1 General Introduction

Synthetic composite materials have played a significant role in the advancement of many areas of industry, including most prominently aerospace, automotive and construction. However they have one major weakness in that their failure can seem unpredictable due to microcracks within the structure which are difficult to detect. Non-destructive evaluation techniques, such as radiography and ultrasonic testing, are time-consuming and require expert technicians and tools. Even then this is not always possible with certain geometries, and most often not economically feasible. This has somewhat inhibited the introduction of these materials into more diverse markets where technological advancement is a less crucial factor in product profitability. Nevertheless this desire to overcome the limitations of composites in order to reap their obvious benefits has led to the conception of an entirely new class of materials; ‘self-healing’ materials.

Several methods for the regeneration of mechanical properties have been proposed, each with their own advantages which make them suitable for particular applications or environments. Active or ‘non-autonomic’ methods have been developed [1,2] where the reformation of bonds within the matrix is instigated by an external stimulus[3], such as Modified Matrix which regains structural integrity with the application of heat to a damage site. Early work on this method used a standard DGEBA-based formulation resin (Epon 828) cured with an acid anhydride (NMA), modified by a high molecular weight linear polymer healing agent (polybisphenol A-co-epichlorohydrin). One of the main disadvantages of this method is that the healing agent imparts a high viscosity to the blend, making it unsuitable for many industrial manufacturing processes, including injection moulding, resin transfer moulding (RTM) and filament winding.

2 Development

In order to address this issue, an investigation has been undertaken into the further modification of this resin in order that the viscosity is reduced without compromising the self-healing ability. This new system is required to have handling properties which make it suitable for use in industrial RTM, which has a fairly low tolerance for the allowable viscosities. Previous work on the formulation of Modified Matrix systems has included a study of the kinetics of the reaction by using lower molecular weight healing agents [4], and the use of varying concentrations of healing agent (Fig. 1). However, despite observation that handling the resin was extremely difficult due to its high viscosity, a rheometric study has never been conducted, as the method was only in the early stages of development.

3 Experimental

3.1 Rheometry

Rheometric comparison of new resin systems against previous self-healing ones and industrial RTM resin displays to what extent the handling properties of the modified self-healing resin have been adapted.

Rheometry was carried out on a TA Instruments AR2000 rheometer in linear temperature ramp experiment for the viscosity profile of the uncured resin using a parallel plate 40mm geometry. Tests were conducted in flow mode using a fixed angular velocity of 5 rad/s.
3.2 Compact Tension Testing

Compact tension testing has been used to monitor the degree of healing in the resin following modification. This method was used as it is an established route and provides information comparable with previous systems. Testing was carried out according to the specification detailed in BS ISO 13586:2000 on a sample of pure resin. This data allowed comparison of the fracture toughness of different resins, and of the healability intrinsic to them by retesting the fracture toughness after a healing heat cycle.

4 Results

Results obtained so far have been to compare the rheometric profile of the previously used resins, and their healability with regard to fracture toughness.

The first attempt at a reduction of the viscosity was to vary the concentration of the healing agent within the composition. Figure 1 shows the viscosity of the resin with varying concentrations, and the healability of fracture toughness of the same concentrations in Figure 2.

The second investigation was into the effects of varying the molecular weight of the healing agent in order to both improve efficiency of the healing and to reduce the viscosity. Rheometric data is shown in Figure 3, with corresponding compact tension results in Figure 4. Note that the colour scheme for the CT data is linked to that of the rheometry.

5 Discussion

It can be seen from Figures 1 & 2 that while concentration of the healing agent always increases the viscosity of the blend, the maximum healing efficiency for this resin peaks at around 7.5% which had been demonstrated in further work. Shown here is the first results for the viscosity of the system which is only in the range suitable for RTM at low concentrations with the high M_w healing agent (44K). However, even at this very low concentration of healing agent, it can be seen that recovery of K_1c is around 45% for the first healing cycle, and 30% for the second. This formulation only drops into the viscosity range for RTM at around 80°C which although would be adequate, for a resin which cures at 120°C, the processing time would be severely reduced.

Data from the compact tension testing of the resin system with a reduced Mw healing agent (Figure 4) can be seen to show that a similar healing efficiency may be obtain with the same amount of a lower molecular weight healing agent. All concentrations were at 7.5%, which was the most efficient concentration for the 44k healing agent from the previous tests.

Viscosities for these new blends can be seen in Figure 3. These new formulations fall into the range suitable for RTM at approximately 75°C. For the results obtained so far differences between the 4K and the 6K healing agent are minimal in terms of the viscosity and the healing efficiency.

Healability of the fracture toughness for both medium weight healing agents was over 50% for the first healing cycle and around 40% for the second.

6 Summary

It has been shown that it is possible to create resins with a self-healing ability by the modified matrix method by lowering the viscosity through a variety of methods. The characterisation of these resins in terms of healing properties of resin has been discussed. Results from the early stages of this investigation have been extremely positive, with healability from newly developed formulations reaching the efficiencies displayed by previous tests, while also reducing the viscosity and therefore improving the handling properties of the uncured resin. Furthermore it has been shown that improved healing efficiency may be gained by the inclusion of higher concentrations of a lower molecular weight healing agent.

The first rheometric study of Modified Matrix self-healing resins has been assessed and it is clear that there are many approaches available in order to further modify the system, and tailor it to specific applications or manufacturing processes. At the time of writing other methods are under investigation and results will be published in due course.
Fig. 1 Viscosity of the resin with varying concentration of healing agent (M_w 44,000). Shaded areas represent the viscosity range suitable (light) and ideal (dark) for RTM manufacture.

Fig. 2 Compact Tension results of the resin with varying concentration of healing agent. Note: Bar colours relate to Figure 1.

Fig. 3 Viscosity of the resin with varying M_w healing agent, at 7.5% concentration. Shaded areas represent the viscosity range suitable (light) and ideal (dark) for RTM.

Fig. 4 Compact Tension results of the resin with varying M_w healing agent. Note: Bar colours relate to Figure 3.
References


