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Transparency and toughness characterization of epoxy resins modified with liquid chloroprene rubber

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Transparent epoxy resins modified with liquid chloroprene rubber (LCR), containing in a category of rubber-toughened resin were found. Transparency and toughness characterization of the modified epoxy resins were investigated as a function of LCR content. Epoxy resins modified with 0–10 vol % LCR showed complete phase-separation microstructure. However, these modified resins were transparent, because the refractive index of LCR was compatible with that of the epoxy resin matrix at room temperature. On the other hand, it was observed that above 10 vol % LCR, a certain amount of LCR dissolved into the epoxy matrix. In this case, the glass transition temperature decreased with increasing LCR content. It was also found that the critical stress intensity factor, K_c, of the modified epoxy resins exhibited a maximum between 10 and 15 vol % LCR.

1. Introduction

It is well known that epoxy resins can be modified with elastomeric polymers for the purpose of toughening. When a modifier is mixed with an epoxy oligomer and a curing reagent, during the very early stage of curing, the elastomeric modifier dissolves completely into the epoxy oligomer. Prior to gelation of the epoxy resin, an *in situ* phase separation of rubbery particles occurs [1]. Thus, in this stage the mixture is a two-phase system, in which the spherical rubber domains, typically a micrometre or so in diameter, are dispersed in the epoxy resin matrix. It has been reported that high toughness of the modified epoxy resin which results in the multiphase microstructure, arises from the greater extent of energy-dissipating deformation occurring in the vicinity of the crack tip [2, 3].

Most elastomer-modified resins are not transparent, because the refractive index of the dispersed rubber phase differs from that of the epoxy matrix phase. It was found earlier that a transparent system of elastomeric modifier and epoxy matrix exists in the category of rubber-toughened resins. There are thought to be two reasons why the elastomer-modified epoxy resin is transparent: (1) elastomer is dissolved homogeneously in an epoxy resin, or the diameter of the dispersed rubber phase is smaller than the wavelength of visible light; (2) in a phase-separation structure, the refractive index of rubber is the same as that of the epoxy resin. In this report, the microstructure and mechanical properties of transparent epoxy resins modified with liquid chloroprene rubber (LCR) are described.

2. Experimental procedure

2.1. Materials

The epoxy resin used in this investigation was a liquid diglycidyl ether of bisphenol A, Epikote 828, supplied by Yuka-Shell Epoxy Co. The resin was cured with 80 p.h.r. hexahydrophthalic anhydride (HHPA) and 1 p.h.r. *N,N′*-dimethyl-benzylamine (DMBA) as an accelerator. The modifier was liquid chloroprene rubber (a liquid rubber with two hydroxy end groups which has $M_n = 5100$), supplied by Denkikagaku Ind. Co. The sets of materials investigated consisted of 100 parts Epikote 828, 80 parts HHPA and 0, 10, 20, 30, 50 parts LCR. Before mixing, LCR was pre-reacted with HHPA at 80 °C for 1 h. Epoxy oligomer, LCR, HHPA and DMBA were thoroughly stirred at 80 °C in a morter *in vacuo*, and then cast between glass plates 6 mm apart. After curing for 3 h at 80 °C, the moulded plate was post-cured for 1 h at 120 °C and for 3 h at 150 °C. To designate the various LCR-modified materials, the notation shown in Table I was adopted. Specimens used for the measurements discussed below were machined from moulded plates.

2.2. Measurements

The refractive index of modified epoxy resins and liquid rubber was measured using an Abbe refractometer with a thermo-controller. Transmittance of various epoxy plates (6 mm thick) was measured using an ultraviolet spectrophotometer (Shimazu UV-210A) at room temperature.

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TABLE I Notation for LCR-modified epoxy resins

Amount of Epikote 828 (p.h.r.)	Amount of HHPA (p.h.r.)	Amount of LCR (p.h.r.)	Amount of LCR (vol %)	Designation	T_g (°C)
100	80	0	0	LCR (0)	134
100	80	10	5.1	LCR (5)	130
100	80	20	9.7	LCR (10)	123
100	80	30	15.3	LCR (15)	120
100	80	50	25.2	LCR (25)	113

1 p.h.r. of DMBA was used for all materials.
T_g was determined by the TMA method.

In uniaxial tensile tests these materials fractured in a brittle manner before the yield point is reached, therefore compression tests (ASTM method D695) were conducted at 23 °C to investigate their plastic deformation behaviour. In addition, flexural moduli were measured at 23 °C according to the ASTM method D790.

