SINTEZA SI CARACTERIZAREA UNUI NOU MATERIAL COMPOZIT PE BAZĂ DE POLI(METIL METACRILAT) ŞI SILICE PENTRU APLICAȚII DENTARE

SYNTHESIS AND CHARACTERIZATION OF A NEW COMPOSITE MATERIAL BASED ON POLY(METHYL METHACRYLATE) AND SILICA FOR DENTAL APPLICATIONS

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The purpose of this study was to improve the knowledge in the field of composite materials based on poly(methyl methacrylate) (PMMA) and silica (SiO_2). For this purpose, two types of silica were taken into account: i) silica was synthesised in situu by sol-gel technique and ii) commercial silica was used. In both cases the polymer matrix was obtained by radical polymerisation.

The composite materials were then characterized from the phases point of view by Fourier transform infrared spectroscopy (FT-IR) and X-ray Diffraction (XRD) and from the morphology and compatibility between phases point of view by scanning electron microscopy (SEM).

The results showed that in situu formation of the silica network is preferred over commercial silica addition because it allows a better compatibility between the organic and inorganic compounds.

Scopul prezentului studiu a fost acela de a îmbunătăți cunoştințele în domeniul materialelor compozite pe bază de poli(metacrilat de metil) (PMMA) şi dioxid de siliciu (SiO_2). În acest sens, au fost utilizate două tipuri de silice: i) una sintetizată in situ prin metoda sol-gel şi ii) silice comercială. În ambele cazuri, matricea polimerică a fost obținută prin polimerizare radicalică.

Materialele obținute au fost caracterizate din punct de vedere fazal prin difracție de raze X (XRD) şi spectroscopie IR cu transformată Fourier (FT-IR) iar din punct de vedere morfologic şi al compatibilității dintre faze prin microscopie electronică de baleiaj (SEM).

Rezultatele au arătat că formarea in situ a rețelei de silice este preferată adiției celei comerciale deoarece permite o mai bună compatibilitate între compuşii organici şi anorganici.

Keywords: *poly(methyl methacrylate), silica, composite material, dental application*

1. Introduction

The composition of dental resin composites has changed dramatically since these materials were introduced to dentistry more than 50 years ago. Until now, the most important changes have focused on the reinforcing filler, which has been reduced in size to obtain materials that are more easily polished and prove better wear resistance. The latter was necessary for materials used in posterior applications, but the former was important for restorations in all areas of the mouth. Present changes are more focused on the polymer matrix, aiming to develop systems with reduced polymerization shrinkage and to make them self adhesive to the tooth structure [1].

A wide range of acrylate polymers are used for medical applications and especially in dentistry [2].

Poly(methyl methacrylate) (PMMA) distinguishes by its water-clear color, high surface resistivity, stability of properties upon severe conditions and resistance to weathering and moisture. Also, PMMA offers some advantages like high strength, good flexibility and excellent dimensional stability. Due to these superior properties, PMMA has been widely used as additive, for coating and polishing agents, binders, sealers, optical fibers, high voltage and outdoor electrical application [3]. Also, it is considered to be an important material for optical devices [4].

The excellent synergetic properties of certain polymer nanocomposites have recently drawn the attention both in industry and in medicine. Nevertheless, the process of obtaining polymer nanocomposites with optimum properties is a challenging task due to the surface energy differences between hydrophilic nanoparticles and hydrophobic polymers. To overcome the incompatibility issue and improve interactions between polymer and nanoparticles, nanoparticles surface modification was considered a good solution in order to enhance nanoparticles dispersion in the polymer matrix and the properties of nanocomposites [5-8].

Traces of unreacted monomer usually lead to side effects and weak properties in the final products which are not desired in many applications,

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especially in medicine [9]. The presence of monomer is a consequence of a small polymerization degree.

Unlike other polymers, PMMA is a representative material used for bone cement due to its self-hardening capacity and excellent mechanical properties. However, direct application to the bone cement is restricted due to the bio-inertness character of PMMA; no biological or chemical bonding occurs at the interface between the PMMA and bone and this causes the PMMA to wear down as a result of repeated interfacial movement. Thereby, the use of PMMA becomes one of the causes contributing to osteolysis and subsequent loosening of the implant [10-12]. Therefore, a lot of studies have been done to provide osteoconductivity to the PMMA bone cement by using bioactive ceramic fillers [13].

