Hydrogen characteristics and ordered structure of mono-mesogen type liquid-crystalline epoxy polymer

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Abstract
Fuel cell systems, such as those used in electric vehicles require lightweight hydrogen fuel storage. Polymer composites are candidate materials for storage vessels requiring high fracture resistance for high pressure cycling, as well as high thermal conductivity. Here, we investigate 4,4'-diglycidyloxybiphenyl (DGOBP) epoxy for such applications, and clarified the relationship between the hydrogen penetration properties and the ordered structure of the epoxy. We controlled the ordered structure of the DGOBP polymer by adjusting the curing temperature of a 4,4'-diaminodiphenyl methane (DDM) curing system. We obtained a series of cured DGOBP with DDM samples with crystallinity values of 19%, 27%, 32%, and 36%, corresponding to curing temperatures of 130, 120, 110, and 100°C, respectively. The thermal conductivities of these samples were 0.26–0.31 W m⁻¹ K⁻¹. Cured DGOBP showed hydrogen contents of 403–1271 ppm (25–75% smaller than that of conventional epoxies). Liquid crystalline epoxy polymers can be a candidate material for hydrogen storage systems requiring well-controlled hydrogen penetration properties.

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Introduction

Hydrogen energy systems are being investigated for next-generation clean energy systems. However, safety is a primary concern for commercial application and must be considered in the design of hydrogen energy systems. For hydrogen energy to be feasible and widely implemented in transport and stationary technologies, it needs to be safely and efficiently stored [1]. Compressed gas is currently the preferred solution for storing hydrogen in fuel cell vehicles (FCV). To satisfy the desired driving range and convenience of FCVs, hydrogen should be stored at 70 MPa and filled at a rapid rate, reaching its storage pressure within 3 min. To avoid thermal damage to the storage vessel, the hydrogen gas needs to be pre-cooled to −40 °C at the hydrogen filling station. Because the compression can greatly elevate the temperature of the gas [2], vessel materials must effectively radiate heat. Moreover, hydrogen storage vessels installed in FCVs need to be lightweight [3] in order to achieve high fuel efficiency.
The current FCV hydrogen vessel is a “type IV vessel”, which consists of a fully-wrapped carbon fibre reinforced plastic, such as an epoxy polymer with a plastic liner [4]. A disadvantage of polymeric materials for this application is that they generally have low thermal conductivity. In contrast, liquid-crystalline epoxy polymers, such as twin-mesogen type liquid-crystalline epoxy polymers, have been reported as strong thermal conductors [5]. Therefore, we consider that liquid-crystal polymers are suitable liner materials or matrices for carbon fibre reinforced plastics in type IV vessels. The high heat dissipation of liquid-crystal polymers should allow a higher pre-cooling temperature during filling, reducing the difficulty of sealing hydrogen gas at low temperature. In addition, it was thought that the highly dense structure of the liquid-crystal polymer should provide an effective barrier to hydrogen permeation [6,7].

In this study, we design a liquid-crystal epoxy polymer suitable as a gas-barrier material for type IV hydrogen storage vessels. A number of studies investigating the hydrogen properties of rubber as a sealing material have been reported [8–14]. It was shown that, when exposed to high-pressure hydrogen gas, the polymer materials were penetrated by hydrogen molecules. The amount of hydrogen penetration into the materials and the volume change ratio have been suggested as criteria for standardising polymer materials for high-pressure hydrogen equipment. Low penetration and volume change ratio are preferred for hydrogen barrier materials from the viewpoint of avoiding fractures and gas leaks. In addition, the thermal conductivity of the hydrogen barrier materials should be much lower than the current state-of-the-art materials considering safety and degradation of the polymers. The hydrogen penetration and thermal conductivity are expected to correlate with the “ordered structure”, such as the crystal domain or liquid-crystal structure of the material.

Understanding the effect of this ordered structure is important for designing a reliable structural material for type IV vessels to store high-pressure hydrogen gas. Here, we investigate the influence of the structure of an epoxy polymer on the hydrogen penetration properties and thermal conductivity. We selected a mono-mesogen type liquid-crystal polymer, which has a controllable ordered structure, as a model material having a similar structure, molecular size and reactive groups as conventional epoxy polymers such as bis(4-diglycidyloxyphenyl)propane. The selected material for this study was 4,4’-biphenol and DDM were purchased from Tokyo Kasei Kogyo Co., Ltd. Chloromethylxirane, tetrabuthylammonium bromide (TBAB), sodium hydroxide and sulfanilamide were purchased from Wako Pure Chemical Industries Co., Ltd. Epikote828, also known as Bisphenol A (BisA), was purchased from Mitsubishi Chemical Co., Ltd. as conventional epoxy polymer. The main ingredient of Epikote828 is 2,2-bis(4-diglycidyloxyphenyl)propane. All compounds were used as received without further purification.

