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In situ coagulation moulding: a new route for high quality, net-shape ceramics

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Abstract

A fast, near-net shape route for the production of advanced ceramic components has been developed that uses carboxylic acid derivatives as coagulants for electrosterically dispersed, high solids content ceramic suspensions. The time dependent in situ hydrolysis of the coagulant D-gulonic-γ-lactone progressively destabilises the suspension to form a viscoelastic solid within which the homogeneity of the initial dispersion is maintained. Constraining this hydrolysis reaction within a non-porous mould leads to the formation of green bodies. After drying, the ceramic components can be sintered without special debinding operations since only a small amount of organic additive, less than 1 wt.% of the total batch mass, is needed. Since the forming process takes place without pressure and at temperatures around ambient conditions, inexpensive moulds and tools can be used. As applied to A16-SG grade α-alumina, this new forming technology, called in situ coagulation moulding, produces components that possess high sintered densities, ~99% theoretical, high average mechanical strengths, $\sigma_{3pt} \approx 450$ MPa, good reliability, Weibull modulus, $m = 10$, and uniform microstructures.

Keywords: A. Suspensions; D. Al_2O_3; Coagulation

1. Introduction

There is a need to produce dense, fine-grained advanced ceramics on a relatively fast production scale, using near-net shape forming routes, and with a reduction in the heterogeneities that are currently present. Graule and co-workers [1–3] have patented a method for the production of complex shaped, high strength, high reliability ceramic components that is based on the destabilisation of a high solids loading, electrostatically stabilised suspension. Destabilisation is brought about by the in situ time dependant formation of potential determining or indifferent ions from initially inactive compounds utilising enzyme-catalysed reactions. The nature of the destabilisation ion determines whether the body produced is flocculated or coagulated. For example, electrostatically stabilised suspensions can be coagulated due to a change in ionic strength according to:

$$H_2NCONH_2 + 2H_2O\ (l) \xrightarrow{\text{urease}} CO_3^{2-} + 2NH_4^+$$

Essentially this reaction is the same at that utilised by Franks and Lange [4] in his Vibraforming route, although in that case heat was used rather than enzymes to obtain appreciable reaction rates. A shift in pH from alkaline to neutral pH, i.e. flocculation, is achievable using the glucose, glucoseoxidase system [2]. The strength of the wet shaped, green body has been found to be dependant on the coagulation method used. Flocculated bodies produced by a pH shift show higher strengths than those coagulated by increasing the salt concentration as a result of the short range hydration forces acting between the particles that occur in the latter case [3].

The current research also relies upon the in situ destabilisation of a high solids loading suspension, however it builds upon previous experience that focused on the coagulation of ceramic suspensions by the direct addition of

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salt to electrosterically stabilised suspensions [5]. The latter process suffered from two inherent drawbacks. Firstly, mixing problems arose because the suspensions became highly viscous too quickly; this led to difficulties in obtaining bodies that were homogenous and free of air entrapment. Secondly, the scope of the process was limited to techniques that involved the subsequent plastic deformation of the pastes, e.g. extrusion. In order to alleviate these problems the use of carboxylic acid derivatives as alternative coagulants has been investigated. It was conceived that the time dependent in situ hydrolysis of this group of compounds would progressively destabilise the suspension to form viscoelastic solids within which the initial homogeneity of the dispersion would be preserved. As a result, the components produced should possess high sintered densities and good mechanical properties. Two previous papers have examined the effect of the coagulant structure on the in situ acidification process [6] and the rheological nature of the suspensions during the coagulation process [7]. This paper examines the practical considerations related to the use of the process for the production of ceramic components.

2. Experimental

Preparation of the initial dispersed suspensions followed the procedure developed by Davies and Binner [8]. Appropriate quantities of deionised water (±0.01 g) and Dispex A40[1] (±0.003 g) were mixed until the dispersant was uniformly distributed and then A-16SG alumina[2] (±0.01 g) blended in until an homogenous suspension resulted. All associated water was allowed for during the batching process calculations, for example, since Dispex A40 is an aqueous solution, the actual quantity of ammonium polyacrylate (NHPA) used corresponded to only 37.6 wt.% of the amount of dispersant added. The composition of the initial dispersed suspensions was 81 wt.% alumina and 1.4 mg g^{-1} ammonium polyacrylate.

