

Photostabilization of an epoxy resin by forming interpenetrating polymer networks with bisphenol-A diacrylate

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Abstract

Bisphenol-A diacrylate (BADA) was synthesized from the reaction of bisphenol-A and acryloyl chloride. Interpenetrating polymer networks (IPNs) based on diglycidyl ether of bisphenol-A (DGEBA) and BADA in weight ratios of DGEBA/BADA = 100/0, 75/25 and 50/50 were prepared by using 4,4'-diaminodiphenylmethane (MDA) and benzoyl peroxide (BPO) as curing agents. Samples were irradiated with ultraviolet in a Q-UVA weather-o-meter to study their aging behavior. Experimental results indicated that the BADA thus incorporated in the IPN structure confers significant photostabilization of the epoxy, as shown by less chain scission at C–O–C in the epoxy, with less property loss in mechanical tests. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: IPN; Aging; Photostabilization; Chain scission

1. Introduction

Epoxy resins exhibit excellent physical properties and good adhesion, and are widely used in such areas as coatings, adhesives, composites, encapsulants, etc. Photodegradation of epoxies is important and was reported by Dickens et al. [1] and also by others [2–6]. A survey of the photo-oxidation of DGEBA indicates damage of the epoxy resin, resulting in chain scission, leading to deterioration of physical properties. It is well known in literature that phenyl benzoates, upon irradiation with ultraviolet, undergo Photo-Fries' rearrangement, leading to the formation of *o*-hydroxyphenyl ketone which contains a hydrogen bonded six-membered ring structure and acts as a UV absorber [7–10]. Incorporation of such a moiety into an epoxy may significantly stabilize the epoxy resin against photodegradation. In view of the structure of bisphenol-A diacrylate, the Photo-Fries' rearrangement would lead to a structure similar to a UV absorber. It is highly likely that an IPN containing such a moiety would act as a photostabilizer. In this article we report such results in our studies.

2. Experimental

2.1. Preparation of bisphenol-A diacrylate (BADA)

Into a 3-l three necked flask, equipped with a mechanical stirrer and a thermometer, 1 mol of bisphenol-A was charged. Enough methyl ethyl ketone (MEK) was added to dissolve the bisphenol-A. Two mol of NaOH (80 g) and 2 mol of triethylamine were added. The mixture was kept below 5°C. Then 2 mol of acryloyl chloride was added dropwise keeping the temperature near 5°C. The acrylation continued for 10 h. The reaction mixture was poured into a large quantity of deionized water. A crude yellow product was obtained with a yield of 96%. A white crystal with m.p. 95–96°C was obtained after recrystallization from *n*-hexane/CH₂Cl₂ (v/v 4/1).

2.2. Preparation of DGEBA/BADA IPNs

Blends of DGEBA/BADA in weight ratios of 100/0, 75/25 were prepared. BPO (1 phr based on BADA) and MDA (in stoichiometric equivalence of DGEBA) were added as curing agents. To prepare specimens, each composition was mixed and deformed thoroughly and poured into Teflon moulds, then procured at 80°C for 4 h, followed by curing at 140°C for another 4 h, and finally post-cured at 180°C for 2 h.

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2.3. Instruments

Functional group changes during aging were monitored with a Fourier transform infrared spectrometer (FTIR, Nicolet 520 with a resolution of 0.5 cm^{-1}). Thin films were spin coated on Al plates and cured, then irradiated in a QUV-A weather-o-meter for various times. The difference spectra were obtained by subtracting the spectrum at time t from that before aging, using benzene absorption at 1609 cm^{-1} as internal standard. Test specimens were prepared according to the method mentioned and were also subject to irradiation in the QUV-A weather-o-meter. Impact resistance was examined with a falling dart type impact tester, with a dart weight of 3.3 kg. The energy under the curve was integrated automatically. Tensile and elongation tests were performed according to an ASTM D638 type 1. The test speed was at 5 mm min^{-1} . An average of 5 test values reported for all mechanical properties.