Dynamic mechanical measurements at 10 Hz were made in the cantilever bending mode at −100–200 °C using a Seiko DMS200 Viscoelasto-spectrometer. The specimen cross-section was 1 mm × 5 mm with a span of 20 mm.

Fracture behaviour was examined using the fracture mechanics approach [4]. Fracture mechanics measurements were made at 23 °C in three-point bending (TPB) at crosshead speed of 1 mm min^{-1}, on sharply notched rectangular bars measuring 12 mm × 12 mm × 52 mm with a span of 48 mm (ASTM E399). Sharp cracks were initiated by tapping with a hammer on a razor blade. The fracture toughness of the cured epoxy resins was evaluated from the critical value, K_{1c}, of the stress intensity factor for the initiation of crack growth, which was determined from TPB specimen according to ASTM E399.

The fracture surfaces of the TPB specimens were observed using a scanning electron microscope (ERAX-3000, Elionix) at a relatively low accelerating voltage of 2 kV. Prior to examination the surfaces were coated with a thin layer of gold in order to improve conductivity and prevent charging.

3. Results and discussion

3.1. Microstructure

The scanning electron micrographs of the fracture surfaces of the rubber-modified epoxy resins are shown as a function of LCR content in Fig. 1. At lower LCR contents, essentially spherical rubber precipitates were found. In the case of LCR (5), dispersed rubber particles with a diameter of 0.5–1 μm were observed. For LCR (10) and LCR (15), dispersed particles were also observed. However, the boundary of the rubber and epoxy matrix became obscure with increasing LCR content. The better solubility of LCR into the epoxy matrix in the case of higher LCR contents is perhaps also responsible for the relatively indistinct epoxy–rubber interface. On the other hand, fracture surfaces of LCR (25) no longer show dispersed particles. The epoxy resins modified with 5–15 vol % LCR shows the microphase separation structure. If the refractive index of the epoxy matrix was different from that of LCR, rubber-modified epoxy resins did not become independent.

3.2. Transparency

It was found that all elastomer-modified epoxy resins were transparent at room temperature. Also, not only above but also below room temperature, LCR (5) and LCR (10) became opaque. A wavelength-dependence of transmittance of cured epoxy plates (6 mm thick) at room temperature are shown in Fig. 2. These rubber-modified epoxy plates appeared to be very transparent to the naked eye, but from this figure, it can be seen that LCR (5) lacked most in transparency and the transmittance increased with increasing LCR content.

3.3. Refractive index

Fig. 3 shows the temperature dependence of the refractive index of the liquid chloroprene rubber and unmodified epoxy resin (Ep-HHPA, LCR(0)). It is clear that n_{25} of LCR was compatible with that of epoxy resin matrix at room temperature. Therefore, in spite of the formation of microphase separation structure, modified epoxy resins became transparent. The n_{25} value of modified epoxy resins are shown in Fig. 4. For LCR(5), n_{25} showed the same value as that of epoxy resin matrix (LCR(0)). However, n_{25} values of LCR(10), LCR(15) and LCR(25) were larger than that of LCR(5). This was considered to be because a certain amount of LCR was dissolved into the epoxy matrix above 10 vol % LCR. An incomplete phase separation was responsible for the decrease in T_g determined by the TMA method.

3.4. Dynamic mechanical properties

Dynamic mechanical properties of the LCR-modified epoxy resins are shown in Fig. 5. Two relaxations were observed; the high-temperature peak, α, is due to the motion of the main polymer chain at the glass transition temperature (T_g, epoxy), the low-temperature peak, β, is due to the motion of the diester segments introduced into the network by HHPA and/or the