The mono-mesogen type liquid-crystal epoxy monomer DGOBP was synthesised as previously described [16]. The synthesis route for the DGOBP monomer and the chemical structures of the DGOBP monomer and curing agent are shown in Scheme 1. The product was purified by reprecipitation from water and methanol.

To observe the ordered structures of the DGOBP samples cured with DDM, the monomer and curing agent were combined at a molar ratio of 2:1. This stoichiometric mixture of DGOBP and DDM was melted and mixed by stirring at 150 °C on a hot plate for 1 min. Afterwards the curing reaction was quenched by liquid nitrogen. To prepare samples for evaluating the conversion of the epoxy group in DGOBP to the amino group in DDM, this same process was employed. However, the curing reaction was undertaken for 2, 3, 5, or 7 min.

Disk-shaped specimens of DGOBP cured with DDM (diameter: 40 mm, thickness: 2 mm) were prepared from a stoichiometric mixture of the polymer and curing agent (molar ratio 2:1). The DGOBP–DDM mixture was prepared as described above, stirred for 3 min, and then cured in a mould for 4 h. The curing temperature was varied: 100, 110, 120, 130, 140, 150 or 180 °C. A stoichiometric mixture of BisA and DDM

![Scheme 1](image)

**Scheme 1** – (a) Synthesis route for the DGOBP monomer. (b) Chemical structure of the BisA monomer. (c) Chemical structure of the DDM curing agent.
Eight scans were performed. The cured polymers were cut into test pieces for subsequent analyses.

Characterization

$^1$H and $^{13}$C nuclear magnetic resonance (NMR)

NMR spectra were obtained using an Avance 500-MHz spectrometer (Bruker BioSpin Co., Ltd.) operated at room temperature ($^1$H NMR at 500 MHz and $^{13}$C NMR at 125 MHz). The chemical shifts were measured relative to the peaks of tetramethylsilane as a standard (6 in 0.00 ppm).

Liquid chromatography

Liquid chromatography was performed using an HPLC system (HLc-8320GPC, Tosoh Co., Ltd.) equipped with two TSKgel SuperH-ZM columns and one TSKgel SuperHZ2000 column. Measurements were acquired in size exclusion chromatography mode with a reflective index detector, tetrahydrofuran elution solvent, flow rate of 0.35 mL min$^{-1}$, and injection volume of 0.1 mL for a 1% w/v sample.

Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the DGOBP monomer, pre-cured samples, and DGOBP cured with DDM were measured using a FT-IR Spectrumin100s (PerkinElmer Co., Ltd.) by the KBr disc method in the wavelength range 450–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Eight scans were performed.

Differential scanning calorimetry (DSC)

DSC measurements of stoichiometric DGOBP and DDM mixtures (5 mg powder samples) were carried out using a DSC 204 HP instrument (Netzsch GmbH) in a nitrogen atmosphere from room temperature to 300 $^0$C. The heating rate was varied: 5.0, 7.5, or 10.0 $^0$C min$^{-1}$. Isothermal DSC measurements were performed on a 5 mg molten DGOBP–DDM sample. The heating rate was 50 $^0$C min$^{-1}$ from room temperature to the test temperature of 130.0, 132.5, 135.0, 137.5, 140.0, 150.0, 160.0, or 170.0 $^0$C, where the sample was held for 20 min in a nitrogen atmosphere. The DGOBP cured with DDM at different curing temperatures and the BisA cured with DDM (10 mg solid samples) were measured at a heating rate of 10 $^0$C min$^{-1}$ from room temperature to 300 $^0$C in a nitrogen atmosphere. The glass transition temperature was determined by the temperature at the half height of the heat capacity change in the DSC curve.

Polarized optical microscopy

The phase transition behaviour of the molten DGOBP–DDM samples was observed using optical microscopy (Eclipse LV150, Nikon Co., Ltd., 10 × eyepiece, 10 × or 20 × objective lenses) equipped with a crossed polarizer and a hot stage (CSS450WCX, Japan High Tech Co., Ltd.). The temperature of the hot stage was calibrated by measuring the melting points of DDM (90 $^0$C), TBAB (104 $^0$C), and sulphanalimide (165 $^0$C).

