ELSEVIER

Polymer Degradation and Stability 69 (2000) 251–253

Polymer Degradation and Stability

Short communication

Protection of epoxy resin against thermo-oxidation via co-curing epoxy/resole (I)

Mu-Shih Lin *, Chun-Chen Chiu

Department of Applied Chemistry, National Chiao-Tung University, Hsinchu 30050, Taiwan

Received 4 January 2000; accepted 24 January 2000

Abstract

Co-cured materials based on 100/0, 50/50 and 0/100 weight ratios of resole/epoxy were prepared by using NaOH and 4,4′-diaminodiphenylmethane (MDA) as curing agents. Samples were spin-coated on Al plates and were subjected to accelerated aging at 150°C in air for 49 days. The functional group changes during thermal oxidation were monitored with FT–IR at various times. Difference spectra were obtained by using aromatic absorption at 1608 cm^{-1} as internal standard. Kinetic study was performed, and a first order of degradation was demonstrated. Experimental results revealed that the degradation rate constants for pure epoxy, 50/50 of resole/epoxy and pure resole are 9.32×10^{-3}, 4.29×10^{-3} and 2.03×10^{-3} h^{-1}, respectively, indicating a significant protection of epoxy against thermal oxidation via co-curing resole/epoxy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Thermo-oxidation; Co-curing; Degradation rate constants

1. Introduction

Hindered phenols are well known as stabilizers for plastics and rubbers [1,2]. Since resole is a thermosetting resin with hindered phenol moieties in the backbone, it would be expected to act as a radical scavenger and hence as a stabilizer for polymers. On the other hand, epoxy resins are strong materials and have been widely used in thermosetting plastics, composites, adhesives, coatings, etc. However, incorporating of low molecular weight hindered phenols into polymer may cause leaching problems [3]. Therefore, we are interested in incorporating polymeric resole into epoxy resin and co-curing the two resins into a network structure to avoid leaching. In this article we report the result of our study.

2. Experimental

Resole was synthesized by a literature method [4,5]. Epoxy in the form of diglycidyl ether of bisphenol-A (DGEBA, Epon 815) with an epoxy equivalent weight (EEW) of 194 was purchased from Shell Co. Weight ratios of resole/epoxy of 100/0, 50/50, and 0/100 were blended and were cured simultaneously by using NaOH (1% on resole) and MDA (stoichiometric balance on DGEBA) as curing agents. Film samples on Al plates were spin-coated and were placed in an accelerated aging oven at 150°C under circulating air for 49 days.

A Nicolet 520 FTIR spectrometer with a resolution of 1 cm^{-1} was used to monitor the functional group changes during thermal oxidation. Difference spectra were obtained by subtracting the absorbances at various time t from that at time zero, using the aromatic absorption at 1608 cm^{-1} as internal standard. Integrated peak areas for the increasing carbonyl absorbance were related to the carbonyl concentration changes. The conversion, α, is defined as

$$\alpha = (A_\text{t} - A_\text{o})/(A_\infty - A_\text{o}) = (C_\text{t} - C_\text{o})/(C_\infty - C_\text{o})$$

where A_o, A_t and A_∞ are peak areas of carbonyl groups at the initial time, time t and after 49 days, respectively; C_o, C_t and C_∞ are the corresponding concentrations.

3. Results and discussion

Thermal oxidation of diamine-cured epoxy resin has been reported in literature [6,7]. The initial stage of

---

* Corresponding author. Tel.: +886-35-712121, ext. 4501; fax: +886-35-723 764.

PII: S0141-3910(00)00058-6

degradation leads to loss of H_2O resulting in the formation of $C=C$; later degradation stages lead to the production of substituted aldehydes, ketones and acids, which cause increasing absorbances at ca. 1700 to 1740 cm^{-1} [6,7]. However, the literature [8–10] reveals extensive thermal oxidation products of resole, which consist mainly of carbonyl groups at ca. 1625 cm^{-1} in the form of substituted benzophenones and quinonoid-type moieties at ca. 1660 to 1690 cm^{-1} [8–10]. Difference spectra for the cured epoxy, cured resole and co-cured resole/epoxy (50/50) are given in Figs. 1–3, respectively. It appears that increasing carbonyl absorbances confirm the reports in literature. However, in comparison of Figs. 1 and 3, obviously, the increase of carbonyl absorbance at ca. 1700 to 1740 cm^{-1} is significantly decreased for the co-cured 50/50 resole/epoxy, based on the same period of thermal oxidation.