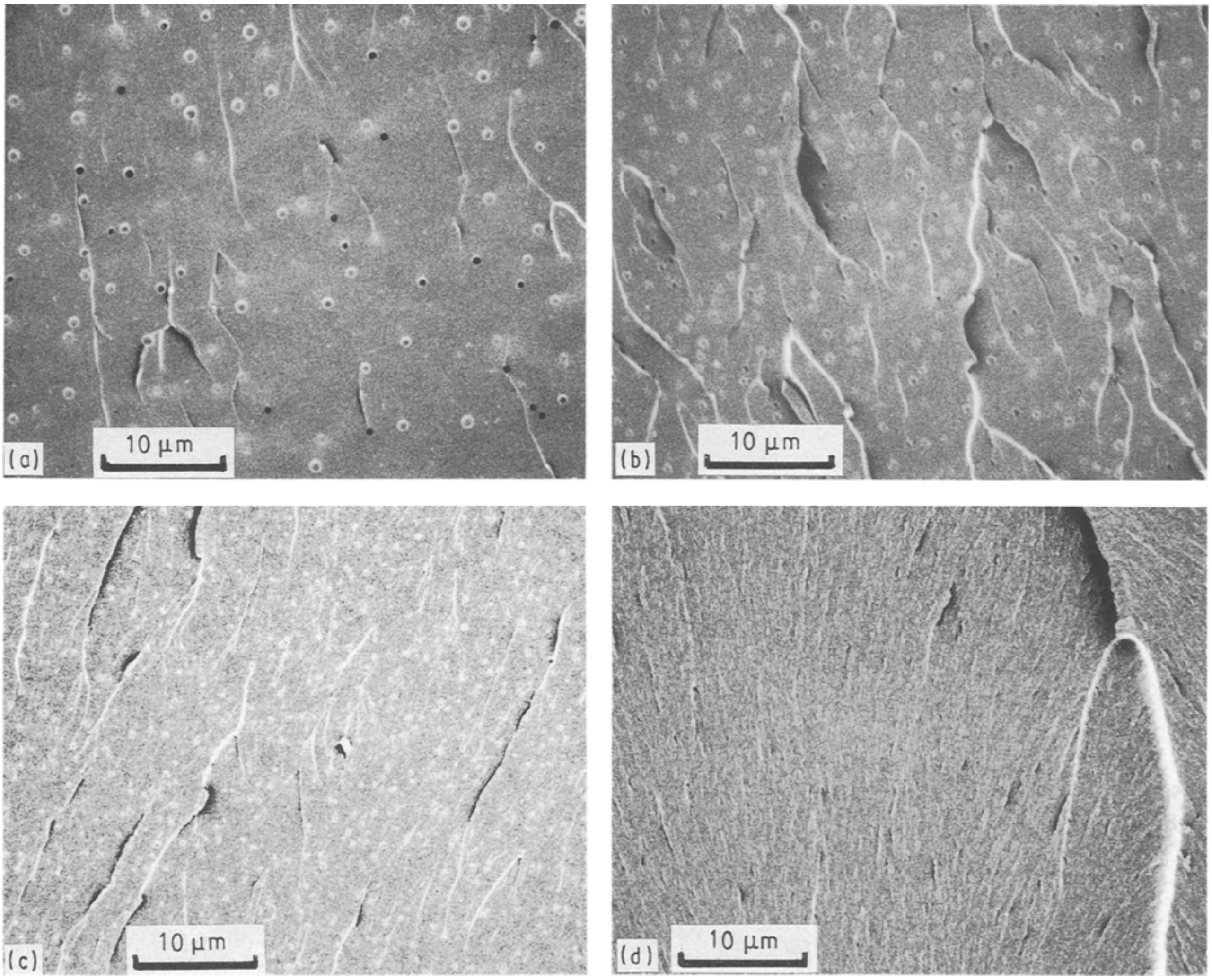

Figure 1 Fracture surfaces of the LCR-modified epoxy resins. (a) LCR (5), (b) LCR (10), (c) LCR (15), (d) LCR (25).

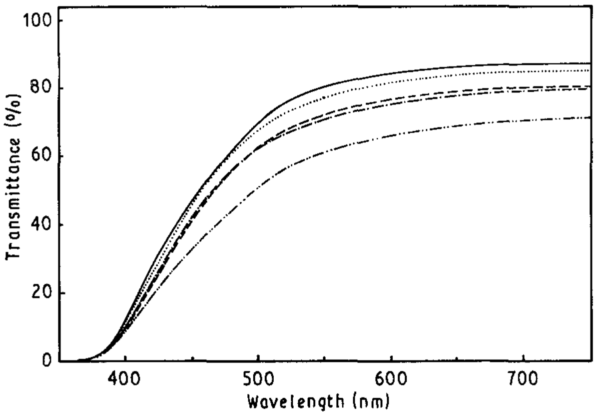

Figure 2 Transmittance of the LCR-modified epoxy resins at room temperature. (——) LCR (0), (–··–) LCR (5), (–·–) LCR (10), (– – –) LCR (15), (····) LCR (25).