Wide-angle X-ray scattering (WAXS)

Samples of DGOBP cured with DDM were cut into disc-shaped specimens (diameter: 13 mm, thickness: 2 mm) for the WAXS measurements. A MultiFlex X-ray diffraction unit ( Rigaku Co., Ltd.) with Cu-Kz radiation was used. Continuous measurements at room temperature were undertaken with a scanning speed of 2 $^0$min$^{-1}$, resolution of 0.02°, and a 2θ range of 10–50°.

Dynamic mechanical analysis (DMA)

DMA was performed using a DVA-200s instrument (IT Keisokuseigyo Co., Ltd.) from 30 to 300 $^0$C at a heating rate of 10 $^0$C min$^{-1}$ in tensile mode, with a strain amplitude of 0.08% and a frequency of 10 Hz. Rectangular specimens cut from cured samples with a cross-sectional area of (1.5 × 1.5) mm$^2$ and a length of 15 mm were used. The samples were fixed at a distance of 10 mm between the grips of the DMA machine and measured a 2 $^0$C intervals. The molecular weight between crosslink points of the cured samples was calculated from the storage modulus (tan δ) at 280 $^0$C (where tan δ converged for every cured polymer). Here, δ is the stress–strain phase lag.

Thermal conductivity measurements

Disc-shaped specimens (diameter of 10 mm; thickness of 0.4 mm) were cut from DG0BP cured with DDM, spray-coated with thin gold and graphite electrodes. The thermal diffusivity of the cured samples was measured by the half-time method using a xenon flash analyser (LFA 467 Hyper Flash, NETZSCH GmbH) at 25 $^0$C. The specific heat capacity was measured by DSC with Al_2O_3 as the reference material, as described in ISO11357-4. The density of DGOBP samples cured with DDM was measured using a Sartorius LA230S balance equipped with the density determination kit YDK01 (Sartorius Co., Ltd.), using ethanol at 25 $^0$C. The thermal conductivity of the cured samples was calculated from the thermal diffusivity, heat capacity, and density. The measurement error of the thermal conductivity was 8%.

Hydrogen content, diffusion coefficient, and volume change after hydrogen exposure

Disc-shaped specimens with a diameter of 13 mm and a thickness of 2 mm were cut from DGOBP cured with DDM and exposed to 90 MPa hydrogen gas at 30 $^0$C for 24 h in a high-pressure vessel. The hydrogen release profile after decomposition was measured using a thermal desorption analyser (JSH-201, J-Science Lab Co., Ltd.). The amount of hydrogen released from the sample was determined by gas chromatography at 30 $^0$C in a flow of argon every 5 min. The diffusion properties of hydrogen were estimated by fitting the data. The hydrogen content immediately after decompression ($C_{HH}^0$; t = 0) and the diffusion coefficient D were estimated by fitting Eq. (1) to the remaining hydrogen content of the specimen using the least-squares method [8].

$$C_{HH}^0(t) = \frac{32}{\pi^2} C_{HH}^0 \sum_{n=0}^{\infty} \exp \left[ -\left( \frac{(2n+1)^2 \pi^2 D t}{4l^2} \right) \right] \frac{1}{(2n+1)^2}$$

where $C_{HH}^0(t)$ (wt. ppm) is the remaining hydrogen content at time t (s), the time elapsed since decomposition. $C_{HH}^0$ (wt. ppm) is the hydrogen content at t = 0, D (m$^2$ s$^{-1}$) is the diffusion coefficient, $\beta_n$ is the root of the zero-order Bessel function, and l (m) and r (m) are the thickness and radius of the specimen, respectively. The measurement errors for the hydrogen
content and diffusion coefficient were estimated from the accuracy of the TDA chromatography and the measurement error of specimens from the propagation of errors from Equation (1). The measurement error for the hydrogen content and diffusion coefficient were 5% and 14%, respectively. The volume change of the disc-shaped specimens after hydrogen exposure was observed at 30 °C by a laser scan micrometre (TM-3000, Keyence Co., Ltd.) with a TM-065 sensor head and an InGaN green LED light source. The disc area was measured at 5 min intervals. The volume was calculated by cubing the square root of the area and was expressed as a proportion of the initial sample dimensions (i.e. the volume change ratio).