Plots of increasing conversion versus time for the three samples are given in Fig. 4. It appears that the formation rates of carbonyl groups are in the order: epoxy > 50/50 co-cured resole/epoxy > resole. In view of the chemical structure of resole, this order is reasonable since resole consists of hindered phenol moieties in its backbone which, of course, are able to act as stabilizer against thermal oxidation [3,4].

Plots of $-\ln(1-\alpha)$ versus time for the increase of carbonyl groups at ca. 1700 to 1740 cm^{-1} are straight lines which fit first-order degradation (Fig. 5). The thermal-oxidation rate constant for each sample can be measured directly from the slope of the corresponding line. The measured rate constants are $k_1 = 9.31 \times 10^{-3}$ h^{-1} for epoxy, $k_2 = 4.29 \times 10^{-3}$ h^{-1} for 50/50 cocured resole/epoxy, and $k_3 = 2.03 \times 10^{-3}$ h^{-1} for resole. Therefore, it is obvious that significant protection of epoxy resin against thermal oxidation can be achieved by incorporating resole into the epoxy via cocuring. A further report on the improved retention of mechanical properties by the same protection method will submitted.

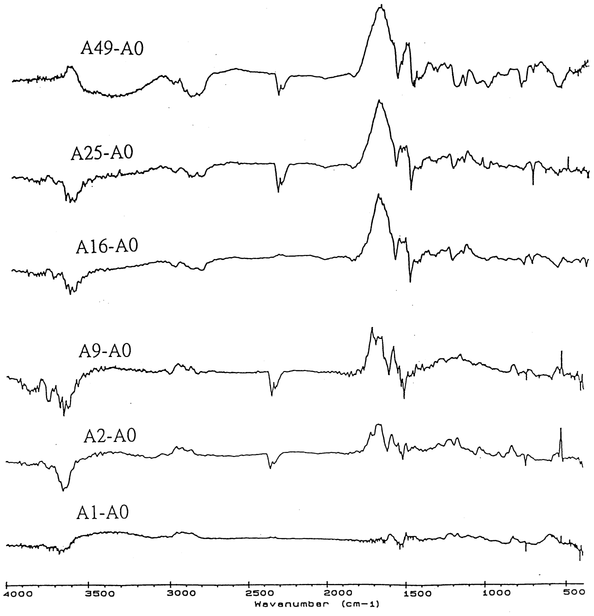

Fig. 2. Difference spectra ($A_t - A_o$, t in days) for resole during thermo-oxidation.

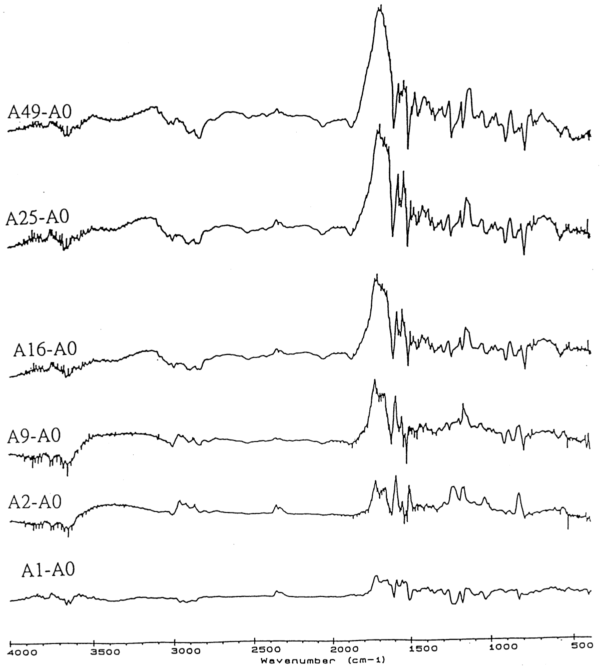

Fig. 1. Difference spectra ($A_t - A_o$, t in days) for epoxy during thermo-oxidation.

