_a for hydrolysis.

The plot in Fig. 2 of rate vs. relative humidity (RH) from Zinbo and Golovoy's data shows surprising non-linearity. The hydrolysis rate must go through the origin, and it is clear that the data deviate strongly from linearity at higher RH. The authors do not discuss

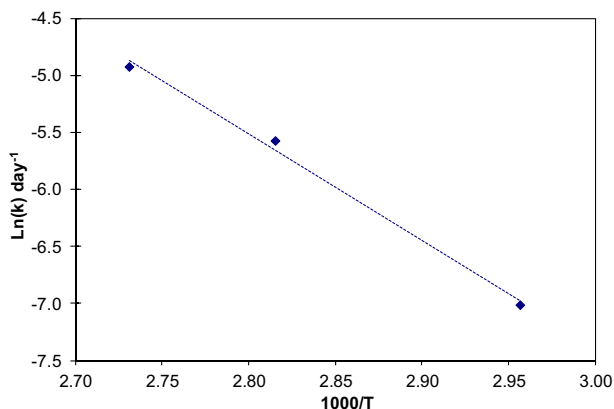


Fig. 1. Arrhenius plot of data from Zinbo and Golovoy [5] for PC hydrolysis at 100% RH. The slope gives an activation energy of 18.5 kcal/mol (77 kJ/mol).

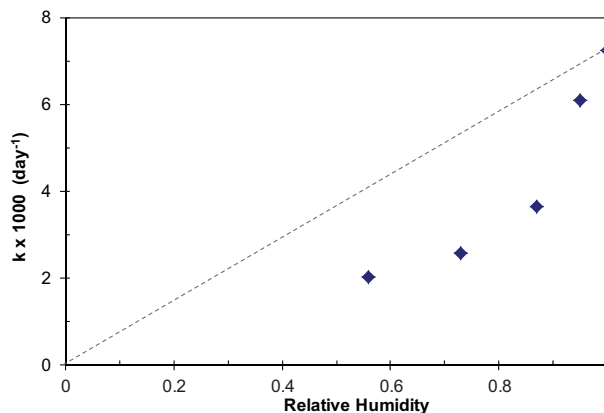


Fig. 2. Plot of data from Golovoy and Zinbo [3] for PC hydrolysis at 100°C .

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