Results and discussion

Synthesis of DGOBP

4,4’-dihydroxybiphenyl and chloromethylloxirane reacted stoichiometrically with NaOH (aq.) and TBAB (see Scheme 1). The product was analysed by liquid chromatography using a differential refractive index detector where the peak area was calculated from the chromatogram. The reaction products of the synthesized DGOBP was confirmed by the 1H and 13C peaks determined by NMR (500 MHz, CDCl3, δ = 118.5 ppm (Ar CH), 150.1 ppm (OCCHHCAr), 69.0 ppm (CH2OCH2O), 50.1 ppm (CH2OCH2O), and 44.7 ppm (CH2OCH2O). The IR (KBr) data are as follows: ν = 3063 cm⁻¹ (w; νas (Ar CH)), 3041 cm⁻¹ (w; νs (Ar CH)), 3008 cm⁻¹ (w; νs (epoxy CH)), 2929 cm⁻¹ (w; νas (CH)), 2877 cm⁻¹ (w; νs (CH)), 1606 cm⁻¹ (s; ν (Ar ring)), 1501 cm⁻¹ (s; δ (Ar ring)), 1244 cm⁻¹ (s; νas (CO)), 1180 cm⁻¹ (m; δ (Ar CH)), 1134 cm⁻¹ (m; δ (Ar CH)), 1037 cm⁻¹ (s; νs (CO)), 911 cm⁻¹ (m; νas (epoxy CO)), 814 cm⁻¹ (s; γ (Ar CH)), and 762 cm⁻¹ (m; τ (Ar CH)), melting point = 160 °C.

Curing behaviour

The curing behaviour was determined by DSC as described in Section Materials and methods. The curing temperature was determined from the exothermic peak of the DSC traces of the stoichiometric DGOBP–DDM mixture [25]. At each heating rate (5.0, 7.5, and 10.0 °C min⁻¹), the exotherm of the curing reaction appears at temperatures above 130 °C, higher than the endotherm related to the melting of the DDM (around 85 °C for this purity of monomer). Fig. 1 shows the isothermal DSC traces of the melting process of the DGOBP–DDM mixtures cured at different temperatures. The isothermal DSC traces show a broad peak related to the curing reaction after the samples melted. The peak width decreased with increasing isothermal temperature, indicating an increase in the reaction rate at higher isothermal temperatures. The DSC traces of the mixtures cured below 135 °C showed an additional exothermic peak, which appeared 3–4 min after reaching the target temperature. This peak was absent in mixtures cured above 137.5 °C, suggesting that it originates from the ordered structure in the samples (as will be discussed later).

The DGOBP–DDM mixtures used in the isothermal curing study were prepared for observation using polarised optical microscopy by mixing at 150 °C for 1 min, followed by rapid cooling in liquid nitrogen [26]. Note that although DGOBP was dissolved in the molten DDM at 150 °C, its melting point is actually 160 °C. Fig. 2 shows polarised optical micrographs of the DGOBP–DDM mixtures obtained at 130 °C and 135 °C. After 3–4 min, a birefringent domain began to emerge in the sample cured at 130 °C and a birefringent texture began to emerge in the sample cured at 135 °C. The ordered structure of such birefringent domains in the sample cured at 130 °C was confirmed by wide angle X-ray patterns reported by Mititelu et al. [15]. A magnified view of the birefringent domain of the sample cured at 130 °C is shown in Fig. 3. The nucleation and growth (to the order of 10 μm) of a spherulite-like structure is clearly visible in these micrographs. The polarised optical micrographs of samples cured at 135 °C showed no definite crystallite structure; the spherulite-like structure was absent in these samples. Li et al. attributed the extra exothermic peak...
in the isothermal DSC traces to the smectic phase [16]. Hence, we infer that the birefringence observed in the polarised optical microscopy images of samples cured at high temperature (above 135 °C) reflects the nematic phase. This suggests that the exothermic peaks in the isothermal DSC traces originate from the crystal phase.

Fig. 4 shows the time–temperature–phase transformation (TTT) diagram indicating the regions of the isotropic, liquid-crystal, and crystal phases of the DGOBP isothermally cured with DDM [28–33]. The solid curves represent the onset of the liquid-crystal phase and the crystal phase transition from the isotropic phase. These onsets were determined from the polarised optical micrographs of the ordered phase observed during isothermal curing. The broken line marks the boundary between the liquid-crystal and crystal phases. Therefore, the ordered structure of DGOBP cured with DDM can be controlled by the curing temperature. Thus, to control the amount of ordered structure in the cured DGOBP with DDM, cured polymer samples were prepared at 100, 110, 120, 130, 140, 150, and 180 °C for 4 h.
Conversion of the epoxy group

