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Short communication

Protection of epoxy resin against thermo-oxidation via cocuring epoxy/resole (II)

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Abstract

Cocured materials based on resole/epoxy in weight ratios of 100/0, 50/50 and 0/100 were prepared by using NaOH and 4,4′-diaminodiphenylmethane (DMA) as curing agents. These cocured samples were subjected to accelerated aging at 150°C in air for 45 days. Continuous increase of carbonyl IR absorption at 1700–1740 cm^{-1} indicated thermal oxidation. The sample with resole/epoxy = 50/50 showed significantly retarded formation of carbonyls. Mechanical property tests of samples during the course of aging, including tensile stress–strain, modulus, and impact resistance confirmed a significant protection of epoxy by incoporating resole into the epoxy via cocuring. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cocured materials; Thermo-oxidation; Formation of carbonyls; Mechanical property tests

1. Introduction

Hindered phenols are well known as effective antioxidants since they are able to scavenge radicals produced during thermal oxidation of polymers [1,2]. However, incorporation of low molecular weight hindered phenols into polymers has the drawback of additive migration problems during processing, or after long-term service [3]. Since resole is a polymeric type of hindered phenol, incorporation of resole into epoxy resin via cocuring would avoid such a drawback. Our previous kinetic studies on the thermo-oxidation for resole/epoxy samples indicated a lower degradation rate constant for the sample of resole/epoxy = 50/50. In this article we further report the results of a series of mechanical tests, which confirmed a significant stabilization of epoxy.

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. Resole/epoxy in weight ratios of 100/0, 50/50, and 0/100 were blended and were cured simultaneously by using NaOH (1% on resole) and MDA (20% on DGEBA) as cocuring agents. Films of the three samples were coated on Al plates. Dumbell specimens according to ASTM-D638 type 1, and specimens for falling dart impact tests of 50×50×3 mm were cast in Teflon moulds. All samples were cured at 110°C for 5 h and then post-cured at 160°C for 3 h. Both film samples and mechanical test samples were then placed in an accelerated aging oven at 150°C under air circulation for 45 days.

A Nicolet 520 FTIR with a resolution of 1 cm^{-1} was used to monitor the carbonyl group changes during thermal oxidation of the film samples. Difference spectra were obtained by subtracting the absorbances at various time t from that at time zero, using the aromatic absorbance at 1608 cm^{-1} as an internal standard. The impact resistance was examined with a computer-added falling dart type impact tester, with a dart weight of 3.3 kg. The value of the dart weight times the height measures the impact energy, which was automatically recorded. The area under this curve (newton vs ms) was integrated and taken as the cracking energy. The tensile stress–strain tests were measured according to the ASTM-D 638 type 1 dumbell specimen. The test speed was set at 5 mm min^{-1}. In all tests, an average of values of five specimens was reported for each sample.

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3. Results and discussions

Resole can be cured by NaOH [6], while epoxy can be cured by diamines [7–9]. Thus, the blends of resole/epoxy were able to be cocured by NaOH/MDA. Our previous kinetic studies on the thermo-oxidation of resole, cocured 50/50 of resole/epoxy and epoxy indicated a first-order thermal oxidation, with degradation rate constants in the order: (A) resole (2.03×10^{-3} h^{-1}) < (B) cocured 50/50 of resole/epoxy (4.29×10^{-3} h^{-1}) < (C) epoxy (9.31×10^{-3} h^{-1}) [10]. In order to reveal how the effect of this kinetic difference on the retention of mechanical properties, tensile and impact tests were conducted. Fig. 1 compares the continuous growth of carbonyl absorbances for (A) resole, (B) cocured 50/50 resole/epoxy and (C) epoxy. It is noted that after the same period of aging, resole indicated a retarded increase of carbonyl absorbance, epoxy showed a rapid increase of carbonyl absorbance, while the cocured 50/50 of resole/epoxy exhibited a carbonyl absorbance increase in between. Fig. 2 compares the retention of tensile moduli for the three samples during 45 days of continuous accelerated thermal oxidation. Sample B with 50/50 of cocured resole/epoxy shows a much better modulus retention than epoxy, indicating a significant protection upon incorporation of resole. This is because resole is basically a polymeric type of hindered phenol which is a stable antioxidant. Even after 45 days of

