Novel Diels-Alder based self-healing epoxies for aerospace composites

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Keywords: self-healing composites, retro-Diels Alder reaction, epoxy

Abstract

Epoxy resins containing Diels-Alder furan and maleimide moieties are presented with the capability to self-heal after exposure to an external heat source. A conventional epoxy amine system has been combined with furfuryl and maleimide functional groups in a two-step process, to avoid major side-reactions, and the concentration of a thermo-reversibly binding cross-linker was considered to balance thermoset and thermoplastic behaviours, and the subsequent self-healing performance.

In the context of self-repair technologies an inbuilt ‘intrinsic’ self-healing system is deemed favourable as the healing agent can be placed in known ‘hot spot’ regions (i.e. skin-stringer run outs, ply drops and around drilled holes) where operational damage predominately occurs in load bearing aerospace structures. In this study, the mechanical and self-healing performance of furan functionalised epoxy resins containing varying amounts (10, 20, 30 or 40 pph) of bismaleimide were investigated using a bulk epoxy polymer tapered double cantilever beam (TDCB) test specimen geometry. Two forms, a thin film and a bulk material, were evaluated to account for future integration methods into fibre reinforced polymer (FRP) composites. The highest healing efficiency, with respect to the obtained initial load value, was observed from the 20 pph bulk material derivative. The polymers were successful in achieving consistent multiple (three) healing cycles when heated at 150 °C for 5 minutes.

This novel investigated Diels-Alder material exhibits favourable processing characteristics for FRP composites as preliminary studies have shown successful coextrusion with reinforcing fibres to form free standing films and dry fibre impregnation.

Introduction

Biomimetic materials are becoming increasingly attractive to engineers due to the expanding possibilities of the existing man-made material design space to include non-standard characteristics by imparting, often embedded, on-demand functionalities such as nature inspired damage tolerant designs, self-sensing and self-healing technologies. The former two technologies have received positive uptake from industry to develop novel ballistic armour concepts [1] and structural health
monitoring systems [2,3] in the aerospace industry, however, self-healing technologies remain in the dormant state of lab scale appropriate experimental investigations. Implementing self-healing technologies into structural components is not a ‘one-size fits all’ approach due to the requirements to tailor the reactive self-healing agents to the in-service operating conditions. Therefore, this research study focuses specifically on an intrinsic self-healing Diels-Alder prepolymer (DApp) based epoxy resin that is compatible with commercially available aerospace grade epoxy resin systems, matches the structural performance of such materials and also does not impact upon the inherent mechanical performance of the host matrix epoxy resin material after embedment. In recent years a number of review papers have considered the advantages and disadvantages of capsule, vasculce and intrinsic self-healing systems [4,5,6,7]. Intrinsic Diels-Alder based self-healing materials for composites have generally received less attention, therefore, we have focussed on this rather unexplored system to restore mechanical performance in epoxy resins.

The Diels-Alder reaction is a thermo-reversible cycloaddition between a conjugated diene and an alkene. Thermally removable epoxy adhesives based on Diels-Alder chemistry have been known for some time and are already (extensively) described in literature. One of the first reports by Aubert [8] dates back to 2003, and details the reaction of a diepoxy- compound formed via the Diels-Alder reaction between two epoxy containing furans and a bismaleimide that results in an epoxy functionalised Diels-Alder adduct that can react further with aliphatic diamines. Since this early work, Wudl et al. [9,10] and Palmese et al. [11,12] have studied thermo-reversible cross-linking systems for epoxy resins, however, practical considerations remain limited due to the use of solvents, encapsulated reagents (uncontrollable mixing) and long healing times. Alternative Diels-Alder based self-healing materials [13,14] have largely consisted of elastomeric hydrogel formulations (ideally suited to coatings or soft robotics) that, although they have a high strain to failure ratio they do not exhibit the high strength and stiffness requirements of high performance thermoset epoxy materials.