Following mixing the slurries were covered to avoid contamination and left to stand at room temperature for 1 h to allow adsorption of the dispersant onto the alumina. In order to breakdown any soft agglomerates, the slurry was then subjected to ultrasonic agitation produced by a Kerry ultrasound unit[3] for 90 s. The vibrational output was at a frequency of 20 kHz and a power level of 150 W. In order to reduce subsequent water evaporation, the samples were covered with Nescofilm[4] and cooled in a refrigerator for 1 h. The dispersed suspensions were stirred and then placed in a 60 ± 10 mmHg vacuum for 1 h in order to remove as much of the entrapped air as possible. Finally the suspensions were re-sealed and allowed to equilibrate in a refrigerator for 24 h.

Based on previous work that examined the consequence of lactone chemistry and concentration on suspension pH and rheology [6,7], D-gulonic-γ-lactone was selected as the coagulant with 2.5×10^{-5} moles per gram of suspension being added and the suspension temperature was varied from 20–80 °C. The dispersed suspensions were covered with Nescofilm to minimise evaporation and partially immersed in a gently agitated water bath to achieve constant temperature conditions prior to the cover being removed and the coagulant thoroughly blended into the suspension for one minute. The suspension containing the coagulant was then poured into moulds and the latter covered in order to preclude undesired viscosity changes due to evaporation and the coagulating suspension allowed to stiffen until the body was sufficiently rigid to allow demoulding.

A variety of materials were used to construct the moulds, including metals, polymers and glass. The most complex shapes produced were fabricated using a mould cast around an existing component, the mould material used in such cases being a silicone rubber[5] that slowly vulcanised at room temperature when intimately mixed with 1–3% of catalyst. The curing rubber was de-aired prior to encapsulating the greased[6] component and left to set for 24 h. Prior to each casting, the mould was thoroughly cleaned and a thin layer of mould releasing agent applied to the surfaces that would be in contact with the coagulating slurry. The demoulding characteristics of a variety of mould materials and release agents[7,8] were investigated in order to find the most effective combination.

Following de-moulding the stiff, wet green parts were initially dried at room temperature; in order to prevent warping they were frequently turned. Thereafter, the samples were dried at 110 °C in an oven to achieve total moisture removal. No attempt was made to use rapid, industrially-relevant, drying procedures, such as the use of a humidity dryer, since the main focus of the work was on the coagulation step itself. Therefore samples were often left in the drier for a week or more prior to further characterisation.

The dried green bodies were sintered in a UAF 16/10[9] static air electric chamber furnace. Since the total quantity of organic material within the dry green component was <1% a very simple binder burnout stage was used. The samples were initially heated at a ramp rate of 3 °C min^{-1} up to 400 °C and held for 30 min before the temperature was subsequently increased at the same ramp rate up to 1540 °C. A holding time of 2 h was used before the samples were

[1] Allied Colloids, Bradford, UK.
[2] Alcoa Manufacturing (GB) Ltd., Worcester, UK.
[3] Kerry Ultrasonics Ltd., Hitchin, Hertfordshire, UK.
[4] Nescofilm™, Nippon Shoji Kaisha Ltd., Osaka, Japan.
[5] Two part RTV silicone rubber system, RS Components, Corby, Northamptonshire, UK.
[6] High vacuum silicone grease, RS Components, Corby, Northamptonshire, UK.
[7] PTFE spray, RS Components, Corby, Northamptonshire, UK.
[8] Chemodex Instant WD, Chemodex Ltd., Worksop, Nottinghamshire, UK.
[9] Lenton Thermal Designs Ltd., Market Harborough, Leicestershire, UK.

allowed to cool at a rate that was prevented from exceeding 10 °C min^{-1} to avoid thermal shock.