The most commonly used ceramics employed in medicine are hydroxyapatite (HA), silica, and bioglass [14]. Silica (SiO_2) is a bioactive material with resistance to high corrosion. Silica bioceramics are used as prosthetic bone and dental implants because they favor the formation of apatite on their surfaces when immersed in simulated body fluid (SBF). SiO_2 improves bioactivity by leading to the appearance of Si–OH groups on the surface of the material. However, because of its poor mechanical properties compared to natural bone, silica cannot be used for load-bearing applications [15].

In the present work, poly(methyl methacrylate)/SiO_2 composite materials were prepared via *in situu* precipitation/polymerization method.

2. Experimental

2.1. Materials

Methyl methacrylate monomer 99% was supplied by Sigma-Aldrich. Silicon dioxide was supplied by Merck. Benzoyl peroxide (initiator) purrum ≥ 97% was supplied by Fluka. The precursor for silica – tetraethyl orthosilicate (TEOS) was supplied by Aldrich. All reagents and precursors were used without any further purification.

2.2. Methods

The dental composite materials based on PMMA and SiO_2 were synthesised starting from methyl methacrylate and a) *in situ* obtained SiO_2 and b) commercial available silica.

For the first case of composites made from precipitated silicon oxide, the synthesis procedure is described below in Figure 1. Into a round-bottom flask equipped with refrigerant, heating plate with magnetic stirrer, thermometer and water bath was first introduced the monomer, then tetraethyl orthosilicate [$Si(OEt)_4$] that was previously dissolved in a minimum volume of distilled water and finally, benzoyl peroxide used as initiator ($C_{14}H_{10}O_4$).

The reaction was carried out for 3 hours at 90°C. At the end, the pH of the entire mass was adjusted to 7.0 with NaOH 0.1 N solution.

In order to obtain the final composites, the sample was centrifuged, dried and grinded.

For the second case of composites made from commercial silica, the synthesis procedure is the same as for the first case with a small change in the order of reagents addition: first it was introduced a minimum volume of distilled water, then the commercial silicon oxide, the monomer and, finally, the initiator (Figure 2).

For both cases, the ratio between the organic matrix and the inorganic component is of 1:1. Benzoyl peroxide was added in a percentage of 1 % reported to the monomer.

The composition, (micro)structures and thermal behaviour of the obtained composite materials were examined by FT-IR, XRD, SEM and ATD-TG.

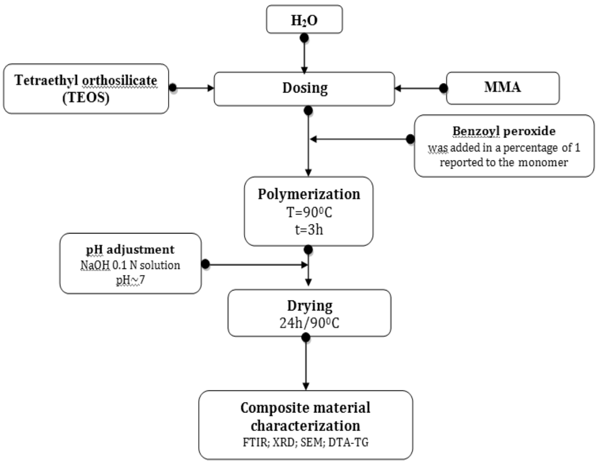

Fig. 1 – Schematical representation of the work procedure for PMMA/*precipitated SiO_2 / Reprezentarea schematică a procesului de obținere al compozitelor PMMA/SiO_2 obținută prin precipitare.*

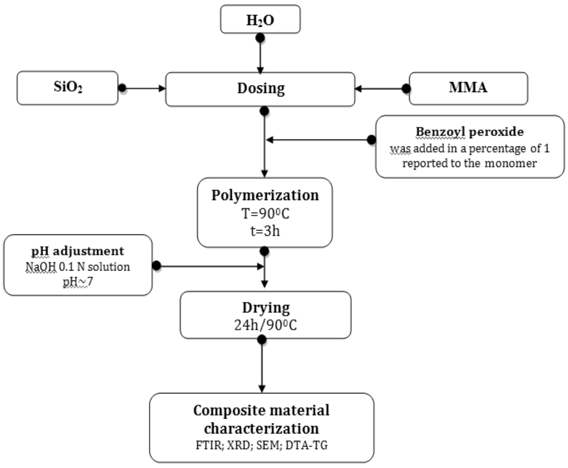

Fig. 2 – Schematical representation of the work procedure for PMMA/commercial SiO_2 / *Reprezentarea schematică a procesului de obținere al compozitelor PMMA/SiO_2 comercială.*

