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Estimating Network Lifetime of AUN in Photo-Aging by Kinetic Modeling and “Degelation” Model

Takato Ishida,* Emmanuel Richaud, Hideaki Hagihara, and Ryoma Kitagaki

The study develops an oxidative kinetic model of acrylic-urethane network during photo-aging. The kinetic model can track chemical reaction dynamics well and also enables to estimate the network lifetime by counting scission/crosslinking events. Estimated network lifetime is semiquantitatively coincided with the one derived from different statistical approach.

then, the initial “loosely” crosslinked network was converted into a brittle network with excessive local crosslinking.^[1] In this paper, we construct a kinetic model of oxidative photo-aging for AUN based on the classical autooxidation (closed radical loop) scheme. The network lifetime triggered by oxidative chain scission predicted by the

reaction kinetic model is comparable with that previously presented by our mesoscale “degelation” model.^[2]

1. Introduction

Acrylic-urethane network (AUN), which is a family of thermosetting polymers with a three-dimensional network structure, is a good choice for outdoor coatings and adhesives because of their flexibility and weatherability. For outdoor applications of AUN coatings, photo-oxidative degradation induced by ultraviolet rays determines the material lifetime. Oxidative degradation is a primary degradation mechanism (so-called “mild” degradation proceeding in several years or more), and it essentially involves molecular chain scissions (β -scission) and crosslinking (as radical termination steps) in elementary reactions. We previously elucidated that significant structural alterations of photo-aged AUN were initiated after a certain number of chain scission events,

2. Experimental: Photo-Aging Conditions and Characterization

Accelerated photo-aging treatments were conducted by using lab-built UV irradiation equipment (the detail was introduced in the previous work^[3]). The UV source was a metal halide lamp (wavelengths less than 295 nm were filtered) with the intensity of 180 W m^{-2} ($\lambda = 300\text{--}400 \text{ nm}$). UV irradiation tests were carried out under temperatures of 20, 40, and 60 °C with low relative humidity (RH) condition. Chemical structure changes were characterized by conventional Fourier Transform Infrared Spectroscopy (FTIR) and Ultraviolet–visible spectroscopy (UV–vis). The transmission FTIR spectra were obtained by using a Nicolet 6700 (Thermo Fisher Scientific, USA). The FTIR spectra were averaged from a total of 64 scans at a resolution of 4 cm^{-1} in the range of $4000\text{--}400 \text{ cm}^{-1}$. UV–vis spectra obtained by using a FP8500 (JASCO, Japan) in the range of 200–800 nm with the scan rate of 400 nm min^{-1} .

3. Results and Discussions

Figure 1 shows the evolution of FTIR spectrum of AUN photo-degraded at 20 °C. These spectra show typical chemical changes for photo-aged AUN, i.e., loss of urethane and C–H bond at α -position of N atom, formation of end-urethane, carboxylic acid, chain imide.^[1,4–6] The similar chemical changes were observed in the samples photo-degraded at 40 and 60 °C, the spectra are presented in Figure S1, Supporting Information.

According to the chemical changes in AUN photo-aging, we here propose a kinetic model for AUN oxidation with mechanistically valid autooxidation scheme. This scheme is basing from the framework of the kinetic model of AUN thermal oxidation constructed in Ishida et al.^[5] Chain-imide groups generated by the cage reaction which is a stable degradation product, is a quite useful marker for evaluating the chemical aging effects. This model takes into account the two parallel reaction paths of the cage reaction and formation of end-urethanes and carboxylic acids involving β -scission that occurs in parallel with the cage reaction. The

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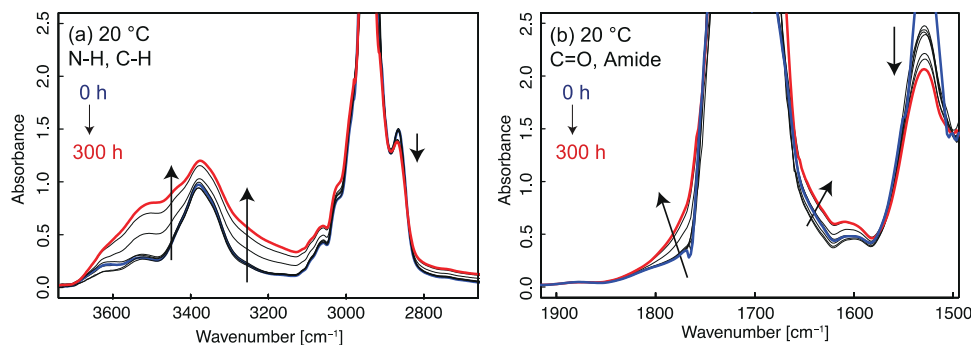
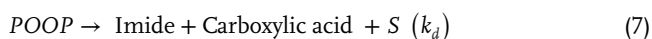
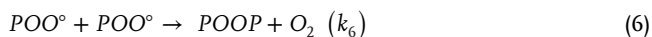
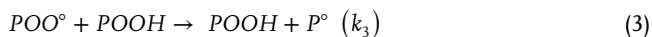
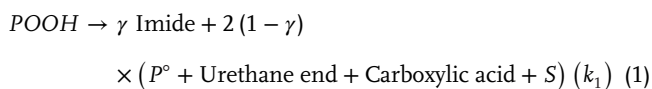