The components were characterised in terms of green and sintered density, sintering shrinkage, mechanical properties and microstructure. Density was measured using a mercury immersion densometer, a minimum of five measurements on different samples being used to obtain an average value. Mechanical testing involved measuring the 3-point flexural strength of 10–20 sintered as-cast specimens per set of processing conditions. The samples measured 75 mm × 7 mm × 5 mm (green dimensions) and 10 were produced simultaneously using a custom built mould. The Weibull modulus was also calculated from the data. Sample preparation for the microstructural analysis involving a scanning electron microscope, SEM, involved wet grinding one face on 30 μm and then 15 μm grinding wheels for 10 min each to provide a flat sample surface. The samples then underwent a number of sequential polishing steps on synthetic lapping wheels using 9, 6, 3 and 1 μm diamond abrasive paste[10] and an alcohol based lubricant.[11] After each polishing stage the samples were cleaned with industrial methylated spirit to avoid contamination of the polishing wheels. The polished samples were thermally etched to reveal the grain boundaries, the heat treatment involved holding for 10 min at 1500 °C with a rapid heating rate of 8 °C min^{-1} and the natural cooling rate of the furnace. The samples were gold coated prior to SEM investigation using an acceleration voltage of 20 kV. The microstructural variables examined included the level of porosity, pore structure, grain size/shape and the nature of the grain boundaries.

3. Results and discussion

The effect of lactone composition and temperature on the nature of the coagulating pH change and its rheology have been discussed elsewhere [6,7], therefore this paper focuses on the actual production of ceramic components. The overall process is summarised in Fig. 1 and its simplicity can be readily seen. Most notably, it does not require any specialist equipment other than appropriate moulds. Fig. 2 illustrates a selection of products that were fabricated using the process. The components were cast using silicone grease mould release agent and a variety of different mould materials.

The effect of mould material and mould release agent are summarised in Table 1. It can be seen that the coagulating bodies were found to adhere to all mould materials when no mould release agent was used. Whilst still unacceptable, sticking was found to be least severe when PTFE was used; this is a natural consequence of the low friction surface associated with this polymer. However, it was found that the application of a layer of high vacuum silicone grease or Chemodex instant WD onto the mould surfaces prevented adhesion. Any residual de-moulding agent present on the surface of the green component was removed during the sintering stage due to thermal degradation and evaporation.

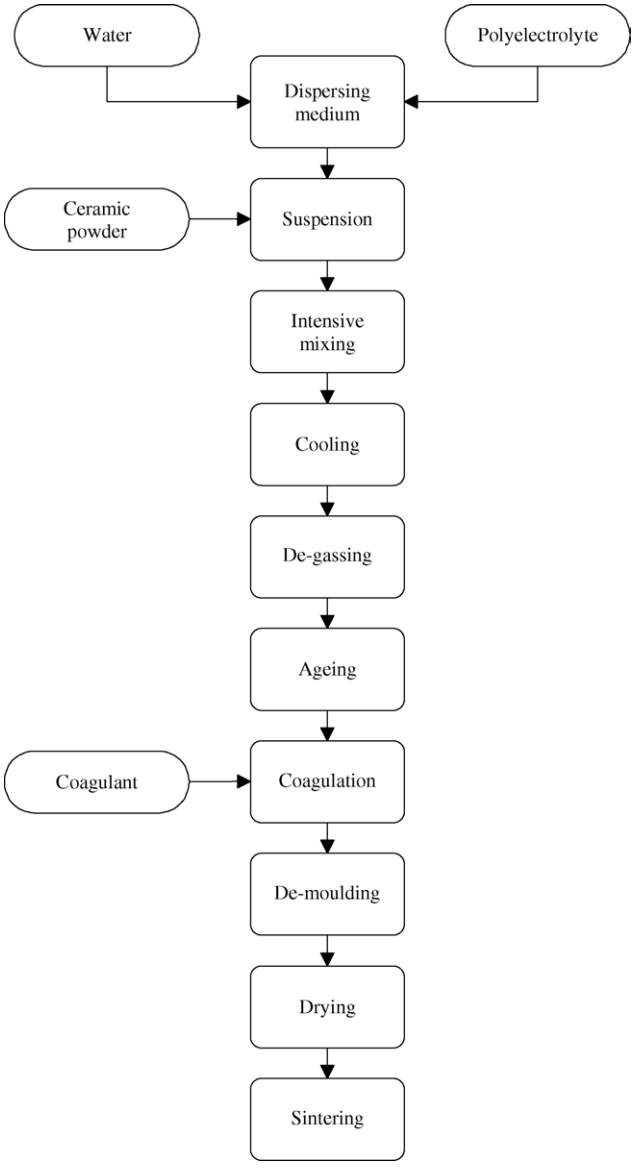

Fig. 1. Flow chart of the in situ coagulation moulding shape formation route.