3. Results and discussion

The synthesized BADA has the following chemical structure

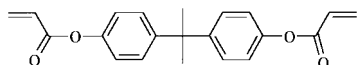


Fig. 1 shows its ^1H NMR spectrum in CDCl_3 . The 6 H's of the two methyl groups occur at $\delta 1.63\text{ ppm}$. The 8 H's of the two phenyl rings (H_d) occur at $\delta 7.01$ and 7.26 ppm

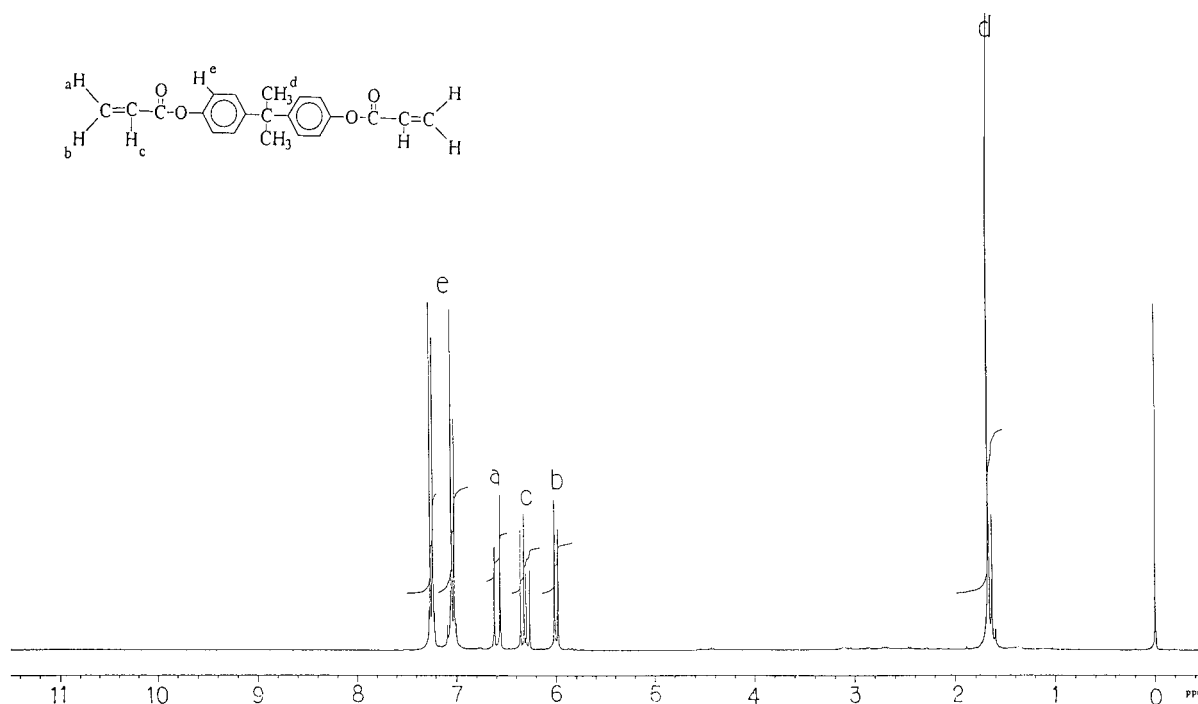
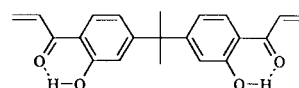


Fig. 1. ^1H NMR spectrum of BADA in CDCl_3 .

(quartet). The 4 H's at the two terminal vinyl hydrogens occur at $\delta 5.98\text{ ppm}$ (*cis* H_b , doublet) and 6.62 ppm (*trans*, H_a , doublet), while the other 2 H's at the two vinyl groups (H_c) occur at $\delta 6.35\text{ ppm}$ (quartet). Fig. 2 shows its FTIR Spectrum. The strong carbonyl absorption of the ester group at 1733 cm^{-1} and the moderate absorption of $\text{C}=\text{C}$ at 1623 cm^{-1} confirm the structure. Free radical polymerization of BADA by BPO resulted in a network structure via a chain mechanism, while curing of DGEBA with MDA resulted in another network structure via step mechanism [11]. Simultaneous curing of various blends of BADA(BPO)/DGEBA(MDA) would lead to various compositions of IPNs via two independent reaction mechanisms. The two components, BADA and DGEBA, have good compatibility, as evidenced by a single glass transition in dsc thermograms (Fig. 3) and a single damping peak from the rheometric dynamic spectroscopy (RDS, Fig. 4) for each IPN [12].

Upon long term irradiation with ultraviolet, the BADA moiety underwent Photo-Fries' rearrangement and led to a six-membered ring structure with an intramolecular H-bonding [10].



