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Electrochemical effects during thermoset moulding

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This paper describes an investigation of the substantial electrochemical potentials which have been found to arise if dissimilar metals are immersed in an electrolyte of polyester resin while it is curing. Sharp initial changes in the e.m.f. indicate the moment of arrival of resin at the electrodes, and the subsequent magnitude can be used to indicate the state of cure. The e.m.f. was found to be influenced by the addition of calcium carbonate filler powder to the base resin, as well as by the choice of electrode metals. Aluminium and copper were selected for practical applications, and tested under transfer moulding conditions. A prototype instrument suitable for incorporating in a mould to indicate the completion of filling and the state of cure in a resin transfer moulding process is described. The results will also have application to other thermoset moulding processes.

1. Introduction

When two dissimilar metals are placed in an electrolyte, a potential difference will exist between them. The magnitude of this will depend on the electrode materials, the electrolytic properties of the liquid in which they are immersed, and other factors such as the impedance of the external circuit.

The electrolytic properties of thermosetting resins were unexpectedly revealed during a series of moulding trials forming part of an investigation of the resin transfer moulding process (RTM) [1–3]. In this work, which was carried out with both heated and unheated moulds, a dry fibre preform was placed in the cavity and a liquid thermosetting polyester resin containing catalyst and accelerator injected. This displaced the air, impregnated the preform and filled the cavity. The exothermic cure reaction that followed caused substantial temperature rises in the moulding, and during many of the trials thermocouples were placed at the mid-plane of the glass-fibre preform to monitor the advance of the resin flow front and indicate the state of cure at a number of chosen locations. It was noticed that the thermocouples often gave spurious readings when the leads were in contact with liquid resin [4]. Further investigations showed that the resin could permeate without difficulty through the braided glass insulation and come into contact with the thermocouple wires. It was assumed that free-radical ions in the curing resin imparted electrolytic properties to the polyester, and the galvanic cell formed with the dissimilar metals interfered with the normal output of the thermocouple. The problem was readily overcome by the use of impervious polytetrafluoroethylene (PTFE) insulation, and for the moment the electrochemical effect was put aside.

Subsequently the phenomenon was re-examined with a view to applying it to process control. Measurements were made of the magnitude of the e.m.f. generated under laboratory conditions in galvanic cells using a variety of metal electrodes and resin electrolytes. A prototype resin cure gauge was constructed and tested under experimental moulding conditions.

2. Resin cast trials

In order to observe the electrochemical effects, a series of probes were made up as shown in Fig. 1 containing two electrodes mounted in a strip connector, and a wire thermocouple. One of the electrodes was made of copper, and the other of a variety of metals. The e.m.f. between the two was monitored through a high impedance circuit using an Akhter PC fitted with a 16-bit Burr Brown analogue-to-digital convertor, connected such that a negative reading indicated that the variable electrode was negative with respect to the copper electrode. Temperature readings from the thermocouple were also recorded by the PC. A new probe was needed for each test.

Resin casts were made using a hot-setting polyester resin (CVP 6345.001, catalysed with 1% TBPEH) in 50 ml polypropylene beakers immersed in an oil bath at 120 °C. The resin was allowed to reach a temperature of approximately 60 °C before the probe was immersed, and the heating was continued until the resin began to cure. The temperature provided a convenient indication of the progress of the reaction, since polyester produces a characteristic exotherm during cure. This was used throughout the trials to relate the e.m.f. to the degree of cure of the resin. The thermocouple also allowed the precise moment of immersion to be established by the rapid temperature rise some 10 or 20 s into the run.

All the traces (Figs 2 to 9 below) show e.m.f. values on the probe before immersion. They are unsteady

