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Accelerated ageing behavior of compatible IPNs based on epoxy and methacrylated epoxy resins

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Methacrylated diglycidyl ether of bisphenol A (MADGEBA) was synthesized from the reaction of the diglycidyl ether of bisphenol A (DGEBA) and methacrylic acid. The MADGEBA was blended with DGEBA in weight ratios of 100/0, 50/50 and 0/100, and cured simultaneously with dicumyl peroxide (DICUP) and hexahydrophthalic anhydride (HHPA) to obtain interpenetrating polymer networks (IPNs). The three samples were irradiated with ultraviolet in a Q-UVA weatherometer for various periods to study their ageing behavior. Experimental results indicate that the methacryloyl moiety thus incorporated confers significant stabilization against photodegradation. © 1998 Elsevier Science Limited. All rights reserved

1 INTRODUCTION

Epoxy resins have been widely used in areas such as coatings, adhesives, composite materials, encapsulants, etc. The photo-oxidation of epoxies is important and was reported by Dickens *et al.*[1] and also by Schultz.[2] A survey of the photo-oxidation of DGEBA indicates damage of the epoxy resin, resulting in chain scissions, leading to deterioration of physical properties. It is also known that acrylic polymers such as poly(methyl methacrylate) have excellent resistance to photo-oxidation[3] and are widely used commercially. Incorporation of the methacryloyl moiety into the epoxy may significantly stabilize the epoxy resin against photo-oxidation. In this article we report our studies on the ageing behaviour of methacrylated epoxy and the compatible IPNs made from epoxy and methacrylated epoxy.

2 EXPERIMENTAL

2.1 Preparation of MADGEBA

Into a 3-l four-necked flask, equipped with a mechanical stirrer, a nitrogen inlet and outlet, and a thermometer, 1 mol of DGEBA (389 g Epon 815 with an EEW of 194.5) was charged and heated to 80°C under nitrogen atmosphere. In the meantime, a mixture containing 2 mol of methacrylic acid (172 g) and 2 mol of NaOH (80 g) was prepared, and after standing for 20 min, the undissolved NaOH was filtered off. The mixture was then added to the flask dropwise, keeping the temperature below 95°C. The methacrylation proceeded for 4.5 h. A large quantity of deionized water was added to extract the unreacted methacrylic acid. The MADGEBA thus obtained was then purified from methanol. The yield of clear syrup product was 85%.

2.2 Preparation of MADGEBA/DGEBA IPNs

MADGEBA/DGEBA weight ratios of 100/0, 50/50 and 0/100 were blended. DICUP (1 phr based on MADGEBA) and HHPA (in stoichiometric equivalence of DGEBA) were used as curing agents. To prepare specimens, each composition was mixed and defoamed thoroughly and poured into Teflon moulds, then precured at 80°C for 4 h, followed by curing at 149°C for another 4 h, and finally post-cured at 180°C for 2 h.

2.3 Instruments

Functional group changes during ageing were monitored with a Fourier transform infrared

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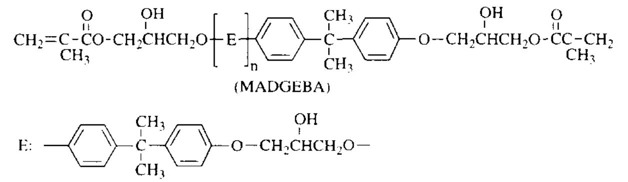
spectrometer (FTIR, Nicolet 520 with a resolution of 0.5 cm^{-1}). Thin films were spin coated on Al plates and cured, then irradiated in a QUV-A weatherometer for various times. The difference spectra were obtained by subtracting the spectrum at time *t* from that before ageing, using benzene absorption at 1609.4 cm^{-1} as internal standard. Test specimens were prepared according to the method mentioned and were also subjected to irradiation in the QUV-A weatherometer. 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 strength and elongation were performed according to an ASTM D638 type 1. The test speed was set at 5 mm min^{-1}. An average of five test values was reported for all impact resistance.