This reaction is well known in literature [10,13]. The *o*-hydroxybenzo ketone thus produced indicated a strong intramolecular hydrogen-bonding between the

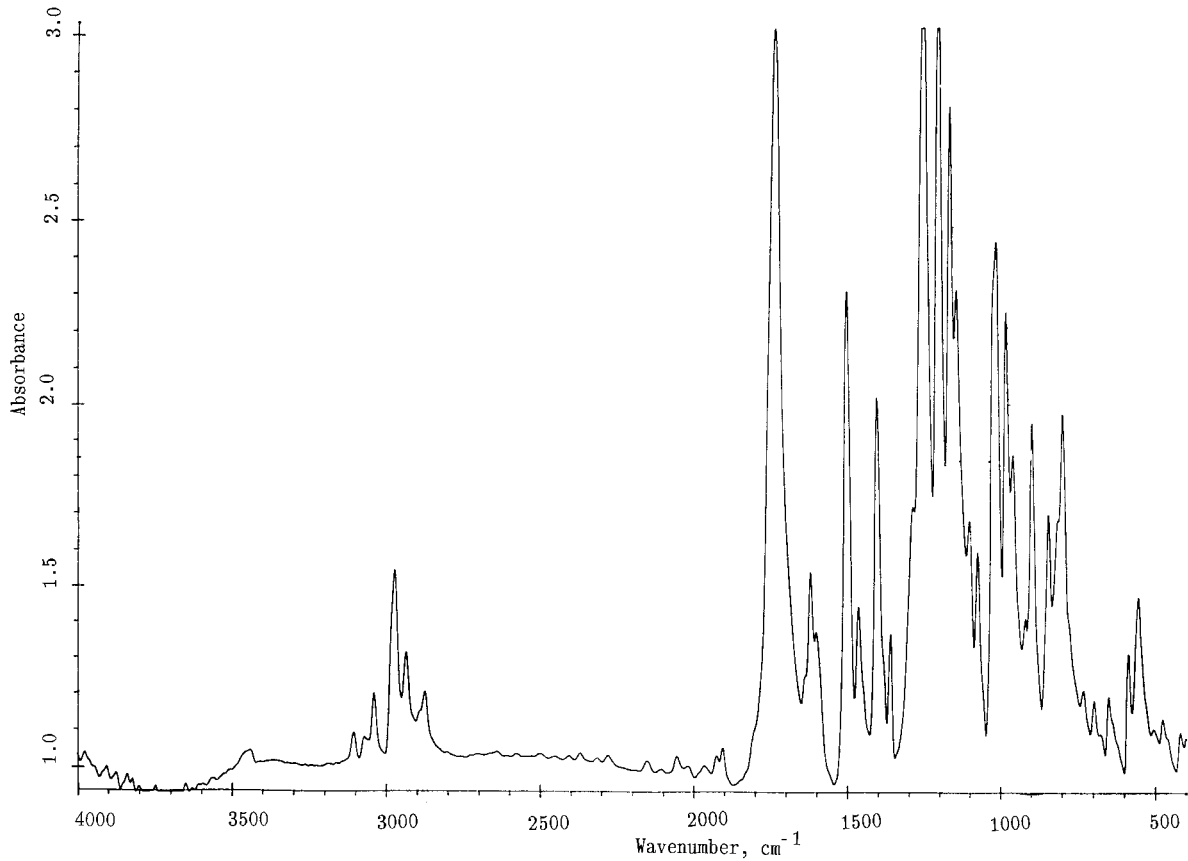


Fig. 2. FTIR spectrum of BADA.

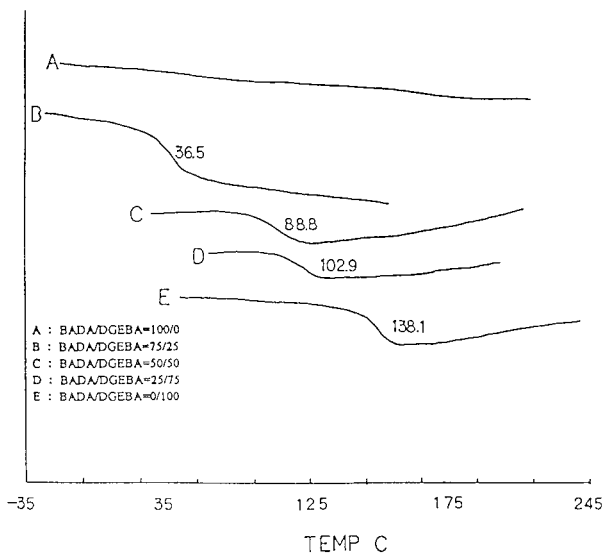


Fig. 3. DSC thermograms for various BADA/DGEBA IPNs.

hydroxyl and carbonyl groups. This intramolecular hydrogen-bonded six-membered ring structure dissipated the UV energy through a physical process [10]. The miscibility of BADA and DGEBA in the IPNs provided good photo protection of the material. Fig. 5