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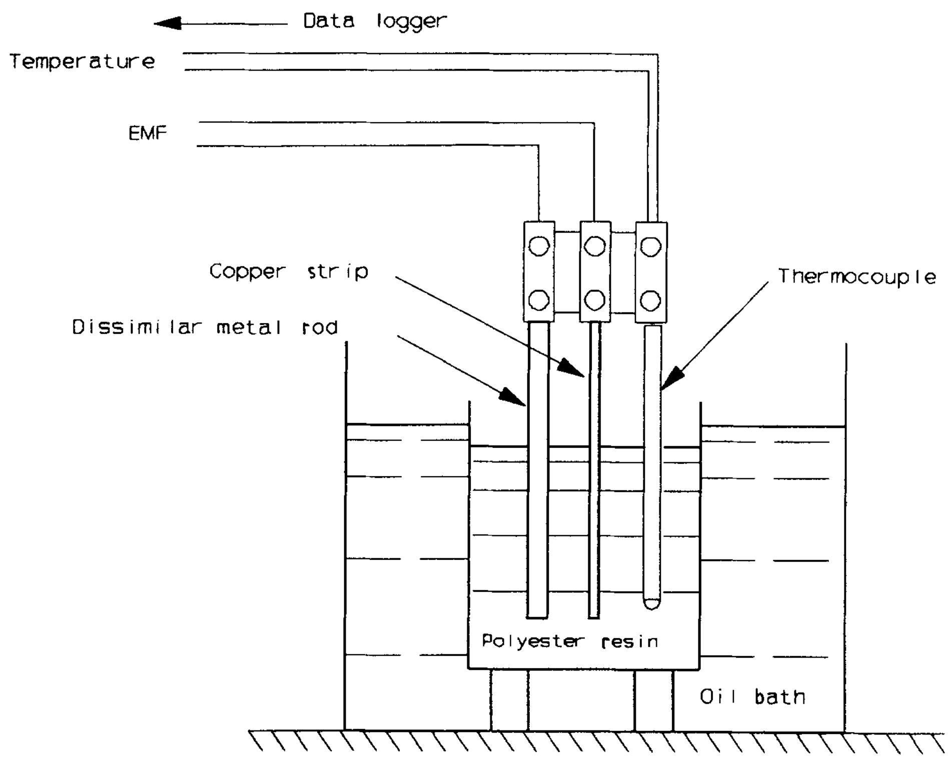

Figure 1 Details of probe construction.

and can be quite large–in some cases over 3 V, the limit of the recorder. They are not directly related to the test described below, but are presumably due either to probe contamination during manipulation or to recorder drift while the high-impedance measuring system is open-circuited. Immediately on immersion a galvanic cell is created and these stray effects are dissipated. The e.m.f. trace decays rapidly, in synchronism with the thermocouple rise, to the electrochemical e.m.f. associated with the early stages of the cure reaction. As the reaction proceeds the output increases progressively, the change being particularly rapid when the thermocouple reading indicates that cure is well advanced. These e.m.f. values depend on the electrode materials, and the electrolyte employed.

2.1. Effects of electrode materials

Four different electrode combinations were used during the trials:

(a) copper/copper (control);
(b) copper/brass;
(c) copper/mild steel;
(d) copper/aluminium.

The results for the copper/copper probe are given in Fig. 2. It had a pre-immersion e.m.f. of about 1.5 to 2.0 V. Then, as might be expected with two electrodes of the same material, the initial electrochemical e.m.f. became zero. However, as the reaction proceeded a small, gently rising e.m.f. peaking at about 0.2 V was generated, falling back to zero when the resin finally solidified. This clearly arose from a lack of symmetry somewhere in the system. There could be different energy levels in the two electrode materials due to variations in the degree of cold work as they were being formed from drawn or rolled copper, or there might be differences in the resin cure regimes round them, since they were an appreciable distance apart.

The results for the other materials, tested under the same conditions, are given in Figs 3 to 5. All showed an open-circuit e.m.f. exceeding 3 V, followed by substantial swings on immersion, steady outputs during heating, and increased e.m.f. during cure. Copper/aluminium gave the highest outputs, in keeping with their wide separation in the electrochemical series, followed by copper/zinc and copper/iron.

These results for each electrode combination are summarized in Table I. In cases (b) and (d) the electrode under test was negative with respect to the copper electrode at all times. In case (c)–copper/steel–the steel went slightly positive with respect to the copper during the exotherm peak.

2.2. Effects of filler loading

The copper/aluminium probe was shown by the above work to be practical and to give a high output. This combination of metals was used in a further series of trials to investigate the effect of adding a commercial calcium carbonate filler powder (Omya BL) to the polyester resin system in the ratios 3:1, 2:1, 1:1 and 1:2 resin:filler by mass. The results are shown in Figs 6 to 9 and the e.m.f. changes upon immersion and cure are summarized in Table II. While there is always a significant swing upon immersion of the probe in the resin, the change becomes less marked during the cure phase as the filler loading is increased. This is not surprising since the addition of any filler will dilute or extend the electrolyte, and its thermal capacity and conductivity can affect reaction speeds. This particular filler may also modify the acidity (polyester resin is slightly acidic while calcium carbonate is alkaline in the presence of moisture), and this may have some