In a recent publication by Turkenburg et al. [15] details for the synthesis of a novel Diels-Alder functionalised epoxy resin material that exhibits a dual character of having thermoset type mechanical properties with the formability and remouldability of a thermoplastic material are presented. Extensive rheology studies demonstrated the capability to induce multiple ‘self-healing cycles’ (i.e. utilising the thermoplastic behaviour) by heating to 150 °C for 5 minutes (Figure 1).
Figure 1: Schematic overview of the Diels-Alder self-healing process (top). Between monomers both permanent and thermo-reversible bounds (bottom left) are established. At high temperature (bottom right) the latter open and enable the system to flow thereby allowing cracks to heal and restore adhesion on sites of delamination [14].

Herein, this research study investigates the mechanical characterisation of the aforementioned Diels-Alder prepolymer material in epoxy resin tapered double cantilever beam (TDCB) test specimen coupons. Throughout the study, the application of the material to relevant aerospace structural component concepts was at the forefront of the experiments. As a result, two forms of the Diels-Alder prepolymer, a bulk material and a thin film, were investigated. It is envisioned that this novel material will be incorporated within FRP composites and, therefore, a thin film is favourable for embedment as an interleave component. The significant variable in these experiments consisted of the concentration of the bismaleimide component, the active cross-linker in the ‘thermoset phase’ and, therefore, the relationship between fracture toughness, initial failure load and healing performance over three heat treatment - re-fracture cycles is evaluated. Furthermore, the impact on the host matrix material in terms of reduction in mechanical performance with respect to the Diels-Alder prepolymer formation is also considered.

Although a relatively high healing temperature may appear to be an issue for commercial implementation, a short healing time (of 5 minutes) is certainly favourable in the scope of maintenance, repair and overhaul (MRO) systems and processes. It is envisioned that an externally mounted controlled heating pad configuration could provide the requirements for this self-healing system once incorporated into FRP composites.
Experimental

Diels-Alder prepolymer synthesis

Diels-Alder prepolymer materials were synthesised from readily available cost effective commercial raw materials; furfuryl amine, diglycidyl ether bisphenol A (DGEBA) and bismaleimide (BMI). The method and analytical analysis is described in detail by Turkenburg et al. [15]. In summary, a bulk reaction process combined furfuryl amine with diglycidyl ether bisphenol A (DGEBA) for 2 hours at 125°C resulted in a yellow polymeric transparent glassy material. Subsequently, the self-healing Diels-Alder resin was processed via batch extrusion at 150°C by using the aforementioned pre-polymer (without further purification) and varied amounts of 1,1’-(methylene-4,1-phenylene) bismaleimide (BMI) (the reversible crosslinker) to get a range of crosslink density values for 10, 20, 30, 40 pph BMI corresponding to 0.32, 0.64, 0.95 and 1.27 equivalents of maleimide groups per furfuryl group respectively.

Solvent exposure tests

In a typical solvent exposure test, dichloromethane is added to 0.1 to 0.5 gram of polymer, \(P_{\text{initial}}\) (total of 4 gram) in a vessel that is closed and kept at ambient conditions for five days after which the sample is decanted. The weight of pieces of swollen polymer is determined, with \(P_{\text{swollen}}\) and without \(P_{\text{final}}\) the absorbed solvent that was removed by placing the samples in oven at 150°C for 1 hour. The reaction of undissolved polymer is calculated \([P_{\text{final}}-P_{\text{initial}}]/P_{\text{initial}}*100\%\) from which the fraction of dissolved polymer is deduced (100% minus fraction of undissolved polymer). Only the undissolved fraction is considered when determining the swelling factor, \(S\), as a measure of the crosslink density of the polymer network. The swelling factor is defined as: \(S = (P_{\text{swollen}}-P_{\text{final}})/P_{\text{final}}\).