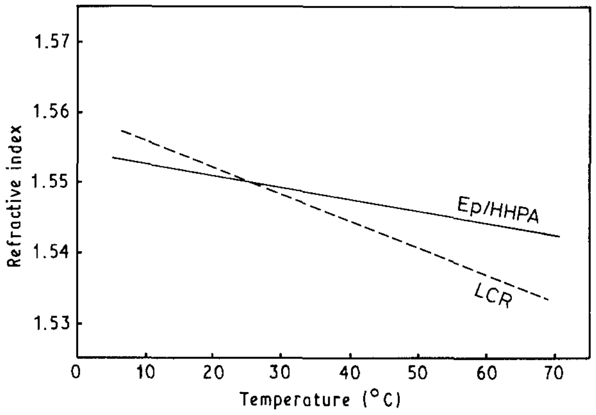

Figure 3 Temperature dependence of refractive index of the liquid chloroprene rubber and unmodified epoxy resin.

motion of the main chain of LCR (T_g peak of the rubbery phase) [5]. In this system, the β-peak temperature of the epoxy matrix is very near the α-peak temperature (T_g, rubber) of the rubber. An addition of LCR into the epoxy resin increased relaxation between α and β relaxation, and also the peak temperature in the α relaxation shifted to a lower temperature. From this figure, it is deduced that a significant amount of LCR was dissolved into the epoxy matrix at high LCR contents.

3.5. Yield strength and Young's modulus

The dependence of rubber content on the compressive yield stress and flexural modulus at 23 ± 1 °C is shown in Fig. 6. The presence of a rubbery dispersed

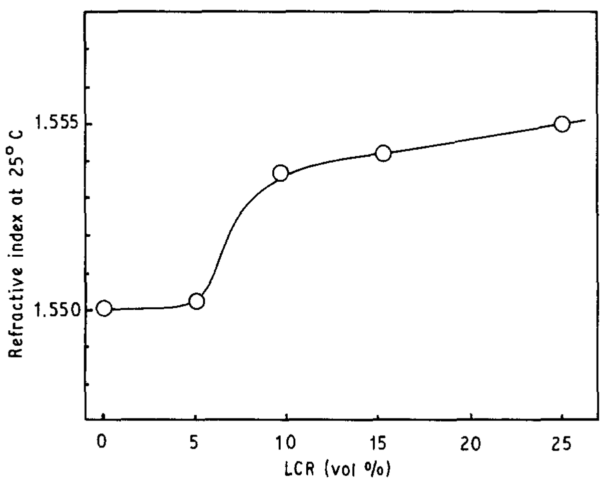

Figure 4 Refractive index of the LCR-modified epoxy resins as a function of LCR content.

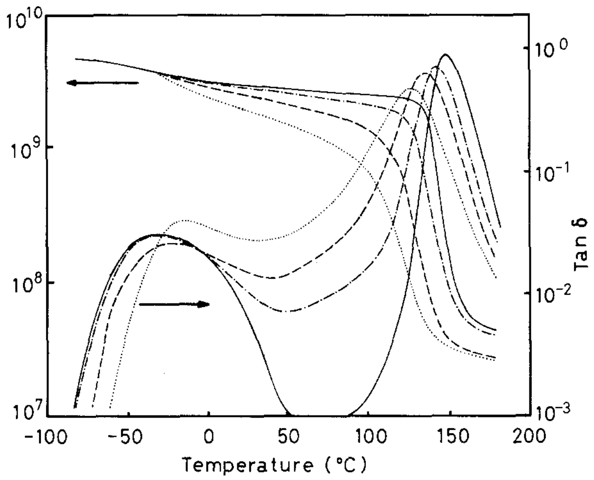

Figure 5 Dynamic mechanical properties of LCR-modified epoxy resins. (——) LCR (0), (–·–) LCR (5), (– – –) LCR (15), (· · · ·) LCR (25).

phase significantly lowers both the modulus and the yield stress of the epoxy materials. In a complete phase-separation system, an approximately linear decrease of the modulus and the yield stress with rubber content is expected, and can be modelled quite well on a volume-fraction basis by Kerner's equation, assuming a negligible modulus for the rubber [6]. However, in this experiment, both modulus and yield stress did not exhibit a linear decrease with increasing LCR content, and showed a more rapid drop of more than 10 vol % LCR. It is concluded that in this LCR–epoxy system, a certain amount of LCR was dissolved into the epoxy matrix and acted as a plasticizer for more than 10 vol % LCR.

