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The application of silicon sol–gel technology to forensic blood substitute development: Mimicking aspects of whole human blood rheology

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ABSTRACT

Solution–gelation chemistry has promising applications in forensic synthetic blood substitute development. This research offers a silicon-based sol–gel approach to creating stable materials that share similar rheological properties to that of whole human blood samples. Room temperature, high water content, silicon sol–gels were created using the organosilane precursors 3-glycidoxypropyltrimethoxysilane and tetraethylorthosilicate along with various concentrations of filler and pigment. Shear-thinning non-Newtonian properties were observed within most formulations of the presented materials. The effects of colloidal concentration, temperature, age and filler addition on the viscosity of the sol–gels were investigated. SEM–EDS analysis was used to identify the behavior of the fillers within the film and support their inclusion for basic bloodstain pattern simulation. A final proposed candidate sol–gel was assessed using a previously reported passive drip simulation test on a hard, dry surface and passed. This works represents encouraging development in providing safe material alternatives to using whole human blood for forensic training and research.

1. Introduction

Forensically relevant synthetic blood substitute (FBS) design and development is an identified need within the bloodstain pattern analysis (BPA) community [1–3]. An FBS can provide a safe and standardized alternative to using human and/or animal blood. Candidate materials for FBS are ideally non-toxic, stable, and physiologically similar to whole human blood. One of the key properties that an effective FBS must be able to simulate is whole blood viscosity. Viscosity plays a significant role in the fluid mechanics of many bloodletting events [4] and directly affects the characteristics of stains found in static patterns [5–7]. Whole blood is described as a non-Newtonian fluid because it exhibits shear-thinning behavior [8]. Since blood-letting mechanisms can occur at a variety of shear rates, it is important then, to create an FBS fluid that successfully mimics this non-Newtonian behavior. Measured values of whole human blood viscosity are quite variable at any given shear rate [9–17]. This is because whole blood viscosity is highly dependent on various physiological conditions of an individual, such as age, health, hematocrit, temperature, presence of anticoagulants and the type of rheometer used for sample measurement [8,11,15,17]. The literature shows that whole blood viscosity is also species dependent [18]. The range of reported whole human blood viscosity values at physiological temperature (37 °C) is found in Table 1.

Silicon solution–gelation (sol–gel) techniques offer polymerization chemistries that can meet many of the physiological requirements of an FBS. Solution–gelation chemistry is marked by a two-step process whereby a *sol* in the form of a colloidal suspension of solid particles in a liquid is created in a way that it eventually polymerizes to the stage of a continuous macromolecule described as a *gel* [19,20]. It typically comprises a series of hydrolysis and condensation reactions between monomeric metal oxide precursors as a result of its surrounding aqueous environment to form the sol. After an aging period the sol turns into gel products, which are often hard inorganic materials that are best suited for thin-film applications [21]. They are primarily used in

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Table 1
A range of reported viscosity values of whole human blood at 37 °C [8,11,15,17].

Shear rate (/s)	Viscosity (mPa s)
0.1–<10	5.46–100
10–<100	7.00 ± 4.24
100–<200	4.63 ± 1.93
>200	4.64 ± 1.93

surface coating technologies, where the thin-films are created through spraying, dipping and spin coating. Silicon-based sol–gel materials are typically used in chemical, biological and optical sensor applications [19,22]. Regardless, their fabrication shows high level of material versatility, which can be tailored to suit forensic training and research needs.

The generic reaction scheme of the sol–gel protocol utilized in this experiment is shown in Fig. 1. Allowing polymerization to occur in a high water content environment slows the gelation process and allows the material to remain a liquid suspended sol for an extended period of time prior to solidification [19,23–25]. This is advantageous for FBS development because, like blood, the inherent nature of the process allows for simulation of clotting and flaking after an extended period of time. For this reason, crosslinking or curing agents were not utilized in this study. This protocol, which creates the base silicon sol–gel material for the FBS, or what we refer to as, GT, is centered on previously established work [26–28]. We extend this work by manipulating the formula and exploring the material's forensic relevance in its applicability in BPA passive dripping simulation. This is a new and novel approach that further extends the versatility of the sol–gel derived material.

2. Materials and methods

2.1. Formulation

All base materials were created using 3-glycidoxypropyltrimethoxy silane (GPTMS, Gelest Chemical) and tetraethylorthosilicate (TEOS, Sigma Aldrich). The silanes were added to a dilute solution of acetic acid in water to facilitate hydrolysis and condensation to form the candidate liquid sol–gel. The sols were allowed to age under constant stirring in room temperature conditions. Raman spectroscopy was used to identify and assess epoxide functionality throughout this process.