Tapered double cantilever beam (TDCB) test specimen manufacture

Silicone moulds, used for casting the TDCB geometry, were formed by pouring Silcoset® 101 silicone potting compound (ACC Silicones), mixed with 0.1 wt% CAA28 catalyst, into computer numerically controlled (CNC) machined aluminium moulds. A degassed mixture of 100 parts EPON 828 (Polysciences Ltd) with 12 parts curing agent diethylenetriamine (DETA - Sigma Aldrich) was poured into the closed mould and left to cure for 24 hours at ambient temperature and 24 hours at 40°C [16]. Precast TDCB epoxy resin test specimens were prepared for the bulk material (occupying the central grooved region) by cutting out the central grooved region using a water-cooled diamond grit saw. The prepared TDCB specimen was placed in one half of the closed silicone mould and Diels-Alder prepolymer material was softened to flow into the cutout region using a temperature controlled (150°C/5 minutes) handheld heat gun (Bosch GHG 660 LCD Professional). Once the cut out region was fully occupied with Diels-Alder prepolymer a second silicone mould was pressed on top to form the symmetrical grooved central trench region (Figure 2). Thin film test specimens were prepared using a similar method, however, a multi-purpose knife was used to separate the symmetrical grooved central section rather than removing the entire grooved central section, as documented above for the bulk material test specimens. In order to cut along the central grooved
section the EPON-DETA TDCB geometry was locally heated to 50°C using a heat gun. This heating step softened the test specimen geometry sufficiently and allowed the central trench cut faces to be separated so that the Diels-Alder prepolymer material can infill the gap. A metal shim (~250um) was inserted at the crack starter region to provide a consistent thickness of the thin film. Diels-Alder prepolymer was then ‘melted’ onto the central grooved section cut faces.

![Figure 2: (i) TDCB test specimen geometry before (right) and after (left) cutting for bulk material specimens, (ii) Aluminium CNC mould (pictured top) and prepared sample for bulk material specimen placed in silicone mould, (iii) Diels-Alder prepolymer ‘flakes’ placed in cut out region, heated with heat gun, (iv) Resultant TDCB bulk material test specimen after pressing molten Diels-Alder prepolymer between silicone moulds.]

**Tapered double cantilever beam (TDCB) test specimen testing**

An Instron 3343 fitted with a 1kN load cell was used to initiate Mode I crack opening displacement. Tapered double cantilever beam (TDCB) test specimens were fixed via a pin attachment fixture and loaded at a displacement rate of 5 μm s⁻¹ [15]. Specimens were precracked with a sharp multi-purpose blade and tested until the crack propagated to the end of the self-healing region. After the initial fracture event the self-healing region was taped up with one-sided adhesive release tape to ‘dam’ the Diels-Alder prepolymer during the healing process. The taped up test specimens were placed in preheated (150°C) silicone (Silcoset® 101) TDCB moulds (to constrain the TDCB geometry) for 5 minutes to facilitate the healing process (Figure 3). Subsequently, the ‘healed’ test specimens were transferred to room temperature silicone moulds to cool. Once the test specimens had cooled to room temperature the test specimens were retested as carried out for the initial fracture. This methodology was repeated for the 2nd and 3rd healing cycles. Self-healing efficiency (η) is determined by initial (P_initial) and healed (P_healed) load values; \( \eta = \frac{P_{healed}}{P_{initial}} \)
Results and Discussion

The main challenge connected with the preparation of a self-healing Diels-Alder (DA) functionalised resin is the activation of selective desired reactions (DA coupling) while avoiding undesired side reactions, such as Michael addition [17] or homo-polymerisation of BMI [18], that occur at high temperatures [19]. To ensure the resultant self-healing polymer had sufficient reactivity after processing careful considerations were taken during the synthesis with respect to the order of the reactions, by using stepwise synthesis and limiting the exposure to oxygen during high temperature processing. Consequently, epoxy and the furfuryl amines were reacted together resulting in an epoxy pre-polymer. It is at this step that the prepolymer is tuned to provide the required quantity of furfuryl side groups for network formation and to keep the viscosity of the prepolymer melt low. In brief, the following step involves the addition of the bismaleimide (BMI) component (the variable in this study) to cross-link the prepolymer and also act as the thermo-reversible self-healing component. Therefore, the relationship between the initial fracture and self-healing efficiency (i.e. mechanical performance) of the DApp is evaluated with respect to the concentration of BMI (expressed in pph, in terms of grams of bismaleimide per 100 gram of prepolymer) to consider the influence of cross-link density.

The self-healing performance of the Diels-Alder prepolymer system was explored using a modified tapered double cantilever beam (TDCB) test specimen geometry (Figure 3) [16]. Two separate configurations were evaluated consisting of a bulk polymer (constrained to the central trench section) and a thin film (~250 μm thickness), to evaluate the self-healing performance. All four Diels-
Alder prepolymer, containing 10, 20, 30 or 40 pph of BMI with respect to the prepolymer were studied in order to select the highest performing candidates for further evaluation (Table 1).