IR spectroscopic measurements were performed using a Thermo Scientific Nicolet iN10 MX FT-IR microscope. The spectra of PMMA/SiO_2 were recorded for both composites over the wavenumber range of 675–4000cm^{-1} with a resolution of 4cm^{-1}.

X-ray diffraction analysis was performed using a PANanalytical Empyrean diffractometer at room temperature. XRD analysis is important for the characterization of materials and can be used to identify the crystalline phases and to determine the crystallinity degree. All samples were ground to fine powders before analysis. XRD determinations are complementary to the information brought by FT-IR analyses.

SEM images were obtained with a HITACHI S2600N with an EDAX probe. All samples were covered with a silver layer prior to imaging. Scanning Electron Microscopy (SEM) analysis was used to determine the morphology of samples. SEM images were also relevant to highlight the compatibility between phases.

Differential thermal analysis (DTA) coupled with thermogravimetric analysis (TGA) were performed in air atmosphere with a Shimadzu DTG-TA-50H at a heating rate of 10°C. Thermal analysis was used to study the behaviour of the samples and to notice quantitative measurements caused by temperature increase.

3. Results and discussions

3.1. Fourier transform infrared spectroscopy – FT-IR

Figure 3 presents the spectrum of the composite material based on PMMA and commercial silica.

The presence of SiO_2 in the polymer matrix is highlighted based on its main absorption band from ~1070cm^{-1}, while the characteristic peak of PMMA appears at ~1730cm^{-1}. It is also worth mentioning that are no bands assigned to the monomer, the main band of methyl methacrylate being at about 1630cm^{-1}, which proves that polymerisation occured with a high conversion degree.

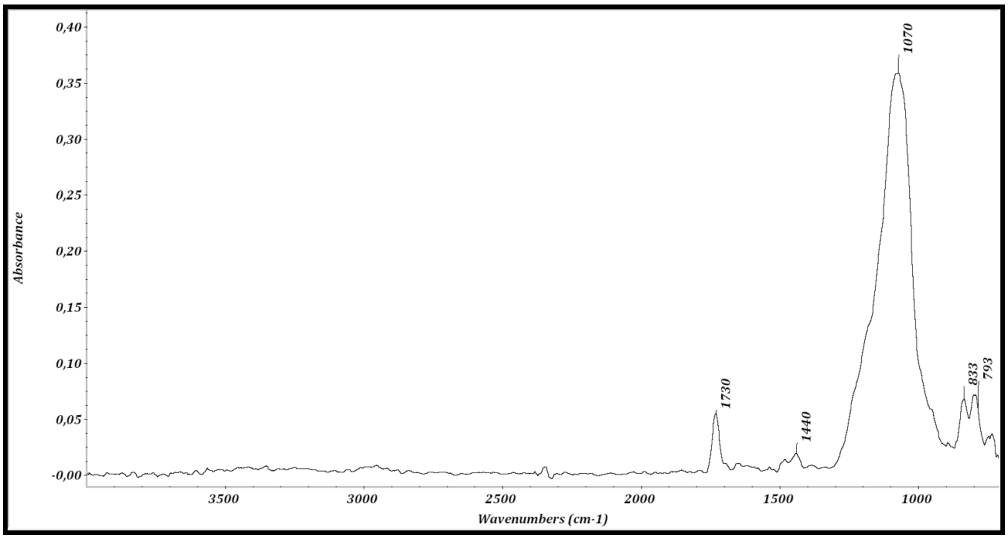

Fig. 3 – FT-IR spectrum of PMMA/commercial SiO_2 composite / *Spectrul FT-IR al compozitului PMMA/SiO_2 comercială*

The main band of silica from ~1100cm^{-1} can be attributed to the stretching of Si-O-Si bonds [16] while the characteristic bands from about 793 and 833cm^{-1} correspond to the bending and stretching of Si-O and Si-OH groups, respectively. The shape and the position of the main Si-O-Si vibrational band at ~1100cm^{-1} shows a stoichiometric silicon dioxide structure [17]. In the case of polymer, the specific band from ~1730cm^{-1} indicates the presence of the acrylate carboxyl group while the peak from ~1440cm^{-1} can be assigned to the bending vibration of the C-H bonds of the –CH_3 group [18].