3 RESULTS AND DISCUSSION

The synthesized MADGEBA has the following chemical structure



(MADGEBA)

The methacryloyl moiety is present at both ends of the DGEBA chain. A comparison of both ^{1}H NMR [Fig. 1 (a) and (b)] and FTIR spectra (Fig. 2) confirms this structure. Photo-oxidation mechanisms for DGEBA have been reported in the literature.[1,2] It is reported that main chain scissions in C–O–C, Ph–O–Ph and side chain scission in CH_3–C–CH_3 occur generally, leading to the production of acids, aldehydes, ketones, alcohols, phenol, etc. Functional group changes during ageing can be revealed from the difference spectra given in Fig. 3. All difference spectra (A_t–A_0) were obtained by substracting the spectrum at *t* days from that unirradiated. The application of FTIR difference spectra to analytical problems was disclosed and discussed by Koenig.[4] The increasing OH absorption at 3500–3200 cm^{-1}, and C=O at 1680–1800 cm^{-1} supported the degradation products reported by Dickens *et al.*[1] and Schultz,[2] while the gradual decrease of C–O–C at 1265 cm^{-1} supports the main chain scission of ether linkage. Figure 4 shows similar difference spectra of MADGEBA. A similar but smaller band decrease was observed because the end groups of the methacryloyl moiety have the ability to dissipate UV energy and cause less damage. A decreasing absorption at 1735 cm^{-1} appears to support the main chain scission at the ester group in the MADGEBA (Fig. 4). Bond breaking of the ester group might subsequently

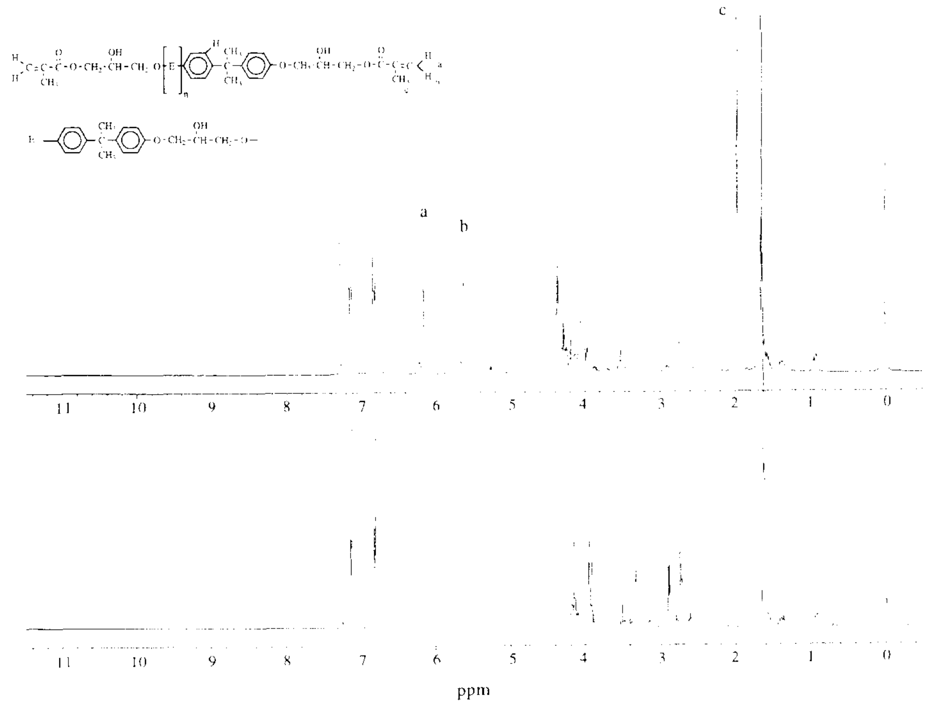


Fig. 1. ^{1}H NMR spectra of (a) MADGEBA and (b) DGEBA.