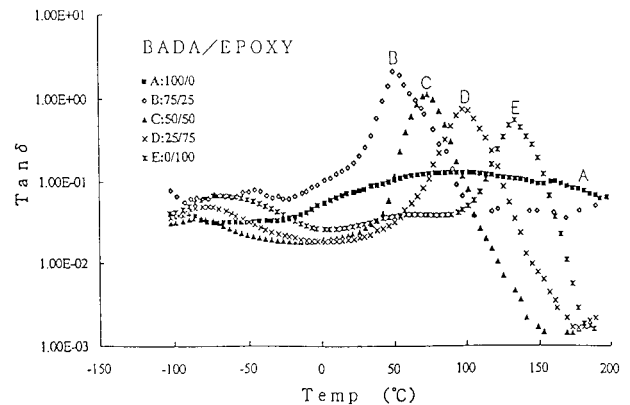


Fig. 4. RDS curves showing the shifts of damping peaks for various BADA/DGEBA IPNs.

shows the difference spectra of FTIR for the cured DGEBA, BADA, and 50/50 IPN. The difference spectra $A_t - A_0$ means the spectra obtained by subtracting the absorbance at t (in days) from that before irradiation. It is obvious from Fig. 5 that the decreasing absorbance at 1265 cm^{-1} indicated the bond breaking of the C–O–C bond in the main chain of cured DGEBA [13]. This type of bond breaking has been well known in literature [1–9]. Continued decrease of absorbance at

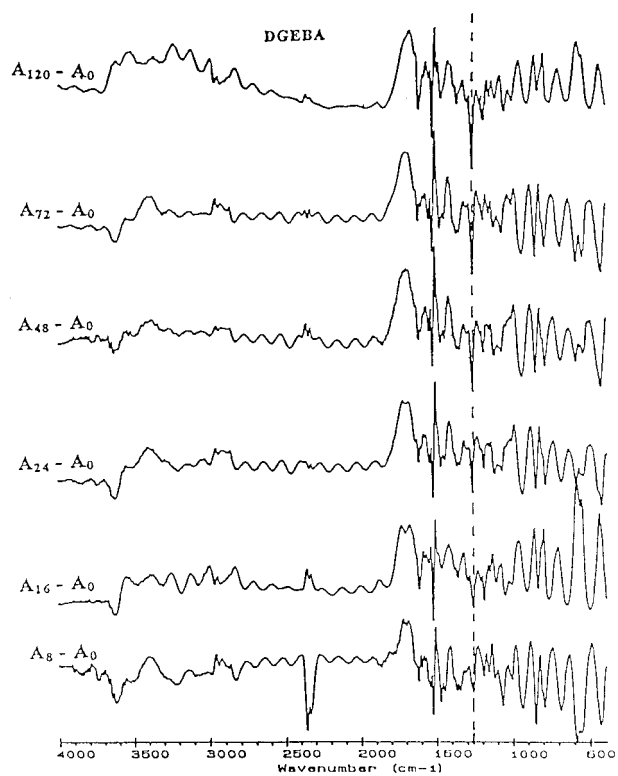


Fig. 5. Difference spectra ($A_t - A_0$ t in days) for pure DGEBA.

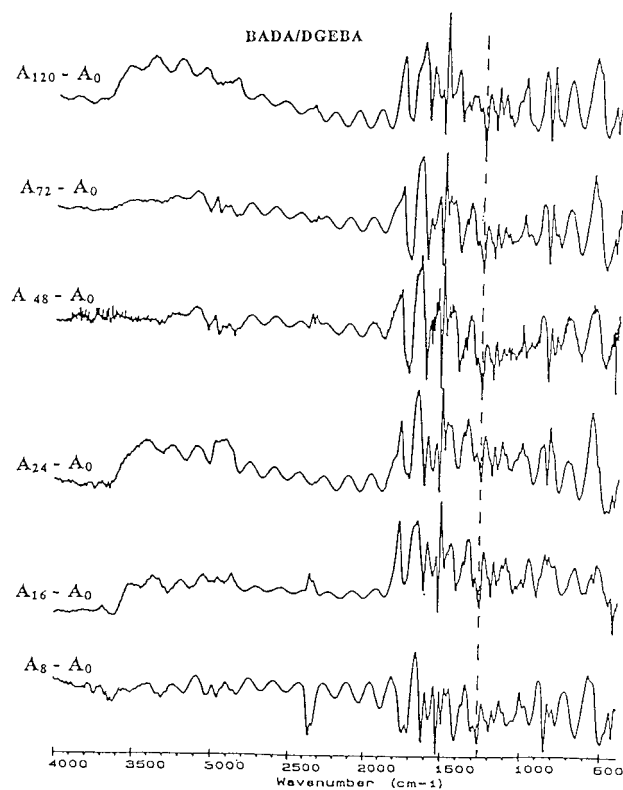


Fig. 6. Difference spectra ($A_t - A_0$ t in days) for 50/50 of BADA/DGEBA IPN.

