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# A COMPARATIVE STUDY OF THE MECHANICAL BEHAVIOUR OF AN EPOXY RESIN CURED BY MICROWAVES WITH ONE CURED THERMALLY

S. L. BAI,* V. DJAFARI, M. ANDRÉANI and D. FRANÇOIS

Laboratoire de Mécanique, URA850, Ecole Centrale Paris, Grande voie des vignes, F-92295 Châtenay-Malabry Cedex, France

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**Abstract**—A comparison of mechanical behaviour was made between an epoxy resin cured by microwaves and one cured thermally. By tensile tests, it was found that the microwave cured resin has a little higher tensile strength and Young's modulus. This difference was considered to be attributed to the greater homogeneity of the microwave cured resin. After ageing in water, the microwave cured resin maintained its advantage of mechanical properties over the thermally cured one. The tensile strength and Young's modulus of both resins increased with the strain rate. The fracture surfaces show some significant mechanisms of rupture and of an ageing effect.

## 1. INTRODUCTION

The utilisation of microwaves for industrial applications has expanded very rapidly recently. But, their applications for polymerisation hold a less important place than other industrial applications such as food curing and drying, vulcanisation of rubber and plastics, etc. However, taking into account the utilisation of epoxy resins as a matrix of composite materials, applications of microwaves to the polymerisation could lead to an important development in the future.

The study of microwave curing of epoxy resins has been carried out with different objectives in mind: the evolution of dielectric properties during the reticulation [1–3], the reaction mechanisms, the kinetics and rate of reticulation [4, 5], the homogeneity of reticulation [6, 7] and the mechanical properties [8–10]. The comparison of reported mechanical properties of thermally cured resins (TCR) and of microwave cured resins (MCR) shows contradictory results.

Singer *et al.* [8] performed tensile tests on DGEBA-DDS resins cured by microwaves and by a classical thermal method. They found that, with the same Young's modulus, MCR has smaller deformation resistance than that of TCR. This difference was considered to be due to the existence of microcracks in MCR. Lewis *et al.* [9] tested DGEBA/4,4′-DDS and 3,3′-DDS. Their results showed the same mechanical behaviour of the resins whatever the curing, in spite of the lower glass transition temperature of MCR. Le Van [10] found by studying a DGEBA-DDM resin that the modulus and resistance in compression of MCR are greater than those of TCR. He assigned these differences to greater homogeneity of MCR.

The present study was carried out for a further comparison of a thermosetting resin (DGEBA-3DCM) cured by microwaves and by a classical thermal method. The tensile tests were carried out at different strain rate and the mechanisms of rupture were examined by using a scanning electron microscope. The ageing effect in water was also studied.

## 2. EPOXY RESINS STUDIED

The epoxy prepolymer used in this study is a diglycidyl ether of bisphenol-A (DGEBA): DER 332 from Dow Chemical. The curing agent is 4,4′-diamino-3,3′-dimethyldicyclohexyl methane (3DCM, Laromin C260, from BASF). Figure 1 shows the structural formulae of both monomers. The formulation is 100 g DGEBA for 34.5 g 3DCM.

The curing cycle and specimen dimensions are reported in Table 1. The microwave curing was performed in an experimental device composed of a generator, a guide and an applicator. The frequency of microwaves is 2500 MHz. The thermal curing was performed in an autoclave. A Mettler TA3000 differential scanning calorimeter was used to measure the glass transition temperature. The same $T_g$ was found for the two resins. For more curing information one can consult Refs [11, 12].

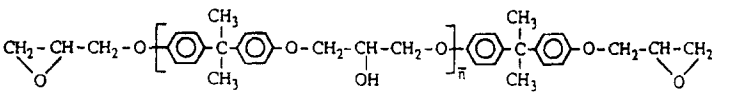
## 3. EXPERIMENTAL

### 3.1. Tensile tests

All tensile tests were carried out using a displacement controlled hydraulic machine (MTS). The chosen strain rates were $2.7 \times 10^{-4}$/sec, $2.7 \times 10^{-3}$/sec and $2.7 \times 10^{-2}$/sec. Three to five specimens machined directly out of the original plaques were tested at each strain rate. The specimen edges were polished before testing in order to avoid premature rupture due to the stress concentration caused by machining scratches. The specimen geometry is shown in Fig. 2.

*New address for correspondence: Department of Mechanics, Peking University, 100871 Beijing, P.R. China.

DER 332 $\bar{n} = 0{,}03$
DOW CHEMICAL
174 g/eq



3DCM
BASF
238 g/moi

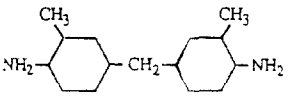


Fig. 1. Molecular structure of the epoxy prepolymer and diamine used for the synthesis of the epoxy networks.

The fracture surfaces of the broken specimens were studied in a scanning electron microscope.