3.2. X-Ray Diffraction – XRD

XRD analyzes – Figure 4, show for all studied masses a predominantly amorphous character by the presence of the diffraction halos in the low angle range.

For the composite materials, X-ray diffraction images presented in figures 4 b) and c) show that diffraction peak intensities characteristic to coesite, a crystalline form of SiO_2 (ASTM [083-1413], ASTM [100-8029]) are low which suggest either a low crystallinity (especially for the commercial silica) or a low crystallite size (especially for the composite material made with *in situ* silica).

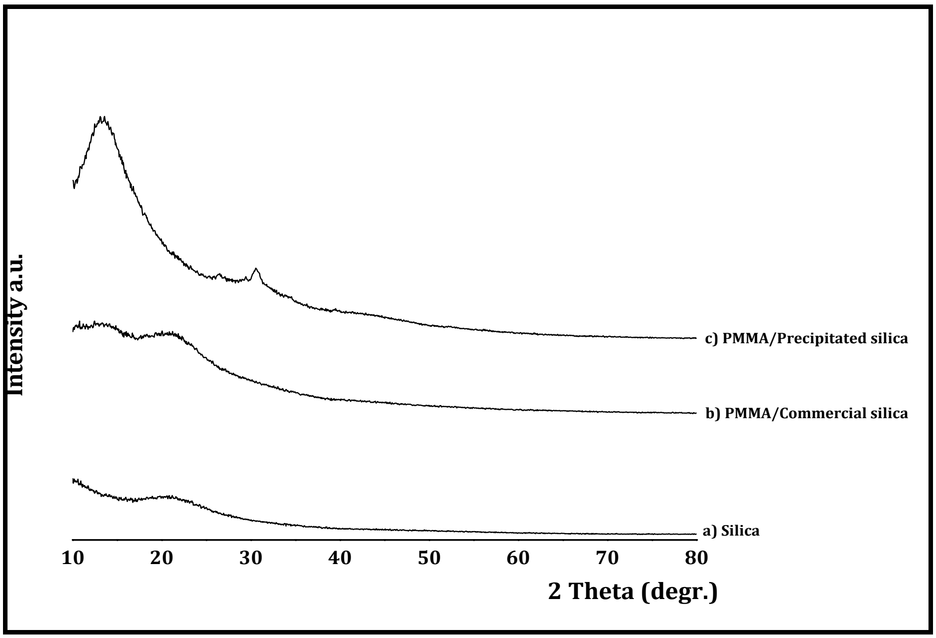

Fig. 4 – Diffractograms of a)SiO_2, b)PMMA/commercial SiO_2 and c)PMMA/precipitated SiO_2 composite / *Difractogramele a)SiO_2, b)compozitului PMMA/SiO_2 comercială şi c)compozitului PMMA/SiO_2 precipitată.*

3.3 *Scanning Electron Microscopy – SEM*

SEM images indicated that PMMA/commercial SiO_2 composite distinguishes by compositional homogeneity. The agglomerates of SiO_2 show sizes of approximately 250 nm (Figure 5).

For the PMMA/precipitated SiO_2 composite, it can be noticed the homogeneous distribution of silica, the latter being embedded uniformly in the polymer matrix (Figure 6).

3.4. Differential Thermal Analysis – DTA-TG

Figure 7 presents the results of DTA-TG analysis for PMMA/commercial SiO_2 composite.
TG analysis showed a mass loss of 44.24% in the range of 20 – 1000°C, 40.37% being in the 200 – 450°C area. In this range (200 – 450°C), DTA curve indicates two endothermic effects (at 279°C and 346°C) accompanied by mass loss that can be attributed to the decomposition of the organic component. The difference of 3.87% can be assigned most likely to the decomposition of some hydroxyl phases. This proves the ratio between polymer and inorganic compound of 1:1.5, close to the theoretical ratio of 1:1 between the two phases.