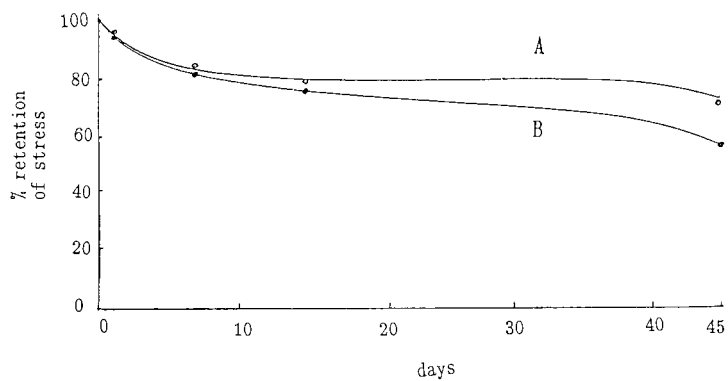


Fig. 7. Plots of % retention of stress at break versus irradiation time. A: IPN, B: DGEBA.

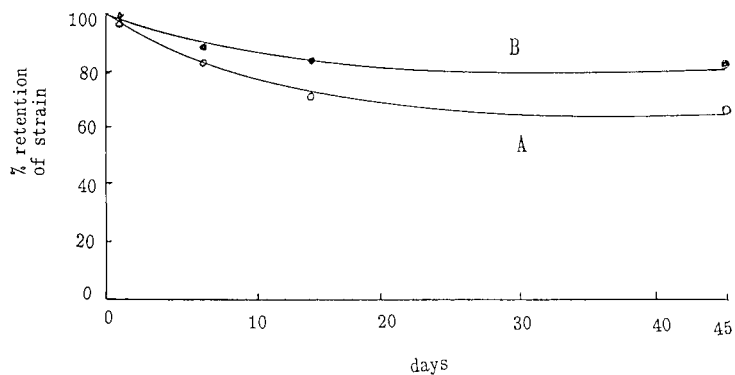


Fig. 8. Plots of % retention of strain at break versus irradiation time. A: IPN, B: DGEBA.

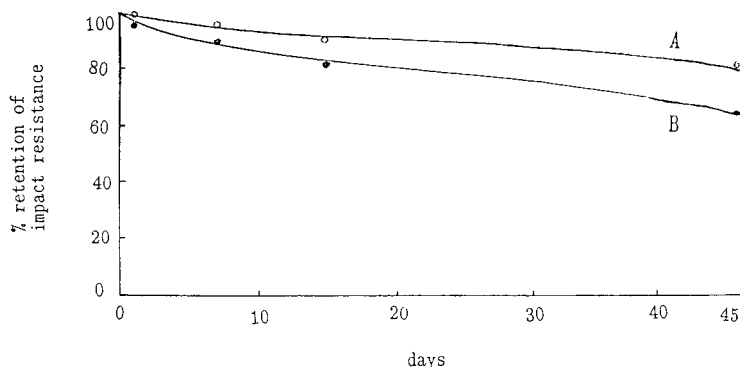


Fig. 9. Plots of % retention of impact resistance versus irradiation time. A: IPN, B: DGEBA.

1265 cm^{-1} with time is clear from Fig. 5. Similar phenomenon, but less decrease at 1265 cm^{-1} in the 50/50 IPN is observed from Fig. 6, indicating less chain scission at C–O–C bond in the IPN. This result strongly supports a significant photostabilization of DGEBA by BADA.

Figs. 7 and 8 show the % retention of stress and of strain for DGEBA/BADA IPNs of 100/0, 75/25 and 50/50 after 45 days of irradiation. Fig. 9 shows the corresponding % retention of impact resistance. All these less mechanical property retention strongly support the photostabilization of the epoxy by forming IPN with BADA.

4. Conclusions

Long term accelerated UV aging of DGEBA resulted in a main chain scission at C–O–C bonds as evidenced from the decreased absorbance at 1265 cm^{-1} in FTIR spectra. Photostabilization of the epoxy resin by forming IPN with bisphenol-A diacrylate can be achieved. This protection resulted in less mechanical property loss of the DGEBA/BADA IPN materials.

Acknowledgements

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