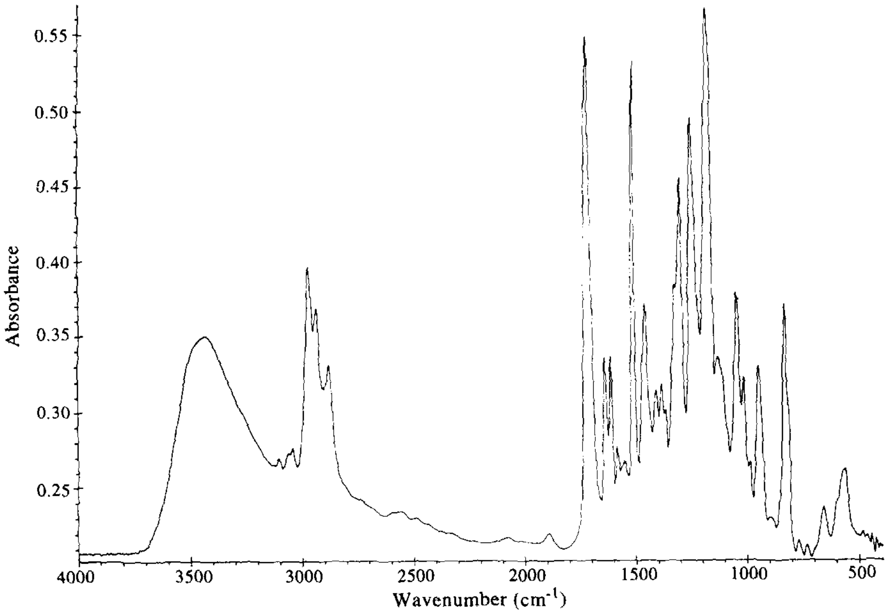


Fig. 2. FTIR spectrum of MADGEBA.

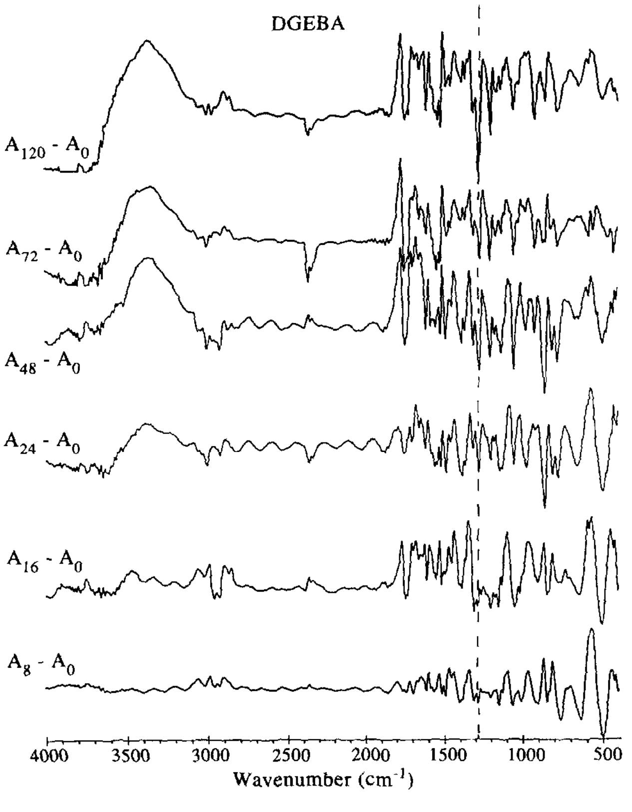


Fig. 3. Difference spectra ($A_t - A_0$) of DGEBA during ageing, where t is in days.

lead to the formation of anhydride linkage, as observed from the strong increase at 1760–1820 cm^{-1}. In the meantime, a comparison of the region 1265 cm^{-1} from Figs 3 and 4 indicates the lower C–O–C bond scission in MADGEBA, because the band at 1265 cm^{-1} decreased less. Therefore, it is clear that the incorporation of the methacryloyl moiety gave significant protection against photodegradation. Similar protection was found in the 50/50 MADGEBA/DGEBA IPN material (Fig. 5).