The body could be demoulded once the gel point[12] had been reached. The advantage of this criterion was that the gel point was found to correspond to the same value of G', ~6 kPa, irrespective of lactone concentration and temperature [7]. It is interesting to note that Graule and Gauckler [1] stated that a very similar minimum compressive strength of ~10 kPa was required for demoulding direct coagulation

[10] Kemet KD diamond pastes, Kemet International, Maidstone, Kent, UK.
[11] Kemet type OS lubricating fluid, Kemet International, Maidstone, Kent, UK.

[12] The gel point represents the crossover point between the dynamic modulii G' and G'', i.e. the point at which the elastic properties dominated the viscous properties and so the system began to behave as a solid.

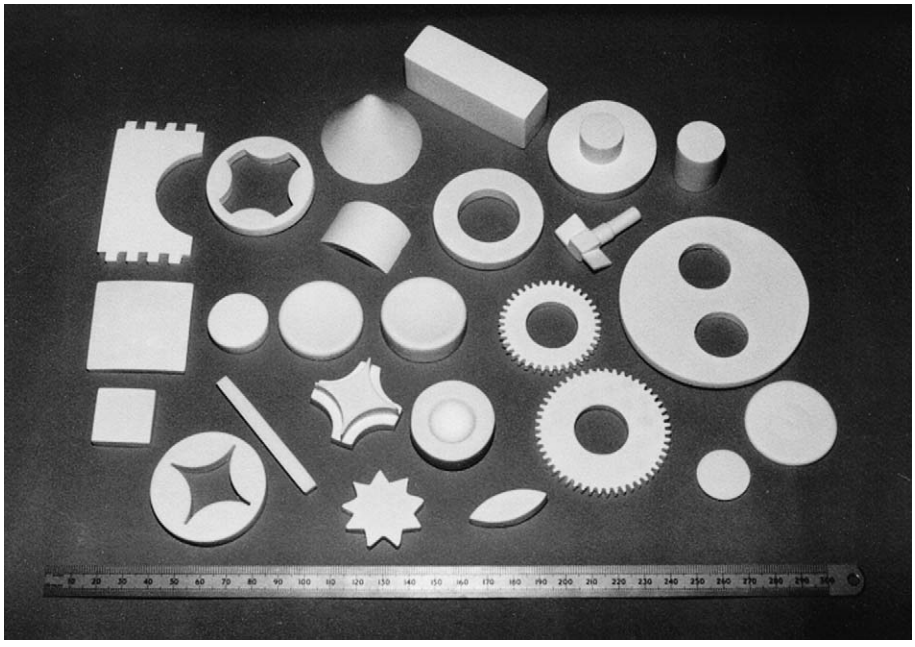

Fig. 2. Components shaped using the in situ coagulation moulding (ICM) process based on D-gulonic-γ-lactone.

Table 1
Comparison of the effectiveness of several mould materials and release agents

Mould material	Release agent	Comments
Brass	None	Green body adhered to mould and removal impossible
Brass	PTFE spray	Green body adhered to mould and removal impossible
Brass	Silicone grease	Green body could be demoulded
Brass	Chemodex	Green body could be demoulded
Brass	Cling film	Green body could not be demoulded without suffering distortion
Perspex	None	Green body adhered to mould and removal impossible
Perspex	Silicone grease	Green body could be demoulded
PTFE	None	Green body adhered to mould slightly and removal difficult
PTFE	Silicone grease	Green body could be demoulded
RTV rubber	None	Green body adhered to mould slightly and removal difficult
RTV rubber	Silicone grease	Green body could be carefully demoulded

cast (DCC) fabricated components. Nevertheless, to achieve high component shape accuracy it was necessary in the present work to use a rigid rather than flexible mould because with the latter it was possible to cause deformation during mould removal.

As expected, the higher the temperature of the suspension, the faster the rate of coagulation, Fig. 3. However, whilst the green bodies were found to possess no noticeable defects at temperatures up to and including 50 °C, above this value macrocracks of increasing severity were observed on the surfaces of the green bodies. This is believed to be attributable to the generation of a moisture gradient throughout the suspension, as a result of the applied heat preferentially evaporating water near the surface.