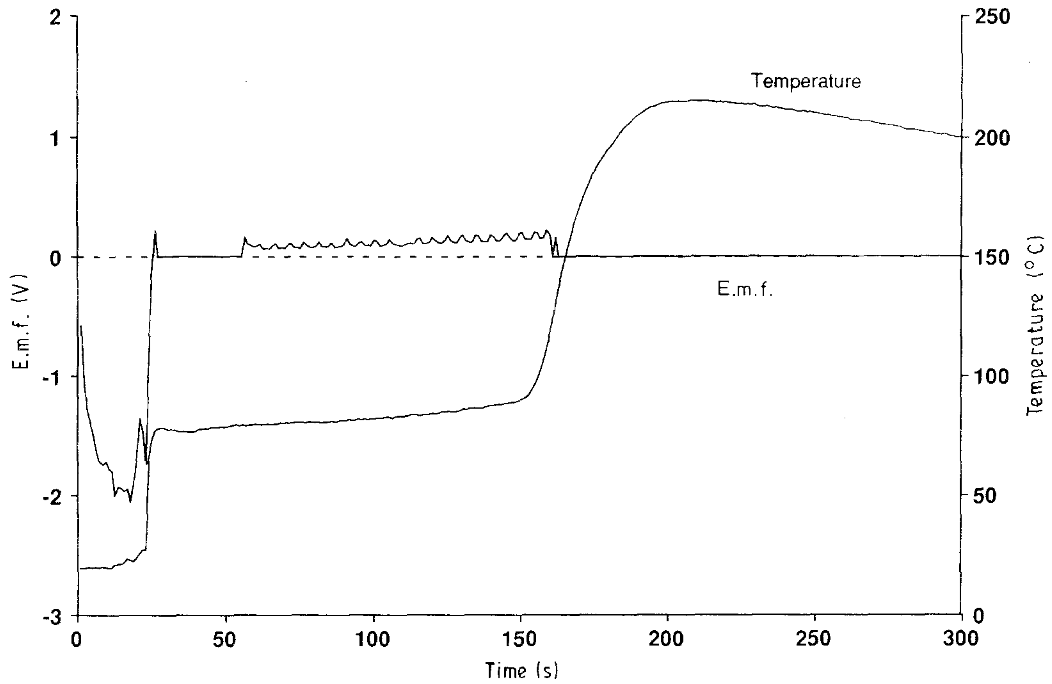

Figure 2 Effects of electrode combination: copper/copper electrodes.

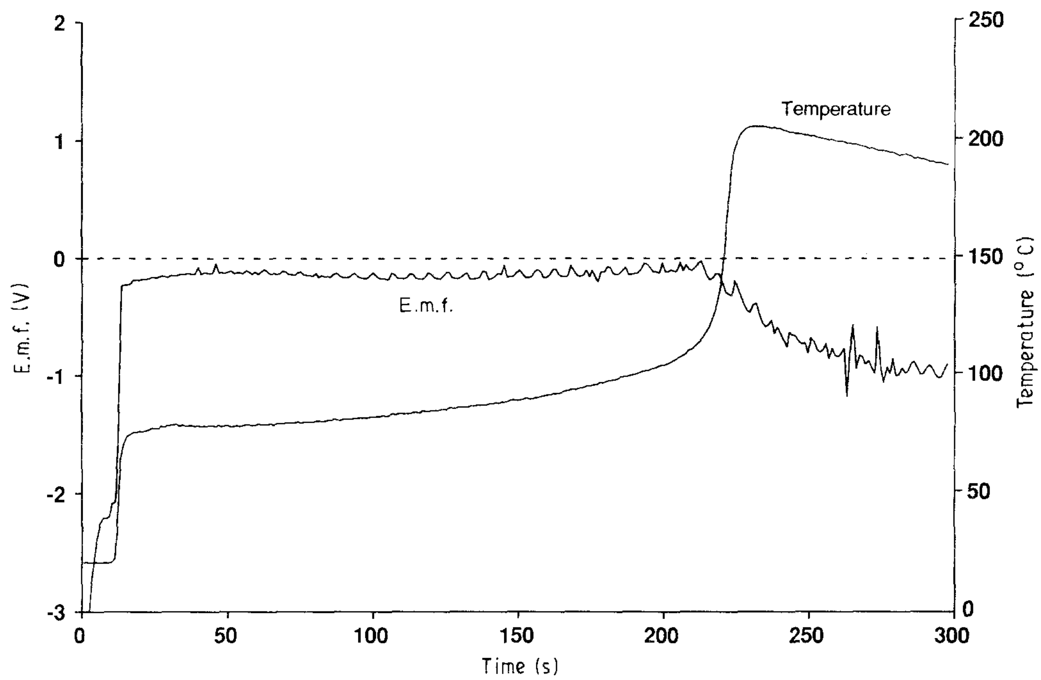

Figure 3 Effects of electrode combination: copper/brass electrodes.

effect on the progress of the cure. It will be noted that the e.m.f. values during cure with the calcium carbonate filler present are reversed in sign compared to unfilled resin, while the pre-immersion values are unchanged.