*3.2. Ageing treatment*

The ageing treatment of MCR and TCR was carried out in distilled water at 20 and 80°C for 15 and 45 days. In order to avoid the machining effect, the resin for the ageing study was machined to form a tensile specimen before the ageing treatment.

## 4. RESULTS

*4.1. Tensile properties*

Figure 3 shows the tensile curves of MCR and TCR obtained at various strain rates. It was found that, on the whole, these curves rose when the strain rate increased. On the contrary, the elongation at fracture decreased. MCR and TCR displayed the same type of mechanical tensile behaviour.

The relationships between the ultimate tensile stress, Young's modulus measured from 0 to 30 MPa of tensile stress and the strain rate show an almost linear increase with the logarithm of strain rate ($\ln \dot{\epsilon}$).

The experimental values are reported in Tables 2 and 3. On the whole, the ultimate tensile stress and Young's modulus of MCR are a little greater than those of TCR.

*4.2. Fractographic observations*

Figure 6 shows the microscopic characteristics of the fracture surfaces of a MCR and of a TCR specimen. They both show the typical fracture surface of brittle epoxy resins, identical for MCR and TCR. Three regions are clearly visible (regions A, B and C).

Region A is the fracture initiation site. This region could be located either in the interior [Fig. 6(a)] or at the edge [Fig. 6(b)] of specimens, where there is probably a defect.

Region B, presenting a mirror smooth appearance, is where the crack became unstable and started to accelerate, still travelling at a slow speed. Small disturbances in the normal stress leave recognisable traces on the fracture front, delineating its position at various stages. These traces are different from Wallner lines which arise from the interference of the crack front with elastic waves released by the fracture itself.

Region C, presenting the "feather structures", is where the crack moved with its steady-state velocity. As the cracking reached high velocity, the distortion of the stress field caused portions of the crack front to deviate randomly above or below the extension of the crack plane [13]. The "feather structures" are due to the shear flowing of resins according to Bascom *et al.* [14] and due to the nucleation of secondary microcracks right ahead where stress concentrations exist according to Roulin [15] and Kinloch [16]. The work of Roulin-Moloney [17] showed also the shear flowing on the fracture structure of the notched specimen.

It was found that the mirror region for TCR is a little greater than that of MCR.

Table 1. Curing process of epoxy resins

| Curing | Specimen (mm) | Process | $T_g$ (°C) |
|---|---|---|---|
| MCR | 90 × 10 × 6 | 200 W, 15 min | 136 |
| TCR | 90 × 10 × 6 | 140°C, 15 min | 136 |

*4.3. Tensile properties after ageing*

Tensile specimens with the same geometry as that of as-cured resin specimens were aged and then tested in tension at room temperature at a $2.7 \times 10^{-3}$/s strain rate.

Figures 7 and 8 show the tensile curves of aged resins. For comparison, the tensile curves of as cured resins are also plotted in the same figures. It was found that the ultimate tensile stress, the ultimate tensile strain and Young's modulus measured in the same way as for as-cured resins decreased after the ageing of resins.

The variation of ultimate tensile stress as a function of ageing duration is shown in Fig. 9. The decrease of the ultimate tensile stress becomes quite low when the ageing time exceeds 15 days. The higher the

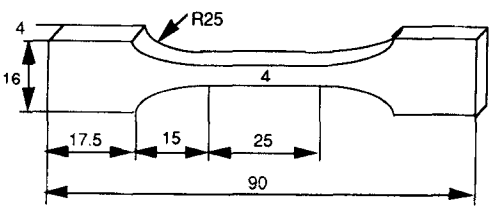



Fig. 2. Specimen geometry (mm).

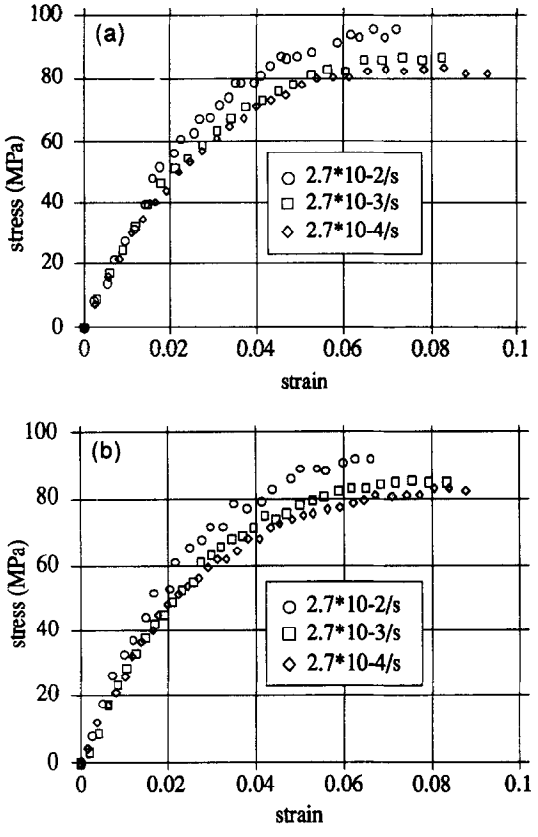



Fig. 3. Stress–strain relationship in tension of studied resins: (a) microwave cured resin; and (b) thermal cured resin.