The initially inactive coagulant could be easily and very homogeneously mixed into the suspension without entrapping significant quantities of air. Hence the average green and sintered densities for the in situ coagulated bodies produced by adding 2.50×10^{-5} mol g^{-1} of D-gulonic-γ-lactone to a suspension at 20 °C were 2.31 g cm^{-3} (58% of theoretical) and 3.92 g cm^{-3} (99% of theoretical) respectively. These values were achieved reproducibly and are indicative of a high degree of particle packing, as illustrated

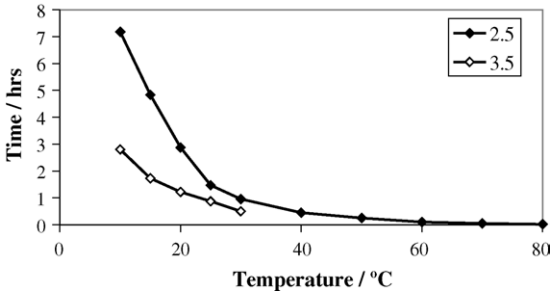

Fig. 3. Variation in time required for the suspension to attain the gel point and so be suitable for demoulding as a function of suspension temperature using 2.50×10^{-5} mol g^{-1} of D-gulonic-γ-lactone. Data for 3.50×10^{-5} mol g^{-1} of D-gulonic-γ-lactone is included for comparison. Note: above 50 °C the samples all demonstrated surface cracking.

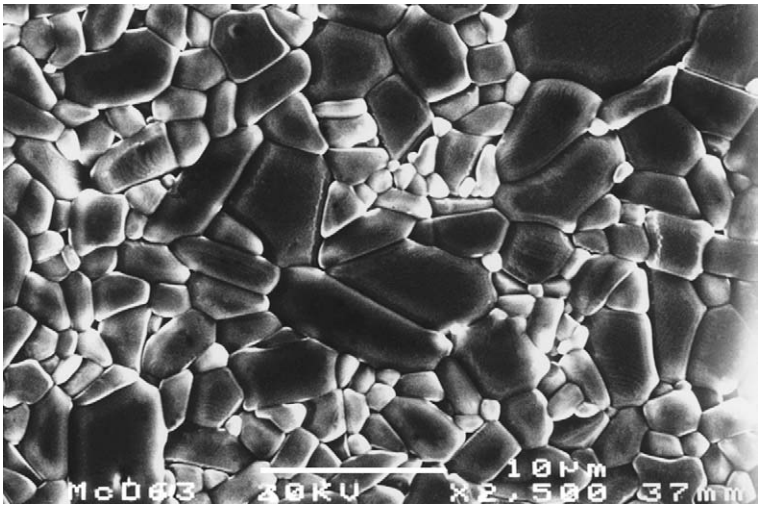

Fig. 4. Sintered microstructure of a sample prepared by in situ coagulation moulding using 2.50×10^{-5} mol g^{-1} of D-gulonic-γ-lactone added to a suspension at 20 °C.

by the typical microstructure shown in Fig. 4. Whilst a small amount of porosity can be observed, mainly at the triple points and within the grains, it is not believed to have affected the strength of the sintered bars because they are smaller than the average grain size, which was 1.3 μm as measured by the random intercept technique. The variation in grain size observed was a result of the grade of alumina used. Sintering shrinkage was also found to be very consistent and isotropic at 17.8%.

The average 3-point bend strength based on 20 as-cast samples that were not machined or polished in any way was found to be 451 MPa. The Weibull modulus, obtained using the least squares regression technique to fit the data points, Fig. 5, yielded a value of 10. Table 2 compares these results with those quoted by several other authors. Note that the grade of the alumina powder and whether a 3- or 4-point bend testing facility was used will have influenced the results obtained.