3. Practical application

Having established that measureable electrochemical effects occurred during the moulding of thermoset polyesters, a prototype sensor or gauge was constructed for use in RTM trials. It was designed to be reusable, and to be an integral part of the wall of an aluminium plaque mould. The sensing unit consisted of a copper plug set flush with the cavity surface and insulated from the mould by Melinex and epoxy resin (Fig. 10). Thus one electrode was provided by the mould and the other by the insulated plug. Leads were connected to both electrodes and thence to the PC for data logging via the analogue-to-digital convertor.

The device was coated thoroughly with the same permanent non-transferable release agent (Frekote) employed on the mould itself, and used during several trials. Sample results are shown in Fig. 11. The traces exhibit the same characteristics as those described above: a step change on encountering electrolyte (resin arrival) and a gradual rise to a peak e.m.f. signalling

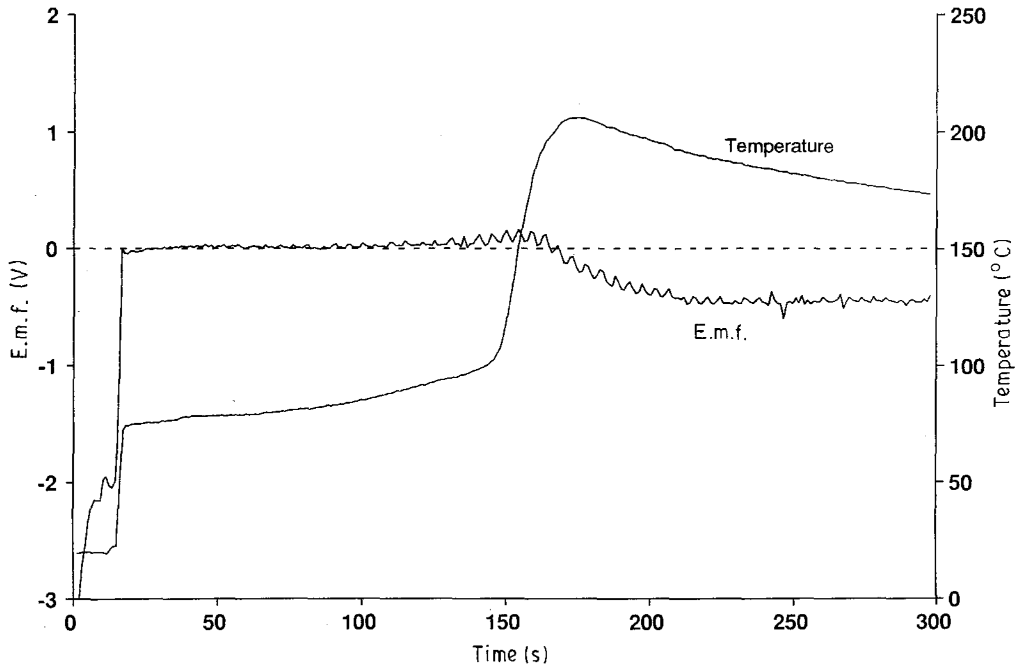

Figure 4 Effects of electrode combination: copper/steel electrodes.