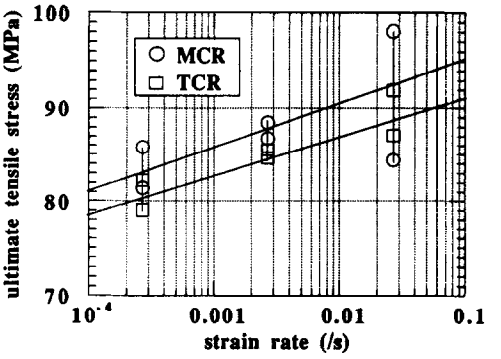



Fig. 4. Ultimate tensile stress as a function of strain rates.

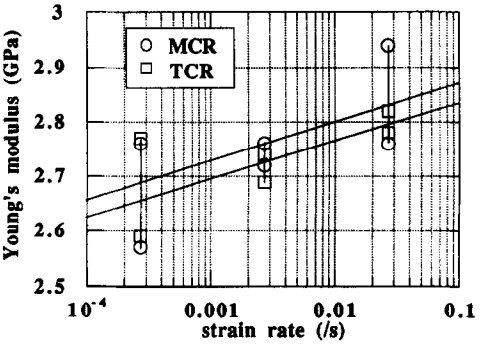



Fig. 5. Young's modulus as a function of strain rates.

ageing temperature, the smaller the ultimate tensile stress.

The same trend was found for Young's modulus as a function of ageing duration and temperature as shown in Fig. 10.

The experimental values are reported in Tables 4 and 5 for the aged resins. By comparing the results with those obtained with the as cured resins, the same trend was found: MCR has better mechanical properties than TCR.

Table 2. Ultimate tensile stress (MPa) as a function of strain rates

| Strain rate | $2.7 \times 10^{-2}$/sec | $2.7 \times 10^{-3}$/sec | $2.7 \times 10^{-4}$/sec |
|---|---|---|---|
| MCR | $92.87^{+5.2}_{-8.5}$ | $87.55^{+0.9}_{-0.8}$ | $83.32^{+2.5}_{-1.9}$ |
| TCR | $88.75^{+3.2}_{-1.7}$ | $84.92^{+0.6}_{-0.3}$ | $80.63^{+1.6}_{-1.6}$ |
| (MCR-TCR)/MCR | 4.4% | 3.0% | 3.2% |

Table 3. Young's modulus (GPa) as a function of strain rates

| Strain rate | $2.7 \times 10^{-2}$/sec | $2.7 \times 10^{-3}$/sec | $2.7 \times 10^{-4}$/sec |
|---|---|---|---|
| MCR | $2.83^{+0.10}_{+0.08}$ | $2.74^{+0.02}_{-0.02}$ | $2.69^{+0.07}_{-0.12}$ |
| TCR | $2.80^{+0.02}_{-0.02}$ | $2.72^{+0.02}_{-0.03}$ | $2.66^{+0.11}_{-0.07}$ |
| (MCR-TCR)/MCR | 1.4% | 0.7% | 1.1% |

Table 4. Ultimate tensile stress (MPa) of aged resins

| Temperature | 20°C | | 80°C | |
|---|---|---|---|---|
| Duration | 15 days | 45 days | 15 days | 45 days |
| MCR | $76.14^{+0.8}_{-0.8}$ | $75.46^{+0.3}_{-0.2}$ | $72.02^{+1.7}_{-1.7}$ | $71.41^{+0.9}_{-0.9}$ |
| TCR | $74.53^{+3.7}_{-3.7}$ | — | $69.47^{+1.3}_{-1.3}$ | $67.85^{+0.0}_{-0.0}$ |
| (MCR-TCR)/MCR | 2.1% | — | 3.5% | 5.0% |

Table 5. Young's modulus (GPa) of aged resins

| Temperature | 20°C | | 80°C | |
|---|---|---|---|---|
| Duration | 15 days | 45 days | 15 days | 45 days |
| MCR | $2.72^{+0.02}_{-0.02}$ | $2.71^{+0.04}_{-0.05}$ | $2.64^{+0.01}_{-0.01}$ | $2.62^{+0.03}_{-0.03}$ |
| TCR | $2.69^{+0.02}_{-0.02}$ | $2.66^{+0.00}_{-0.00}$ | $2.60^{+0.05}_{-0.05}$ | $2.55^{+0.03}_{-0.03}$ |
| (MCR-TCR)/MCR | 1.1% | 1.8% | 1.5% | 2.7% |

*4.4. Fractographic examination after ageing*

The fracture surfaces of aged resins displayed, as in the case of as cured resins, three regions with the same characteristics. But, more detailed examinations result in some remarks concerning the aged resins (Fig. 11). The main ones are as follows:

- the fracture surfaces of TCR presented more important irregularities than those of MCR, which means that TCR is more susceptible to ageing by hydrodegradation.
- the transition from region A to region B became more marked with the increase of ageing duration and temperature. The region B of aged resins is greater than that of as cured ones.
- the region C is always more undulating for the aged resins compared with as cured ones.
- the "feather structures" became finer with the increase of ageing duration and temperature.