Figure 1. Time dependent FTIR spectra in photo-aging under 20 °C in the regions of a) 1900–1500 cm⁻¹ and b) 3600–2800 cm⁻¹.

elementary reactions steps considered in this model are:



Here, we denote hydroperoxides as POOH, substrates as PH, macroradicals as P[°], peroxide radicals as POO[°], peroxide structure as POOP. *k*_(i) are the rate constants corresponding to each reaction, and *k*_d is assumed to be comparable with *k*₁, in accordance with our previous work.^[5] γ is the yield of the cage reaction, which corresponds to occurrence of β -scission at a probability of $1 - \gamma$ per each POOH decomposition event. Kinetics of AUN photooxidation can be simulated by solving differential equations which is equivalent with the above elementary reactions. We adopt that the initial conditions and the yield γ are exactly the same as^[5] ($\gamma = 0.78$), and the numerical time-integration is performed using MatLab ode23s solver. Among the rate constants shown here, *k*₁ corresponding to the radical initiation process, is initiated by photon absorption, and it is necessary to take into account the excitation process by photon absorption, as suggested by François–Heude et al.^[7] Here, the frequency of photon absorption process is evaluated using the overlap integral of the absorption spectrum of the sample from UV–vis measurements and the radiation spectrum of the light source. As shown in **Figure 2**, as the progress of photo-aging, the aged AUN exhibits stronger absorption of wavelength components longer than 300 nm. Using the UV–vis spectrum (*A*_{UV–vis}(λ)) and the radiation spectrum of

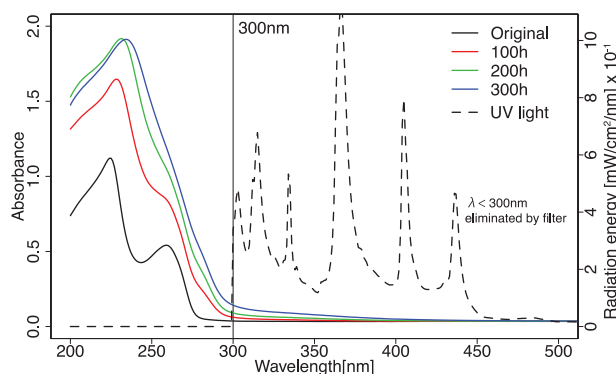


Figure 2. Spectral distribution of the light source and change in UV–vis spectra during photo-aging treatment at 60 °C.

the light (*E*(λ)), the overlap integral *J* and the rate constant *k*₁ of the radical initiation process can be expressed as:

$$J(t) = \int_{\lambda_{\min}}^{\lambda_{\max}} E(\lambda) A_{UV\text{-vis}}(\lambda) d\lambda \quad (8)$$

$$k_1(T, J) = k_1^{(0)} J(t) \exp\left(-\frac{E_1}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (9)$$

where $\lambda_{\min} = 300$ [nm], $\lambda_{\max} = 800$ [nm], *k*₁⁽⁰⁾ is the parameter corresponding to the frequency factor of the initiation process, *E*₁ is the activation energy, *R* is the gas constant, *T*_{ref} is the reference temperature. The evaluated photon absorption *J*(*t*) is shown in **Figure S2**, Supporting Information and it can be seen that they indeed increase as degradation progresses (see Supporting Information).

Figure 3 shows the time evolution of target chemical species estimated as the same procedure in our previous report^[5] and predicted by the proposed kinetic model. Considering the physically reasonable hierarchy between parameters, the set of rate constants (shown in **Table 1**) are determined to track the experimental results well, as shown in **Figure 3**. The kinetic model can reproduce chemical reaction kinetics well (succeeded in reproducing the accumulation of imide and the loss of C–H bonds).

Finally, the time evolution of elastically active chain concentration (EAC) is discussed as a validation as shown **Figure 4**.