The first study considered the bulk polymer configuration that contained the DApp in the central trench region. The central trench section was reduced to exclusively fill the grooved feature due to prior preliminary results showing that when using the previously documented [16] test set up premature fracture occurred at the loading arms. Although the Diels-Alder prepolymer contains epoxy groups to aid compatibility with epoxy resin systems, the bonding affinity between the regular central trench bulk polymer and the TDCB epoxy resin was not great enough to facilitate successful crack propagation. The revised configuration proved successful in obtaining self-healing efficiency values for each DApp formulation. In the context of implementation into epoxy materials the fracture toughness is considered in terms of load due to the nature of the crack to propagate to interface regions.

Table 1: Test specimen configurations

<table>
<thead>
<tr>
<th>Designation</th>
<th>g BMI / 100g DApp</th>
<th>Maleimide groups/ furfuryl groups</th>
<th>TDCB test specimen configurations*</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bulk material</td>
</tr>
<tr>
<td>10-100</td>
<td>10</td>
<td>0.32</td>
<td>x</td>
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<tr>
<td>20-100</td>
<td>20</td>
<td>0.64</td>
<td>x</td>
</tr>
<tr>
<td>30-100</td>
<td>30</td>
<td>0.95</td>
<td>x</td>
</tr>
<tr>
<td>40-100</td>
<td>40</td>
<td>1.27</td>
<td>x</td>
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* Healing conditions: 150°C for 5 minutes, 3 consecutive healing cycles

After the solvent exposure tests (Figure 4) the sample of 10pph has absorbed all the dichloromethane that was added forming a single phase that may be a polymer solution of BMI connected prepolymer chains that barely add up to a network, or, a gel consisting of a very loosely crosslinked polymer network which has internal pockets available to accommodate a large volume of solvent in the swollen state. In case of 20, 30 and 40 pph, a large fraction of soluble material is still observed. Short chains that did not participate in the polymer network formation have been extracted by the solvent. The majority of these samples however, remained undissolved after five days of exposure to dichloromethane indicating that the concentration of Diels-Alder adduct bonds established is much higher compared to the material corresponding to 10pph of BMI. The maximum fraction of insoluble material is found for 30pph which has a maleimide to furfuryl ratio closest to one. Eventhough the amount of material participating in the formation of a polymer network may be of comparable level for 20pph and 40pph of BMI, the crosslink density may be lower in case of 20pph because it has a much larger swelling ratio, absorbing up to 15 grams of solvent per gram of undissolved polymer as opposed to a swelling ratio of 3 in case of 40pph.
Figure 4: Solvent exposure effects after five days in dichloromethane in relation to the amount of cross-linker added to the system. The swelling factor, $S$, of the fraction that has not dissolved in dichloromethane has been added in the figure.

It is expected that a higher mechanical performance is obtained when the crosslink density of the polymer is higher and when a larger fraction of the material has participated in network formation. The 30-100 analogue showed to have the highest average initial failure load of $47 \pm 6$ N from 5 test specimens (Figure 5) when compared to the 20-100 analogue with a value of $34 \pm 7$ N. When considering the healed results for three successive healing cycles (150°C/5 minutes) for both analogues the apparent healing efficiencies with respect to the observed load values are comparable within the data error. For example, the first heal for the 30-100 analogue resulted in a healing efficiency of 73% (i.e. 34 N) and the first heal for the 20-100 analogue resulted in a healing efficiency of 122% (i.e. 41N). The second and third healing cycles resulted in progress reductions in healing efficiency values (of ~5-20%). This confirms the previously discussed findings from the viscosity results stating that irreversible side-reactions and increased irreversible network formation are responsible for the reduction in healing efficiency values.