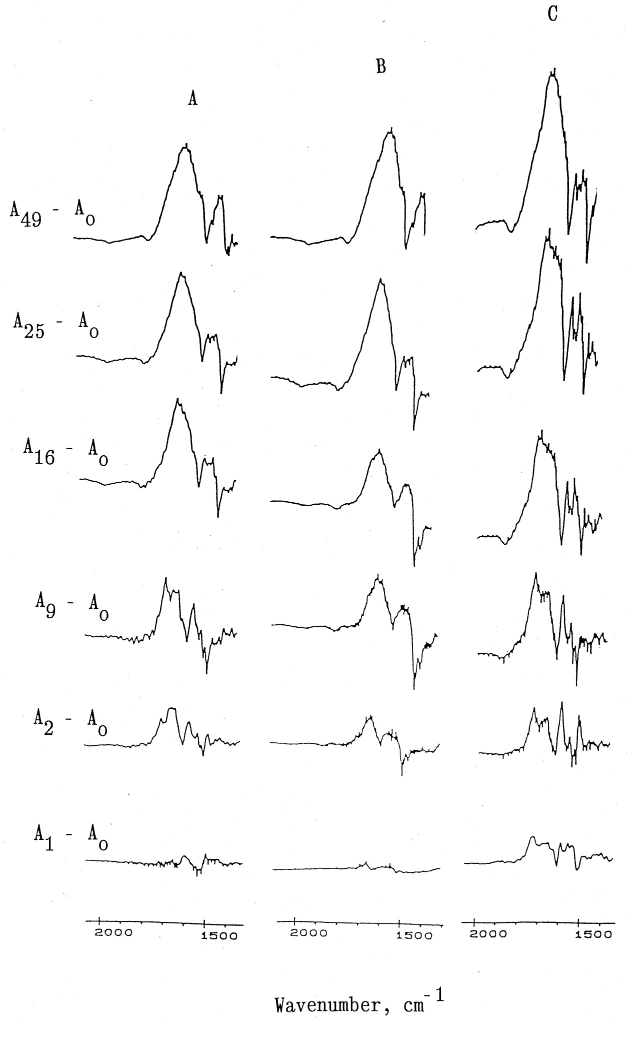

Fig. 1. Difference spectra of FTIR (A_t–A_o, with *t* in days) showing the enhanced IR carbonyl absorbance at ca. 1700–1740 cm^{-1}, (A) resole, (B) cocured 50/50 of resole/epoxy, (C) epoxy.

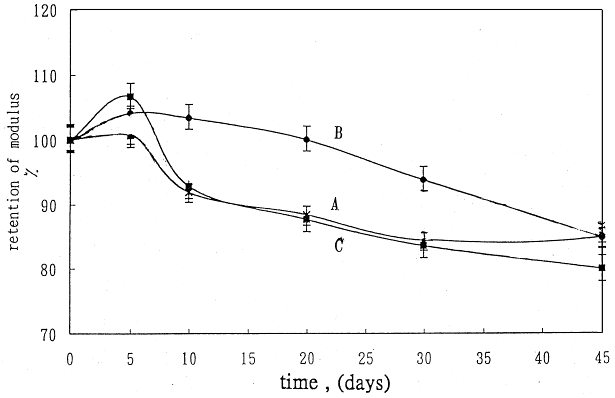

Fig. 2. Plots of % retention of tensile modulus versus aging time. (A) resole, (B) cocured 50/50 of resole/epoxy, (C) epoxy.

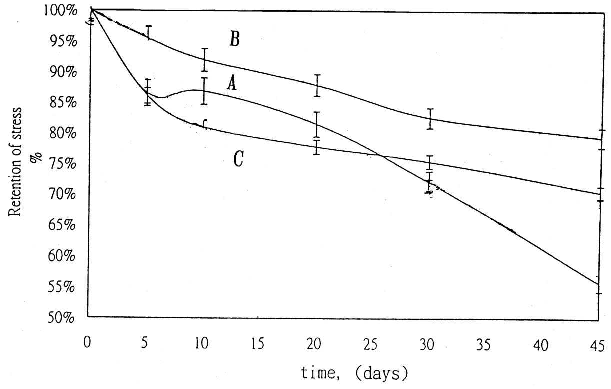

Fig. 3. Plots of % retention of tensile stress versus aging time. (A) resole, (B) cocured 50/50 resole/epoxy, (C) epoxy.