The conversion of the epoxy group was determined from the FT-IR and DSC measurements. The conversion of the amine-based curing system has been studied by many authors [34–37]. In terms of the methodology of these studies, the calibration curve for the conversion of the epoxy group by the consumption of the DGOBP monomer and DDM was defined in this study. The area under the exothermic peak in the DSC traces of the pre-cured samples was assumed as the residual heat of the curing reaction. The total heat of reaction was assumed to be the residual heat of the curing reaction of the uncured DGOBP–DDM mixtures. The overall conversion was calculated from dividing the residual heats by the total heats of the curing reaction. In the FT-IR spectra of the pre-cured samples, we computed the ratio of the peaks attributed to the CO stretching vibration of the epoxy group (at 910 cm⁻¹) and the in-plane vibration of the phenyl ring (at 1610 cm⁻¹). The decrease in the height of the 910 cm⁻¹ peak was attributed to the consumption of monomer. The peak at 1610 cm⁻¹ was adopted as the internal standard for the spectra. Using the calibration curve method, the conversion of the epoxy group can be evaluated regardless of the overlap of the peaks originating from other chemical species. By analysing the changes in the 910 cm⁻¹/1610 cm⁻¹ peak ratios, we derived the epoxide conversion in the DGOBP cured with DDM.

Fig. 5 shows the FT-IR spectra of the DGOBP cured with DDM at different temperatures. The KBr disc method used to acquire the data allowed us to evaluate the conversion both on the surface and in the bulk of the samples. The cured samples show reduced absorption intensity of the epoxide group at 910 cm⁻¹. The percentage conversion values of the epoxide groups at each curing temperature, obtained by the peak ratio of 910 cm⁻¹/1610 cm⁻¹, are summarised in Table 1. Above 140 °C, the epoxide group was completely consumed. Even at lower curing temperatures, more than 94% of the epoxide groups were consumed during the curing process. From these results, it can be concluded that the curing of DGOBP with DDM was successful at all temperatures investigated here.

Observation of the ordered structure

Fig. 6 shows the WAXS patterns of DGOBP cured with DDM at different temperatures. Samples cured below 130 °C exhibited three diffraction peaks, at 2θ = 19°, 22°, and 27°, corresponding to d-spacings of 0.46, 0.40, and 0.32 nm, respectively. At curing temperatures below 130 °C, crystalline phases should be present in the cured polymer. The d-spacing of the sample cured above 140 °C was attributed to the stacking of mesogen groups, implying that the liquid crystal structure was frozen in the cured polymer [7]. We evaluated the degree of crystallinity by integrating the intensity of the crystal peak and broad peak (halo patterns) from the WAXS patterns [38]. The crystallinity values of our DGOBP–DDM samples were 19%, 27%, 32%, and 36%, where the degree of crystallinity increased as the curing temperature decreased. This crystallization gives rise to the exothermic peaks observed in the isothermal DSC traces (see Fig. 1). Douglas et al. and Cho et al. have reported a relationship between the phase transition and the gel point [31,33]. Smaller spherulite particles were formed in DGOBP cured at 130 °C compared to those in samples cured at 100 °C. This was attributed to a decline in the mobility of the molecular chains as a result of gelation, preventing an increase in the spherulite size.

Fig. 7 shows the storage modulus and tan δ from DMA measurements (Fig. 7 a, b, respectively) of DDM-cured BisA
Table 1 – Epoxide conversion and thermal, physical, and structural properties of DGOBP cured with DDM.

<table>
<thead>
<tr>
<th>Curing temperature (°C)</th>
<th>Conversion (%)</th>
<th>$E'$ at r.t.a</th>
<th>$T_g^d$ (°C)</th>
<th>$E'$ at $T_g^d$ (Pa)</th>
<th>$T_c^i$ (°C)</th>
<th>$E'$ at $T_c^i$ (Pa)</th>
<th>$E'$ at $T_m^f$ (Pa)</th>
<th>$\rho_{Me}^e$ (g mol$^{-1}$)</th>
<th>$T_d^b$ (°C)</th>
<th>$D_c^j$ (nm)</th>
<th>$d_i^k$</th>
<th>$\rho^k$</th>
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<tbody>
<tr>
<td>100</td>
<td>94</td>
<td>$1.94 \times 10^9$</td>
<td>127</td>
<td>$1.42 \times 10^9$</td>
<td>213</td>
<td>$2.77 \times 10^6$</td>
<td>$1.98 \times 10^6$</td>
<td>86</td>
<td>144</td>
<td>35.8</td>
<td>0.46</td>
<td>1.270</td>
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<tr>
<td>110</td>
<td>95</td>
<td>$1.99 \times 10^9$</td>
<td>151</td>
<td>$1.25 \times 10^9$</td>
<td>216</td>
<td>$2.82 \times 10^6$</td>
<td>$2.01 \times 10^6$</td>
<td>86</td>
<td>149</td>
<td>31.8</td>
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<td>120</td>
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<td>214</td>
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<td>208</td>
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<td>$2.18 \times 10^6$</td>
<td>66</td>
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<td>18.7</td>
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<td></td>
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<td>162</td>
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<tr>
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<td>140</td>
<td>$5.63 \times 10^7$</td>
<td>–</td>
<td>$4.90 \times 10^6$</td>
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<td>317</td>
<td>132</td>
<td>0.0</td>
<td>0.50</td>
<td>1.191</td>
</tr>
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</table>