Whilst die pressing is a fast and highly automated shape formation process that is generally preferred by industry, it actually gives the lowest values recorded in the table. It is now generally accepted that improvement in green state homogeneity can be obtained by using suspension-based techniques. Slip casting is probably the benchmark for such processes, however, whilst it results in an improvement in mechanical properties over die pressing, it is an inherently

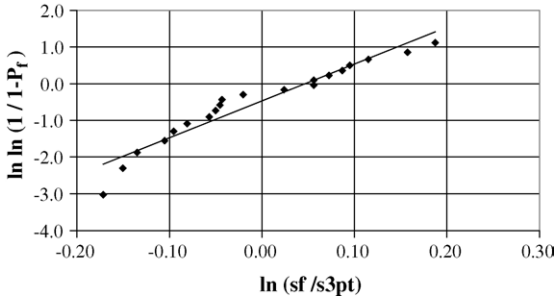

Fig. 5. Weibull analysis for sintered specimens prepared by in situ coagulation moulding using 2.50×10^{-5} mol g^{-1} of D-gulonic-γ-lactone added to a suspension at 20 °C.

Table 2
Comparison of the mechanical properties of alumina bodies fabricated using different shape forming processes

Process	Sintered density (g cm^{-3})	Strength (MPa)	Weibull modulus m	Reference
Die pressing	3.85	235	5.6	Alcoa data sheet CHE 920
Aqueous injection moulding using agar binder	3.81	240	6.2	[9]
Gelcasting	–	248	–	[10]
Extruding directly (salt) coagulated suspensions	3.83	355	6	[11]
Injection moulding using polyacetal and catalytic debinding	3.91	400	11	[12]
Extrusion of alumina–boehmite mixtures	3.94	402	8	[13]
Slip casting	3.92	422	–	[14]
In situ coagulation moulding, ICM	3.92	451	10	Current work
Direct coagulation casting, DCC	3.97	485	8.5	[15]
Quickset	–	489	10	[16]
Centrifugal slip casting	3.97	541	23.9	[17]
Direct coagulation casting followed by hot isostatic pressing	3.98	685	40	[17]
Viscous polymer processing, VPP	–	1042	12	[18,19]

slow technique. Interest has recently been shown in centrifugal casting because the resulting bodies possess fewer defects, which is reflected by the higher component strengths and reliabilities, and is considerably faster. However, this processing route is limited by the size of the components that can be made and the capital cost of the equipment. The highest observed strengths are associated with the VPP processing route, which utilises high shear rates to reduce agglomerate size. However, the production of components is restricted to those techniques that plastically deform the resulting paste. A variety of researchers have demonstrated that colloidal suspensions can be set within the mould cavity [1,4,15,16]. These forming technologies are characterised by the ability to produce large, complex shaped components possessing thin and thick sections that exhibit improved properties compared to conventional forming technologies. Relative to these shape formation routes, it can be seen that in situ coagulation moulding produces components possessing similar mechanical properties.

4. Conclusions

A new flexible ceramic forming process, in situ coagulation moulding (ICM), has been developed and patented [20,21] for the production of advanced ceramic components. The process couples a stable, high solids loading, dispersed ceramic suspension and an initially inactive carboxylic acid derivative coagulant. Time dependent in situ hydrolysis of the coagulant progressively destabilises the suspension to form a viscoelastic solid within which the homogeneity of the initial dispersion is maintained. The new method is characterised by a near-net shape capability of forming complex parts with low defect microstructures. After drying, ceramic components can be sintered without special debinding operations since only a small amount of organic additive, less than 1 wt.% of the total batch mass, are needed. As applied to A16-SG grade α-alumina this new forming technology produces components that possess sintered densities, strengths and reliabilities similar to various other colloidal approaches. Specifically, densities of ∼99% theoretical, high average mechanical strengths of ∼450 MPa and a good Weibull modulus of 10. Since the forming process takes place without pressure and at temperatures around ambient conditions, inexpensive moulds and tools can be used.

The first step in the process is the ability to produce a high solids content, low viscosity suspension. Since in situ coagulation moulding does not rely on the dewatering of the suspension, all water present in the initial suspension will also be present in the green body prior to drying. To keep down energy costs and drying times, it is therefore important that the suspension has as high a solids content as possible whilst still being highly fluid, i.e. possessing low viscosity, elasticity and yield point, to ensure good mould filling. In the present work, the precursor suspensions used contained 81 wt.% solids contents and 1.4 mg g^{-1} of ammonium polyacrylate, molecular weight 3500. Coagulation was then achieved by the in situ hydrolysis of 2.50×10^{-5} mol g^{-1} of D-gulonic-γ-lactone. Optimisation of the concentration of coagulant present and coagulation temperature allowed components to be made in as little as 10 min, additional research may well result in further reductions in time.

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