3.6. Fracture toughness

The critical stress intensity factor, K_{Ic}, at crack initiation is plotted against the LCR content for the rubber-modified epoxy resins, shown in Fig. 7. The fracture toughness of the LCR-modified epoxy resins increased vigorously with increasing LCR content, and reached a maximum between 10 and 15 vol % LCR, and then dropped off with increasing LCR. These

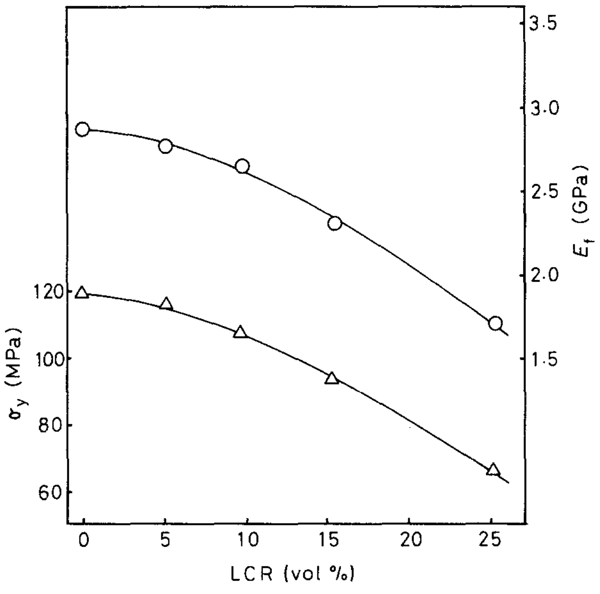

Figure 6 (△) Compressive yield stress, σ_y, and (○) flexural modulus, E_f as a function of LCR content.

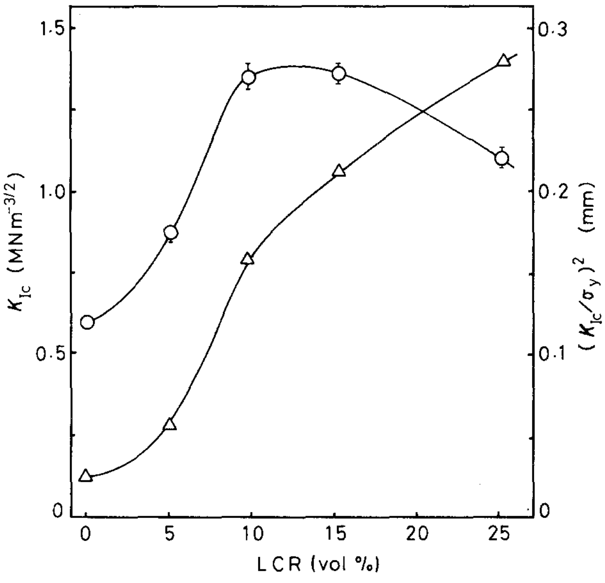

Figure 7 (○) Fracture toughness, K_{Ic}, and (△) relative toughness, $(K_{Ic}/\sigma_y)^2$, as a function of LCR content.

toughness values were somewhat lower than those published by other investigators. For example, it was reported that in the CTBN-modified epoxy resins cured with piperidine, $K_{Ic} = 2.5–4$ MN m$^{-3/2}$ [7]. In this CTBN system, cavitation and plastic shear yielding of the epoxy matrix occurred around the crack tip and a large amount of energy was dissipated for this deformation. In the LCR–epoxy system, no large shear yielding was observed, so the value of K_{Ic} did not become so large. As the yield stress of the epoxy–HHPA matrix is very high, the occurrence of shear yielding is not easy. The parameter, $(K_{Ic}/\sigma_y)^2$, which represents the relative toughness of materials, was calculated. Fig. 7 shows also the relationship between $(K_{Ic}/\sigma_y)^2$ and LCR content. The value of $(K_{Ic}/\sigma_y)^2$ increased with increasing LCR content. This is considered to be due to the addition of a large amount of LCR, giving a significant decrease in the yield stress of the epoxy matrix.

4. Conclusions

It was found that transparent epoxy resins may be toughened by a liquid chloroprene rubber (LCR). Epoxy resins modified with 5–10 vol % LCR had a phase-separation microstructure. At room temperature, these epoxy resins became transparent, because the refractive index of the epoxy resin phase was the same as that of LCR. Above 10 vol % LCR, a certain amount of LCR dissolved into the epoxy matrix. In this case, the LCR-modified epoxy resins did not exhibit a complete phase-separation microstructure. Fracture toughness of the modified epoxy resins increased with increasing LCR content, and reached a maximum between 10 and 15 vol % LCR.

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