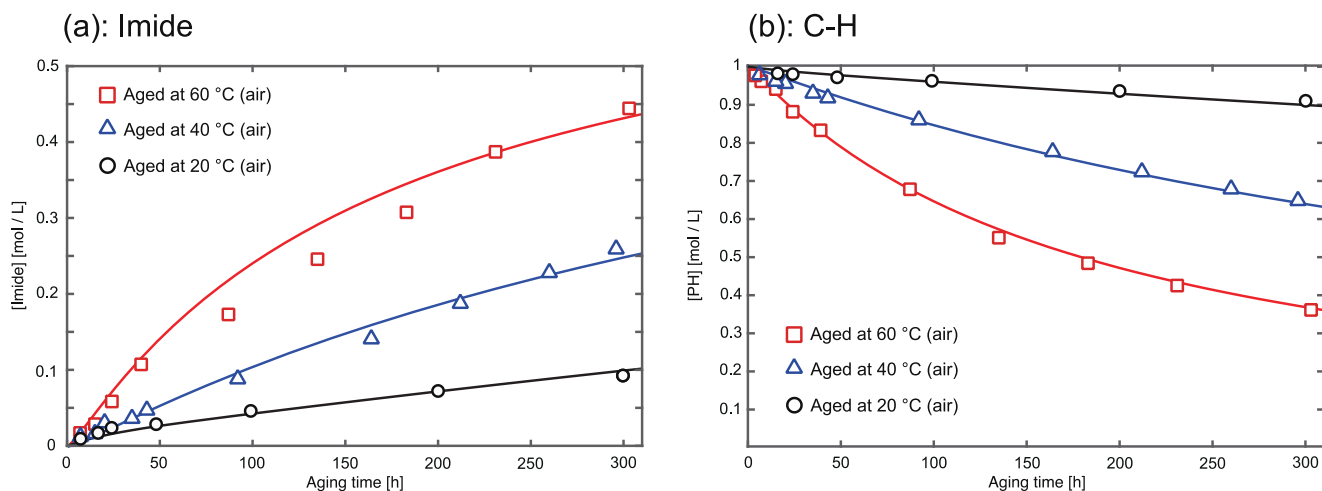


Figure 3. Change in concentrations of target species in AUN photo-aging (20, 40, and 60 °C) a) imide, b) PH; solid lines: simulation curves; plots: experimental data.

Table 1. Rate constants and activation energies (E_a) used for the simulation and determined by the numerical reverse method at 60 °C.

Rate constants	$k_1^{(0)}$	k_2	k_3	k_4	k_5	k_6
[mol L ⁻¹ s ⁻¹]	6.0×10^{-5}	10^6	48.0	8.4×10^8	2.2×10^8	1.3×10^8
E_a [kJ mol ⁻¹]	13.7	0	40.3	0.49	1.89	5.27

It is calculated assuming that three EACs are lost per scission event and two EACs are generated per crosslinking event because AUN has the trifunctional network. According to Figure 4, the EAC has completely disappeared at 52 h in photo-aging under 60 °C and at 155 h in photo-aging under 40 °C. The complete disappearance of EAC corresponds to a kind of transition phenomenon “degelation” in which the gel converted into sol triggered by chain-scission. The time of EAC disappearance semiquantitatively coincides with the “degelation” time previously estimated by the mean-field approach in our system (Table 2). This result suggests that the kinetic model

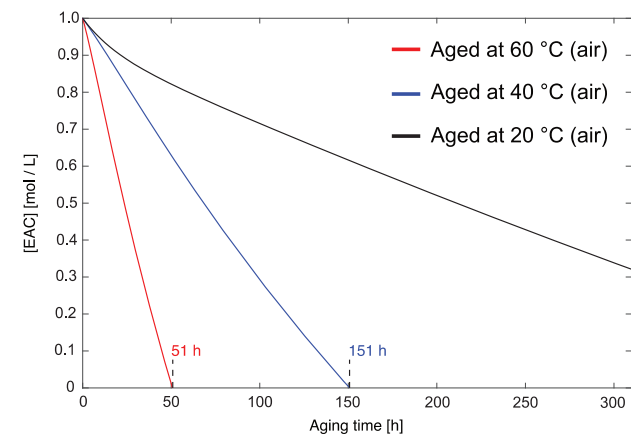


Figure 4. Change in the concentrations of EAC in AUN photo-aging (20, 40, and 60 °C).

Table 2. Estimated network lifetime of AUN in photo-aging.

	20 °C	40 °C	60 °C
This work (microscale) [h]	–	51	151
Mean-field approach ^[2] [h]	–	45	211

can predict reasonable network lifetimes of AUN in photo-aging.

4. Conclusion

A developed kinetic model solves the elementary reaction kinetics of radical-mediated autoxidation reactions. The kinetic model can reproduce chemical reaction kinetics well. It enables us to estimate the network lifetime, corresponding to the complete disappearance of the elastic chains, by counting scission/crosslinking events. The time of complete loss of EAC roughly corresponds to the network lifetime estimated by different mean-field based approach (which uses Flory’s classical gelation theory in reverse). It means the proposed kinetic model of AUN photo-aging can reasonably estimate network lifetime.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.



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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors. Supporting Information is available from the Wiley Online Library or from the author.

Keywords

acrylic-urethane network, kinetic modeling, network lifetime, photodegradation

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