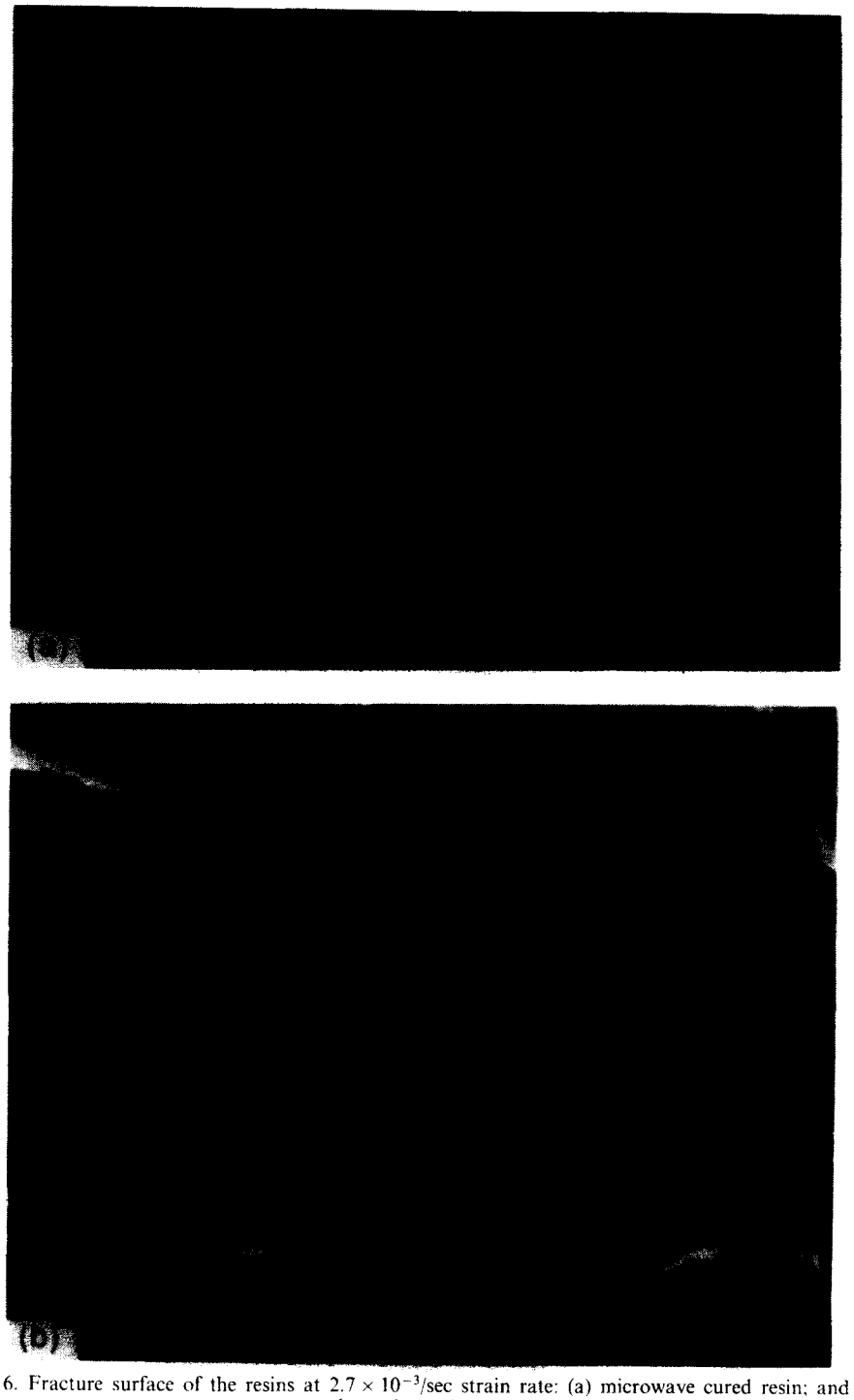



Fig. 6. Fracture surface of the resins at $2.7 \times 10^{-3}$/sec strain rate: (a) microwave cured resin; and (b) thermal cured resin.