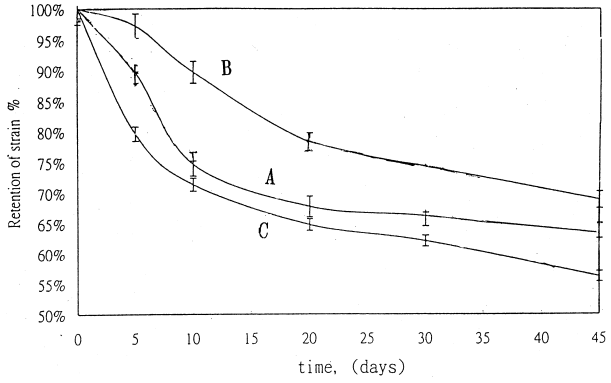

Fig. 4. Plots of % retention of tensile strain versus aging time. (A) resole, (B) cocured 50/50 resole/epoxy, (C) epoxy.

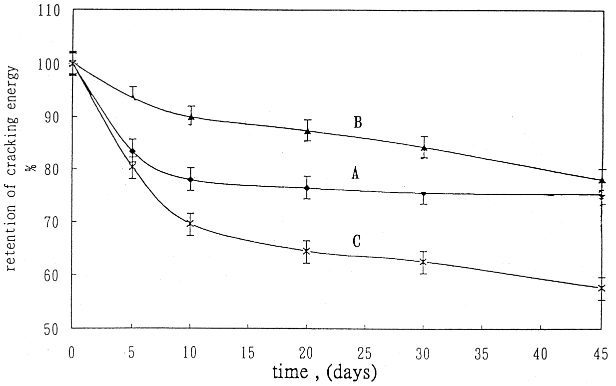

Fig. 5. Plots of % retention of cracking energy versus aging time. (A) resole, (B) cocured 50/50 resole/epoxy, (C) epoxy.

accelerated thermal aging, the incoporated resole still exhibited its stabilization effect without evaporation or leaching from the cocured material. Although resole had the lowest thermo-oxidation rate constant, its modulus retention is less than the cocured 50/50 of resole/epoxy because resole is substantially not a strong material. In comparison of Figs. 3 and 4, for the tensile stress and tensile strain, similar results were observed, with the fact that sample B showed the best retention of tensile stress and strain. Fig. 5 shows the percentage retention of cracking energies for falling dart impact tests. Again, sample B exhibited much better retention of cracking energy than resole and epoxy. This is because resole is not a strong material, while epoxy experienced serious thermal oxidation. Results on mechanical behavior tests are rather consistent with the findings of increased carbonyl absorbance as discussed in Fig. 1.

4. Conclusion

Although resole showed the lowest thermo-oxidation rate, it has poor retention of mechanical properties because resole is a brittle material. Significant protection of epoxy against thermo-oxidation was observed by incorporating resole into epoxy via cocuring, which subsequently led to significant retention of mechanical properties.

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References

[1] Schnable W, editor. Polymer degradation. New York: Macmillan Pub, 1981. p. 49.
[2] Hawkins WL, editor. Polymer stabilization. New York: John Wiley & Sons, 1972 (Chapter 2). p. 54–63.
[3] Hawkins WL, editor. Polymer stabilization, New York: John Wiley & Sons, 1972 (Chapter 8). p. 371–5.
[4] Steiner PT. J Appl Sci 1975;7:19.
[5] Fyfe CA. J Appl Polym Sci 1983;28:2611.
[6] Fukuda A, Hasegawa K. J Appl Polym Sci 1985;30:3943–52.
[7] King JJ, Bell JP. In: Bauer RS, editor. Epoxy resin chemistry, vol. 114. Washington, DC: American Chemical Society, 1978. p. 2223–62 (Chapter 16).
[8] Riccardo CC, Adabbo HE, William JJ. J Appl Polym Sci 1984;29:2481.
[9] Goub MA, Lerner NRJ. Appl Polym Sci 1986;32:215.
[10] Lin MS, Chiu CC. Polym Degrad Stab 2000;69:251.