a: The storage modulus measured at 30 °C.
b: The glass transition temperature as measured by the peak of tan δ.
c: The storage modulus measured at the glass transition temperature.
d: The melting temperature of the crystal structure.
e: The storage modulus measured at 30°C (before melting).
f: The molecular weight between crosslink points.
g: The glass transition temperature from DSC measurement.
h: The degree of crystallinity calculated from WAXS measurement.
i: The d-spacing as measured by peak top of halo pattern from WAXS measurement.
j: The density.
k: The density.

The temperature dispersion of tan δ of DGOBP cured with DDM below 130 °C (see Fig. 7 b) showed two peaks, one at approximately 210 °C corresponding to melting of the crystal phase and the other the glass transition of the amorphous phase (which depended on the curing temperature). The peak height of tan δ (indicating the glass transition) of the amorphous phase was smaller than that of the crystal phase at temperatures ≤120 °C. The tan δ curves of DGOBP cured with DDM above 140 °C exhibited a single peak, indicating that these samples lacked the crystal phase. The tan δ curve of BisA cured with DDM exhibited a single peak, however, the DSC trace (Fig. 7 c) showed an endothermic peak before a change in the heat capacity. This peak can be assigned to the enthalpy relaxation, according to a previous study of a similar cured BisA system [39,40]. The glass transition temperature of DGOBP cured with DDM derived from DSC measurements depends on the curing temperature. This phenomenon has also been observed in conventional epoxy polymer systems [41]. The relationship between curing temperature and glass transition temperature is in agreement with the DMA measurements. Neither of the DSC traces for cured BisA or DGOBP showed an exothermic peak of melting. Both the DMA and DSC measurements and DGOBP samples and their corresponding DSC traces (Fig. 7 c). The peak height of tan δ of DGOBP was smaller than that of BisA. The storage modulus of DGOBP cured with DDM widely varies from 150 to 250 °C; the resulting peak in the tan δ curves is thought to indicate the glass transition temperature. The storage moduli of the samples at room temperature increased slightly with increasing curing temperature in the case of the DGOBP sample, which means that the amount of liquid crystal or crystal structure does not affect the storage modulus of the sample at room temperature. The decreasing storage modulus in the rubbery region differs between the crystalline samples and the liquid crystalline samples. The molecular weight between crosslink points of DGOBP cured with DDM at 130 °C showed the lowest value of all samples tested. It was thought that the lower curing temperature samples formed low chemical crosslink points, attributed to the inhibition of the curing reaction as a result of the increased crystallinity.

The temperature dispersion of tan δ of DGOBP cured with DDM below 130 °C (see Fig. 7 b) showed two peaks, one at approximately 210 °C corresponding to melting of the crystal phase and the other the glass transition of the amorphous phase (which depended on the curing temperature). The peak height of tan δ (indicating the glass transition) of the amorphous phase was smaller than that of the crystal phase at temperatures ≤120 °C. The tan δ curves of DGOBP cured with DDM above 140 °C exhibited a single peak, indicating that these samples lacked the crystal phase. The tan δ curve of BisA cured with DDM exhibited a single peak, however, the DSC trace (Fig. 7 c) showed an endothermic peak before a change in the heat capacity. This peak can be assigned to the enthalpy relaxation, according to a previous study of a similar cured BisA system [39,40]. The glass transition temperature of DGOBP cured with DDM derived from DSC measurements depended on the curing temperature. This phenomenon has also been observed in conventional epoxy polymer systems [41]. The relationship between curing temperature and glass transition temperature is in agreement with the DMA measurements. Neither of the DSC traces for cured BisA or DGOBP showed an exothermic peak of melting. Both the DMA and DSC measurements and DGOBP samples and their corresponding DSC traces (Fig. 7 c). The peak height of tan δ of DGOBP was smaller than that of BisA. The storage modulus of DGOBP cured with DDM widely varies from 150 to 250 °C; the resulting peak in the tan δ curves is thought to indicate the glass transition temperature. The storage moduli of the samples at room temperature increased slightly with increasing curing temperature in the case of the DGOBP sample, which means that the amount of liquid crystal or crystal structure does not affect the storage modulus of the sample at room temperature. The decreasing storage modulus in the rubbery region differs between the crystalline samples and the liquid crystalline samples. The molecular weight between crosslink points of DGOBP cured with DDM at 130 °C showed the lowest value of all samples tested. It was thought that the lower curing temperature samples formed low chemical crosslink points, attributed to the inhibition of the curing reaction as a result of the increased crystallinity.
demonstrated that we can obtain DGOBP cured with DDM with a crystal structure, which is supported by the WAXS results.