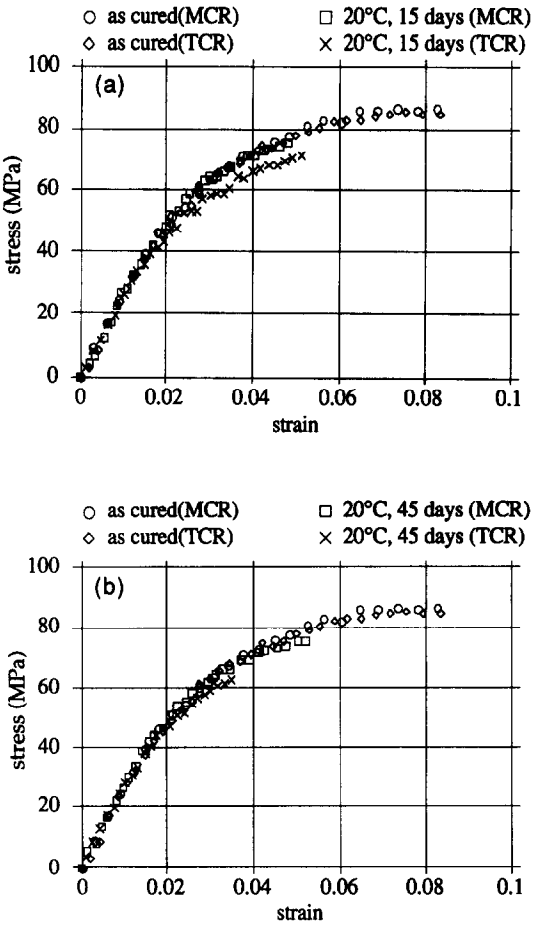



Fig. 7. Tensile curves of aged resins at 20°C: (a) ageing at 20°C for 15 days; and (b) ageing at 20°C for 45 days.

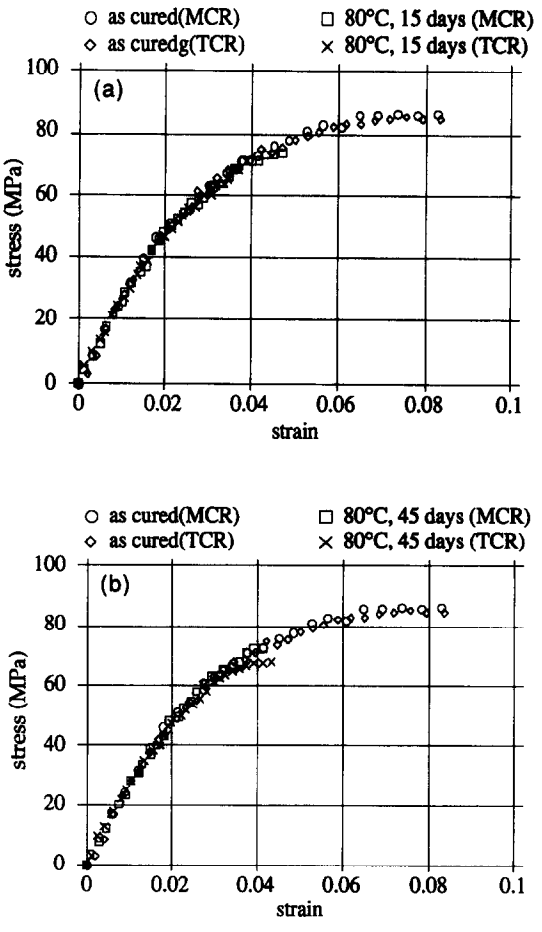



Fig. 8. Tensile curves of aged resins at 80°C: (a) ageing at 80°C for 15 days; and (b) ageing at 80°C for 45 days.

## 5. DISCUSSION

For both as cured and aged resins, the difference of tensile strength between MCR and TCR is always greater than that of Young's modulus. This remark makes us think about the effect of microdefects which exists in the interior of resin specimens. In general, the tensile strength is sensitive to the micro-

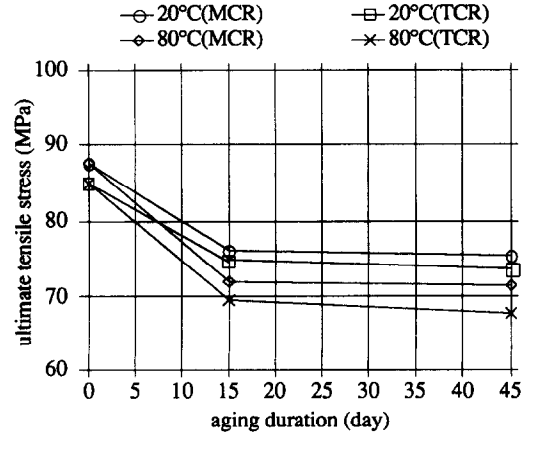



Fig. 9. Ultimate tensile stress as a function of the ageing duration. (The value of TCR at 20°C for 45 days is estimated. The specimens were ruptured at the grip section.)