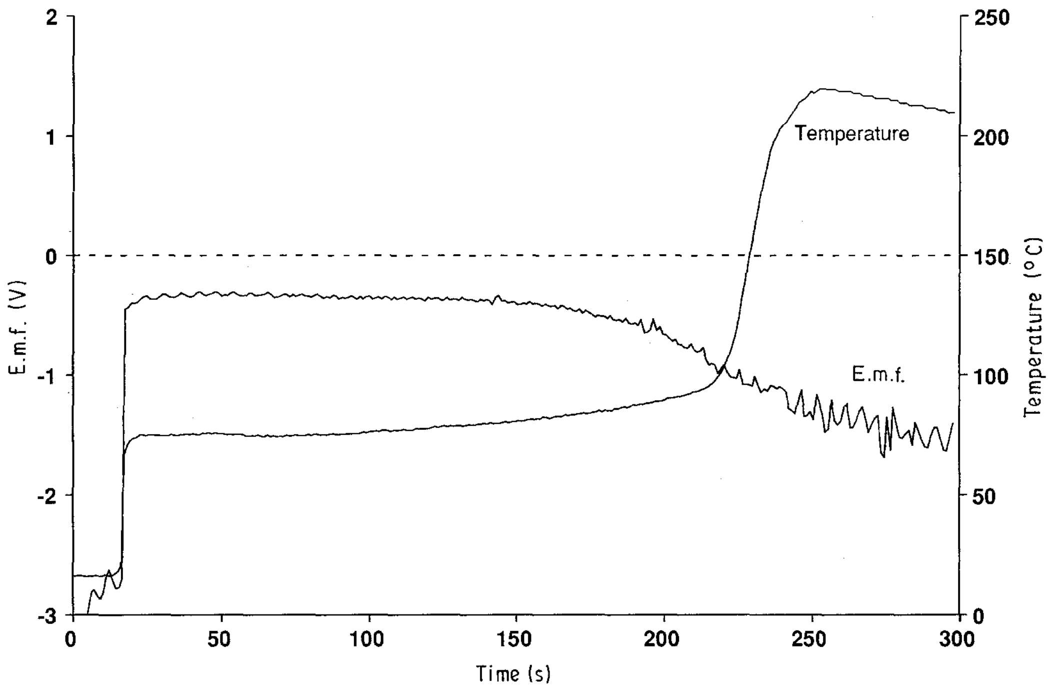

Figure 5 Effects of electrode combination: copper/aluminium electrodes.

resin cure. The release agent did not impair performance and the unit appeared to have good potential for process control purposes.

Two uses are seen for such a gauge. Firstly it can signal the arrival of resin at the edge of the RTM mould so that the injection operation can be automatically terminated. Alternative capacitative proximity switches are available but are subject to temperature limitations due to the use of electronic components in the sensing unit. Secondly, minimizing the RTM cycle time requires some means to detect resin cure so that the mould can be opened at the earliest possible moment. A thermocouple sensing the moulding exotherm temperature can be used, but this technique is unreliable because it depends on the kinetics of the cure reaction and the thermal characteristics of the mould. The thermocouple tip must be close to, or buried within, the moulding, and thermally insulated from the mould, or the thermal conductivity and mass of this will prevent its temperature from

TABLE I Summary of e.m.f. values for different electrode combinations

Probe combination	E.m.f. (V)			Fig.
	Pre-immersion	Initial reaction	Final cure	
Copper/copper	− 1.8	0.0	+ 0.2	2
Copper/brass	− 2.2	− 0.2	− 1.0	3
Copper/steel	− 2.0	0.0	− 0.5	4
Copper/aluminium	− 2.8	− 0.3	− 1.4	5

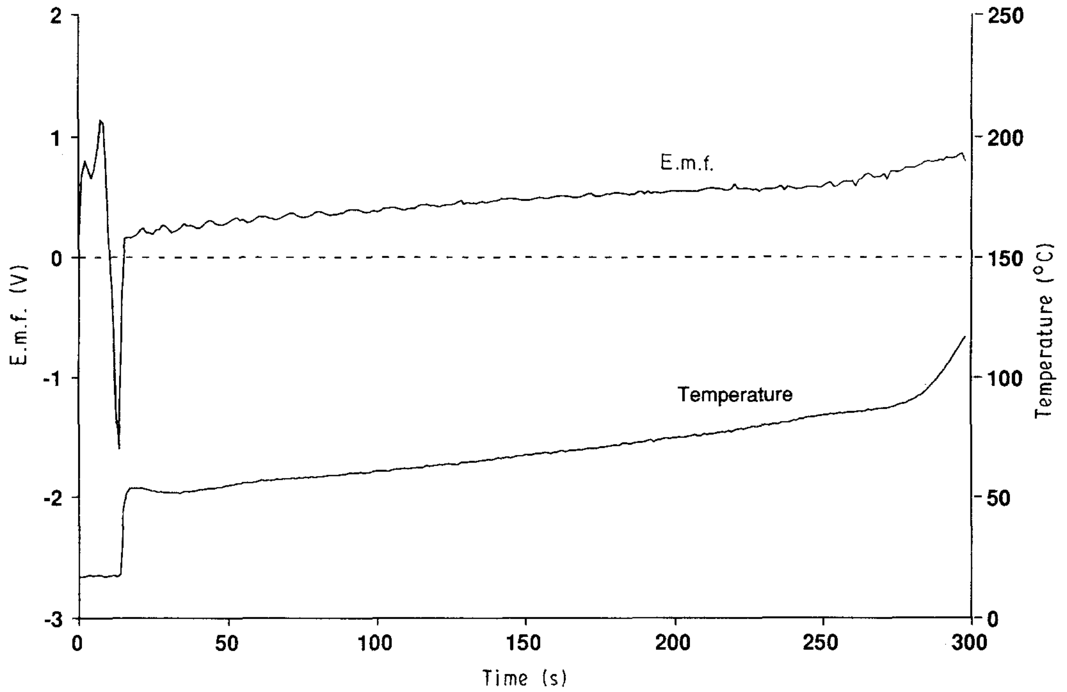

Figure 6 Effects of filler loading: 3:1 resin:filler by mass.