Along with the epoxide conversions, Table 1 lists the storage moduli at room temperature, the glass transition temperatures, and molecular weight between crosslink points estimated from the storage moduli in the rubbery state. The glass transition temperatures estimated by the DSC measurements and the degree of crystallinity calculated from the WAXS measurements are also listed in Table 1. The degree of crystallinity can be calculated from the density of crystalline and amorphous phases; although the precise density of the crystal structure has not been clarified for DGOBP cured with DDM. However, the sample densities follow the trend of the WAXS measurements. Both sets of results support a crystalline phase in DGOBP cured with DDM, which diminishes as the curing temperature increases. Reducing the curing temperature increased the density of DGOBP cured with DDM, which is synonymous with increasing the degree of crystallinity. To clarify this point, BisA cured with DDM (also presented in Table 1) is less dense than DGOBP cured with DDM and exhibited no evidence of a crystal phase in the WAXS measurements. From the WAXS, DMA, and density measurements, we infer that DGOBP cured with DDM at low temperature comprises both crystalline and amorphous component. Thus, we can control the degree of crystallinity of DGOBP cured with DDM by adjusting the curing temperature.

**Thermal conductivity**

Fig. 8 shows the thermal conductivity of DGOBP cured with DDM at different curing temperatures. The mean value of the thermal conductivity from 100 °C to 130 °C was 0.26–0.28 Wm⁻¹ K⁻¹ which is slightly lower than that of samples cured from 140 °C to 180 °C, 0.27–0.31 Wm⁻¹ K⁻¹. A
decline in the thermal conductivity with increasing crystallinity for polyethylene terephthalate has been reported by Choy [42]. This decline in the thermal conductivity is attributed to the static scattering of phonons from the crystal interface. However, the thermal conductivity of the DGOBP-DDM system always exceeded that of BisA-DMM (within experimental uncertainty) for the conditions of these experiments. The improvement in thermal conductivity for different monomers is attributed to the densely packed atoms in the liquid crystal structures and crystal structures.

Hydrogen properties

Fig. 9 presents the hydrogen release profiles obtained from TDA measurements of the DGOBP cured with DDM by showing the remaining hydrogen content in the specimens after decompression from exposure to high-pressure hydrogen gas. The slope of the hydrogen release profiles moderately decreases with increasing degree of crystallinity, indicating a small diffusion coefficient of hydrogen in the polymer. The contents and diffusion coefficients of hydrogen in DGOBP cured with DDM obtained by least-squares fitting, are listed in Table 2.

![Fig. 9 – Time dependence of the remaining hydrogen content in DGOBP cured with DDM at different curing temperatures.](image)

Fig. 10 shows the hydrogen content and diffusion coefficient of hydrogen as functions of the curing temperature. Both of these properties decrease with increasing crystallinity of the DGOBP sample, and both are lower in DGOBP cured with DDM than in BisA cured with DDM. The differences in the hydrogen content values are larger than the estimated error in this study, and are hence significant. The hydrogen content of DGOBP cured with DDM are 25–75% smaller than that of conventional epoxy polymer. The volume change ratios of DGOBP cured with DDM at each curing temperature depended on the hydrogen content, and in the case of samples cured below 130 °C, the volume change ratio decreased due to the high crystallinity. The hydrogen properties were not significantly correlated with the molecular weight between crosslink points.