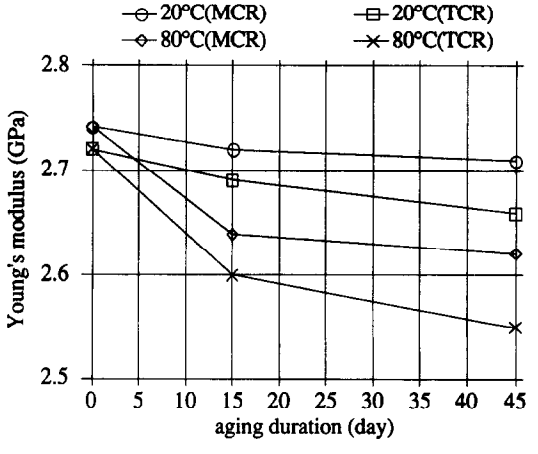



Fig. 10. Young's modulus as a function of the ageing duration.


Fig. 11(a and b). *(See caption on p. 883.)*

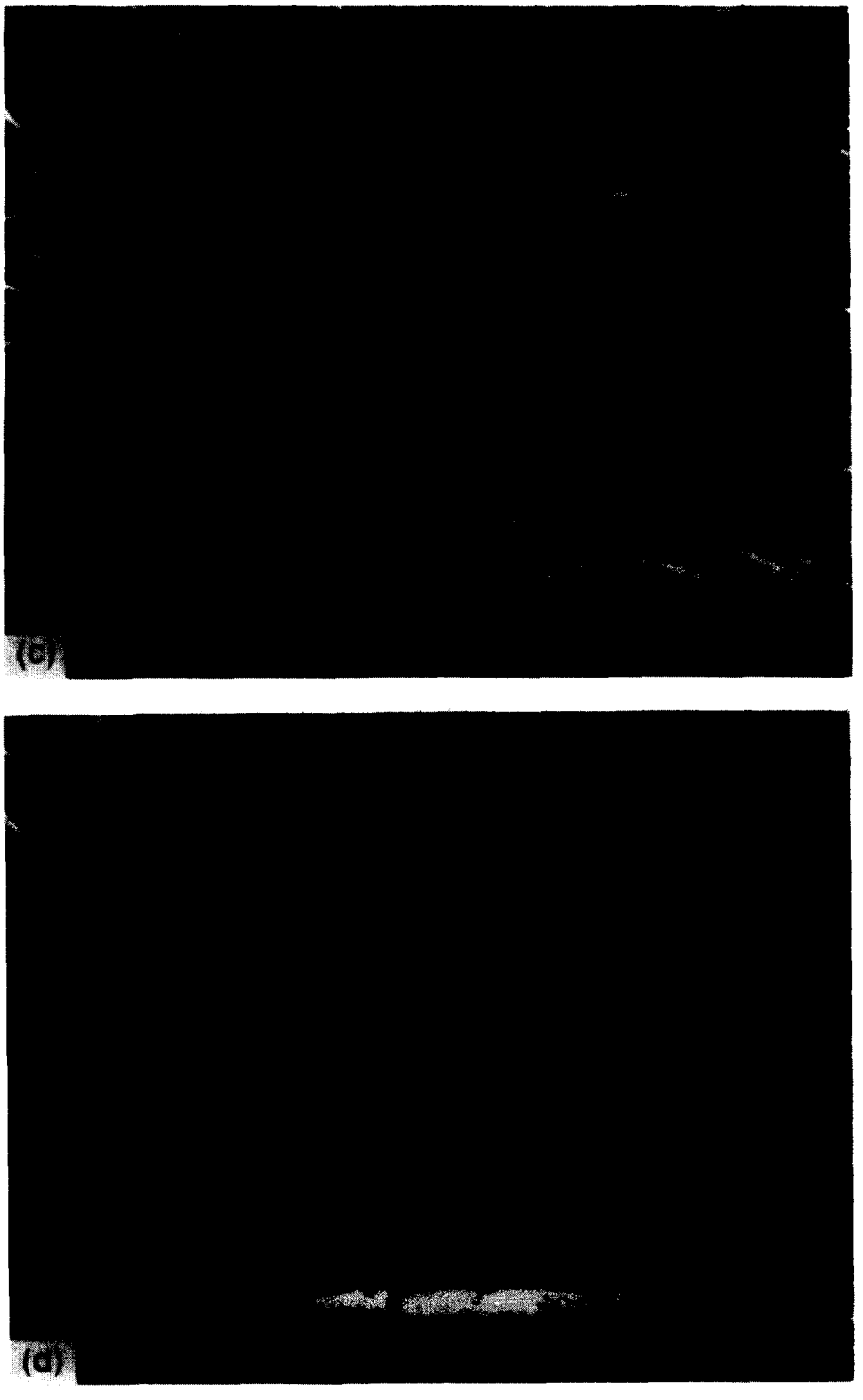



Fig. 11(c and d). *(See caption on p. 883.)*

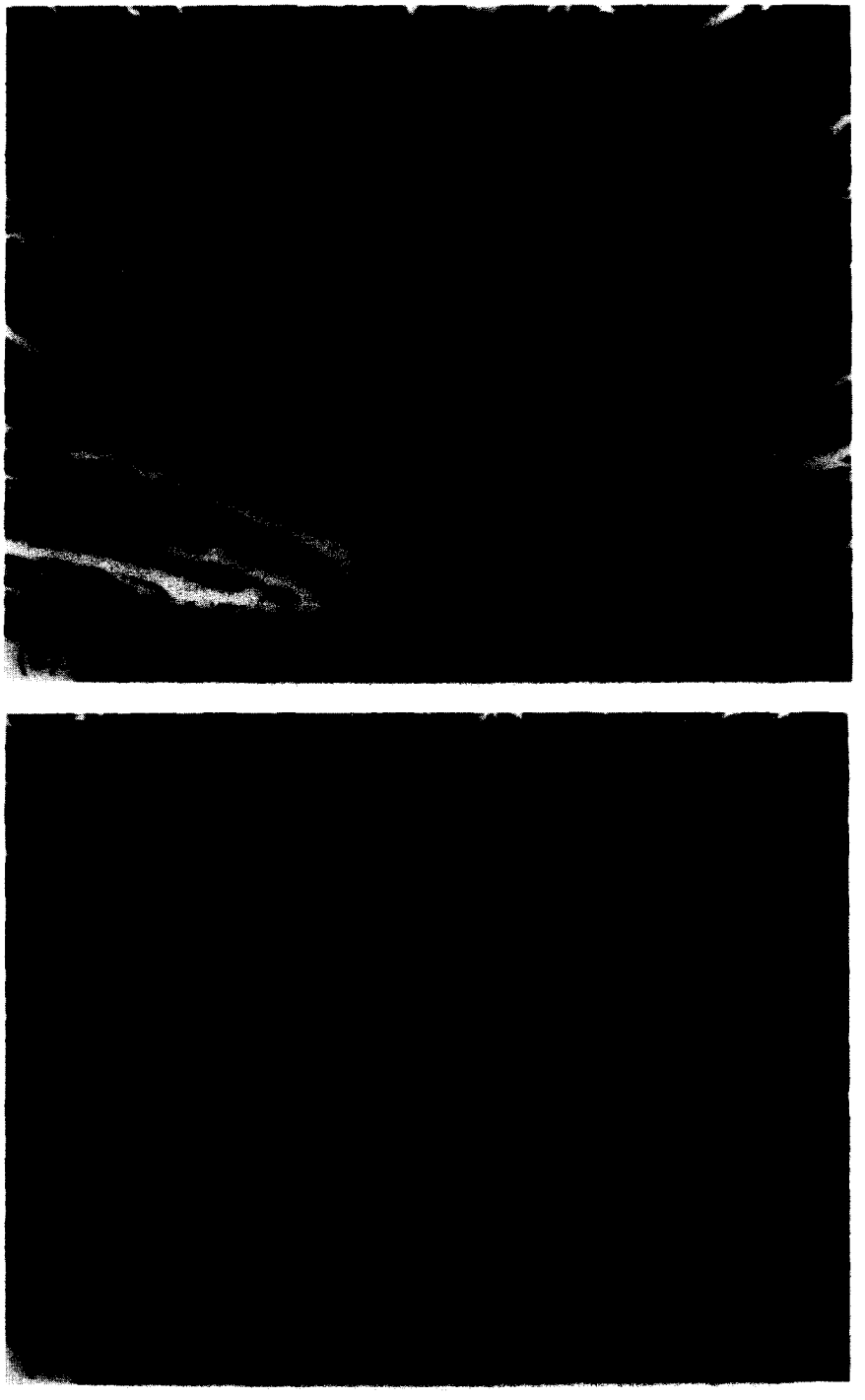


Fig. 11(e and f). *(See caption opposite.)*

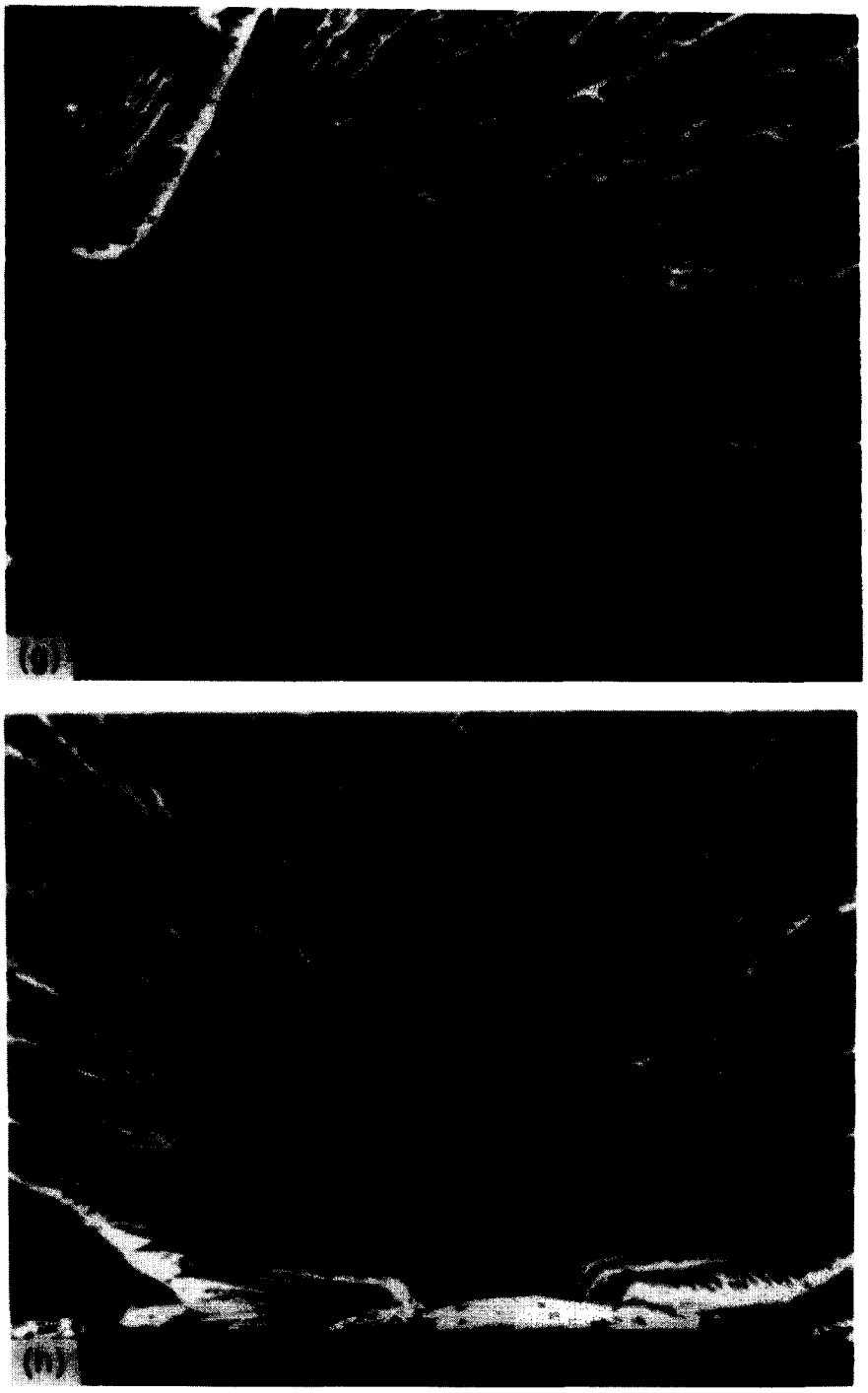


Fig. 11(g and h).

Fig. 11. Fracture surfaces of aged resins: (a) MCR aged at 20°C for 15 days; (b) MCR aged at 20°C for 45 days; (c) MCR aged at 80°C for 15 days; (d) MCR aged at 80°C for 45 days; (e) TCR aged at 20°C for 15 days; (f) TCR aged at 20°C for 45 days; (g) TCR aged at 80°C for 15 days; and (h) TCR aged at 80°C for 45 days.

defects which can create the stress concentration and cause the premature fracture of tensile specimens. In contrast, the effect of the microdefects on the elastic modulus is not important when the number