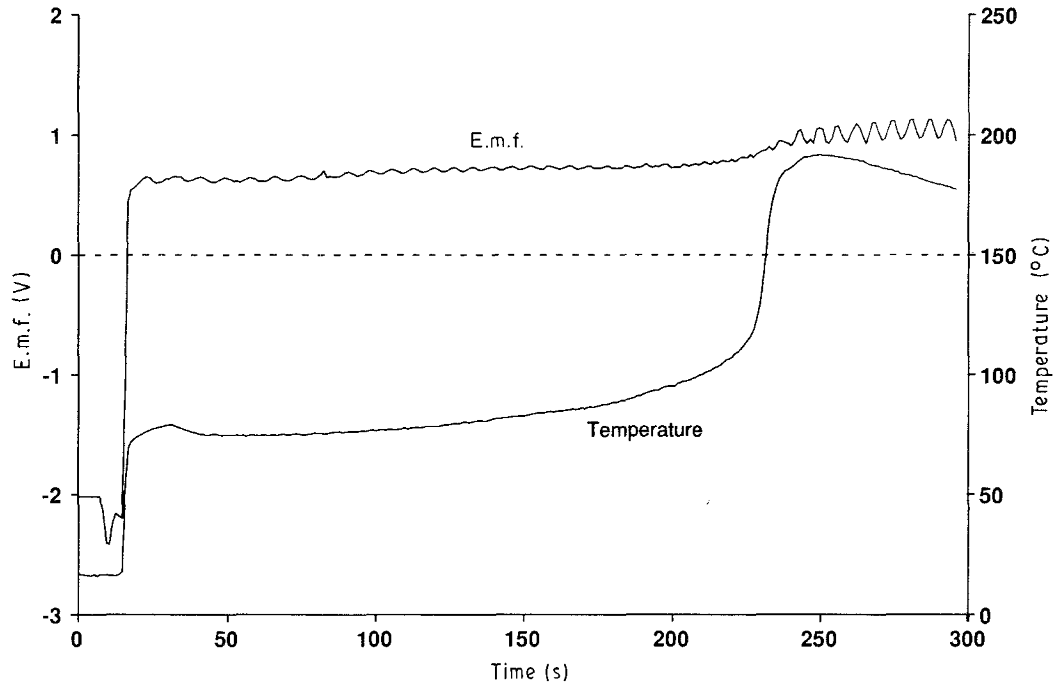

Figure 7 Effects of filler loading: 2:1 resin:filler by mass.

changing much during the cycle. This is difficult to engineer for repeated use. The electrochemical technique offers the facility to combine both functions in one device which can be compact, robust, and permanently installed in a mould. If flush-mounted it will not interfere with the geometry of the moulding and will provide an economic, reusable solution.

4. Conclusions

The investigation has shown that by introducing electrodes of dissimilar metals in a polyester resin during polymerization, signals can be generated to detect both the presence of the resin and its state of cure. The former depends on there being a significant e.m.f. on the probe under open-circuit conditions before immersion. This generally appears to be the case, but if necessary it could be supplied from an external high-impedance source. E.m.f. values generated during cure are smaller, and the unit needs to have a reasonable sensitivity. A copper/aluminium couple has been shown to provide a useful (and economic) combination, and higher e.m.f. values are probable if electrode materials can be used which are more widely separated in the electrochemical series, such as silver and magnesium. The output may be affected by the presence of mineral filler in the resin system.