Fig. 11 shows the hydrogen properties as a function of the degree of crystallinity of DGOBP cured with DDM. The hydrogen penetration properties are strongly inversely correlated with the amount of crystal structure in the polymer, despite the low correlation with the molecular weight of crosslinking points. The inverse relationship between crystallinity and hydrogen content likely reflects the difficulty of penetrating the crystalline phase. The relationship between crystallinity and gas properties has been reported for polyethylene by Michaels et al. [43,44]. It is thought that hydrogen also penetrates the amorphous region or the liquid crystal region of the cured epoxy polymer, indicating that the hydrogen penetration properties could be estimated from the amount of hydrogen entering these regions. In other words, the hydrogen penetration property of DGOBP cured with DDM can be determined from the degree of crystallinity.

Conclusions

In this study, we investigated the relationship between the hydrogen penetration properties and the ordered structure of a mono-mesogen type liquid-crystalline epoxy polymer, a candidate material for hydrogen storage vessels. We selected 4,4’-diglycidoxybiphenyl (DGOBP) as a model epoxy polymer and prepared a series of samples with controlled ordered structures. The ordered structure of DGOBP was controlled by

<table>
<thead>
<tr>
<th>Curing temperature (°C)</th>
<th>ρMC (g mol⁻¹)</th>
<th>Dc (%)</th>
<th>K* (W m⁻¹ K⁻¹)</th>
<th>Di (m² s⁻¹)</th>
<th>Ci (wt.ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>86</td>
<td>35.8</td>
<td>0.26</td>
<td>3.77 × 10⁻¹²</td>
<td>403</td>
</tr>
<tr>
<td>110</td>
<td>86</td>
<td>31.8</td>
<td>0.28</td>
<td>3.89 × 10⁻¹²</td>
<td>458</td>
</tr>
<tr>
<td>120</td>
<td>71</td>
<td>27.4</td>
<td>0.27</td>
<td>4.58 × 10⁻¹²</td>
<td>511</td>
</tr>
<tr>
<td>130</td>
<td>66</td>
<td>18.7</td>
<td>0.27</td>
<td>5.17 × 10⁻¹²</td>
<td>629</td>
</tr>
<tr>
<td>140</td>
<td>72</td>
<td>0.0</td>
<td>0.31</td>
<td>9.90 × 10⁻¹²</td>
<td>1271</td>
</tr>
<tr>
<td>150</td>
<td>105</td>
<td>0.0</td>
<td>0.29</td>
<td>1.07 × 10⁻¹¹</td>
<td>1183</td>
</tr>
<tr>
<td>160</td>
<td>162</td>
<td>0.0</td>
<td>0.29</td>
<td>1.13 × 10⁻¹¹</td>
<td>1206</td>
</tr>
<tr>
<td>BisA (100)</td>
<td>317</td>
<td>0.0</td>
<td>0.21</td>
<td>4.35 × 10⁻¹¹</td>
<td>1682</td>
</tr>
</tbody>
</table>

*a* The molecular weight between crosslink points.

*b* The degree of crystallinity calculated from WAXS measurement.

*c* The thermal conductivity.

*d* The diffusion coefficient of hydrogen molecular.

*e* The hydrogen content.
adjusting the curing temperature of the 4,4’-diaminodiphenyl methane (DDM) curing system. Crystal structures were observed in DGOBP cured with DDM below 130 °C, and the degree of crystallinity decreased with increasing curing temperatures. We obtained a series of samples having 19%, 27%, 32%, and 36% crystallinity, corresponding to curing temperatures of 130, 120, 110, and 100, respectively. The thermal conductivity values of DGOBP cured with DDM were in the range of 0.26–0.31 Wm⁻¹ K⁻¹, regardless of their degrees of crystallinity. Cured DGOBP showed hydrogen contents in the range of 403–1271 ppm, which is 25–75% smaller than that of conventional epoxy polymer. The hydrogen content and diffusion coefficient of DGOBP cured with DDM reduced with increasing crystallinity, indicating that both factors can be controlled by the degree of crystallinity.

Because the ordered structure governs the diffusivity of hydrogen in liquid-crystal epoxy polymer, we conclude that the degree of crystallinity of the polymer strongly correlates with the hydrogen penetration. According to these results, DGOBP polymer with liquid-crystal structure can be a candidate polymer material for components in hydrogen systems, which require well-controlled hydrogen penetration properties. This suggests that we can design a suitable epoxy polymer with low hydrogen penetration properties by understanding and carefully controlling the development of the liquid-crystalline phase.

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**REFERENCES**


[9] Yamabe J, Matsumoto T, Nishimura S. Application of acoustic emission method to detection of internal fracture of...


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