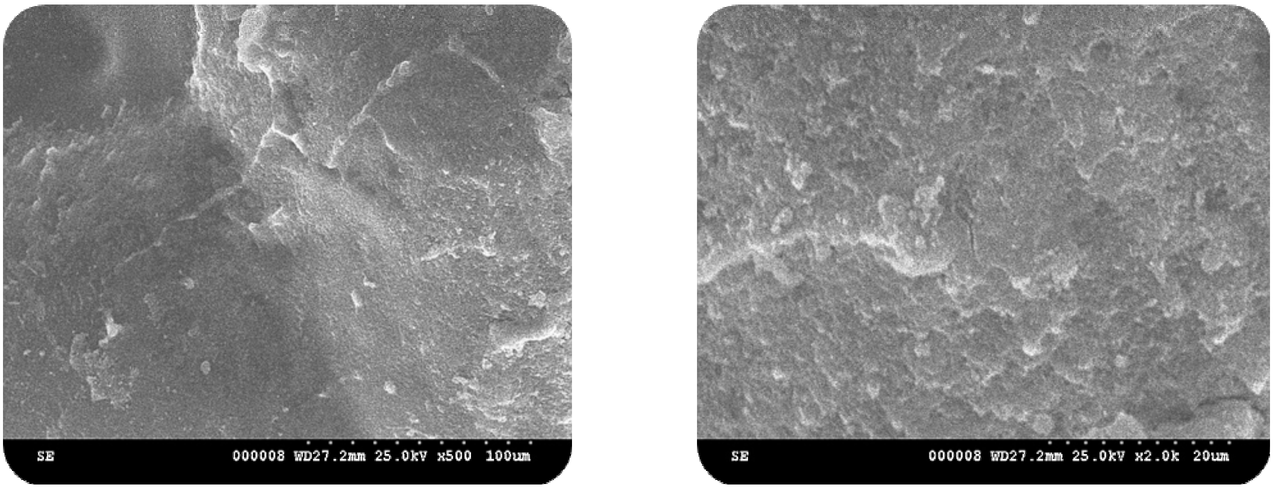

Fig. 5 – SEM images of PMMA/commercial SiO_2 composites / *Imagini SEM ale compozitelor PMMA/ SiO_2 comercială.*

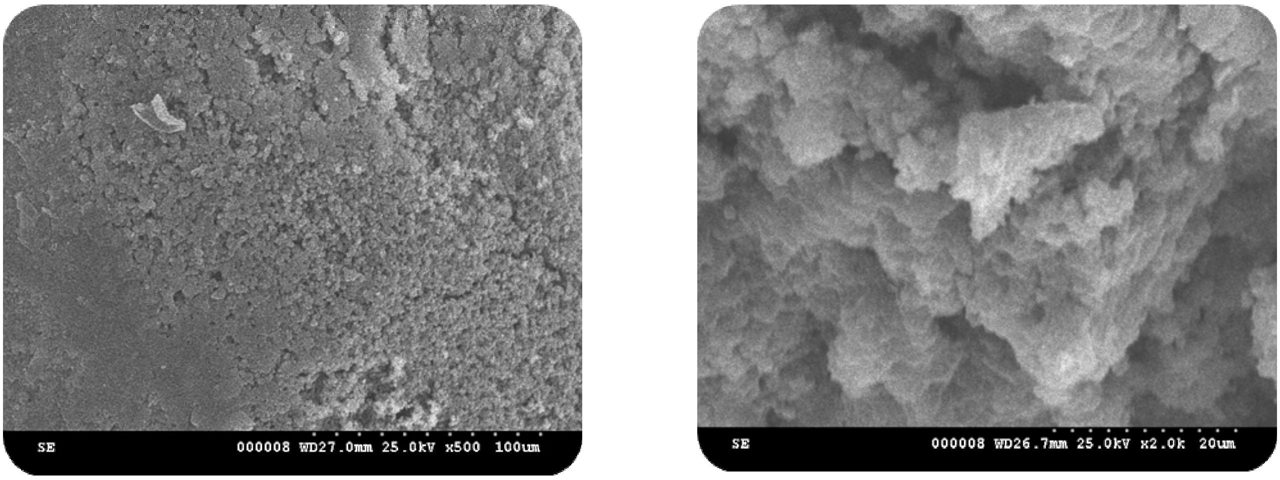

Fig. 6 – SEM images of PMMA/synthesized SiO_2 composites / *Imagini SEM ale compozitelor PMMA/ SiO_2 sintetizată*