Aliquots of the sol–gel were used to measure fluid viscosity formed under a range of process conditions including aging time (0–72 h), temperature (10 °C–37 °C), and filler concentration (0–10% weight by volume (w/v)). A total of seventy-two samples were run for characterization, fifty-six of them in ambient temperature conditions. Low alcohol formulations, what we refer to as low ROH or LAGT, were generated by distillation under reduced pressure to remove the alcohol hydrolysis byproducts in the solution. Alcohol removal was assessed using IR spectroscopy. The retentate, or LAGT was re-suspended in Millipore water to restore a portion of the original volume. Water was added to achieve final volumes ranging from 20% to 100% final volume/initial formulation volume. Fillers were added to the sol–gel formulation to achieve the drying and visual appearance of whole blood. The fillers added to the sol–gel included magnesium silicate (talc, Sigma Aldrich) and watercolor pigments (Yarka and Winsor Newton). Nine samples of candidate FBS sol–gels were created with 60–65% v/v LAGT and the inclusion of up to 2% w/v talc and 1% w/v pigment.

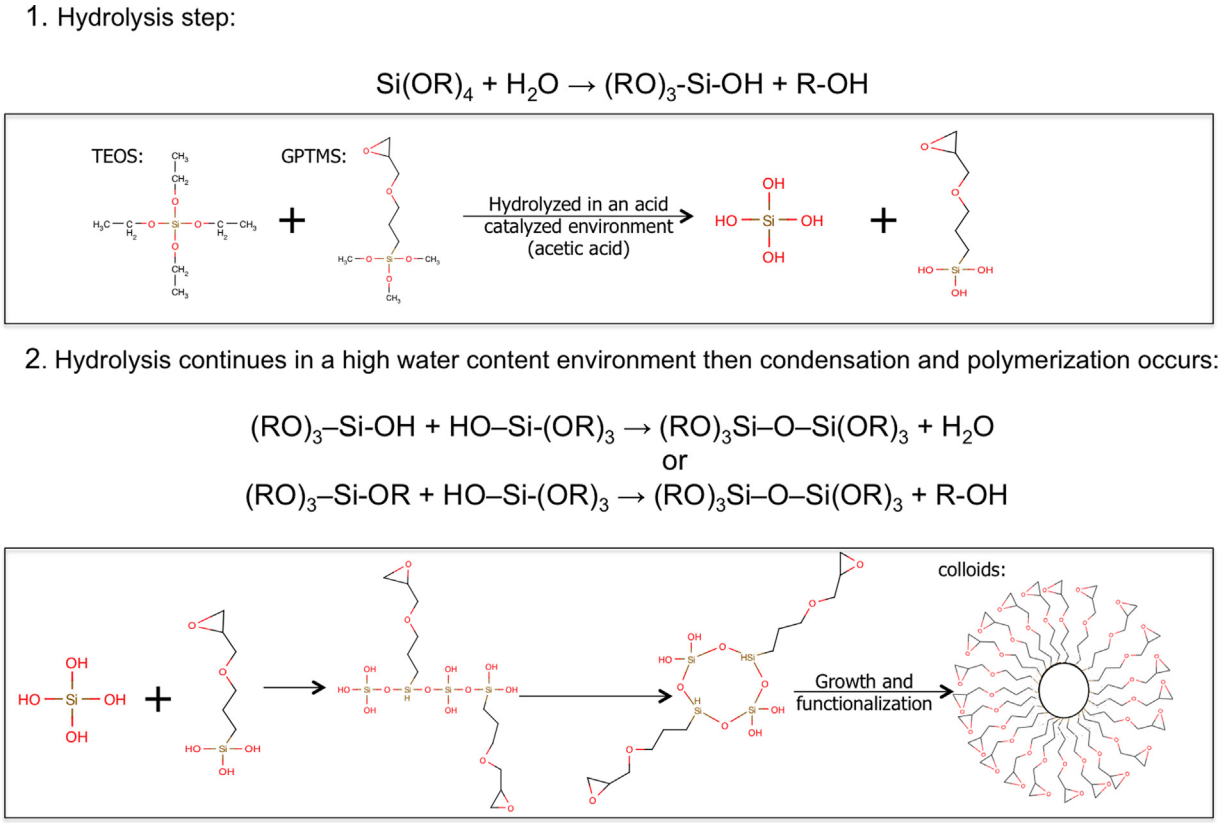

Fig. 1. The polymerization scheme utilized in the creation of the FBSs generated in this experiment.