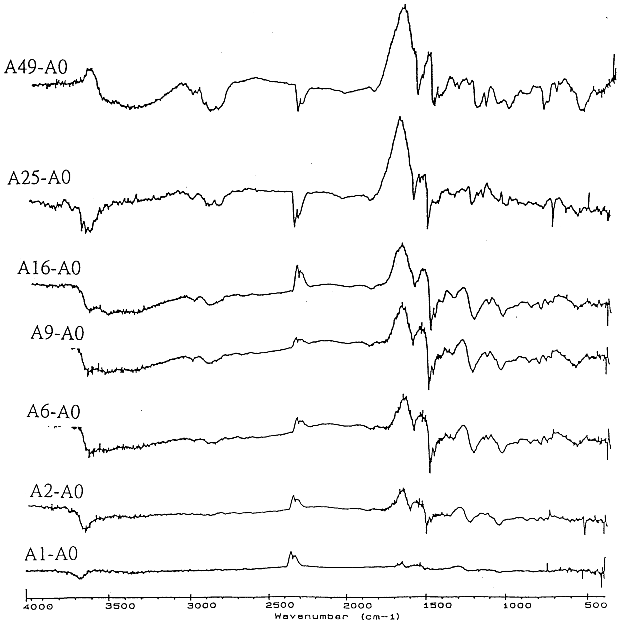

Fig. 3. Difference spectra ($A_t - A_o$, t in days) for cocured 50/50 resole/epoxy during thermo-oxidation.

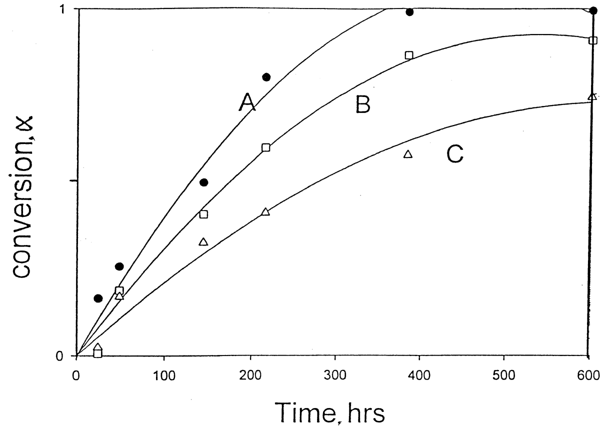

Fig. 4. Conversion of carbonyl formation, α, versus time for (A) epoxy, (B) 50/50 resole/epoxy, and (C) resole.

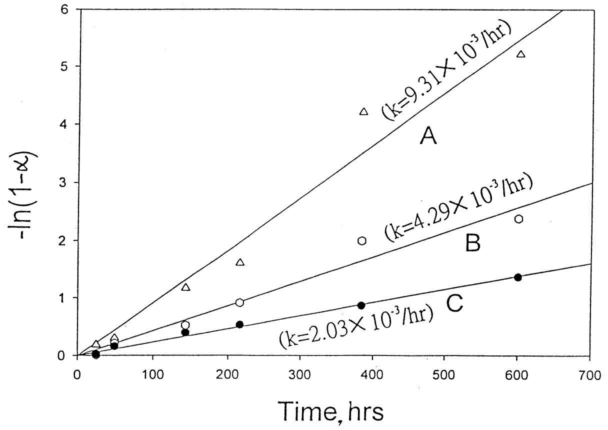

Fig. 5. Plots of $-\ln(1-\alpha)$ versus thermo-oxidation time at 150°C for (A) epoxy, (B) 50/50 resole/epoxy, and (C) resole.

4. Conclusions

Significant protection of epoxy resin against thermo-oxidation via co-cured resole/epoxy was found by monitoring the rates of carbonyl group formation with FT–IR. Thermo-oxidation rate constants for different samples were also determined from a kinetic study, indicating lower thermo-oxidation rate constant after resole was co-cured into the epoxy resin.

Acknowledgements

The authors thank the National Science Council for financial support under contract number NSC 88-2216-E-009-023.

References

[1] Schnabel W, editor. Polymer degradation. Hanser International New York: (USA distribution, Macmillan Publishing), 1981. p. 48–50.
[2] Hawkins W, editor. Polymer stabilization. New York: Wiley-Interscience, 1972. p. 108–13.
[3] Hawkins WL, editor. Polymer stabilization. New York: Wiley-Interscience, 1972. p. 57–9.
[4] Pilato LA, editor. Synthesis by step polymerization. New York: Temecon Group, 1989. p. 60–2.
[5] Fyfe CA. J Appl Polym Sci 1983;28:2611.
[6] Grassie N. Polym Degrad Stab 1986;14:125.
[7] Peltonen K. Analyst 1964;110:1173.
[8] Conley RT. J Appl Sci 1964;8:2163.
[9] Conley RT. J Appl Sci 1965;9:1117.
[10] Conley RT. J Appl Sci 1965;9:2799.