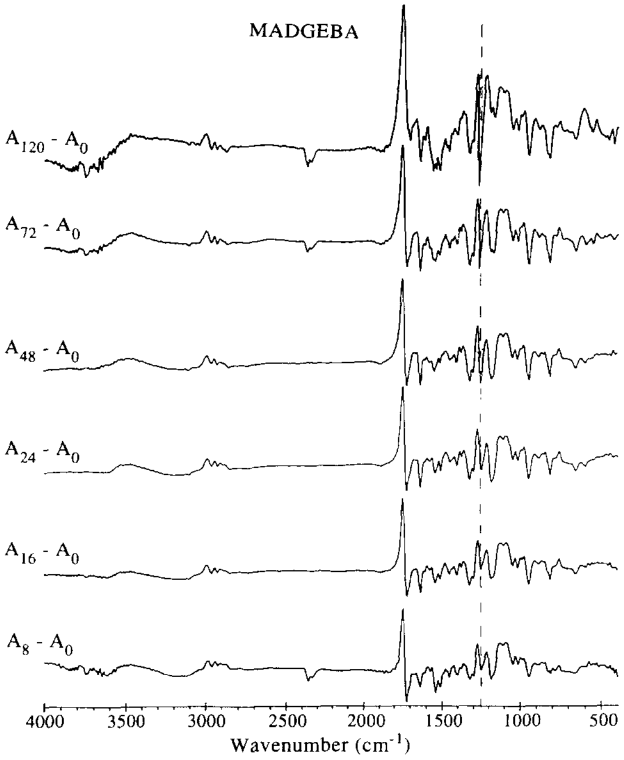


Fig. 4. Difference spectra (A_t-A_0) of MADGEBA during ageing, where t is in days.

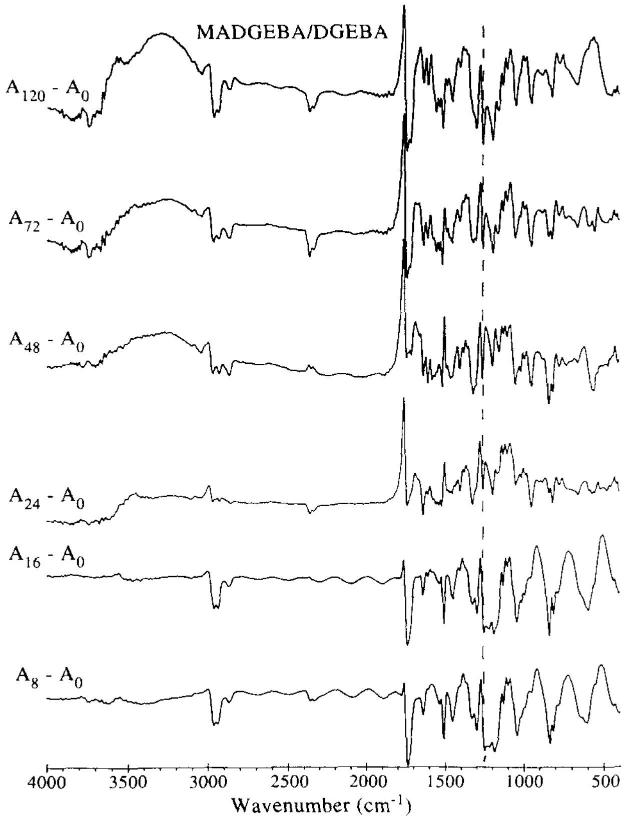


Fig. 5. Difference spectra (A_t-A_0) of MADGEBA/DGEBA (50/50) IPN during ageing, where t is in days.