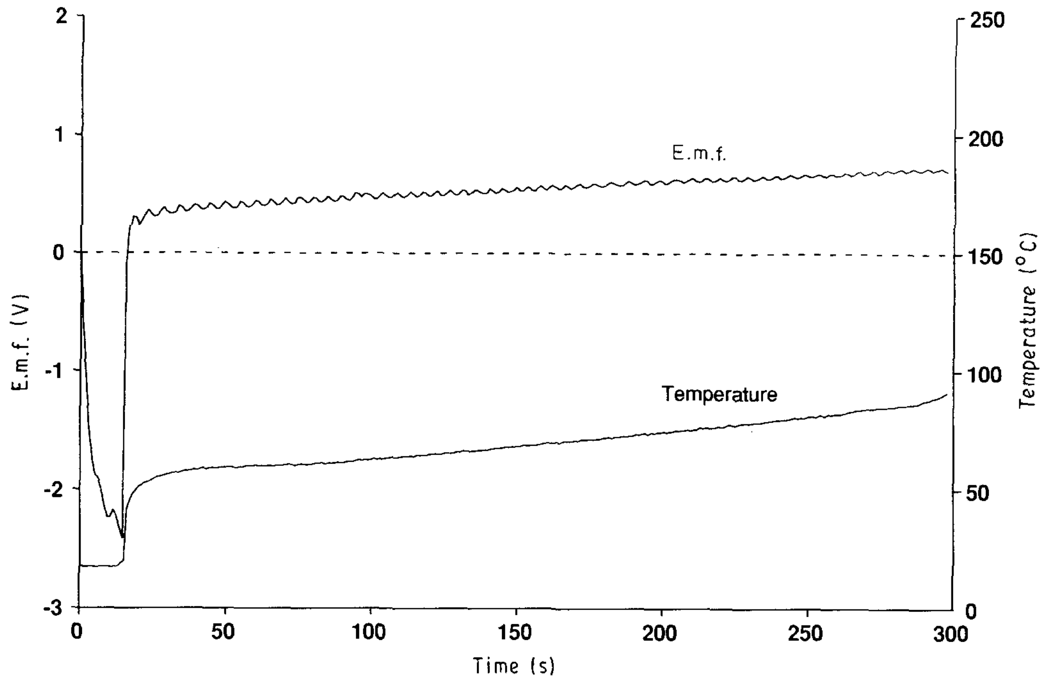

Figure 8 Effects of filler loading: 1:1 resin:filler by mass.

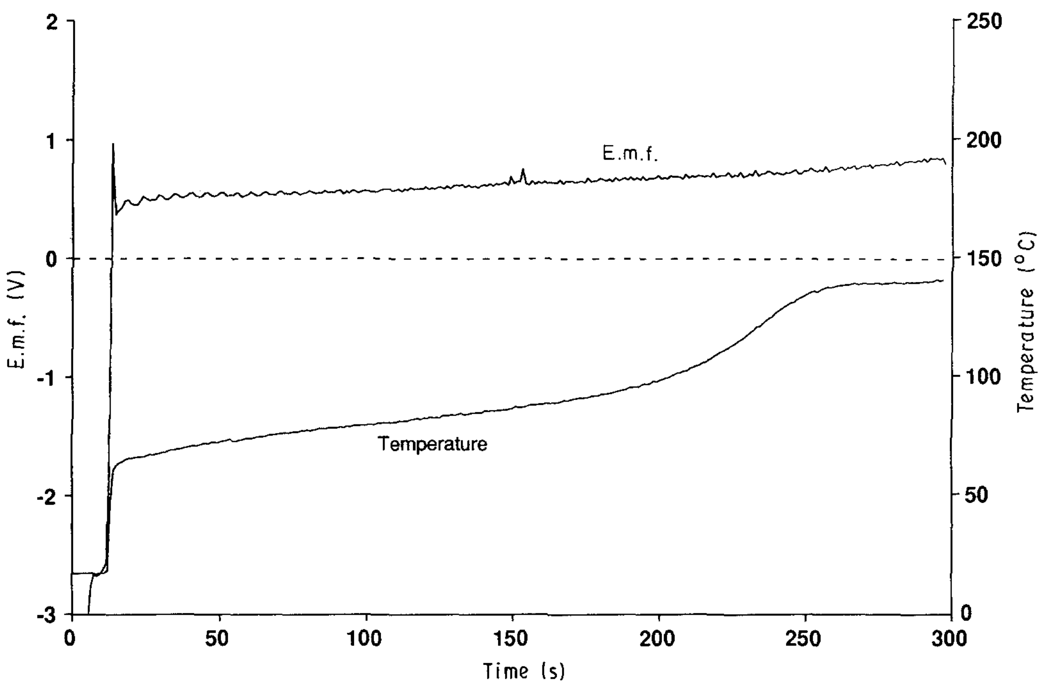

Figure 9 Effects of filler loading: 1:2 resin:filler by mass.