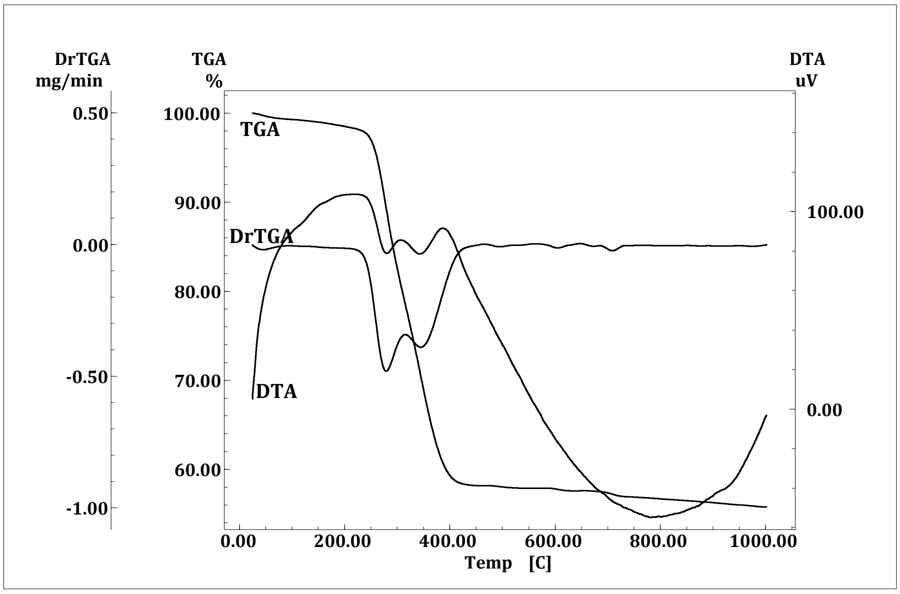

Fig. 7 – DTA, TGA and DTG curves of the PMMA/commercial silica composite */ Curbele DTA, TGA şi DTG ale compozitului pe bază de PMMA/silice comercială.*

4. Conclusions

This study presented the synthesis of PMMA/silica composite materials by two different routes. Regardless of the selected synthesis route, the final PMMA:SiO2 ratio was 1:1 which confirmed that MMA was totally converted into polymer.

Present results indicate that the inorganic particles that were synthesized *in situu* led to a more uniform distribution in the polymer matrix.

The analyzed composite materials highlighted a good potential to be used as cements or adhesives in dentistry.

Further researches will be conducted in this direction in order to incorporate new compounds with antiseptic properties. Also, surface modification of inorganic particles is taken into consideration in order to achieve a more efficient compatibility with the polymer matrix.

Acknowledgements

This work has been funded by the Sectorial Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/107/1.5/S/76903.

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MANIFESTĂRI ŞTIINȚIFICE / SCIENTIFIC EVENTS

IOP Institute of Physics

Advanced Materials for Demanding Applications

7–9 April 2014, Glyndwr University, St Asaph, UK

Organised by Nanoscale Physics and Technology Group.

The objective of the conference will be to bring together researchers with interests in composites and other specialist materials, with technology demonstrators working in demanding engineering applications requiring high specific strength or stiffness, high temperature performance, high tolerance geometrical stability or other unusual and challenging requirements.

The target number of attendees will be 80-120: a small enough gathering that it is possible for all of the delegates to meet each other. Some of the attendees will be young researchers working or aiming to work in interdisciplinary topics in this area. Others will be more established researchers or industrial technology developers. The aim is to bring the diversity of depth of expertise, breadth of application requirements, together with ambition, energy, experience and expertise.

The conference will include discussion time, to focus on what the challenges are for future engineering capability, and what the necessary technology enablers could be. This could form the basis for future collaborative project team building, maximising the interdisciplinary and international credentials for successful proposal bidding.

The format of each day of the conference will include a plenary lecture on a specialist subject, made more accessible to an expert but non-specialist audience. The research paper presentation sessions will follow, with round table discussion sessions and Keynote presentations later in the day. A range of social events will also take place.

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