Figure 6 shows the comparison of absorbance decreases at 1265 cm^{-1} for (a) pure MADGEBA, (b) the MADGEBA/DGEBA = 50/50 IPN, and (c) the pure DGEBA. Of the three materials, the pure MADGEBA showed the best resistance to photo-oxidation, followed by the IPN, because the pure MADGEBA contained the largest amount of methacryloyl moiety. The IPN material (b) also showed good stabilization against photo-oxidation. It appears reasonable to infer that the miscibility of MADGEBA and DGEBA at the molecular level[5] permits the close contact of methacrylic moiety to DGEBA chains. This allows the methacryloyl moiety to protect the IPN from UV damage.

Both MADGEBA and DGEBA materials are relatively brittle, while the MADGEBA/DGEBA IPN material is tough and possesses enhanced impact resistance because of the network interlock between components.[5] Figure 7 shows the changes of impact resistance for the various IPNs after different ageing times. It is clear from Fig. 7 that both MADGEBA (curve a) and DGEBA (curve e) lost much impact resistance, while the other IPNs (curves b–d) retained impact resistance after 45 days of accelerated ageing, especially the IPN of 50/50 MADGEBA/DGEBA, which showed even better resistance than the IPN of 75/25 MADGEBA/DGEBA, even though the 75/25 MADGEBA/DGEBA IPN contains more methacryloyl moiety. This is because MADGEBA is a brittle material. Figures 8–10 show the plots of tensile strength loss and tensile modulus loss, and elongation loss versus exposure days for various IPNs. The epoxy retained 76% of its original tensile strength after 45 days of exposure. MADGEBA retained only 83% of its original tensile strength because it is a brittle material (Fig. 10). The IPNs of MADGEBA/DGEBA = 75/25, 50/50 and 25/75

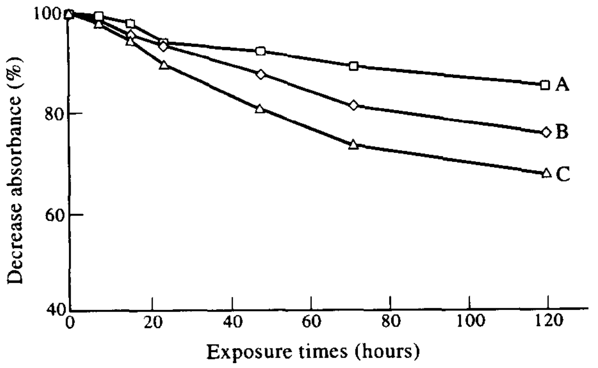


Fig. 6. Comparison of decreased absorbances at 1265 cm^{-1} for C–O–C scission. (A) MADGEBA, (B) MADGEBA/DGEBA (50/50) IPN and (C) DGEBA.

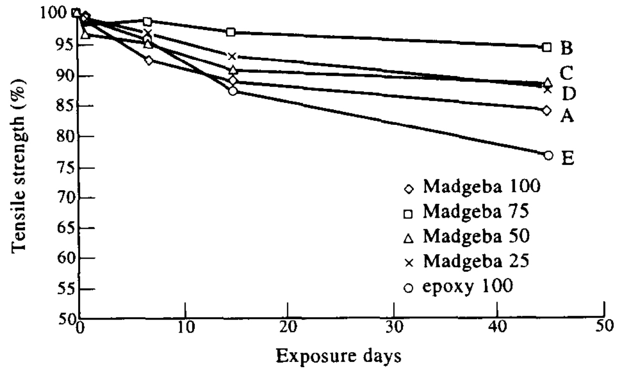


Fig. 8. Plots of percentage tensile strength versus exposure days for various IPN compositions in MADGEBA/DGEBA ratios, (◇) 100/0, (□) 75/25, (△) 50/50, (×) 25/75 and (○) 0/100.