To fully confirm the effect of cross-linker concentration, swellability and mechanical performance on self-healing behaviour the 10-100 and 40-100 analogues were evaluated. Firstly, the 10-100 analogue that showed the highest degree of swellability also exhibited the lowest average initial failure load with a value of $25 \pm 4$ N. Subsequently, healing efficiency values of ~80% (i.e. 20 N) resulted. This is attributed to the reduction in cross-linking between the available BMI and furfuryl functional groups despite the reduction in viscosity. In comparison, the 40-100 analogue showed to have an initial failure value of $44 \pm 3$ N and healing efficiency values of 59% ($1^{st}$ - 26 N), 63% ($2^{nd}$ - 28 N) and 77% (34 N). Therefore, it is evident that at a concentration of 40 g BMI to 100 g prepolymer an increase in swelling is observed due to the number of crosslink donors (dienophiles) not being in balance with the number of crosslink accepting groups (dienes). As a result the prepolymer chains become saturated with bismaleimides up to the point where furfuryl groups can accommodate for linking but not for cross-linking.
The second study considered the embedment of a thin film (~250 μm thickness) of DApp cast within an EPON-DETA epoxy resin TDCB test specimen (Figure 6). This configuration was selected as an interim progression from bulk material testing to embedding interleaved material or infused fibres into FRP composites. Similarly to the bulk material TDCB test campaign the 20-100 and 30-100 analogues were tested initially to evaluate mechanical performance with respect to self-healing efficiency. The 20-100 analogue exhibited the highest average initial failure load (from 5 test specimens) with a value of 36±5 N, a slight improvement compared to the initial failure load achieved for the 30-100 analogue (28±2N). These results appear to be in direct contrast to those obtained for the bulk material test specimens and is likely to be attributed to the increased compliance of the lower cross-linked 20-100 analogue in comparison to the 30-100 analogue. Thin film analogues are essentially adhering two ‘crack surfaces’ and, therefore, the reduced thickness of the embedded thin film feature provides a greater compliance and reduced rigidity prior to initial failure. The healing results for both the 20-100 and 30-100 analogues, however, are comparable within the data error when considered with respect to their associated initial fracture values. Healing efficiency values of 104% (1st - 37N), 82% (2nd - 30 N) and 76% (3rd - 27 N) were obtained respectively for the 20-100 analogue, and 117% (1st - 33 N), 123% (2nd - 34 N) and 107% (3rd - 30 N) for the 30-100 analogue.

In order to provide further clarity to the relationship between BMI-DApp cross-linking and mechanical performance, the 10-100 and 40-100 analogues were also tested in thin film form. As shown previously the healing efficiency remains largely consistent over three healing cycles, however, values appear to be 20-30% lower than the values obtained for 20-100 and 30-100 analogues (Figure 7). These healing results further reiterate that the form of the self-healing material (i.e. bulk material or thin film) has a large influence on the outcomes from mechanical testing. Therefore, what may appear to be significant differences between bulk material analogues, is observed to be much more subtle in thin film configurations.
Scanning electron micrographs of the 30-100 bulk material and thin film analogues are shown in Figures 8 and 9, respectively. The fracture surfaces represent the different failure mechanism and energy released during fracture. Figure 8, that features the bulk material specimen, shows a distinct cohesive failure with riverlines running parallel to the direction of the propagating crack as the crack deviates from the starter crack (right side of image) to the DApp/TDCB epoxy resin interface (i.e. on the left side of the representing out-of-plane fracture). These features represent a high energy release event, typical of a brittle failure experienced in the load-displacement plot (Figure 5). Figure 9, however, shows a quasi-adhesive failure and the crack propagates between interface regions, this failure contributes towards the increased surface roughness of the Diels-Alder prepolymer shown.

Although the observed failure values appear somewhat lower (up to 50%) to those observed from the benchmark values (Figure 4), the specific application of this technology is of key importance to achieving performance benefits and enhanced FRP durability. It is envisioned that self-healing technologies will be localised to areas of high stress concentration in FRP composite components where these likely early failure regions (i.e. stringer run out regions, ply drops etc.) will benefit hugely from self-repair mechanisms, and typically do not fully represent the overall host matrix mechanical performance. Consequently, in the scope of self-healing research activities direct comparison to benchmark values may not be truly representative of ‘real-life’ technology application. Therefore, the preliminary investigation detailed above proves the successful development of a viable Diels-Alder self-healing agent for FRP composite components. On-going and future studies are considering the implementation of this technology into prepreg-based FRP aerospace structural components.
Figure 7: A summary of healing efficiency (left axis) and initial fracture load values (right axis) for bulk material and thin film TDCB test specimens. Three healing cycles are presented. Labelled average values are taken from 5 data points.