of microdefects is small. Therefore, it is possible that more microdefects exist in TCR than in MCR, which means that MCR is more homogeneous. The same point of view was given by Le Van [10].

During the ageing in water, two mechanisms were observed by authors [18]: the resin dissolution and the mass uptake with the associated expansion of specimens. The measurement of the mass uptake on a small specimen of 5 g showed that MCR absorbed less water than that of TCR, which was considered by them to be due to also the greater homogeneity of MCR.

For the ageing effect on the mechanical properties, it was considered by other authors [19, 20] that when the epoxy resin is aged in water, on one hand, the water molecules diffuse into the microvoids which exist in the resin networks. On the other hand, the interactions between the water and the polar segments of resin chains result in the plasticisation of resins. These two phenomena, being more important with the increase of ageing time and temperature, cause certainly a decrease of mechanical properties of aged resins.

## 6. CONCLUSIONS

The microwave polymerisation improved slightly the mechanical properties of as cured and aged epoxy resin (DGEBA-3DCM). This improvement is considered to be due to a better homogeneity of microwave curing.

According to the microscopic observations of the fracture surfaces, the mechanisms of rupture are identical for MCR and TCR. The three characteristic regions, typical of brittle fracture, are always present.

Whatever the curing mode (microwaves or thermal), the ultimate tensile stress and Young's modulus increase almost linearly with the logarithm of the strain rate.

The mechanical properties of aged epoxy resins drop with the increase of ageing duration and temperature.

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