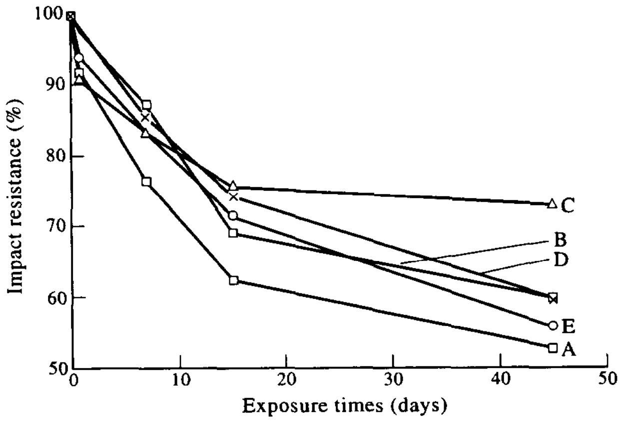


Fig. 7. Plots of percentage impact resistance versus exposure days for various IPN compositions in MADGEBA/DGEBA ratios, (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75 and (E) 0/100.

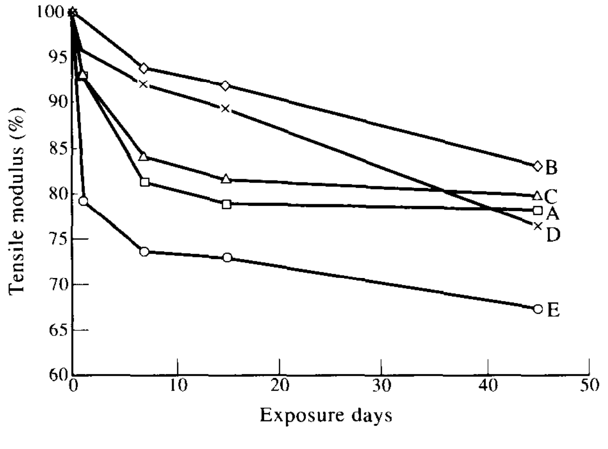


Fig. 9. Plots of percentage tensile modulus versus exposure days for various IPN compositions in MADGEBA/DGEBA ratios, (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75 and (E) 0/100.

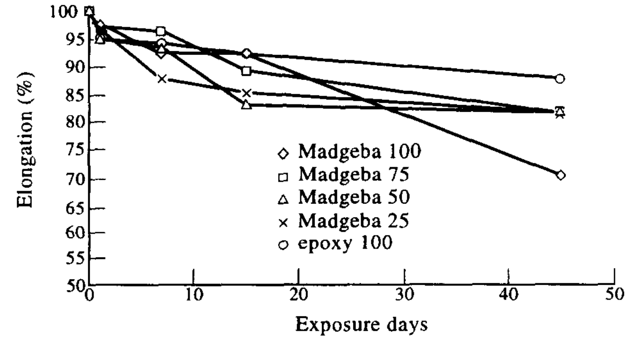


Fig. 10. Plots of elongation versus exposure days for various IPN compositions in MADGEBA/DGEBA ratios, (◇) 100/0, (□) 75/25, (△) 50/50, (×) 25/75 and (○) 0/100.

retained 93.4, 87.6 and 86.9% of their original tensile strengths, respectively. Tensile modulus measurements (Fig. 9) indicated a similar tendency. It appears that the methacryloyl moiety thus incorporated stabilized the IPN materials significantly. Mechanical tests are consistent with the finding of band changes at 1265 cm^{-1} by FTIR (Figs 3–6).

4 CONCLUSIONS

The accelerated ageing study of DGEBA by FTIR agreed with the degradation mechanisms proposed by Schutz and Dickens and co-workers. The main chain scission at C–O–C was monitored from the decreasing band at 1265 cm^{-1}. Ageing experiments revealed that incorporation of the methacryloyl moiety into the DGEBA either at chain ends or by means of IPN resulted in significant protection of the epoxy from UV damage. Mechanical tests of specimens confirmed the result of FTIR study.

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