Figure 8: Microscopy investigation of the fracture plane for a 30-100 bulk material TDCB test specimen after re-test. Left main image: Scanning electron micrograph (SEM) of the fracture plane. Upper right and lower right inset images: SEM of the fracture plane at higher magnifications, illustrating riverlines aligned parallel to the crack direction (right to left of images).
Figure 9: Microscopy investigation of the fracture plane for a 30-100 thin film TDCB test specimen after re-test. Left main image: Scanning electron micrograph (SEM) of the fracture plane. Upper right and lower right inset images: SEM of the fracture plane at higher magnifications, illustrating quasi-adhesive fracture.

Processability, future implementation and outlook

The obtained materials exhibit unique characteristics of both traditional thermoset epoxies having a high crosslink density as well as the typical behaviour of thermoplastics that soften and flow at elevated temperatures. The crosslink density, which is of importance for the chemical inertness and mechanical behaviour of composites, was studied previously by solvent exposure tests [15]. The processability of the Diels-Alder prepolymer is largely determined by the viscosity of the prepolymer, which showed that without the presence of BMI gradual decreases of over three orders of magnitude are observed when increasing the temperature from 60°C to 120°C. Throughout the entire temperature range the liquid behaviour of the prepolymer remains. The flow properties of the cross-linked prepolymer are dramatically changed and two regimes can be discriminated within each heat cycle of the combined systems: the temperature independent plateaus at low temperature indicating the presence of a solid, and a liquid state at temperatures above the retro-DA temperature (ca. 100°C) where viscosity scales with temperature. The high temperature regime is dominated by the reverse Diels-Alder reaction. Reversible crosslinks are broken and the material behaves as a prepolymer melt in which free BMI is dissolved. BMI, having a rigid molecular structure and a high melting point (158°C), acts effectively as a thickener explaining the higher viscosity in the liquid state with respect to the curve of the prepolymer itself. Therefore, when evaluating the self-healing DApp for further implementation an appreciation is required for the processing requirements in addition to the self-healing performance (Figure 8).

The use of preimpregnated fibre preforms (i.e. prepreg) in the aerospace industry is expansive and ever growing to provide consistently high quality, certified composite components. Therefore,
designing a self-healing system to be compatible with such a material process would be hugely attractive to minimise the requirements to develop entirely ‘new’ manufacturing methods for self-healing composites. As shown in Figure 10, the aforementioned Diels-Alder prepolymer is capable of being extruded and processed into a stable thin film that can be machined to a specific geometry to be interleaved or infused to form a prepreg material. Therefore, demonstration of the prepolymer in epoxy resin TDCB test specimens, to provide a self-healing ‘mechanical zip’, is the first step to the further development of this material for the in-situ repair of FRP composite materials.

![Figure 10](image)

(i) Microscopic image after extrusion, (ii) Prepolymer with 30 pph reversible BMI crosslinker coextruded with glass fibres, (iii) Free standing film obtained after hot compression of the extruded material, (iv) Freestanding film embedded in test specimen of conventional prepreg.

**Conclusions**

In conclusion, a selection of bismaleimide cross-linked furan functionalised epoxy resins were synthesised and investigated for their mechanical performance and recovery of mechanical performance via three repeatable healing cycles, attributed to the thermoplastic behaviour. Building on the previous rheological studies that demonstrated the thermo-reversible nature of the crosslinks allows for substantial flow of the material at elevated temperatures, the self-healing functionality showed great promise for implementation into FRP composites. Although a knock-down in mechanical performance was observed for self-healing specimens when compared with the benchmark epoxy resin, it is expected this will be less of an issue for FRP composites that possess a much lower resin volume fraction of ~37%. The potential for a composite that has the capability to repair multiple times has to be appreciated when compared to a marginally higher performing composite that when become damaged needs to be taken out of service and manually repaired at great expense. In our future work we aim to demonstrate this feature to further advance the field of self-healing composites in a commercial environment.
Acknowledgments

The authors would like to acknowledge the financial support of the European Union under the framework programme 7 (FP7) self-Healing POLymers for Concepts on self-Repaired Aeronautical compositES (HIPOCRATES) project. (Grant number: ACP3-GA-2013- 605412-HIPOCRATES)

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