TABLE II Summary of e.m.f. values for different filler loadings

Filler loading by mass		E.m.f. (V)			Fig.
Resin:filler	phr[a]	Pre-immersion	Initial reaction	Final cure	
1:0	0	− 2.8	− 0.3	− 1.4	5
3:1	33	− 1.6	+ 0.2	+ 0.8	6
2:1	50	− 2.2	+ 0.7	+ 1.0	7
1:1	100	− 2.3	+ 0.3	+ 0.8	8
1:2	200	− 2.7	+ 0.5	+ 0.7	9

[a] Parts per hundred of resin.

Lower-impedance measuring equipment could be used if the impedance of the external circuit through the moulding were reduced by making the electrodes longer and the space between them narrower. An etching, embossing or printing process could overlay a filigree pattern of one metal upon the surface of the other with a thin insulating film between them. However, using readily available voltage sensing equipment, the strength of the existing signal appears to be sufficient for practical application.

The principle has been employed to produce a prototype sensing unit for industrial use. It has been installed in a mould and has demonstrated its potential for process control in thermoset moulding operations. It was used in a hot RTM process but could be applied to other closed-mould processes such as injection or compression moulding, to detect the presence of resin at a given point in the mould and to indicate its state of cure. It is also possible to combine the two electrodes in a separate plug to make an independent

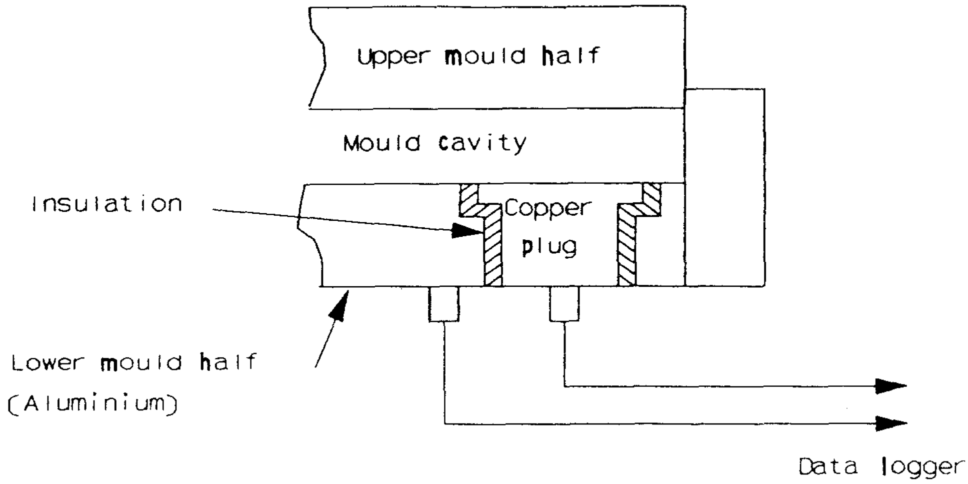

Figure 10 Prototype gauge construction.

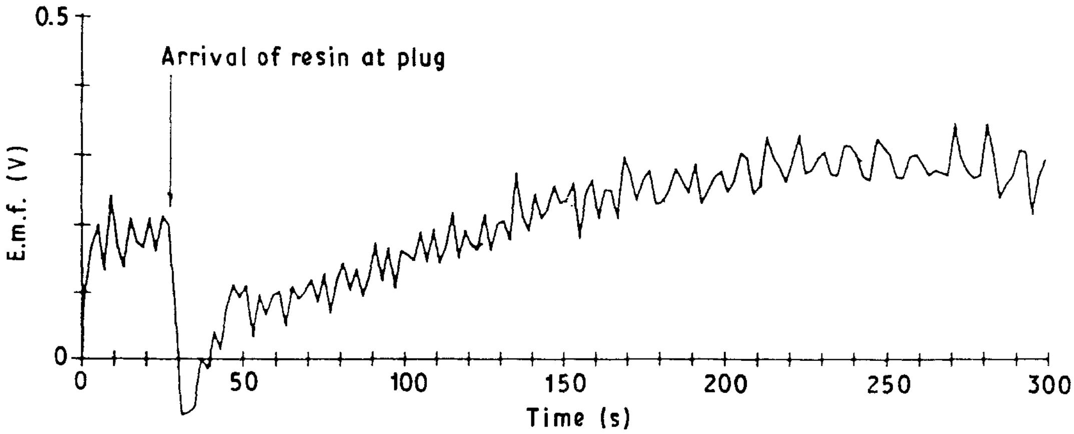

Figure 11 E.m.f. produced by prototype gauge during moulding trials.

unit which can be installed as required in any mould, including those made of non-electrically conducting materials such as plastics.

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